SMS 2019
SMART MATERIALS AND SURFACES

EGF2019
EUROPEAN GRAPHENE FORUM

NanoMedicine
2019

SMS 2019 / EGF 2019 / NanoMed 2019

Joint International Conferences and Exhibition

23 - 25 Oct. 2019

Lisbon - Portugal

Book of Abstracts

Organizer

SETCOR
Conferences & Exhibitions

SMS 2019 / EGF 2019 / NanoMed 2019
Joint Conferences Program

08:30 - 12:00	**Registration**	**Registration Area**

October 23, 2019 **SMS 2019 / EGF 2019** **Plenary session I**		
Conference Room Porto		
Session's Chairs: **Prof. Paula Ferreira, Minho University, Portugal** **Prof. Riccardo Nobile, University of Salento, Italy** **Prof. Peng Feng, Tsinghua University- Beijing, China**		
09:30 - 10:00	Smart Nano-Structured Coatings for Corrosion Protection, Anti-Fouling and Sensing **M.G.S. Ferreira**	**Prof. Mário G.S. Ferreira**, University of Aveiro, **Portugal**
10:00 - 10:30	New thermosets from ionic liquids S.Livi, S. Pruvost, J.F. Gérard and **J.Duchet-Rumeau**	**Prof. Jannick Rumeau**, University of Lyon, **France**
10:30 - 11:00	**Coffee Break / Posters Session I**	**Coffee Break Area**
11:00 - 11:30	Highlighting novel static and fluidic properties of liquids using solid wall interactions **L. Noirez**	**Dr. Laurence Noirez,** Léon Brillouin Lab, CEA/CNRS, **France**
11:30 - 11:45	Design and Realization of White Quantum Dot Light-Emitting Electrochemical Cell Hybrid Devies **S. Gellner**, J. Frohleiks, S. Wepfer, G. Bacher and E. Nannen	**Ms. Sandra Gellner**, University of Applied Science Niederrhein, **Germany**
11:45 - 12:00	Mesoporous Silica Nanoparticles based on Ionic Microbial Agents **S. Gago**, B. Mora, P. Rações, M.M.L. Ribeiro Carrott and L. C. Branco	**Dr. Sandra Gago**, Faculty of Sciences and Technology of NOVA University, **Portugal**
12:00 - 12:15	Inherently Chiral Ionic Liquids with Axial, Helical and Central Stereogenicity for Highly Efficient Enantioselective Sensors **S. Rizzo**, P.R. Mussini, S. Arnaboldi, M. Longhi, F. Fontana, R. Cirilli and A. Forni	**Dr. Simona Rizzo**, CNR-Institute of Molecular Science and Technologies, **Italy**
12:00 - 14:00	**Lunch Break**	**Restaurant**

October 23, 2019 **SMS 2019 / NanoMed 2019 joint session I** **Advances in Functional and Multifunctional Materials / Composite Materials / Nanosystems**		
Conference Room Porto		
Session's Chairs: **Prof. Etelvina Gomes, University of Minho, Portugal** **Prof. Jannick Rumeau, University of Lyon, France** **Dr. Laurence Noirez, Léon Brillouin Lab- CEA/ CNRS, France** **Dr. Christos Riziotis, National Hellenic Research Foundation, Greece**		
14:00 - 14:30	High Performance Fiber-Reinforced Polymer for Integration of Structure and Functions **P. Feng** and Z. Li	**Prof. Peng Feng,** Tsinghua University- Beijing, **China**
14:30 - 14:45	Tungsten Carbide Microparticles Introduction's Effect on Steel Hardness and Resistance to local Impacts A. Anikeev**, I. Chumanov** and V. Sedukhin	**Mr. Ilia Chumanov**, South Ural State University, **Russia**

14:45 - 15:00	Biopolymers for the Development of Stimuli Responsive Composites **A.C. Pinho** and A.P. Piedade	**Dr. Ana Catarina Pinho**, University of Coimbra, **Portugal**
15:00 - 15:15	Modulation of Protein Sorption at Magnetic-Responsive Hydrogels A. C. Manjua, V. D. Alves, J.G. Crespo and **C.A.M. Portugal**	**Dr. Carla Portugal**, FCT / NOVA University, **Portugal**
15:15 - 15:30	Metallization of thermoset composites through it surface functionalization **H. Perrin**, S. Klein and R. Vaudemont	**Dr. Henri Perrin**, **Luxembourg** Institute of Science and Technology
15:30 - 15:45	Dithia[3.3]paracyclophane Core: a Versatile Platform for Fine Triplet State Tuning and Through Space TADF Emission. M. Auffray, D.H. Kim, J.U. Kim, F. Bencheikh, **D. Kreher**, Q. Zhang, A. D'Aléo, J-C. Ribierre, F. Mathevet and C. Adachi	**Dr. David Kreher**, Sorbonne University, **France**
15:45 - 16:00	A Nontoxic Reversible Thermochromic Binary System via π-π Stacking of Sulfonephthaleins **B. Liu**, H. Ranji-Burachaloo, P.A. Gurr, E. Goudeli and G.G. Qiao	**Mr. Bingxin Liu**, The University of Melbourne, **Australia**
16:00 - 16:30	**Coffee Break / Posters Session I**	**Coffee Break Area**
16:30 - 16:45	Single Particle Microscopy & Spectroscopy of Morphology and Size Controlled Perovskite Crystals: PEROVSKOPY **E. Debroye**, H. Bhatia, M. Keshavarz, C. Martin-Alvarez, J. Steele, H. Yuan, M. Roeffaers and J. Hofkens	**Dr. Elke Debroye**, KU Leuven, **Belgium**
16:45 - 17:00	Influence of the Nanotopography of Wrinkles on a-C:H coated Polymers on the Differentiation of non-embrionic Stem Cells **J.M. Lackner** and R. Major	**Dr. Juergen M. Lackner,** Joanneum Research Forschungsgesellschaft mbH, **Austria**
17:00 - 17:15	3-nitroaniline crystals embedded in electrospun nanofibers as strong piezoelectric and nanoemitters of second harmonic light R. Baptista, C. Bernardo, **E. Matos Gomes**, P.Lopes and M.S. Belsley	**Prof. Etelvina Gomes**, University of Minho, **Portugal**
17:15 - 17:30	Optimization of electrochemical flow capacitor (EFC) design via Finite element modeling **F. Summer,** J.Torop, V.Zadin and A, Aabloo	**Ms. Faiza Summer**, University of Tartu, **Estonia**
17:30 - 17:45	Strong Piezoelectric Response from Electrospun Fibers of Hybrid Polymer Embedded Dipeptide Boc-Diphenylalanine Nanotubes **R. Baptista**, E. de Matos Gomes, M.M.M. Raposo, S. P.G. Costa, P. Lopes, B. Almeida and M. S. Belsley	**Dr. Rosa Baptista**, University of Minho, **Portugal**
17:45 - 18:00	Analysis of various Aspects in Metals Creation with Given Microheterogeneity Degree **A. Anikeev** and I. Chumanov	**Mr. Andrei Anikeev**, South Ural State University, **Russia**
18:00 - 18:15	Adapting the properties of 3d-printed tailored lightweight mechanical metamaterials **E. Truszkiewicz**, M.Berer, G. Meier, M. Vetter, M. Rossegger, S. Schlögl, P.Fuchs and G.Pinter	**Ms. Eliza Truszkiewicz**, Polymer Competence Center Leoben, **Austria**
18:15 - 18:30	Concept and economic evaluation of an automotive composite part with integrated wireless sensor system **M. Hardt**, P. Middendorf, and R. Bjekovic	**Mr. Maximilian Hardt**, Daimler AG, **Germany**

October 23, 2019
SMS 2019- Session Optically Engineered Surfaces
Manufacturing of 3D nanostructured optics (H2020 project PHENOMENON)

Conference Room Obidos A

Session's Chairs:
Mr. Pablo M. Romero, AIMEN Technology Centre, Spain

09:00 - 09:10	Introduction of the session: Optically Engineered Surfaces - Manufacturing of 3D nanostructured optics (H2020 project PHENOMENON) **P. Romero**	**Mr. Pablo M. Romero,** AIMEN Technology Centre, **Spain**
09:10 - 09:45	Multiphoton Lithography-Materials and applications **M. Farsari**	**Dr. Maria Farsari**, IESL-FORTH, **Greece**
09:45 - 10:10	Massively parallel multiphoton photoplotting: rationale, techniques and implementation obstacles **K. Heggarty**	**Prof. Kevin Heggarty**, IMT Atlantique, **France**
10:10 - 10:30	3D microfabrication by two-photon induced polymerization of subwavelength diffractive elements with high aspect ratio for surface optics **P. Baldeck**	**Dr. Patrice Baldeck,** ENS, Lyon, **France**
10:30 - 11:00	**Coffee Break / Posters Session I**	**Coffee Break Area**
11:00 - 11:40	Emerging metasurface technologies and the role of simulations in their development **L. Pennik**	**Dr. Lieven Pennik,** PlanOpSim, **Belgium**
11:40 - 12:00	Tiny fiber Sensors by laser processing **J.M. López-Higuera**	**Prof. José Miguel López-Higuera**, University of Cantabria, **Spain**
12:00 - 12:20	Optical grade microsctructure fabrication through injection molding techniques **F. Gontad**	**Dr. Francisco Gontad,** AIMEN Technology Centre, **Spain**
12:20 - 12:40	Novel methods to prepare photoelectrodes for solar fuels **S. Eslava**	**Dr. Salvador Eslava, University of Bath, UK**
12:00 - 14:00	**Lunch Break**	**Restaurant**

October 23, 2019
EGF 2019 - Session I
Graphene Synthesis, Growth, Functionalization and Characterization

Conference Room Obidos A

Session's Chairs:
Prof. Pedro Alpium, International Iberian Nanotechnology Laboratory, Portugal
Prof. Paula Pereira Marques, University of Aveiro, Portugal
Prof. Eva Rauls, University of Stavanger, Norway

14:30 - 15:00	NanoSonic - Graphenest NanoSonication Technology Clean graphene nanoparticles production for application across electronics, aerospace and textile industries A. Bernardes, R. Silva, **B. Figueiredo**, J. França and V. Abrantes	**Mr. Bruno Reis Figueiredo**, Graphenest – Advanced Nanotechnology, **Portugal**
15;00 - 15:15	Bias-controlled doping of graphene with thin ice: a theoretical DFT study **E. Rauls**, U. Gerstmann, A. Jaadouni and W.G. Schmidt	**Prof. Eva Rauls**, University of Stavanger, **Norway**
15:15 - 15:30	Soliton fractional charges in graphene nanoribbon and polyacetylene: similarities and differences **S.-R. Eric Yang**	**Prof. S.-R. Eric Yang**, Korea University, **Rep. of Korea**

15:30 - 15:45	Simulation and Growth of Graphene for Silicon Microeletronic Applications **G. Lippert**, J. Dabrowski, A. Becker, M. Lisker, Ch. Wenger, A.Mai and M. Lukosius	**Dr. Gunther Lippert**, IHP – Leibniz-Institut für innovative Mikroelektronik, **Germany**
15:45 - 16:00	Graphene Oxide as the Catalyst of Ethane Dehydrogenation **A.A. Abakumov**, I.B. Bychko and P.E. Strizhak	**Mr. Alexander Abakumov**, L.V. Pisarzhevsky Institute of PhysicalChemistry, **Ukraine**
16:00 - 16:30	**Coffee Break / Posters Session I**	**Coffee Break Area**
16:30 - 16:45	Catalytic activity of carbon nanomaterials in the ethylene and acetylene hydrogenation **I. Bychko** and P. Strizhak	**Dr Igor Bychko**, L. V. Pisarzhevsky Institute of Physical Chemistry, **Ukraine**
16:45 - 17:00	Improving Mechanical Properties of Carbon Fiber Reinforced Epoxy Polymer Composite with Carbon Nanotubes **K. Yüceer** and D. Çöker	**Ms. Kevser Yüceer**, Middle East Technical University,**Turkey**
17:00 - 17:15	Analytical approach for nonlinear optical selection rules of excitons in monolayer transition metal dichalcogenides **A. Taghizadeh** and T. G. Pedersen	**Dr. Alireza Taghizadeh**, Aalborg University, **Denmark**
17:15 - 17:30	Exploration of Graphene for the Improvement of Plasma Facing Components in Fusion Plasmas **M. Navarro**, M. Zamiri, K. Hall, R. Doerner, O. Schmitz, M. Lagally, J. Santarius and G. Kulcinski	**Dr. Marcos Navarro**, University of Wisconsin-Madison, **USA**
17:30 - 17:45	Graphene properties from curved space Dirac equation **A. Gallerati** and F. Laviano	**Dr. Antonio Gallerati**, Politecnico di Torino, **Italy**
17:45 - 18:00	Identification of Active Electrocatalytic Sites Using Electrochemi-cal Scanning Tunneling Microscopy **R.M. Kluge**, R.W. Haid and A.S. Bandarenka	**Ms. Regina Kluge**, Technical University of Munich**, Germany**
18:00 - 18:15	Monitoring Folds and Strain Localization in 2D Transition Metal Chalcogenides (TMDCs) using Second Harmonic Generation **A. R. Khan** and Y. Lu	**Mr. Ahmed Raza Khan**, Australian Nat. University, Canberra **Australia**
18:15 - 18:30	Novel Economic Simple Strategy for Mass Synthesis of Nitrogen-doped Graphene: Controllable Growth Mechanism and Structure **M. A. A. Mohamed**, F. Carrasco-Marín, N. A. Elessawy and H. A. F. Hamad	**Dr. Marwa Mohamed**, City of Scientific Research and Technological Applications, **Egypt**
18:30 -18:45	Homogeneous Anti Corrosion Coating of Spontaneously Dissolved Defect Free Graphene **M. Bin Subhan**, P. Cullen and C. Howard	**Dr. Mohammed Bin Subhan**, University College London, **UK**

October 23, 2019
SMS 2019 - Session I
Smart coatings and surfaces

Conference Room Obidos B

Session's Chairs:
Prof. Mario G.S. Ferreira, University of Aveiro, Portugal
Prof. Jean-Manuel Raimundo, Aix Marseille University, France
Prof. Monika Walesa-Chorab, Adam Mickiewicz University-Poznan, Poland

14:00 – 14:15	Supported lipid monolayers as sensing and selective layers for ISFET sensors V. Kilinc, T. Nguy, A. Kenaan, S. Lamant, C. Henry-de-Villeneuve, G. Monier, M. Petit, Y. Wakayama, **J. M. Raimundo** and A. Charrier	**Prof. Jean-Manuel Raimundo**, Aix Marseille University, **France**
14:15 – 14:30	Polyvinyl alcohol / barium titanate composite films: filler content, particle size and surface modification effects on dielectric-electrical properties **K. Gille**, C. Lapeyronie, S. Scheffler, M. Rajaoarivelo, W. Neri, A. Bentaleb, I. Ly, A. Derré, J. Yu-an, P. Poulin and C. Jaillet*	**Dr. Christèle Jaillet,** CRPP-CNRS- University of Bordeaux, **France**

14:30 – 14:45	Smart corrosion inhibition and structural effect of lithium in PMMA-silica coatings **A. Trentin**, K. Marcoen, S. V. Harb, M. C. Uvida, C. V. Santilli, H. Terryn, T. Hauffman and P. Hammer	**Ms. Andressa Trentin**, São Paulo State University, **Brazil**
14 :45-15 :00	High-rate deposition of high-quality oxide layers using reactive high-power impulse magnetron sputtering **J. Rezek**, J. Houška and J. Vlček	**Dr. Jiri Rezek**, University of West Bohemia, **Czech Republic**
15:00 – 15:15	Multifucnctional Smart Materials for the Corrosion Inhibition of Metal Artefacts **C. Giuliani**, G. Di Carlo, C. Riccucci, M. Pascucci, E. Messina and G. M. Ingo.	**Dr. Chiara Giuliani**, Institute of nanostructured materials/ CNR-Rome, **Italy**
15:15 – 15:30	Electrochromic thin films – methods of preparation and properties **M. Wałęsa-Chorab**	**Prof. Monika Walesa-Chorab**, Adam Mickiewicz University-Poznan, **Poland**
15:30 – 15:45	Robust and versatile grafted bacteriostatic polymer surfaces based on ionenes **S. Bernardi**, M.N. Bellon-Fontaine and G. Carrot	**Ms. Sarah Bernardin**, CEA/ Paris-Saclay University, **France**
15:45- 16:00	Innovative polymer coatings for packaging **V. Beghetto**, V. Gatto, S. Conca, N. Bardella and R. Samiolo	**Dr. Valentina Beghetto**, University Ca' Foscari of Venice, **Italy**
16:00 – 16:30	**Coffee Break / Posters Session I**	**Coffee Break Area**
16:30-16:45	Development of repellent surfaces **A. Antelava**, A. Wojdyła-Cieślak, G. Durand, A. Constantinou and A. Taylor	**Ms. Ana Antelava**, London South Bank University, **United Kingdom**
16:45-17:00	Photochemically Initiated Conversion of Coordination Compounds – A Low Temperature Route to Metal Oxide Thin Films **P. With**, J. Lehnert, L. Seifert, S. Dietrich, H. Krautscheid, S. Naumov, A. Prager, G. Mirschel, L. Prager and U. Helmstedt	**Dr. Patrick With**, Leibniz Institute of Surface Engineering (IOM), **Germany**

October 24, 2019 SMS 2019/ EGF 2019 Joint Plenary Session		
Conference Room Porto		
Session's Chairs: **Prof. Michael Sinapius, Technische Universität Braunschweig, Germany** **Dr. Christos Riziotis, National Hellenic Research Foundation, Greece** **Prof. José Miguel López-Higuera, University of Cantabria, Spain**		
09:00 - 09:30	Applications in Nanotechnology of Focused Electron and Ion Beam Induced Deposition **J. M. De Teresa**	**Prof. Jose María De Teresa Nogueras**, University of Zaragoza, **Spain**.
09:30 - 10:00	Multifunctional Adaptive Sandwich Structures: Modeling and Optimization **A.L. Araújo**	**Prof. Aurelio Araujo**, University of Lisbon, **Portugal**
10:00 - 10:30	Adsortion of sodium diclofenac in aqueous medium using graphene oxide nanosheets A.C.S. Guerra, M.B. de Andrade , T.R.Tonial dos Santos, N.C. Homem, M.F. Vieira, A.M.S.Vieira, R. G. Gomes, F.de Jesus Bassetti, **M.T.S. Pessoa Amorim** and R. Bergamasco	**Prof. Maria Teresa Amorim**, Minho University, **Portugal**
10:30 - 11:00	**Coffee Break / Posters Session II**	**Coffee Break Area**
11:00 - 11:30	Novel Power Generator using Dielectric Elastomers **S. Chiba**, M. Waki and K. Fujita	**Prof. Seiki Chiba**, Chiba Science Institute, **Japan**
11:30 - 12:00	Active Composite Materials for 4D-printed Structures **M. Sinapius** and R. Mitkus	**Prof. Michael Sinapius,** Technische Universität Braunschweig, **Germany**
12:00 - 12:30	Free-standing nanostructures at Atomic Scale: from growth mechanisms to properties S. Martí-Sánchez, M. Botifoll, C. Koch and **J. Arbiol**	**Prof. Jordi Arbiol,** ICREA and ICN2, CSIC and BIST, Catalonia**, Spain**
12:00 - 14:00	**Lunch Break**	**Restaurant**

October 24, 2019 SMS 2019 / EGF 2019- Joint Session II Novel Materials / Graphene for Energy and Environment applications		
Conference Room Porto		
Session's Chairs: **Prof. Seiki Chiba, Chiba Science Institute, Japan** **Prof. Michael Sinapius, Technische Universität Braunschweig, Germany** **Dr. Adela I. Carrillo Gomez, ERC Executive Agency- Brussels, Belgium**		
14:00 - 14:30	Engineering photoanodes for photoelectrochemical solar water splitting **S.Eslava**	**Dr. Salvador Eslava,** University of Bath, **UK**
14:30 - 15:00	European Research Council session **A. I. Carrillo Gomez**	**Dr. Adela I. Carrillo Gomez,** ERC Executive Agency, Brussels, **Belgium**
15:00 - 15:30	A dream that became reality with the help of ERC! **E. Fortunato**	**Prof. Elvira Fortunato**, New Univ. of Lisbon, **Portugal**
15:30 - 16:00	The need of sustainable materials for flexible electronics **E. Fortunato**	**Prof. Elvira Fortunato**, New Univ. of Lisbon, **Portugal**
16:00 - 16:30	**Coffee Break / Posters Session II**	**Coffee Break Area**
16:30 - 16:45	Better in Vacuum - how vacuum can improve investigation of 2D materials using conductive Atomic Force Microscopy (AFM) **R.Bourrelier**, J;Ludwig, M.Mascaro, U.Celano, I.M. Hermes, A W. Vandervorst and K.Paredis	**Dr. Romain Bourrelier**, Park Systems France SARL, Orsay, **France**

16:45 - 17:00	Buckled MoS2 nanoribbons for bistable vibration energy harvesters **G. Abadal**, R. López and X. Cartoixà	**Dr. Gabriel Abadal**, Autonomous University of Barcelona, **Spain**
17:00 - 17:15	Electric charges recovering from aqueous media using conductor oxides **V. Ledoux** and A. Evstratov	**Dr. Valentin Ledoux**, Institut Mines-Telecom Mines Alès, **France**
17:15 - 17:30	Bio-inspired microshapes converted to functional materials for catalysis and photovoltaics **H.C. Hendrikse**, L. Helmbrecht, A. van der Weijden, M. Ronda Llorett and W.L. Noorduin	**Mr. Hans Hendrikse,** AMOLF, **The Netherlands**
17:30 - 17:45	Size-dependent Electronic Properties of Strongly Confined Graphene Quantum Dots and their Application in Electrochromic and Photovoltaic Devics Z. Ji, E. Dervishi, S. K. Doorn and **M. Sykora**	**Dr. Milan Sykora**, Comenius University, **Slovakia**
17:45 - 18:00	Printed electrolyte-gated field-effect transistors from graphene oxide formullations electrochemical tuning of charge transport S. Vasilijević, **N. Battaglini**, G. Mattana, G. Anquetin and B. Piro	**Dr. Nicolas Battaglini**, ITODYS, University Paris Diderot, **France**
18:00 - 18:15	Soft Transducers having Stretchable & Flexible CNT Electorodes **M. Takeshita**, S. Chiba, M. Waki, M. Uejima and K. Arakawa	**Mr. Makoto Takeshita**, Zeon Corporation-Tokyo, **Japan**
18:15 - 18:30	Graphene flake with an adatom illuminated by an optical pulse **M. Kosik**, M. Pelc, M. Müller, C. Rockstuhl, K. Słowik and A. Ayuela	**Ms. Miriam Kosik**, Nicolaus Copernicus University, **Poland**
18:30 - 18:45	Graphene Radio-Frequency Transistors with Self-Aligned Channel and Core-Shell Nanowire Gate **V. Silva**, L. Baptista, J. Borme, C.-D. Liao, P. Mendes and P. Alpuim	**Mr. Vitor Silva**, University if Minho, **Portugal**

October 24, 2019

SMS 2019 Session II

Smart sensors, smart Textiles, wearables & Internet of things

Conference Room Obidos A

Session's Chairs:
Prof. Aurelio Araujo, University of Lisbon, Portugal
Prof. Kaspar Jansen, Delft University of Technology, The Netherlands
Prof. Maria Teresa Amorim, Minho University, Portugal

14:00 - 14:30	Smart Sensors using Light technologies: a comprehensive vision **J.M. López-Higuera**	**Prof. José Miguel López-Higuera**, University of Cantabria, **Spain**
14:30 - 15:00	Engineering Photonic Structures and Functional Materials Towards Smart Physical and Chemical Sensors **C. Riziotis**	**Dr. Christos Riziotis**, National Hellenic Research Foundation, **Greece**
15:00 - 15:15	Printed Electrodes for Hot Electron Electrochemistry Applications **S. Kulmala**, P. Grönroos, K. Salminen and N. E-Habiba	**Prof. Sakari Kulmala**, Aalto University, **Finland**
15:15 - 15:30	Combinatorial Gas Phase Electrodeposition for Fabricating Multimodal Three Dimensional Nano-Bridge Gas Sensors **N. A. Isaac**, L. Schlag, J. Reiprich, S. Katzer, H. Nahrstedt, J. Pezoldt, T. Stauden and H. O. Jacobs	**Mr. Nishchay Angel Isaac**, Technische Universität Ilmenau, **Germany**
15:30 - 15:45	Challenges and Opportunities in Reproducible Electrochemical Ink Formulation and Processing for Multiplexed Designs **N. Broughton**, D Barwick, R. Kadara and B. Bender,3	**Ms. Nicola Broughton**, Centre for Process Innovation- Wilton, **UK**
15:45 - 16:00	Incorporating Functionalized Polydiacetylene in Alginate Beads For Bacterial Detection **A. Al Choueiry**, M. Bassil, E. El Kaady, G. Moarbess and M. El Tahchi	**Dr. Antoine Al Choueiry**, Lebanese University, **Lebanon**
16:00 - 16:30	**Coffee Break / Posters Session II**	**Coffee Break Area**

16:30 - 16:45	Smart sensors based on structural embossing and supramolecular controlled order loss **Y. Foelen**, D.A.C. Van Der Heijden and A.P.H.J. Schenning	**Mr. Yari Foelen**, Eindhoven University of Technology, **The Netherlands**
16:45 - 17:15	The next generation of Smart Textiles **K.M.B. Jansen**	**Prof. Kaspar Jansen**, Delft University of Technology, **The Netherlands**
17:15 - 17:30	Development of Flexible Textile Aluminium-Air Battery Prototype A. Vališevskis, U. Briedis, **M. Carvalho** and F.Ferreira	**Prof. Miguel Carvalho**, University of Minho, **Portugal**
17:30 - 17:45	Connecting the world to garments – capturing, filtering, defining, translating, mapping and actuating in, on and off the textile **E. Lindell**, L. Guo, R. Holt, Z. Ling, E Kontopoulos and N-K. Persson	**Ms. Eva Lindell**, University of Borås, **Sweden**
17:45 - 18:00	Towards responding fabrics – textile processing of thin threadlike pneumatic actuators C. Backe, L. Guo, E.W.H. Jager and N-K. Persson	**Ms. Carin Backe**, University of Borås, **Sweden**
18:00 - 18:15	Towards the development of smart textile wound dressings using temperature an pH responsive hydrogel **D. Štular**, I. Jerman, B. Simončič and B. Tomšič	**Dr. Danaja Stular**, University of Ljubljana, **Slovenia**
18:15 - 18:30	Untethered stimuli-responsive liquid crystal polymer actuators **M. Pilz da Cunha**, M. G. Debije and A.P.H.J. Schenning	**Ms. Marina Pilz da Cunha**, Eindhoven Uni. of Tech., **The Netherlands**
18:30 - 18:45	Towards measuring flexoelectric coefficient of single carbon nanotubes **R. El Beainou**, J.-Y. Rauch, S. Dembélé, O. Lehmann, L. Hirsinger and M. Devel	**Dr. Raya El Beainou**, FEMTO-ST Institute-Besançon, **France**

October 24, 2019

NanoMed 2019 / EGF 2019 Joint Plenary session

Bioinspired materials/ Nanotechnology in Therapy / Pharmaceutical Nanotechnology

Conference Room Obidos B

Session's Chairs:
Prof. Nuno Santos, iMM- Lisbon, Portugal
Dr. Silvia Panseri, ISTEC-CNR, Italy
Prof. Susana G. Santos, i3S - INEB, University of Porto, Portugal

09:00 - 09:30	Graphene surfaces for detection of biomolecules **P. Alpium**	**Prof. Pedro Alpuim,** Intl. Iberian Nanotechnology Lab., **Portugal**
09:30 - 10:00	Graphene-based sheets for biomedical applications: case studies. **Paula A. A. P. Marques**	**Prof. Paula Pereira Marques,** University of Aveiro, **Portugal**
10:00 - 10:30	Challenges on Graphene-Based Nanomaterials in Nanomedicine **D. Iannazzo**	**Prof. Daniela Iannazzo**, University of Messina, **Italy**
10:30 - 11:00	**Coffee Break / Posters Session II**	**Coffee Break Area**
11:00 - 11:30	Measuring forces at the nanoscale for cardiovascular risk evaluation **N. Santos**	**Prof. Nuno Santos**, iMM-Lisbon, **Portugal**
11:30 - 11:45	Proton stimulation therapy for iron-oxide mineral forming Alzheimer's disease **J.K. Kim**, Y. Choi and J.-G. Jeon	**Prof. Jong-Ki Kim**, Catholic University of Daegu, **Rep. of Korea**
11:45 - 12:00	Radiolabelled Gold Nanoparticles for Image-guided Chemoradiotherapy of Glioblastoma Multiforme **A. Paulo**, A. Belchior, A. D'Onofrio, C. Mendes, C. Oliveira, F. Marques, F. Silva, M. P. C. Campello, Lurdes Gano, M. Ravera and P. Raposinho	**Dr. Antonio Paulo**, Technical Superior Institute-Lisbon, **Portugal**
12:00 - 14:00	**Lunch Break**	**Restaurant**

October 24, 2019, 13:45 - 13:55
Conference Group Photo
At the conference venue
All conference participants are requested to be present for the Conference Group Photo

October 24, 2019 NanoMed 2019 - Session II: Nanotechnology in Therapy / Pharmaceutical Nanotechnology		
Conference Room Obidos B		
Session's Chairs: **Prof. Pedro Alpuim, International Iberian Nanotechnology Laboratory, Portugal** **Prof. Paula Pereira Marques, University of Aveiro, Portugal** **Prof. Daniela Iannazzo, University of Messina, Italy**		
14:00 - 14:30	NanoMedicine, Science & Regulation: the translation issues for the next generation of technologies **R. Gaspar**	**Prof. Rogerio Gaspar,** University of Lisbon, **Portugal**
14:30 - 15:00	Ceramic biomaterials instruct cell behavior in regenerative medicine **S. Panseri**	**Dr. Silvia Panseri**, ISTEC-CNR, **Italy**
15:00- 15:30	Nanomaterials for and from immune cells: nanoparticles and extracellular vesicles **S. G. Santos**	**Prof. Susana G. Santos**, i3S - INEB, University of Porto, **Portugal**
15:30 - 15:45	Gellan Gum-based In-situ Gelling Systems containing Self-Assembling Mixed Nanomicelles: A Novel combined system for the Ocular Delivery of Cyclosporine-A **E. Terreni**, E. Zucchetti, D. Monti, S. Burgalassi, S. Tampucci and P. Chetoni	**Dr. Eleonora Terreni**, University of Pisa, **Italy**
15:45 - 16:00	Development of bio-based hybrid microparticles as poorly water-soluble drug delivery systems **K. Doufène**, V. Lapinte, J-J. Robin, J. Chopineau, J-M. Devoisselle, C. Tourné-Péteilh and A. Aubert-Pouëssel	**Mr. Koceïla Doufène**, ICGM, Univ Montpellier, **France**
16:00 - 16:30	**Coffee Break / Posters Session II**	**Coffee Break Area**
16:30 - 16:45	Carbon nanotubes as a scaffold for hESC differentiation toward photoreceptor precursor cells **Y.Chemla** , E.Shawat , A. Markus, Y. Kostikov, F. Nairouz, S. Aviad.slotky, D.Nessim and Y.Mandel	**Mr. Yoav Chemla**, Bar ilan University, **Israel**
16:45 - 17:00	Synthesis and preliminary biological evaluations of PSMA-targeted NIR upconverting nanoparticles for optical/scintigraphic imaging of prostate cancer **A. Cordonnier**, D. Boyer, S. Besse, A. Briat, F. Degoul, R. Mahiou, A. Maisonial-Besset, B. Maunit, L. Mazuel, M. Quintana, M. Vivier, E. Miot-Noirault and J-M. Chezal	**Mr. Axel Cordonnier,** Clermont Auvergne University, **France**
17:00- 17:15	A rational approach towards breast cancer treatment **E. Costa**, C.O. Silva, M. Cardoso, P. Faísca, C. Pinto Reis, A.S. Cabrita and I.V. Figueiredo	**Dr. Eduardo Costa**, University of Coimbra, **Portugal**
17:15 - 17:30	Magnetic microparticles for magneto-mechanical treatment of glioblastoma cells **C. Thébault**, C. Naud, E. Billiet, H. Joisten, M. Carrière, B. Dieny, Y. Hou and, R. Morel	**Dr. Caroline Thebault**, Univ. Grenoble Alpes, **France**
17:30 - 17:45	Active Pulmonary Targeting against Tuberculosis (TB) via Triple–Encapsulation of Q203, Bedaquiline and SPIOs in Nanoparticle Aggregates **W. Poh**, N.A.B Rahman, Y. Ostrovski, J. Sznitman, K. Pethe and S.C.Joachim Loo	**Mr. Wilson Poh**, Nanyang Technological University, **Singapore**

17:45 - 18:00	Novel Strategies Towards Surface Modification of Polymeric Biomedical Devices Based on Nylon 6 and Polycaprolactone S. Swar, **V. Máková**, B. Holubová, P. Šubrtová and J. Horáková	**Dr. Veronika Máková**, Technical University of Liberec, **Czech Republic**
18:00 - 18:15	Characterization and Modeling of Local Electronic Properties of Native Bone Tissue in Intact and Damaged Areas **A.A. Pavlychev**, X.O. Brykalova and D.O. Samoilenko	**Prof. Andrey Pavlychev**, St.Petesburg State University, **Russia**

October 24, 2019, 19:30 - 22:00

Conference Diner

At the conference venue

All conference participants are welcome to attend (subject to confirmation)

October 25, 2019 SMS 2019 - Session III: Novel Materials Biomaterials Properties and Applications		
Conference Room Obidos A		
Session's Chairs: **Prof. Andrey Pavlychev, St.Petesburg State University, Russia** **Prof. Galina Mihaleva, Nanyang Technological University, Singapore** **Dr. Christos Riziotis, National Hellenic Research Foundation, Greece**		
09:00 - 09:30	Challenges and opportunities for x-ray spectro-microscopies in magnetism and spintronics **P. Fischer**	**Dr. Peter Fischer**, Lawrence Berkeley National Laboratory, **USA**
09:30 - 10:00	From the Atomic Structure to the Optoelectronic Properties Studies of Carbon and Related Nanostructures via TEM **R. Arenal**	**Dr. Raul Arenal**, Zaragoza University, **Spain**
10:00 - 10:30	**Coffee Break**	**Coffee Break Area**
10:30 - 11:00	Supramolecular dehydropeptide hydrogels: synthesis, properties and biomedical applications **P.M. Ferreira**, J. A. Martins and E.M.Castanheira	**Prof. Paula Ferreira**, Minho University, **Portugal**
11:00 - 11:15	Mussel-inspired injectable hydrogel glue for Tissue Repair **K.Wei**, B. Senturk, M.T. Matter, X. Wu, I.K. Herrmann, M. Rottmar and C.Toncelli	**Dr. Kongchang Wei**, Empa, Swiss Federal Laboratories for Materials Science and Technology, **Switzerland**
11:15 - 11:30	Ca 2p Photoelectron Spectroscopy of Surfaces of Cortex and Subchondral Femoral Bone in Intact and Damaged Areas X.O. Brykalova, N.N. Kornilov and **A.A. Pavlychev**	**Prof. Andrey Pavlychev**, St.Petesburg State University, **Russia**
11:30 - 11:45	A new design of a petal valve designed for pulsatile heart assist pumps application, presents and future development **R. Major**, M. Gawlikowski, A. Mzyk, S. Kakinoki and J. M. Lackner	**Prof. Roman Major**, Institute of Metallurgy and Materials Science Polish Academy of Sciences, **Poland**
11:45 - 12:00	Advanced micromanufacturing strategies for the production of biomimetic and bioresorbable vascular stents and peripheral nerve implants **I.Quintana**, R.Ortiz, X.Mendibil, R.Diez and S.Merino	**Dr. Iban Quintana**, IK4-TEKNIKER, **Spain**

October 25, 2019 EGF 2019 / NanoMed 2019 Joint Session III		
Conference Room Obidos B		
Session's Chairs: **Prof. Nuno Santos, iMM- Lisbon, Portugal** **Prof. Daniela Iannazzo, University of Messina, Italy**		
09:00 - 09:15	Graphene and graphene/drug conjugates for cancer phototherapy D. Bogas, R. Costa-Almeida, C. Couto, J.R. Fernandes, M.C.L. Martins, I.C. Gonçalves, F.D. Magalhães and **A.M. Pinto**	**Dr. Artur M. Pinto**, University of Porto, **Portugal**
09:15 - 09:30	Graphene Quantum Dots for Multiphoton Imaging: Myths and Facts **E. Maçôas**, C. Santos, C. Correia, I. Mariz, S. Pinto, and J. G. Martinho	**Dr. Ermelinda Macoas,** Instituto Superior Técnico, **Portugal**
09:30 - 09:45	Graphene coated CMOS ISFETs for pH sensing **C. Panteli**, P. Georgiou and K. Fobelets	**Mr. Christoforos Panteli**, Imperial College London, **UK**
09:45 - 10:00	Antibacterial activity of polyethersulfone membranes modified with graphene oxide nanosheets **N.C. Homem**, T.D. Tavares, R. Bergamasco and M.T.P. Amorim	**Mrs. Natália Homem**, University of Minho, **Portugal**

10:00 - 10:30	Coffee Break	Coffee Break Area
10:30 - 10:45	Influencing Radiosensitizing Properties in Cancer Cells **M. Vetrik**, L. Kobera, R. Konefal, V. Lobaz, M. Hruby and G. Pratx	**Dr. Miroslav Vetrik**, Institute of Macromolecular Chemistry CAS, **Czech Republic**
10:45 - 11:00	pH-responsive ultrasound contrast agents for bio-sensing applications **J.A. Walker**, K.Kemp and S.R. Corrie	**Ms. Julia A. Walker**, Monash University, **Australia**
11:00 - 11:15	Bactericidal Titania Textiles for Hospital use **J.C. Matos**, C. Oliveira and M.C. Gonçalves	**Ms. Joana Matos**, Lisbon University, **Portugal**
11:15 - 11:30	Prospects and Challenges of Multi-Omics Data Integration in Nanotoxicology S. Canzler and **J. Hackermüller**	**Dr. Jörg Hackermüller**, Helmholtz Centre for Environmental Research-UFZ, **Germany**
11:30 - 11:45	Graphene Oxide Film and Graphene Nanoparticles with Silver Nano-particles as the Potential Bacteriostatic Ingredient of Food Packaging **K. Mitura**, J. Kornacka, J. Kalisz, E.Kopczyńska, E, Czerwińska, L.Volesky and T.Bakalova	**Dr. Katarzyna Mitura**, Koszalin University of Technology, **Poland**
11:45 - 12:00	Challenges on graphene oxide film in the food package system K. Mitura, E. Kopczyńska, J. Kornacka, J. Kalisz, E. Czerwińska and **E. Ziółkowska**	**Ms. Elzbieta Kopczynska**, Koszalin University of Technology, **Poland**

October 23, 2019
SMS 2019 / EGF 2019 / NanoMed 2019 - Joint Posters Session I
Synthesis / Characterization / Properties

Posters Room Cascais

N.	Title	Author, Affiliation, Country
1.	Numerical and experimental validation of SMArt thermography for the control of GFRP composite laminate M. De Giorgi, R. Nobile, and **A. Saponaro**	**Prof. Riccardo Nobile**, University of Salento, **Italy**
2.	Magnetic and Electrical Properties of postannealed Co2MnSi Heusler alloy films **G. Grigaliūnaitė-Vonsevičienė**, B. Vengalis, A. Maneikis and R. Juškėnas	**Dr. Grazina Grigaliunaite-Vonseviciene**, Vilnius Gediminas Technical University, **Lithuania**
3.	Microstructure and mechanical properties of Fe-based amorphous alloy produced using the direct metal deposition method **W. Pilarczyk**	**Prof. Wirginia Pilarczyk**, Silesian University of Technology, **Poland**
4.	Modification and characterization of VACNTs for application as water harvesting surfaces from dew and fog R.A. Pinheiro, V.J. Trava-Airoldi and **E.J. Corat**	**Dr. Evaldo Corat**, National Institute for Space Research- São José dos Campos, **Brazil**
5.	In-pack Ohmic Heating of Packaged Food Using Carbon Black Loaded Polyethylene Films **M. Gratz** and H. Jaeger	**Mr. Maximilian Gratz**, University of Natural Resources and Life Sciences (BOKU), **Austria**
6.	Structural, magnetic and electrochemical properties of AlCoCrFeNiSi high entropy alloys **R. Babilas**, A. Radoń and W. Łoński	**Dr. Rafal Babilas**, Silesian University of Technology, **Poland**
7.	Tunable and functionalizable polydopamine thin films by means of electropolymerization. **T. Marchesi D'Alvise**, S. Harvey, K. Wunderlich and T. Weil	**Mr. Tommaso Marchesi**, Max Planck Institute for Polymer Research, **Germany**
8.	The Effect of Plasma Electrolytic Polishing on the Surface Properties of Steel after Nitrocarburising **S. Kusmanov**, S. Silkin and I. Tambovskiy	**Prof. Sergei Kusmanov**, Kostroma State University, **Russia**
9.	Microstructure and Corrosion Resistance of Zn-Al-Mg Alloy Coated Steel Product and Its Applications K. Kim, S. So, I. Park, J. Yoon, **M. Oh**, Y. Jang and M. Lee	**Prof. Min-suk Oh**, Chonbuk National University, **Rep. of Korea**
10.	Modified Epoxy Coating with high Efficiency Isocyanate Micro-capsules for Corrosion Protection of Steel **M. Attaei**, L. M. Calado, M. Taryba A. C. Marques and M.F. Montemor	**Ms. Mahboobeh Attaei**, Lisbon University, **Portugal**
11.	Terbium doped calcium germinate (Ca2GeO4) as a potential candidate for LED application I. Koseva, P. Tzvetkov, P. Ivanov, **R. Tomova**, A. Yordanova and V. Nikolov	**Prof. Reni Tomova**, The Institute of Optical Materials and Technologie, **Bulgaria**
12.	Structure and luminescent properties of Eu3+ doped glass in the system WO3-La2O3-B2O3-Nb2O5 L. Aleksandrov, R. Iordanova, M. Milanova, P. Ivanov, P. Petrova and **R. Tomova**	**Prof. Reni Tomova**, The Institute of Optical Materials and Technologie, **Bulgaria**
13.	Dry Transfer of Chemical Vapor Deposition Graphene onto Silicon Wafers Treated by Silane Coupling Agents **M. Ishihara** and M. Hasegawa	**Dr. Masatou Ishihara**, National Institute of Advanced Science and Technology (AIST), **Japan**
14.	SnOx thin films using RF sputtering as transparent conductive materials **Y. Zakaria**, A. Slaoui, S. Ahzi, A. Samara, V. Bermudez Benito and S. Mansour	**Mr. Yahya Zakaria**, Hamad Bin Khalifa University, **Qatar**
15.	The Barrier and Electrochemical Properties of CVD Graphene on Metallic Substrates **P. Ozga**, A. Hara, Z. Świątek and J. Pstruś	**Dr. Piotr Ozga**, Polish Academy of Sciences, **Poland**
16.	Graphene surface analysis and layer counting using scanning low energy electron microscopy **L. Průcha**, J. Piňos, M. Kizovský and E. Mikmeková	**Mr. Lukas Prucha**, Institute of Scientific Instruments of the CAS, **Czech Republic**

17.	Adjustable Hydrogenation of Monolayer Graphene Depending on Back-Gate Voltage **H.Choi** and J.Hong	**Ms. Harim Choi**, Yonsei University, **Rep.of Korea**
18.	Low contact resistance for graphene on Pt bottom electrode and its effects on device performance **J.Cha**, J. Son and J. Hong	**Mr. Jongin Cha**, Yonsei University, **Rep. of Korea**
19.	Plasmon-enhanced Substrates for the Super-resolution Fluorescence Imaging C-Y.Lin, G. Abrigo and **F-C. Chien**	**Mr. Fan-Ching Chien**, National Central University, **Taiwan**
20.	Synthesis of silver nanoparticles and nanocomposites with unique structure and optical properties by UV-irradiation method **A. Radoń**	**Mr. Adrian Radoń**, Silesian University of Technology, **Poland**
21.	SbSI nanowires composites for energy harvesting and sensors **B. Toroń**. P. Szperlich, M. Jesionek, M. Kozioł and M. Nowak	**Dr. Bartłomiej Toroń**, Silesian University of Technology, **Poland**
22.	Density Functional Study of Two Dimensional Monolayer PtX2[X= S, Se and Te]. **H. Alaqi** and W.A.Diery	**Ms. Hadeel Alaqi**, King Abdulaziz University, **Saudi Arabia**
23.	EIS Characterization of Passive Films Formed on AlxCoCrFeNi Alloys **M.López Ríos**, N.Florido Suárez, I.Voiculescu, V.Geanta and J.C.Mirza Rosca	**Dr. Miguel Lopez**, Las Palmas de Gran Canaria University, **Spain**
24.	Effects of Nickel Content on the Microstructure, Microhardness and Corrosion Behavior of High-entropy AlCoCrFeNix Alloys **M.López Ríos**, P.P.Socorro Perdomo, V.Lucero Baldevenites, I.Voiculescu, V.Geanta and **J.C.Mirza Rosca**	**Dr. Miguel Lopez**, Las Palmas de Gran Canaria University, **Spain**
25.	Thin ice under pressure on graphene: a theoretical NMR study A. Jaadouni, E. Rauls, W.G. Schmidt and **U. Gerstmann**	**Dr. Uwe Gerstmann,** University of Paderborn, **Germany**

October 24, 2019 SMS 2019 / EGF 2019 / NanoMed 2019 – Joint Posters Session II Properties and applications		
Posters Room Cascais		
1.	Morphology and growth of carbon nanotubes synthesis by impinging flame **L. Marques**, A. Duarte and E. Fernandes	**Dr. Luísa Marques,** Techcinal superior institute Lisbon, **Portugal**.
2.	Investigation of Polyoxometalate-Silica Thin Films for Chemical Gas Sensors **S. Krutovertsev**, L. Krutovertseva and O. Ivanova	**Dr. Sergey Krutovertsev**, JSC "Ecological sensors and systems", **Russia**
3.	Piezotronics effects in Schottky diodes fabricated in AlGaN/GaN heterstructures **B.K. Paszkiewicz**, B. Paszkiewicz, M. Wosko and **R. Paszkiewicz**	**Prof. Bogdan Paszkiewicz,** ,Wroclaw University of Science and Technology, **Poland**
4.	Redox peptide film as platform for C-Reactive protein immunosensors J.P. Piccoli, A.C.Soares, O.N. Oliveira, P.R. Bueno and **E.M. Cilli**	**Prof. Eduardo Cilli**, São Paulo State University, **Brazil**
5.	Graphene and Graphene Derivates-based Gas Sensors: State of the Art and Realistic Outlook **S. Luby** and J. Ivanco	**Prof. Stefan Luby**, Slovak Academy of Sciences, **Slovakia**
6.	Novel Type of SnO2 Rheotaxially Grown and Vacuum Oxidated Films for NO2 Sensing at Room Temperature **B. Lyson-Sypien** and M. Kwoka	**Dr. Barbara Lyson-Sypien**, Silesian University of Technology, **Poland**
7.	Surface Modification of Biodegradable Magnesium Mesh for Guided Bone Regenration by Hydrothermal Treatment **Y. Jang**, I. Park, S. Wu, M. Lee, J. Ji, M. Oh and J. Yoon	**Dr. Yong-Seok Jang**, Chonbuk National University, **Rep. of Korea**
8.	Material and Biological Characteristics for Scaffold composed of Tooth and Tricalcium Phosphate Powders **M. Lee**, J. Gong, Y. Jang, I. Park, J. Ji and T. Bae	**Prof. Min-Ho Lee**, Chonbuk National University, **Rep. of Korea**
9.	Chitosan/ Hydroxyapatite/Magnetite Biocompatible Scaffolds for Bone Tissue Engineering **A. Pistone**, D. Iannazzo, C. Celesti, E. Piperopoulos, D. Ashok, A. Cembran, A. Tricoli and D. Nisbet	**Prof. Alessandro Pistone**, University of Messina, **Italy**
10.	Effects of Magnetic Nanoparticles and External Magnetic Fields on Glioblastoma Wnt Signaling Pathway **S.H.Yang**, Y. Choi, M. Park, H.W. Rho, H-Y. Son and Y-M. Huh	**Mr. Seung Hyun Yang**, Yonsei University-Seoul, **Rep.of Korea**
11.	Cell-penetrating Peptides and their Influence on Polyomavirus-based Nanosystems **M. Hubalek Kalbacova**, J. Vanova, A.Hejtmankova, J. Zackova Suchanova, P. Sauerova, J. Forstova and H. Spanielova	**Prof. Marie Hubalek Kalbacova**, Faculty of Medicine- Chareles University, **Czech Republic**
12.	Drug-carrying gold-iron nanowires for local treatment of glioblastoma multiforme **J. M. Taylor**, M. Williams, M. P. Ryan and A. E. Porter	**Mr. Jonathan Taylor**, Imperial College London, **UK**
13.	Methylene blue-loaded PLGA nanoparticles as adjunct in periodontal antimicrobial photodynamic therapy **C.R.Fontana**, J.S. M Giusti, N.S. Soukos, M.M. Amiji and V.S. Bagnato	**Prof. Carla Fontana,** Universidade Estadual Paulista (UNESP), **Brazil**
14.	Properties of Ion Pair Amphiphile Complexes as Possible Drug Delivery Systems **J. Krouská**, M. Havlíková, J. Szabová, L. Mravcová, C.-H. Chang and F. Mravec	**Dr. Jitka Krouska,** Brno University of Technology, **Czech Republic**
15.	Solid Lipid Nanoparticles for Topical Antiseptic Delivery and Release in Wound Healing **M. Rysová**, H. Tománková, M. Schaabová, M. Buzgo and T. Zajíc	**Ms. Miroslava Rysova**, Technical University of Liberec, **Czech Republic**
16.	AT101-loaded cubosomes: translational diffusion investigated with NMR technique and in vitro therapeutic efficiency **D.K. Flak**, V. Adamski, G. Nowaczyk, K. Szutkowski, M. Synowitz, J.Held-Feindt and S. Jurga	**Dr. Dorota K. Flak**, Adam Mickiewicz University Poznań, **Poland**

17.	Electrochemical immunosensors for detection of drug resistant bacterial infection **R. Grinyte**, B. Pérez-López, J.L. Muñoz-Gomez, M. McConnell, J. Dominguez, J.J. Infate, J. M. Cabot and M. Masa	**Dr. Ruta Grinyte**, Technological Center LEITAT, **Spain**
18.	Fabrication and characterization of micro/nanofibrous scaffolds made using drawing method and its application for tissue engineering **A. Shynkarenko**, D. Azulay, S. Hauzerova, A. Klapstova, M. Moucka and D. Lukas	**Mr. Andrii Shynkarenko**, Technical University of Liberec, **Czech Republic**
19.	Combined silk fibroin/nanohydroxyapatite scaffold with antibiotic addition for bone regeneration **D.Polakova**, I.Vichova, M. Schaabova, P. Kejzlar, L. Martinova and M.Rysova	**Mrs. Dagmar Polakova**, Technical University of Liberec, **Czech Republic**
20.	Novel nanofibers from polyamide/polyethylenimine for enzyme immobilization **M.Maryšková**, **M.Schaabová**, H.Tománková, V.Novotný and M.Rysová	**Dr. Marketa Schaabova**, Technical University of Liberec, **Czech Republic**
21.	DNA Tetraplex-based Biosensors for Cell Analysis **A. Dembska**, A. Świtalska, A. Fedoruk-Wyszomirska and B. Juskowiak	**Dr. Anna Dembska**, Adam Mickiewicz University, **Poland**
22.	Wrapping, Inhibition and Adsorption of Bacteria by Polycationic Graphene Sheets via Electrostatic Attraction O. Wagner, **R. Ahmed**, L. C. Camacho, A. Vaishampayan, D. Wight, E. Grohmann and R. Haag	**Mr. Rameez Ahmed**, Freie University Berlin, **Germany**
23.	Environmentally-friendly reduced graphene oxide functionalized with hyaluronic acid for targeted cancer photothermal therapy **R. Lima-Sousa**, D. de Melo-Diogo, C. G. Alves, E. C. Costa, P. Ferreira, R. O. Louro, A. G. Mendonça and I. J. Correia	**Ms. Rita Lima-Sousa**, University of Beira Interior, **Portugal**
24.	POxylated Graphene Oxide for cancer phototherapy and combina-torial drug delivery **D. de Melo-Diogo**, E. C. Costa, C. G. Alves, R. Lima-Sousa, P. Ferreira, R. O. Louro and I. J. Correia	**Dr. Duarte de Melo-Diogo**, University of Beira Interior, **Portugal**

SMS 2019 / EGF 2019
Plenary session I

Smart Nano-Structured Coatings for Corrosion Protection, Anti-Fouling and Sensing

Mário G.S. Ferreira

Department of Materials and Ceramic Engineering / CICECO, University of Aveiro, Campus Santiago, 3810-193 Aveiro, Portugal

Abstract:
The active corrosion protection of metallic substrates can be achieved by addition of corrosion inhibitors to protective coatings. However, direct mixing of an inhibitor with coating formulations can lead to important drawbacks decreasing barrier properties of the coating and diminishing activity of the inhibitor. Also, soluble inhibitors can cause phenomena like osmotic blistering or be leached out spontaneously to the environment, which limits long-term performance and is environmentally pernicious. To overcome this problem and achieve controlled release of inhibitor different strategies of inhibitors storage in nanocontainers have been developed in order to produce smart self-healing coatings. In this work novel protective nanostructured coatings with self-healing ability are presented. This effect is obtained based on nanocontainers that release entrapped corrosion inhibitors in response to local pH changes or presence of corrosive species. The development of new nanocontainers for organic and inorganic corrosion inhibitors achieved is described, especially the most promising from industrial point of view, based on Layered Double Hydroxides (LDH). The combination of different nanocontainers in the same coating system has proved to be effective to accomplish further functions as antifouling and sensing.

Keywords: smart coatings, corrosion, protection, anti-fouling, self-healing, inhibitors, nanocontainers, LDH, sensing.

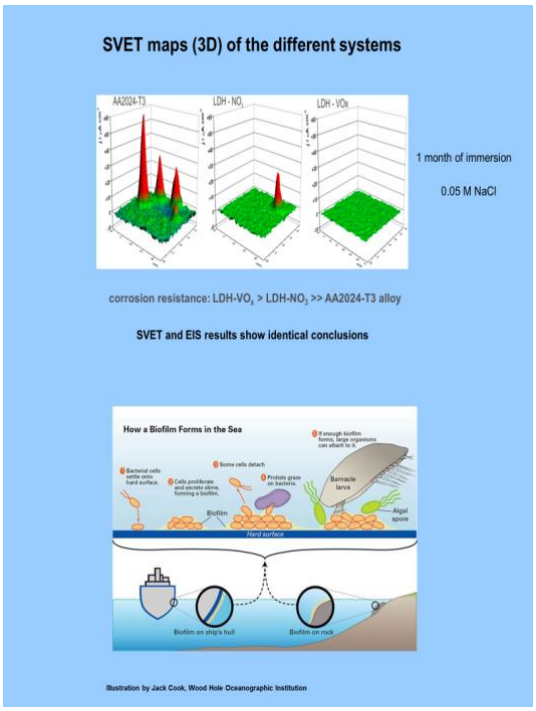


Figure 1. SVET maps of AA2024 alloy in NaCl solution and in presence of inhibitor containing LDH (upper part) and biofilm formation in seawater (lower part).

References:

1. J. Tedim, S. K. Poznyak, A. Kuznetsova, D. Raps, T. Hack, M. L. Zheludkevich and M. G. S. Ferreira (2010) *ACS Appl. Mater. Interfaces*, 2, 1528.
2. F. Maia, A.P. Silva, S. Fernandes, A. Cunha, A. Almeida, J. Tedim, M.L. Zheludkevich, M.G.S. Ferreira (2015) *Chemical Engineering Journal*, 270, 150.
3. Maia, F., Tedim, J., Bastos, A.C., Ferreira, M.G.S., Zheludkevich, M.L (2013) *Nanotechnology*, 24, 415502 (9pp)

NEW THERMOSETS FROM IONIC LIQUIDS

S.Livi, S. Pruvost, J.F. Gérard, J.Duchet-Rumeau
IMP UMR CNRS 5223 Université de Lyon – INSA Lyon, F-69621 Villeurbanne (France)

Abstract:
Thermoset polymers such as epoxies are widely used as matrices of fiber-reinforced composites, coatings, encapsulants, and adhesives in aerospace, aeronautics, automotive industry, etc. Nanostucturation of those polymer networks allows to design high performances materials as combined functionalities could be introduced at nanoscale. Recently, ionic liquids appear as new attractive additives within polymers, in particular thanks to their excellent properties such as low volatility, their non-flammability, their good ionic conductivity, their excellent thermal stability as well as their versatility. It becomes possible to tune the affinity with the polymer matrix by the control of the chemical nature of the counteranion and/or the cation. In this talk, different routes of the use of ionic liquids within epoxy networks will be described [1]: i) as a promoter of epoxy polymerization by replacing the conventional hardener. ILs were considered to be inserted in the network from its participation to the cationic polymerization of epoxies or from the synthesis of epoxy-functionalized ionic liquids which can be copolymerized with diamines [2-5], ii) as an additive of nanostructuration in polymer networks from a (nano)phase separation process alone or supported by metal-oxo clusters, *i.e.* polyhedralsilsesquioxanes, POSS [6]. For example, phosphonium based ionic liquids combined with phosphinate, carboxylate, and phosphate counter anions could be considered. Due to the presence of ionic nanostructures formed by the ionic liquid within the thermoset networks, these ones could combine series of functionalities such as a high surface hydrophobicity, an excellent thermal stability (i.e. above 350 °C) with a significant fire retardancy, a shape memory and self healing behavior and an improved deformation ability, as well as a thermomechanical behavior tuned from the chemical structure of ILs.

Keywords: ionic liquids, multifunctional additive, epoxy resin, reactivity, gelation mechanism, nanostructuration, building block, relationship between structure and properties.

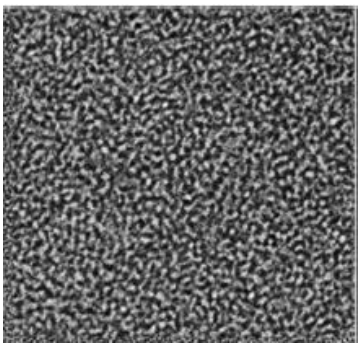


Figure 1: Figure illustrating the nanophase separation of phosphonium cation combined with phosphate anion with a content of 10 phr from the DGEBA based epoxy network [4]

References:

1. G.B. Soares, S. Livi, J. Duchet, J.F. Gérard, *Macromol. Mater. Engng*, 2011, 826-834
2. A. Silva, S. Livi, D.B. Netto, B.G. Soares, J. Duchet, J.F. Gérard, *Polymer*, 2013, **54**, 2123-2129
3. S. Livi, A.A. Silva, Y. Thimont, T.K.I. Nguyen, B.G. Soares, J.F. Gérard, J. Duchet, *RSC Advances*, 2014, **4** (53), 28099-28106
4. T.K.L. Nguyen, S. Livi, B. Soares, S. Pruvost, J. Duchet, J.F. Gérard, *ACS Sustainable Chemistry & Engineering*, 2016, **4** (2), 481-490
5. S. Livi, C. Chardin, L. C. Lins, N. Halawani, S. Pruvost, J. Duchet, J.F. Gérard, J. Baudoux, *ACS Sustainable Chem. Eng*., 2019, **7** (3), 3602–3613
6. H. Chabane, S. Livi, H. Benes, C. Ladaviere, P. Ecorchard, J. Duchet, J.F. Gérard, *Europ. Polym. J.*, 2019,

Highlighting novel static and fluidic properties of liquids using solid wall interactions

L. Noirez
Laboratoire Léon Brillouin, Univ. Paris-Saclay, CEA-CNRS, F-91191 Gif-sur-Yvette, France

Abstract
The properties of the liquids in the vicinity of an interface might be very different from those measured in a large volume. Near the interfaces, the nature of the interactions can dramatically affect both dynamic and static liquid properties. Significant deviations from homogeneous temperatures have been experimentally highlighted revealing that similar to external fields such as electric, magnetic, or flow fields, the vicinity of a solid surface can preclude the liquid molecules from relaxing to equilibrium, generating located non-uniform temperatures away from the solid surface [1]. This effect reveals also a high degree of connectivity between liquid molecules in agreement with the identification of elastic correlations (low frequency shear elasticity) in various liquids and viscoelastic fluids [2].
The high degree of connectivity between liquid molecules (elastic correlations) challenges the molecular approaches and imposes the consideration of collective modes similarly as in solids. More parameters (lengthscale dependence, interfacial force boundaries, compressibility effects) have to be taken into account making the liquid characterization more complex but also richer of potential applications. The effects are particularly revealed at the sub-millimeter scale, impacting microfluidics in particular the flow mechanisms of physiological fluids.
Keywords: liquids, viscoelastic fluids, solid wall, wetting, long range interactions, collective effects.

References:

1. L. Noirez, P. Baroni, JF Bardeau, Highlighting non-uniform temperatures close to liquid/solid interfaces. Appl. Phys. Lett. 110, 213904 (2017) DOI:10.1063/1.4983489
2. L. Noirez, P. Baroni, H. Mendil-Jakani. The missing parameter in rheology: hidden solid-like correlations in liquid polymers and glass formers. Polym Int (2009) 58:962

Design and Realization of White Quantum Dot Light-Emitting Electrochemical Cell Hybrid Devies

S. Gellner[1,2,3], J. Frohleiks[2,3], S. Wepfer[2,3], G. Bacher[2] and E. Nannen[1,2,3]

[1] University of Applied Science Niederrhein, Faculty of Electrical Engineering and Computer Science, Krefeld, Germany
[2] University of Duisburg-Essen, Werkstoffe der Elektrotechnik and CENIDE, Duisburg, Germany
[3] University of Duisbrug-Essen, Research Group „Solid State Lighting", Duisburg, Germany

Abstract:
Light-Emitting Electrochemical Cells (LECs) are a promising device concept for low-cost, large area, flexible and stretchable lighting solutions due to a simple device architecture and solution-based processing. The idea of combining an organic emitter with mobile ions, which facilitate the injection of electronic charge from the electrodes into the emissive layer, results in one-component devices with air-stable electrodes. The realization of white light emitting LECs is quite challenging due to the lack of deep-blue emitters, which are efficient, bright and long-term stable at the same time.
We present an alternative device concept for white light emission, which units an ionic transition metal complex (iTMC) LEC based on Iridium with blue colloidal quantum dots (QDs) in a new type of QD-LEC hybrid device (QLEC). Due to the unique operation mechanism of LECs, it is necessary to analyze theoretically and practically the optimal arrangement of the active layers aiming a balanced electronic charge ratio in both emissive layers. This careful arrangement results in light emission from both emitters already at voltages below 3 V. The QLEC devices show homogeneous white light emission with luminance above 850 cd m^{-2} and a maximum external quantum efficiency greater than 0.2 %. The devices achieve emission with a high color rendering index up to 80 indicating good light quality. The hybrid devices show superpositioned transient behavior of typical QLED and LEC reference devices and a lifetime greater than 20 h at constant-voltage operation.

Keywords: light-emitting hybrid devices, quantum dots, light-emitting electrochemical cells, white light emitters, iTMC.

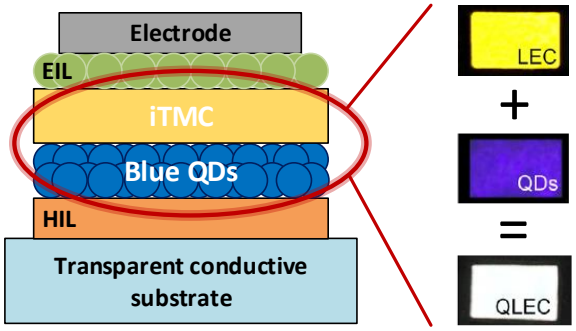


Figure 1: Figure illustrating the device concept of a hybrid QLEC (based on Frohleiks et al., 2018). The idea is to combine the high-performing yellow-orange emitting iTMC-LEC with blue quantum dots to generate bright white light with high CRI.

References:

1. Costa, R.D., Ortí, E., Bolink, H.J., Monti, F., Accorsi, G., and Armaroli, N. (2012). Luminescent Ionic Transition-Metal Complexes for Light-Emitting Electrochemical Cells. *Angewandte Chemie International Edition* 51, 8178–8211.
2. Tang, S., and Edman, L. (2016). Light-Emitting Electrochemical Cells: A Review on Recent Progress. *Topics in Current Chemistry* 374.
3. Frohleiks, J., Wepfer, S., Kelestemur, Y., Demir, H.V., Bacher, G., and Nannen, E. (2016). Quantum Dot/Light-Emitting Electrochemical Cell Hybrid Device and Mechanism of Its Operation. *ACS Applied Materials & Interfaces* 8, 24692–24698.
4. Frohleiks, J., Gellner, S., Wepfer, S., Bacher, G., and Nannen, E. (2018). Design and Realization of White Quantum Dot Light-Emitting Electrochemical Cell Hybrid Devices. *ACS Applied Materials & Interfaces* 10, 42637–42646.

Mesoporous Silica Nanoparticles based on Ionic Microbial Agents

S. Gago,[1,*] B. Mora,[1] P. Rações,[1] M.M.L. Ribeiro Carrott,[2] L. C. Branco[1]

[1] LAQV-REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal

[2] LAQV-REQUIMTE, Centro de Química de Évora, Instituto de Investigação e Formação Avançada, Departamento de Química, Escola de Ciências e Tecnologia, Universidade de Évora, Colégio Luís António Verney, 7000-671 Évora, Portugal

Abstract:
Infectious diseases are the second major cause of death worldwide and the antibiotic treatment sometimes fails due to drug resistant strains or to insufficient activity or concentration of antibiotics at the site of infection. Most of the active pharmaceutical ingredients (APIs) are available in the solid form. However, the solid forms of APIs usually suffer from polymorphic conversion, low solubility and a variety of factors that affect the final bioavailability. Many of the phase II trials of new APIs fail due to their low efficacy often related to low bioavailability and thus low solubility. Co-crystals, amorphous forms and new delivery routes may hold part of the answer to overcoming some obstacles, but it has recently been showed that the use of the ionic liquids (ILs, are defined as organic salts with melting point below 100ºC) building up platform may offer more APIs design options. The combination of ILs and APIs have been recently reported [1,2]. This novel API-ILs can improve the original drug performance in terms of its stability, solubility, permeability and delivery [1,2]. Mesoporous silica nanoparticles (MSNs) offer several advantages to drug formulations, as they can function as antimicrobial agents, while also increasing therapeutic effects, targeted delivery to the site of infection, controlled release that lowers adverse side effects by minimizing nonspecific interactions and decreasing the required treatment dose [3]. The development of novel silica nanomaterials based on ionic microbial systems appears as an innovative route for the development of new and more efficient drug delivery systems. In this work several APIs-ILs based on L-tryptophan and ciprofloxacin in homogeneous phase and supported on MSNs have been developed (Figure 1). All compounds and resultant hybrids were characterized by several characterization techniques such as ^{1}H NMR, elemental analysis, X-ray powder diffraction, FT-IR, DLS, N_2 adsorption experiments and TEM.

Keywords: protein folding, nanoporous sol-gel glasses, silica-based biomaterials, circular dichroism spectroscopy, surface hydration, crowding effects, micropatterning, biomedical applications.

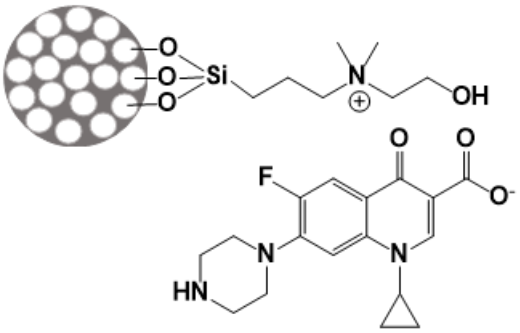


Figure 1: Example of supported API-ILs based on Ciprofloxacin

References:

1. Ferraz, R.; Branco, L. C.; Prudêncio, C.; Noronha, J. P.; Petrovski, Ž. (2011) Ionic Liquids as Active Pharmaceutical Ingredients, *ChemMedChem*, 6, 975-985.
2. Marrucho, I. M.; Branco, L. C.; Rebelo, L. P. N. O. (2014) Ionic liquids in pharmaceutical applications, *Annu. Rev. Chem. Biomol. Eng*, 5, 527-546.
3. Zhou, Y.; Quan, G.; Wu, Q.; Zhang, X.; Niu, B.; Wu, B.; Huang, Y.; Pan, X.; Wu, C. (2018) Mesoporous silica nanoparticles for drug and gene delivery, *Acta Pharm. Sin. B.*, 8, 165–177.

Acknowledgements: This work was supported by the **Associate Laboratory for Green Chemistry- LAQV** which is financed by national funds from FCT/MCTES (UID/QUI/50006/2019, UID/QUI/0619/2019).

Inherently Chiral Ionic Liquids with Axial, Helical and Central Stereogenicity for Highly Efficient Enantioselective Sensors

S. Rizzo,[1,*] P.R. Mussini,[2] S. Arnaboldi,[2] M. Longhi,[2] F. Fontana,[3] R. Cirilli,[4] A. Forni,[1]

[1] CNR, Institute of Molecular Science and Technologies, Milan, Italy
[2] University of Milan, Dept. of Chemistry, Milan, Italy
[3] University of Bergamo, Dept. of Engineering and Applied Science, Dalmine, Italy
[4] Italian National Institute of Health, National Centre for the Control and Evaluation of Medicines, Rome, Italy

Abstract:
We recently defined as "inherently chiral" functional materials the compounds in which the stereogenic scaffold responsible for chirality and the molecular group responsible for their specific properties coincide.[1] This structural combination results in outstanding enantioselection properties, much higher than those exhibited by the compounds in which stereogenic unit and functional group are independent molecular portions. We first tested the validity of this concept in the design of macrocyclic fully conjugated poly-thiophenes in which chirality results from a tailored distortion of regio-regular oligo-thiophene sequences. They were employed as highly stereoselective electrode surfaces.[2]
We decided to apply the inherent chirality concept to Chiral Ionic Liquids (CILs), experimenting first the effects produced by a stereogenic axis and then extending the research to completely new Inherently Chiral Ionic Liquids (ICILs) based on helices and classical stereocenters. In our project the ICILs based on a stereogenic axis are characterized by suitably substituted 3,3'-bipyridinium (**1**) or 1,1'-bibenzimidazolium (**2**) atropisomeric scaffolds.[1] Considering that pyridinium and imidazolium groups are classical IL functionalities, and that a pair of them are involved in the hindered rotation around the interannular bond, responsible for chirality, it is evident that the attribute of ICILs to these compounds is correct. Aza- and di-aza-hexahelicenium cations (**3**) also fulfill the requirements to be defined as ICILs, since the pyridinium unit is essential part of the helical scaffold. As for ICILs based on stereogenic centers, we have planned the alkylation of configurationally stable phosphanes (**4**) as the key step to easily obtain them. Synthesis and characterization of all new ICILs and electrochemical enantio-differentiation experiments of the antipodes of several chiral probes are discussed in comparison with the behaviour of classical CILs.

Keywords: Ionic liquids, Chiral additives, Inherent chirality, Chiral electrochemistry and electroanalysis, aza-hexahelicenium cation, phosphonium cation

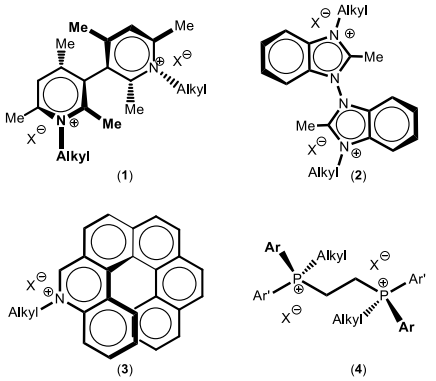


Figure 1: Prototypes of Inherently Chiral organic salts characterized by 3,3'-bipyridine (1), 1,1'-bibenzimidazole (2), 5-aza-hexahelicene (3) and phosphane (4) scaffolds.

References:

1. Rizzo, S. et al. (2017) "Inherently Chiral" Ionic-Liquid Media: Effective Chiral Electroanalysis on Achiral Electrodes, *Angew. Chem. Int. Ed.,* 56, 2079-2082.
2. F. Sannicolò et al., (2014) Potential-driven chirality manifestations and impressive enantioselectivity by "inherently chiral" electroactive organic films of innovative design, *Angew. Chem. Int. Ed.*, 53, 2623-2627.

SMS 2019 / NanoMed 2019 joint session I
Advances in Functional and Multifunctional Materials / Composite Materials / Nanosystems

High Performance Fiber-Reinforced Polymer for Integration of Structure and Functions

Peng Feng,* Zhiyuan Li,

Tsinghua University, Department of Civil Engineering, Beijing, China

Abstract:
FRP (Fiber-reinforced polymer) composites had been used widely in many areas including aerospace, infrastructures, vehicles, marine and offshore structures, etc. They have the significant advantage of high strength and light weight in term of mechanical behavior, which inherits from the high performance of carbon fiber or glass fiber. Besides it, FRP has many functional behaviors, such as corrosion resistance, electromagnetic property, designable, and fatigue resistance. The integration of structure and function is an opportunity of FRP applications. Hence, FRP in civil engineering is becoming a mainstream material expanding the possibilities of human being. Using FRP can solve the problems which the traditional structural materials cannot deal with. The latest researches on FRP for integration of structure and functions are reviewed. The developing trends are analyzed based on the recent projects supported by the National Natural Science Foundation of China. Furthermore, the related real applications are introduced.

Keywords: corrosion resistance; electromagnetic property; designable material; fatigue resistance; large scale structure; offshore structure.

Figure 1: Figure illustrating a real application of FRP enclosure system for bridge, which is a typical application of integration of structure and function.

References:

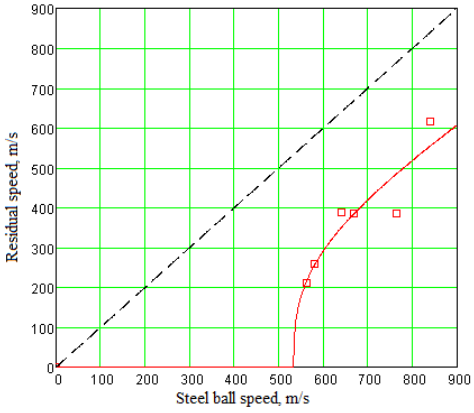
1. Shi CHENG, Peng FENG, Zhiyuan LI, Jike DU. Mechanical behavior of cylindrical GFRP chimney liners subjected to axial tension. *Composites Part B: Engineering,* 2019, 177: 107411.
2. Zeyuan WANG, Peng FENG, Yi ZHAO, Tao YU. FRP-confined concrete core-encased rebar for RC columns: concept and axial compressive behavior. *Composite Structures*, 2019, 222: 110915.
3. Peng FENG, Lili HU. Steel columns strengthened / reinforced by prestressed CFRP strips: concepts and behaviors under axial compressive loads. *Composite Structures*, 2019, 217: 150-164.
4. Jie WANG, Peng FENG, Tingyu HAO, Yudong HAN. Axial compressive behavior of seawater coral aggregate concrete filled FRP tubes. *Construction and Building Materials*, 2017, 147: 272-285.
5. Peng FENG, Jie WANG, Ye TIAN, David LOUGHERY, Yi WANG. Mechanical behavior and design of FRP structural members at high and low service temperatures. *Journal of Composites for Construction, ASCE*, 2016, 20(5): 04016021.
6. Peng FENG, Xinmiao MENG, Hanqing ZHANG. Mechanical behavior of FRP sheets reinforced 3D elements printed with cementitious materials. *Composite Structures*, 2015, 134: 331-342.
7. Peng FENG, Shi CHENG, Yu BAI, Lieping YE. Mechanical behavior of concrete-filled square steel tube with FRP-confined concrete core subjected to axial compression. *Composite Structures*, 2015, 123: 312-324.
8. Peng FENG, Jie WANG, Yi WANG, David LOUGHERY, Ditao NIU. Effects of corrosive environments on properties of pultruded GFRP plates. *Composites Part B: Engineering*, 2014, 67: 427-433.

Tungsten Carbide Microparticles Introduction's Effect on Steel Hardness and Resistance to local Impacts

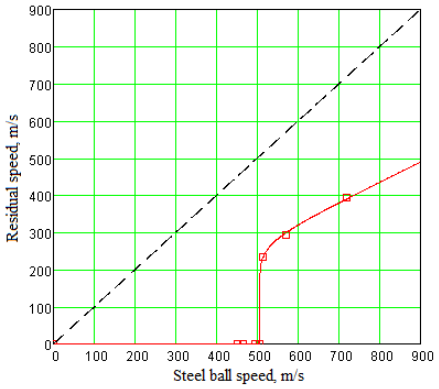
A. Anikeev,[1] I. Chumanov,[1] V. Sedukhin[1]

[1] South Ural State University, Department of Engineering and Technology of Materials Production, Chelyabinsk, Russia

Abstract:
The article presents one of the technological methods for the metals manufacture (matrix melt) by active micro and nanoparticles contributing in order to increase their strength characteristics. The samples obtained, saturated with refractory tungsten carbide microparticles, showed high hardness and resistance to local impacts characteristics with a stable type of fracture.
In this paper, we consider one of the technological methods for the metals manufacture (matrix melt) with active micro- and nanoparticles, contributing to an increase in their strength properties and a noticeable decrease in the obtaining the material cost.
Samples were obtained by melting in an induction furnace, then casting was carried out in a horizontal type centrifugal casting plant, with a mold speed of 800 rpm. Casting 1 - standard, without the dispersed particles introduction; casting 2 - with reinforcing particles concentration WC = 0.1 wt. % During deformation, the wall thickness of the casting reduced from 20 mm to 5 mm.



a)



b)

Figure 5: Ballistic breakdout curves: a - sample No. 1, b - sample No. 2.

The resulting materials were tested on a special ballistic stand and ballistic breakthrough curves were constructed.

When comparing the residual velocity (speed of the flying plug) with impactor speeds of 700-900 m/s in the case of a plate, which has reinforcing particles, this indicator is lower, and that indicates the increase in ballistic resistance of this material type and the resistance increase to local impacts.
Thus, a sample saturated with tungsten carbide refractory microparticles has higher hardness characteristics and resistance to local impacts with a stable spall fracture type compared to ordinary steel mark 1020 sample.

Keywords: casting, micro and nanoparticles, tungsten carbide, crystallization, hardness, fracture.

ACKNOWLEDGMENTS
This work was supported by the Ministry of Education and Science of the Russian Federation (project no. 11.9658.2017/8.9).

References:

1. Ballistic Resistance of Body Armor (2008), NIJ Standard-0101.06.
2. GOST R 50744-95 «Armor Wear. Classification and General Technical Requirements» (1995) [in Russian].

Biopolymers for the Development of Stimuli Responsive Composites

A.C. Pinho, A.P. Piedade*

CEMMPRE-University of Coimbra, Department of Mechanical Engineering, Coimbra, Portugal

Abstract:
3D printing of polymers can now be considered as a common processing technology for the conformation of parts/devices. Besides all the recent possibilities available by 3D printing, this technology itself has been able to provide the freedom of processing any device or part without concern regarding the complexity of the shape and, simultaneously, is a very restrictive technology when adaptive and shape change during use is considered [1].
A newly emerging trend in this area is 4D printing that relies on introducing stresses into a printed 1D, 2D, sometimes 3D, structure. When an external stimulus is applied the stress is released and the structure further evolves with time (the fourth dimension) into the desired tridimensional shape. In the literature, most of the work related to 4D printing describes the use of shape memory polymers or shape memory nanocomposites.
This work represents an approach undertaken with the aim of investigating the production and characterization of biopolymers that will be used as reinforcement in the production of polymeric nanocomposites. They will be used in the additive manufacturing (3D) of nanocomposites in order to investigate their ability to promote the bridge between 3D and 4D printing. It is intended that the produced part/component will change its properties/characteristics due to the action of an external stimuli such as variations of pH, light or moisture.
In this presentation, the first approaches in the use of microorganisms for the production of biopolymers will be addressed. Its use as reinforcement of a hydrophobic polymer, poly(ε-caprolactone) (PCL) for the preparation of nanocomposites is presented, as well as the preliminary tests regarding the shape-morphing ability of the printed structures due to an external stimulus.

Keywords: biopolymers, nanocomposites, stimuli responsive materials, clean and sustainable production.
Acknowledgements: This work was developed under the project PTDC/CTM-COM/30767/2017 cofunded by FEDER, throught Portugal-2020 programme, POCI-01-0145-FEDER-030767 and by FCT,I.P. through National funds (PIDDAC).

References:

1. Piedade A.P. (2019) 4D Printing: The Shape-Morphing in Additive Manufacturing, *J. Funct. Biomat. 10, 9;* doi:10.3390/jfb10010009

Modulation of Protein Sorption at Magnetic-Responsive Hydrogels

A. C. Manjua[1,2], Vitor D. Alves[3], João G. Crespo[1], Carla A. M. Portugal[1,*]

[1] LAQV-REQUIMTE, FCT.NOVA, Department of Chemistry, Caparica, Portugal
[2] iBB-Institute for Bioengineering and Biosciences, IST-Universidade de Lisboa, Department of Bioengineering, Lisboa, Portugal
[3]LEAF-Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal

Abstract:
Magnetic hydrogels are soft materials with ability to undergo volume and shape changes when exposed to an external magnetic field [1,2]. These magnetic driven effects result from the hydrogel contraction-distention imposed by the magnetic field forces.
The present work discusses the impact of magnetic field in the hydrophilic and structural character of polyvynil alcohol (PVA) hydrogels doped with iron oxide nanoparticles (MNPs) and the way it seems to influence protein sorption processes, i.e. protein adsorption and absorption to these hydrogels.
Magnetic PVA hydrogels showed to be able to reversibly switch surface wettability when exposed to cyclic variation of magnetic field intensity [3]. The magnetic induced increase of surface wettability was interpreted as a possible consequence of the increase of surface roughness caused increase load of MNPs at the surface due to the magnetic shrinking of the hydrogel volume (Figure 1). The magnetic field was also shown to stimulate protein desorption allowing for a reversible modulation of protein sorption-desorption processes when exposed to magnetic field cycles. The total amount of protein is desorbed from the hydrogel after the 1st OFF/ON magnetic field cycle, along the ON magnetic field stage at 0.45T. Protein sorption was restored by switching OFF the magnetic field and a desorption of 76.1% was reached after the 2nd cycle [3].
The capacity of these hydrogels to modulate surface wettability and protein sorption on demand and controlled way motivate the use of these materials for the design of functional devices for processes whose performance relies on an efficient control of protein-surface interactions and protein mobility through porous media, e.g. tissue engineering processes and biosensors.

Keywords: magnetic hydrogels, magnetic field, protein sorption, surface roughness, surface hydrophilicity, bioprocessing, biomedical applications.

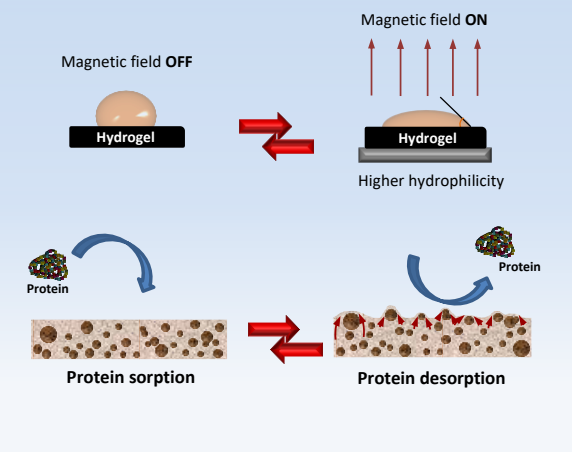


Figure 1: Schematic illustration of the effect of the magnetic field on the surface wettability and capacity to tune on demand protein sorption-desorption processes at hydrogel surfaces. Adapted from [3].

References:

1. Szabó, D., Szeghy, G., Zrínyi, M. (1998) Shape Transition of Magnetic Field Sensitive Polymer Gels. *Macromolecules*, 31, 6541-6548.
2. Filipcsei, G., Csetneki, I., Szilágyi, A., Zrínyi, M. (2007) Magnetic responsive-field smart polymer composites. *Adv Polym Sci* , 206, 137–189.
3. Manjua, A. C., Alves,V. D., Crespo, J. G., Portugal, C.A.M. (2019) Magnetic responisve PVA hydrogels for remote modulation or protein sorption. *ACS Appl. Mater. Interfaces*, 11, 23, 21239-21249.

Metallization of thermoset composites through it surface functionalization

H. Perrin,[1,*] S. Klein, R. Vaudemont,[1,]

[1] Luxembourg Institute of Science and Technology, Material research and technology, Bascharage, Luxembourg

Abstract:
General aviation aircraft, large commercial jets and wind turbines are vulnerable to lightning strike. Unlike their metal counterparts, composite structures in these applications do not readily conduct away the extreme electrical currents and electromagnetic forces generated by lightning strikes. Composite materials are either not conductive at all (e.g., fiberglass) or are significantly less conductive than metals (e.g., carbon fiber), so current from a lightning strike seeks the metal paths available. For that reason, lightning strike protection (LSP) has been a significant concern since the first composites were used on aircraft more than 30 years ago.
The CO3 project will thus offer an enabling automated process for the next generation of airplane.
In this work, as part of the CO3 Project, authors are focusing their attention on the composite surface functionalization enabling a deposition of coating through Supercritical Nitrogen jet as dry and efficient carrier gaz.
The challenge of this work consist to develop, optimize and validate coating process approach on carbon fibers reinforced thermoset. In order to generate a strong mechanical anchoring of the metal coating without any degradation of the CFRP substrate.
Due to the intrinsic thermos-mechanical properties of high performance thermoset compare to thermoplastic, the erosion damage at the composite surface could occurs during deposition inducing surface defect as well as composite internal damage. This phenomenon highlights the lack of thermoset-metal adhesion as well as a poor deposition efficiency.
This study propose to investigate and optimize the in-situ surface functionalization through thin thermoplastic layer incorporated during the manufacturing of the CFRP substrate. An analyse the relationship between the composite manufacturing conditions, in particular the cure state of the matrix and the resulting thermoplastic coating adhesion properties is proposed, as prelimiry studied in the litteratur [1]. The selected resin is the RTM6-2 from Hexcel. A metallic powder (copper) are selected as metallization material and is projected on the top of functionalized CFRP substrate using an optimized cold gas spraying deposition assisted SCN jet process parameters. Depending on the CFRP manufacturing conditions, process deposition efficiency as well as coating properties (electrical conductivity, coating morphologies, coating adhesion) are compared together with the reference.
The conclusion of this study highlights the significant role of composite manufacturing surface functionalization enabling a metallization process efficiency and resulting metallic coating properties.

Keywords: lightning strike protection, thermoset composite

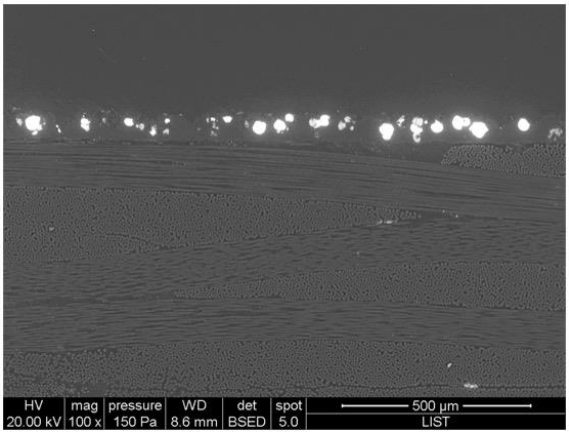


Figure 1: Figure illustrating a copper coating on a functionalized CFRP substrate

References:

1. Fernandez Villegas, I., & Rubio, P. V. (2015). High-Temperature Hybrid Welding of Thermoplastic (Cf/Peek) To Thermoset (Cf/Epoxy) ICCM 19th, 19–24.

Dithia[3.3]paracyclophane Core: a Versatile Platform for Fine Triplet State Tuning and Through Space TADF Emission

Morgan Auffray[a], Dae Hyeon Kim[b], Jong Uk Kim[b], Fatima Bencheikh[b][c], David Kreher[a], Qisheng Zhang[d], Antho D'Aléo[e], Jean-Charles Ribierre[b][c], Fabrice Mathevet[a], Chihaya Adachi[b][c]

[a] Sorbonne Université, Institut Parisien de Chimie Moléculaire (IPCM), UMR 8232, Equipe Chimie des Polymères, 4 place Jussieu, 75005 Paris (France)
[b] Department of Applied Chemistry, Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motooka, Nishi Fukuoka 819-0395 (Japan)
[c] ERATO, Adachi Molecular Exciton Engeneering Project, Nishi Fukuoka 819-0395 (Japan)
[d] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027 (P. R. China)
[e] Aix Marseille Univ., CNRS, CINaM UMR 7325, Campus de Luminy, 13288 Marseille (France)
[f] Center for Quantum Nanoscience, Institute for Basic Science, Seoul 03760 (Republic of Korea)

Abstract:
Since the pioneering work of Tang and VanSlyke[1] and later on by Friend et al.[2], fluorescent-based organic light-emitting diodes (OLEDs) have been intensively studied. After the second generation of OLEDs based on phosphorescent materials ,[3] recently an alternative approach allowing 100% of IQE in OLEDs has been successfully developed based on metal-free, thermally activated delayed fluorescence (TADF) emitters, leading to the third generation of OLEDs.[4] The common strategy consists in maintaining a weak electronic communication between Donor and Acceptor groups by a central core , either through an intensely twisted conjugated linker[5], or a single σ-bond[6], or via through-space interactions.[7]
In this context, novel TADF isomers using a dithia[3.3]-paracyclophane building block as a versatile 3D platform to promote through-space interactions is presented.[8] Such a 3D platform allows to bring together the D and A units into close proximity and to probe the effect of their orientation, contact site and distance on their TADF emission properties. This study provides evidence that dithia[3.3]paracyclophane core is a promising platform to control intramolecular through-space interactions and obtain an efficient TADF emission with short RISC lifetimes. In addition, this study demonstrates that this design can tune the energy levels of the triplet states and leads to an upconversion from 3CT to 3LE that promotes faster and more efficient RISC to the 1CT singlet state.

Keywords: paracyclophane, through-space TADF emission.pi-conjugated materials.

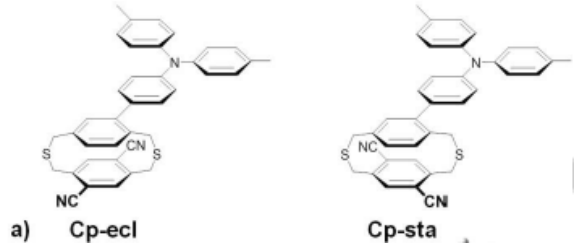


Figure 1: a) Molecular structures compared.

References:

1. C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913-915.
2. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539-541.
3. C.Adachi, M. A. Baldo, M. E. Thompson, S. R. Forrest, *J. Appl. Phys.* **2001**, *90*, 5048-5051.
4. C. Adachi, *Jpn. J. Appl. Phys.* **2014**, *53*, 60101.
5. a) H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **2012**, *492*, 234-238; b) L.-S. Cui, H. Nomura, Y. Geng, J. U. Kim, H. Nakanotani, C. Adachi, *Angew. Chem. Int. Ed.* **2017**, 56, 1571-1575.
6. Nakagawa, T.; Ku, S.-Y.; Wong, K.-T.; Adachi, C. *Chem. Commun.* **2012**, *48*, 9580-9582.
7. K. Kawasumi, T. Wu, T. Zhu, H. S. Chae, T. Van Voorhis, M. A. Baldo, T. M. Swage, *J. Am. Chem. Soc*. **2015**, *137*, 11908-11911.
8. Vögtle, F. *Cyclophane Chemistry*; Wiley: New York, **1993**.
9. a) J. Zyss, I. Ledoux, S. Mukamel, G. P. Bartholomew, G. C. Bazan, *J. Am. Chem. Soc*. **2000**, *122*, 11956-11962.
10. Morgan Auffray, Dae Hyeon Kim, Fatima Bencheikh, David Kreher, Antho D'Aléo, Jean-Charles Ribierre, Fabrice Mathevet, Chihaya Adachi, *Chem. Asian J.* **2019**, 14, 1 – 6.

A Nontoxic Reversible Thermochromic Binary System via π-π Stacking of Sulfonephthaleins

Bingxin Liu,[a] Hadi Ranji-Burachaloo, [a] Paul A. Gurr, [a] Eirini Goudeli, [a] and Greg G. Qiao *[a]

[a] Department of Chemical Engineering, The University of Melbourne, VIC 3010, Australia.

Abstract:
The mechanisms of thermochromic materials are mostly based on Bragg reflection, surface plasmon absorption, molecular structure changes, conformational stretching or aggregation. [1] Here, the first example of dye-solvent binary systems with clear and reversible thermochromism around ambient temperatures is reported with an alternative mechanism of solubility-dependent π-π stacked agglomeration of sulfonephthalein dyes controlled by melting or crystallisation processing of the solvent. This system comprises of commercially available sulfonephthaleins dissolved in liquid linear chain esters, acids or alcohols which demonstrate colour changes at different temperatures when the solvents transition between solid to liquid states. Molecular dynamics (MD) simulations, ultraviolet visible (UV-Vis) spectroscopy, ^{1}H nuclear magnetic resonance (NMR) spectroscopy, fourier transform infrared spectroscopy (FTIR-ATR) and X-ray diffraction (XRD) were used to prove the colour changing is related to the formation or disappearance of π-π stacked crystals of the sulfonephthalein dyes rather than dye ring-opening mechanism. The colour changing speed of these binary systems can be adjusted by varying the dye concentration. Cell toxicity testings confirmed the sulfonephthalein dyes are less toxic to NIH-3T3 cells than Cyanidin chloride, which is the only reported nontoxic food dye affording thermochromism, while this is based on an alternative mechanism. [2] With the choice of nontoxic solvent, this binary system can form a nontoxic thermochromic material.

Keywords: thermochromic, reversible, nontoxic, π-π stack, sulfonephthalein.

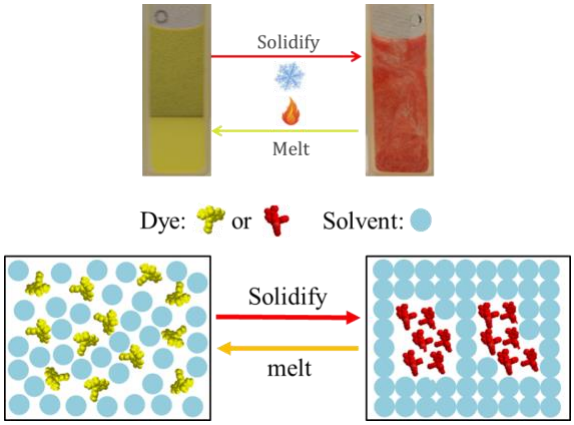


Figure 1: The photographic images of dye-solvent binary system that shows clear reversible thermochromism between liquid and solid states. The corresponding schematic diagram illustrates the colour change mechanism of solubility-dependent π-π stacked agglomeration or disagglomeration of sulfonephthalein dyes controlled by melting or crystallisation processing of the solvent.

References:

1. Seeboth, A.; Lötzsch, D.; Ruhmann, R.; Muehling, O., Thermochromic Polymers—Function by Design. Chemical Reviews 2014, 114, (5), 3037-3068.
2. Seeboth, A.; Lötzsch, D.; Ruhmann, R., First example of a non-toxic thermochromic polymer material–based on a novel mechanism. Journal of Materials Chemistry C 2013, 1, (16), 2811-2816.

Single Particle Microscopy & Spectroscopy of Morphology and Size Controlled Perovskite Crystals: PEROVSKOPY

E. Debroye,[1*] H. Bhatia,[1] M. Keshavarz,[1] C. Martin-Alvarez,[1] J. Steele,[2] H. Yuan,[1] M. Roeffaers,[2] J. Hofkens[1]

[1] KU Leuven, Department of Chemistry, Leuven, Belgium
[2] KU Leuven, Centre for Surface Chemistry and Catalysis, Leuven, Belgium

Abstract:
After seminal reports of their interesting physical properties published in 2009 and 2012,[1] an explosion of scientific interest into metal halide perovskites (MHPs) in the past decade has seen this family of materials emerge as the most exciting avenue for next-generation solar cells. The strong promise for MHP materials arise from their fundamental physics; from high absorption coefficients at visible wavelengths, long carrier diffusion lengths and small exciton binding energies, to its simple solution-based processing. An early surge of research activity was inspired by an empirical race to produce photovoltaic devices with ever-higher photo-conversion efficiencies. Consequently, perovskite engineering significantly outpaced the understanding of their physical properties. In response, the focus of researchers is steadily shifting toward the intrinsic properties of perovskites, as these will ultimately define their performance in any photonic application. In this light, recent research in our laboratory aims at connecting the microstructure of perovskite crystals with their physical properties, by addressing three overarching goals: (1) Development of systematic experimental protocols for controlled synthesis of a variety of highly crystalline, monodisperse and defect-poor perovskite crystals with well-defined morphology, with sizes covering a few nanometres over microns to millimetres. (2) In-depth investigation on these materials using an arsenal of single particle microscopy and spectroscopy techniques. Complementary information obtained from such experiments will provide true understanding of how perovskite composition and morphology influence the fate of the photo-generated charge carriers, and this structure-property relationship can be used to develop better perovskite materials. (3) Finally, this knowledge is applied to the development of better-performing photonic devices. In this contribution, I will report recent progress in perovskite synthesis[2] and single particle micro- and spectroscopy.[3]

Keywords: perovskite (nano)crystals, single particle microscopy, spectroscopy, photophysical pathways, structure-property relationship, photonic devices.

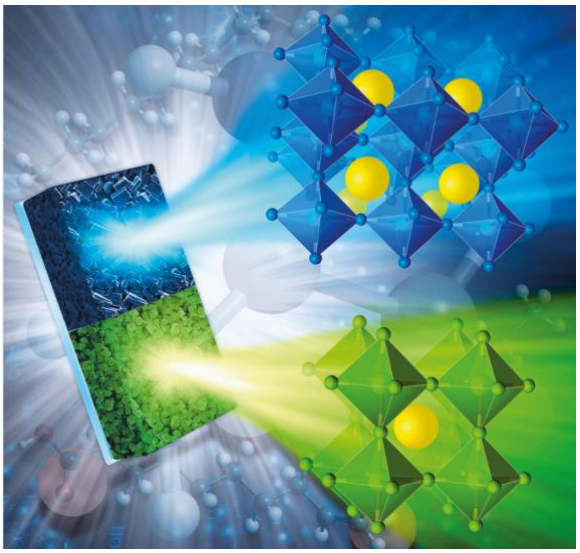


Figure 1: Unraveling the structure-property relationship of perovskite nanocrystals for a rational development of better perovskite materials toward more efficient optoelectronic devices such as LEDs or X-ray photodetectors.

References:

1. A. Kojima et al. (2009) *J. Am. Chem. Soc.* 131, 6050–6051; H.-S. Kim et al. (2012) *Sci. Rep.*, 2, srep00591.
2. E. Debroye et al. (2017) *ChemNanoMat*, 3, 223–227; H. Bhatia et al. (2019) *Chem. Mater*.
3. H. Yuan et al. (2016) *J. Phys. Chem. Lett.*, 7, 561–566; H. Yuan et al. (2018) *Adv. Mater.*, 30, 1705494; J. Steele et al. (2018) *Adv. Mater.*, 30, 1804450.

Influence of the Nanotopography of Wrinkles on a-C:H coated Polymers on the Differentiation of non-embrionic Stem Cells

J.M. Lackner[1,*] R. Major[2]

[1] JOANNEUM RESEARCH Forschungsges.m.b.H., Institute of Surface Technologies and Photonics, Niklasdorf, Austria

[2] Polish Academy of Sciences, Institute of Metallurgy and Materials Sciences, Krakow, Poland

Abstract:

The plasticity of non-embryonic stem cells and their potential to de-differentiate provides new therapeutic strategies in regenerative medicine. Derived from human endothelial cells, differentiated progenitor cells provide reliable, reproducible and physiologically appropriate source of cells for the treatment of vascular disease, atherosclerosis, coronary heart disease, hypertension and inflammatory diseases.

The aim of the work was to explore and characterize the influence of defined surface topography of thin haemocompatible thin films (a-C:H) for effective capturing progenitor cells from whole human blood for differentiation into vascular endothelium.

200 nm thin a-C:H films (amorphous hydrogenated "diamond-like" carbon) were deposited by magnetron sputtering of a pyrolytic carbon target in ($Ar+C_2H_2$) atmosphere on soft, 1 mm thin thermoplastic polyurethane foil substrates. Homogenous surface topography of the films with uniaxial wave structure was achieved by prestraining of the foils before deposition and release of the strain afterwards, which leads due to different elastic moduli (E) of substrate and film to the formation of "wrinkles" [1-4]. This method and the achievable uniaxial wrinkle wavelength λ(d) and amplitude A(d) are physically well described, as shown in the simulations of the achieved topography – especially the alternating wrinkle A(d) at different pre-strain at fixed film thickness d and thus λ in Fig 1.

Besides topography analysis with AFM and roughness, revealing the above simulated wrinkling amplitudes, the interaction of endothelium progenitor cells (i-Cells) with the defined topography, mimicking tissue niches of the ECM was investigated by a VascuLife VEGF Medium Complete Kit (LifeLineCell Technologies, US).

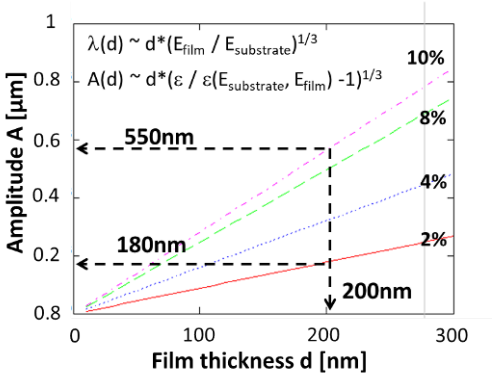


Figure 1: Wrinkle amplitude A as a function of pre-strain (2-10%) for a-C:H films (d = 200 nm) on TPU substrate.

The degree of differentiation was tested using anti-CD62E (E-selectin) and anti-CD31 (PECAM-1) antibodies [5]. The results are presented in Fig. 2: PECAM-1 positive cells (yellow) indicate diversification into endothelial cells, E-Selectin (red) leukocyte-endothelial cell adhesion molecules, ZO-1 staining (green) tight intercellular junctions, and blue staining the cell nuclei.

As visible, especially the 5% pre-straining result in a very regular network of PECAM-1 expression (leukocyte-endothelial cell adhesion molecules). There is a probability that deformation limit exists between 5% and 8% strain. In the case of the 8% deformation, the degree of cell differentiation and the likelihood of the appropriate cell-cell interactions formation that indicate the cell monolayer creation is weakened.

Summing up, the influence of the surface tomography on the cell-material interaction was observed. The surface tomography influences on the cell differentiation effect as well as the monolayer formation. Both phenomena could have the significant meaning on potential use of biomaterial in cardiovascular regeneration. At the work, the biomaterial should not come into direct contact with blood. The biomaterial

should create an appropriate environment for the self-formation of the endothelium. Endothelium is the natural layer that is able to self-regulate the clotting process. Therefore, the appropriate differentiation of progenitor cells into endothelium and the generation of appropriate cell-cell interactions is crucial, which was shown to be influenced by nanotopography.

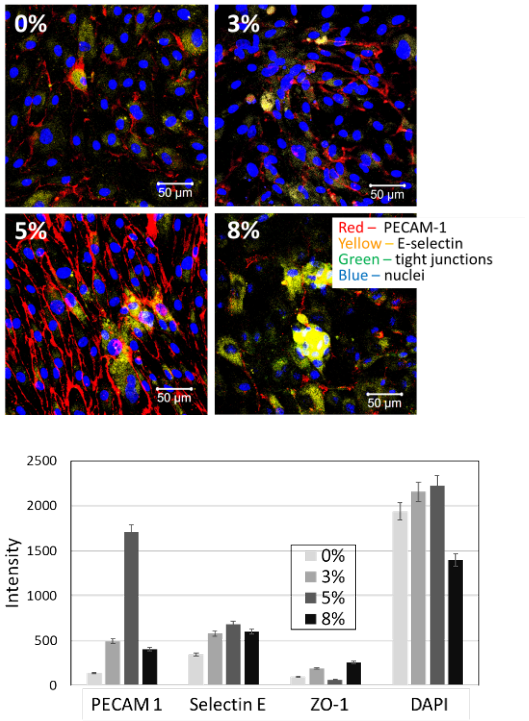


Figure 2: Degree of differentiation by expression of PECAM1 (red), Selectin-E (yellow), ZO-1 (green) and DAPI (blue, indicating cell nuclei)

Keywords: surface nanotopography, stem cells, diamond-like carbon, cell differentiation

References:

1. R. Major, J. M. Lackner, M. Sanak & B. Major, Biomimetics in thin film design: Niche-like wrinkles designed for i-cell progenitor cell differentiation. Materials Science and Engineering: C, 80 (2017) 379-386.
2. J.M. Lackner, Industrially-styled room-temperature pulsed laser deposition of titanium-based coatings, Vacuum 78 (2005) 73–82.
3. J.M. Lackner, W. Waldhauser, R. Major, L. Major, P. Hartmann. Wrinkling and fracture of pulsed laser deposited films in comparison to human skin. Surf. Coat. Technol. 215 (2015) 192–198.
4. R. Major, K. Trembecka-Wojciga, M. Kot, J.M. Lackner, P. Wilczek, B. Major, In vitro hemocompatibility on thin ceramic and hydrogel films deposited on polymer substrate performed in arterial flow conditions. Mater. Sci. Eng. C 61 (2016) 15–22.
5. M. Sanak, B. Jakiela, W. Wegrzyn, Assessment of hemocompatibility of materials with arterial blood flow by platelet functional tests Bull. Pol. Acad. Sci. Tech. Sci. 58 (2) (2010) 317–322.

3-nitroaniline crystals embedded in electrospun nanofibers as strong piezoelectric and nanoemitters of second harmonic light

Rosa Baptista,[1] Cesar Bernardo,[1] Etelvina de Matos Gomes,[1] Paulo Lopes,[2] Michael S. Belsley[1]

[1]Univ Minho, Centre of Physics, Campus Gualtar, P-4710057 Braga, Portugal
[2]Univ Minho, Inst Polymers & Composites I3N, Campus Azurém, P-4800058 Guimarães, Portugal

Abstract

Nanofibers consisting of optically active nonlinear organic 3-nitroaniline (3NA) molecules embedded in polycaprolactone (PCL) as a host polymer were produced by the electrospinning technique. The electrospun nanofibers have an average diameter of 225 nm, are bead free and optically transparent in the near UV-visible optical spectrum. Fiber mats with 40 cm^2 area may easily be fabricated using a rotatory grounded drum. The electrospinning technique is an effective method to fabricate all-organic molecular functional devices based on polymer nanofibers with guest molecules possessing strong nonlinear optical and/or polar properties [1].

In this communication, the production and characterization of nanofibers exhibiting strong piezoelectric and quadratic optical nonlinearity response will be presented. The effective second order nonlinear susceptibilitie was measured on a single nanofiber as a function of polarization using a femtosecond mode-locked Ti:Sapphire laser system with a fundamental wavelength centered at 800nm. The results show that these hybrid functional 3NA_PCL nanofibers can produce a strong and highly polarized second harmonic response with higher effective nonlinear coefficients than bulk crystals. The estimated effective second order susceptibility coefficient for one polarization configuration was found to be approximately a factor of 4 times greater than the largest tensor element for pure crystalline 3NA (Figure 1).

The piezoelectric response of 3NA_PCL fiber mats is very significant as output voltage of 6V and current up to 60nA were measured upon an applied periodical force of (Figure 2).

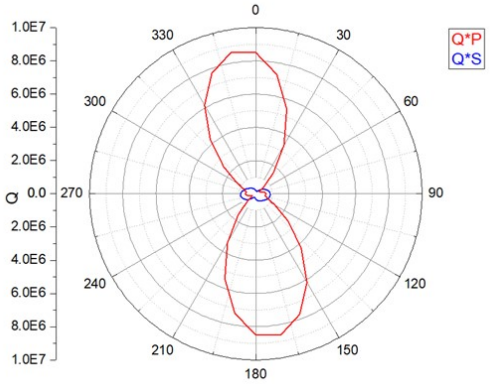


Figure 1. Polar plot of the nonlinear optical response of 3NA_PCL nanofibers.

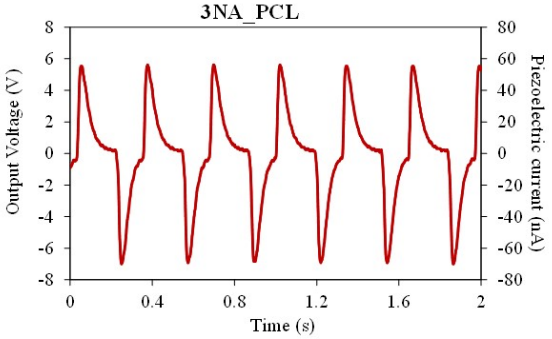


Figure 2. Piezoelectric response of 3NA_PCL nanofibers.

Keywords: electrospinning, functional nanofibers, nonlinear optical properties, piezoelectricity

References:

1. D.V. Isakov, E.D. Gomes, L.G. Vieira, T. Dekola, M.S. Belsley, B.G. Almeida, ACS Nano 5, 73 (2011).
2. Carenco, J. Jerphagnon, and A. Perigaud, J. Chem. Phys. 66, 3806 (1977).

Optimization of electrochemical flow capacitor (EFC) design via Finite element modeling

F. Summer,[1,*] J.Torop,[1] V.Zadin,[1] A, Aabloo,[1]
[1]IMS Lab, Institute of Technology, University of Tartu, Nooruse 1, 50411, Tartu, Estonia.
faiza.summer@ut.ee

Abstract:
Electrochemical flow capacitor (EFC) is the electrical energy storage introduced for grid scale systems due to its rapid charge/discharge and easy recovery of stored energy [1]. The EFC shares the concept of high power supercapacitor and scalability of flow batteries, together providing rapid decoupling of power at the order of milliseconds and longer life time. To develop the EFC technology, studies were mainly focused on the electrode material, chemical activation, porosity and morphology of electrode material. The higher percentage of mass loading showed the improved capacitance of the EFC device for desalting of brackish water due to surface chemistries [2]. The lower concentration of electrolyte in the slurry showed the direct relation of resistivity with the depth of flow channel, which directly influence the conductivity of the device [3]. Mathematical modeling approach was used to analyze the over-potential profile of the static and flowing slurry in the half cell configuration [4]. Diffusion becomes the prominent phenomenon when ionic conductivity is higher than the electronic conductivity in the static slurry, while for the flowing slurry advection phenomenon also takes place due to mass transfer at different flow rates [5].
This study is related to the study of EFC performances on the base of Finite element method (FEM) based theoretical model. The adsorption of electrolytic ions on the carbon electrode as studied by Johnson and Newman is utilized to build the non-faradic model of Flow capacitor (FC) [6]. The capacitive source in the flow channels kick starts to measurable current during the charging of the carbon electrodes. The diffusion mechanism of electrolytic ions is analyzed for different geometry dimension at small flowrate of slurry. The low electronic charge transfer from current collector to the carbon is solved by mixing the slurry at low mixing rate.

Keywords: Finite element method, Ionic transportation, Geometry optimization, Electrochemical Flow capacitor (EFC), current collector design.

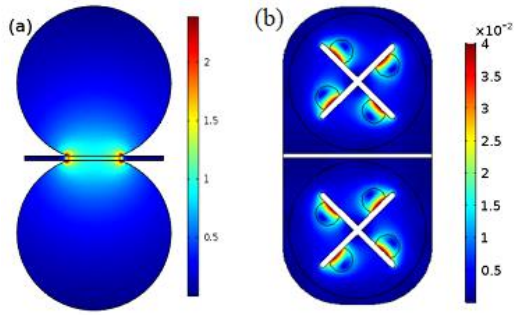


Figure 1: The current density distribution due to electronic charge transfer to electrode phase in two different geometries. (a) Static slurry while charging, (b) Mixing slurry while charging.

References:

1. V. Presser, C.R. Dennison, J. Campos, K.W. Knehr, E.C. Kumbur, Y. Gogotsi, The electrochemical flow capacitor: A new concept for rapid energy storage and recovery, Adv. Energy Mater. 2 (2012) 895–902.
2. K.B. Hatzell, M.C. Hatzell, K.M. Cook, M. Boota, G.M. Housel, A. McBride, E.C. Kumbur, Y. Gogotsi, Effect of oxidation of carbon material on suspension electrodes for flow electrode capacitive deionization, Environ. Sci. Technol. 49 (2015) 3040–3047.
3. C.R. Dennison, M. Beidaghi, K.B. Hatzell, J.W. Campos, Y. Gogotsi, E.C. Kumbur, Effects of flow cell design on charge percolation and storage in the carbon slurry electrodes of electrochemical flow capacitors, J. Power Sources. 247 (2014) 489–496.
4. N.C. Hoyt, J.S. Wainright, R.F. Savinell, Mathematical Modeling of Electrochemical Flow Capacitors, J. Electrochem. Soc. 162 (2015) A652–A657.
5. N.C. Hoyt, J.S. Wainright, R.F. Savinell, Current Density Scaling in Electrochemical Flow Capacitors, J. Electrochem. Soc. 162 (2015) 1102–1110.
6. A.M. Johnson, J. Newman, Desalting by Means of Porous Carbon Electrodes, J. Electrochem. Soc. 118 (1971) 510–517.

Strong Piezoelectric Response from Electrospun Fibers of Hybrid Polymer Embedded Dipeptide Boc-Diphenylalanine Nanotubes

Rosa Baptista,[1] Etelvina de Matos Gomes,[1] Maria Manuela M. Raposo,[2] Susana P.G. Costa,[2] Paulo Lopes,[3] Bernardo Almeida,[1] Michael S. Belsley[1]

[1]Univ Minho, Centre of Physics, Campus Gualtar, P-4710057 Braga, Portugal
[2]Univ Minho, Centre of Chemistry, Campus Gualtar, P-4710057 Braga, Portugal
[3]Univ Minho, Inst Polymers & Composites I3N, Campus Azurém, P-4800058 Guimarães, Portugal

Abstract:
Dipeptide biomaterials are strong piezoelectric materials that can transform applied mechanical forces into electricity. We have developed hybrid electrospun mats (Figure 1) of several cm^2 containing Boc diphenylalanine nanotubes dispersed within biocompatible polymers, which exhibit strong piezoelectric properties when a mechanical force is applied [1,2]. We have used the electrospinning technique to produce the nano/microstructured hybrid materials. These two dimensional structures are able to generate voltage, current and density power of up to 30V, 300nA and 2.3μW/cm^2, respectively (Figure 2), and can power several liquid-crystal display panels.
We found that the enhanced piezoelectric response of dipeptide polymer fibers functional composite are the combination of dipeptide nanotubes piezoelectric properties and enchanced mechanical strength of the polymer matrix. The electrospun mats of peptide-polymer composite may be used as bio energy sources for biomedical and clean energy applications [3].

Keywords: piezoelectricity, dipeptides, biomaterials; electrospinning, nanofibers, energy harvesting.

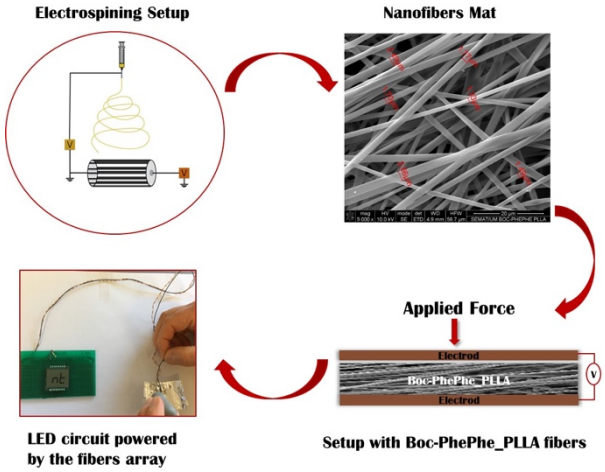


Figure 1: Electrospining setup; SEM images at high magnification level (50,000x) of Boc-PhePhe_PLLA electrospun fibers; Schematic piezoelectric setup with Boc-PhePhe_PLLA fibers mat and LED circuit powered by the fibers array.

References:

1. M. Yemini, M. Reches, J. Rishpon, E. Gazit, Novel Electrochemical Biosensing Platform Using Self-Assembled Peptide Nanotubes, *Nano Lett*. 5 (2005) 183-186.
2. A. Kholkin, N. Amdursky, I. Bdikin, E. Gazit, G. Rosenman, Strong Piezoelectricity in Bioinspired Peptide Nanotubes, *Acs Nano*. 4 (2010) 610-614.
3. E. de Matos Gomes, T. Viseu, M. Belsley, B. Almeida, M.M.R. Costa, V.H. Rodrigues, D. Isakov, Piezoelectric and pyroelectric properties of DL-alanine and L-lysine amino-acid polymer nanofibres, Mater. Res. Express. 5 (2018) 045049.

Analysis of various Aspects in Metals Creation with Given Microheterogeneity Degree

A. Anikeev,[1] I. Chumanov[1]

[1] South Ural State University, Department of Engineering and Technology of Materials Production, Chelyabinsk, Russia

Abstract:
The article discusses various aspects of the metals creation with given microheterogeneity degree, obtained by introducing dispersed particles into the melt. When creating such materials, it is important to take into account many aspects: the conditions for the dispersed particles separation from supersaturated solution, the particles interaction level with metal, the feed rate to the melt, distribution control, the particles number in the melt volume, the microheterogeneity influence on the properties' level, and other aspects. The article analyzes modern approaches for solving each aspect, proposes the methodology for calculating the crystallization rate and particle distribution when fed into the metal during centrifugal casting. Based on the developed methodology, computer model was built allowing to predict the particles distribution depending on many factors.

Keywords: dispersed particles, cast alloys, wetting, injection rate, microheterogeneity, distribution density

Acknowledgments
This work was supported by the Ministry of Education and Science of the Russian Federation (project no. 11.9658.2017/8.9).

References:

1. Watanabe, Y., Sato, H. (2011), Review Fabrication of Functionally Graded Materials under a Centrifugal Force, *in book "Nanocomposites with Unique Properties and Applications in Medicine and Industry" (ed. by John Cuppoletti, InTech)*, 372-378.
2. Chumanov, I., Anikeev, A. (2015), Fabrication of functionally graded materials by introducing wolframium carbide dispersed particles during centrifugal casting and examination of FGM's structure, *Procedia Engineering,* 2, 816-820.
3. Kiviö, M., Holappa, M., Yoshikawa, T. (2012), Interfacial Phenomena in Fe-TiC Systems and the Effect of Cr and Ni, *High Temp. Mater. Processes,* 31(4-5), 645-656.
4. Sobczak, N., Nowak, R., Radziwill, W. (2008) Experimental complex for investigations of high-temperature behaviour of molten metals in contact with refractory materials, *Mater. Sci. Eng., A,* 495(1-2), 43-49.
5. Kiviö, M., Holappa, L., Louhenkilpi S. (2016), Studies on interfacial phenomena in titanium carbide/liquid steel systems for development of functionally graded material, *Metall. Mater. Trans. B,* 47, 2114-2122.
6. Han, Q., Hunt, D. (1995), Particle pushing: critical flow rate required to put particles into motion, *J. Cryst. Growth,* 152(3), 221-227.
7. Wilde G., Perepezko H. (2000), Experimental study of particle incorporation during dendritic solidification, Mater. Sci. Eng., A, 283(1-2), 25-37.
8. Catalina, A., Mukherjee, S., Stefanedcu, D. (2000), A dynamic model for the interaction between a solid particle and an advancing solid/liquid interface, *Metall. Mater. Trans. A,* 31(10), 2559-2568.
9. Wang, Q., Zhang, L. (2016), Determination for the Entrapment Criterion of Non-metallic Inclusions by the Solidification Front During Steel Centrifugal Continuous Casting, *Metall. Mater. Trans. B*, 31 (10), 1933-1949.
10. Wang, Q., Zhang, L. (2016), Detection of Non-metallic Inclusions in Centrifugal Continuous Casting Steel Billets, *Metall. Mater. Trans. B,* 47(3), 1594-1612.
11. Martinez, E., Peaslee, D., Lekakh, S. (2011), Calcium Wire Ladle Treatment to Improve Cleanliness of Centrifugally Cast Steel, *Transactions of American Foundry Society,* 119, 513-520.

12. Türker, M., Çapan, L. (2017), Effect of inclusions on mechanical properties of Nb stabilized austenitic stainless steels (316Nb) with centrifugal and sand casting techniques, *Matériaux et Techniques,* 105(3), #2017035.
13. Anikeev, A., Seduhin, V., Sergeev, D. (2016), Increase in wear resistance by introduction of titanium carbide dispersed particles, *Mater. Sci. Forum,* 843, 269-273.
14. Al-Mangour, B. Grzesiak, D. (2016), Selective laser melting of TiC reinforced 316L stainless steel matrix nanocomposites: Influence of starting TiC particle size and volume content, *Mater.Des.,* 104, 141-151.
15. Li, H., Li, P., Chen, W. (2017), Effect of WC and Co on the microstructure and properties of TiC steel-bonded carbide, *Mater. Sci. Forum,* 898, 1468-1477.

Adapting the properties of 3d-printed tailored lightweight mechanical metamaterials

E. Truszkiewicz,[1] M.Berer, [1] G. Meier[1], M. Vetter,[1]
M. Rossegger,[1] S. Schlögl,[1] P.Fuchs,[1] G.Pinter,[1]

[1] Polymer Competence Center Leoben GmbH, Leoben, Austria

Abstract:
The continous development of additive manufacturing over recent years increased considerably both, the process quality and the quality of printed products. Typical features of 3d-printing techniques such as fast prototyping, less waste of the material, possibility to create very complicated components, not possible to produce with conventional methods, are already very well known. However, the 3d-printig techniques can also be used for the production of lightweight structures. With 3d-printing, defined mechanical properties can be achieved through specific geometry design. For example for a honeycomb geometry this is reduction of weight and material costs, keeping at the same time relative good out-of-plane compression and shear properties. The artificially structured materials with unique properties in comparison to traditional components are called metamaterials. Their properties are defined mainly from the designed structure.
In this project, four polymers were processed with in total three different 3D-printing techniques. Each polymer was printed in four differently designed structures. For each combination of geometry and material/printing method the mechanical behavior was studied. The present study shows the results of the mechanical characterization for one of these specimen groups – polylactic acid structures printed with fused filament fabrication.

Keywords: additive manufacturing, 3d-printing, mechanical metamaterials, polylactic acid, lightweight conctructions

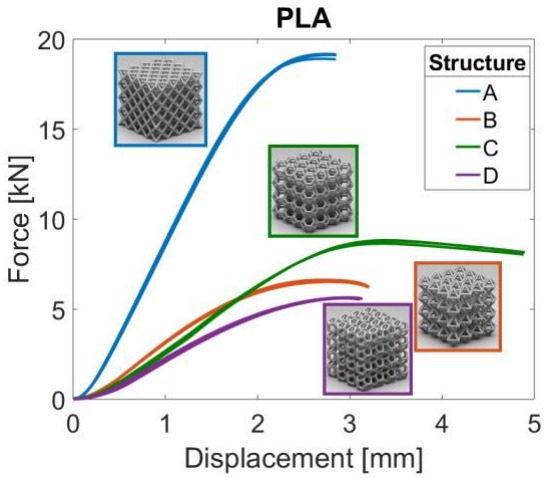


Figure 1: Mechanical properties of different PLA structures printed with fused filament fabrication - the figure shows the curves of the compression tests until the point of ultimate compressive strength.

References:

1. Jiang, Y., Wang, Q. (2016) Highly-stretchable 3D-architected Mechanical Metamaterials, *Scientific Reports,* 6
2. Christensen, J., Kadic, M., Kraft, O., Wegener, M. (2015), Vibrant times for mechanical metamaterials, *MRS Communications*, 5, 453-462.
3. Pham M.S., Liu Ch., Todd I., Lertthanasarn J. (2019), *Nature*, 7739, 305-311
4. Bertoldi K., Vitelli V., Christensen J., van Hecke M. (2017), Flexible mechanical metamaterials, *Nature Reviews Materials*, 2, 11

Concept and economic evaluation of an automotive composite part with integrated wireless sensorsystem

M. Hardt,[1,*] Prof. P. Middendorf, [2] Prof. R. Bjekovic[3],
[1] Daimler AG, Stuttgart, Germany
[2] Institut of Aircraft Design, University of Stuttgart,
[3] University of Applied Science Ravensburg-Weingarten

Abstract:
In addition to traditional research and development topics, such as lightweight construction, the automotive industry is currently facing a variety of challenges in the areas of connectivity, autonomous driving, mobility services and electrification. These development directions will be further intensified in the future, leading to a significant increase in electronic and sensor components in vehicles [1]. Continuing miniaturization of components on the one hand and reduction of costs on the other hand enable completely new possibilities for integrated functionalities.
One research approach that takes into account both the requirements for consistent lightweight construction and for integrated functionalities is sensor integration in fiber composite materials. Due to their high lightweight potential as well as the specific manufacturing process using different plies of materials, fibre reinforced composites (FRPs) are the ideal material for sensor-integrated components [2], [3].
In the context of this work, the integration of a wireless sensor system into an automotive series component made of carbon fiber reinforced plastic (CFRP) is presented. It is shown how a component platform with a multifunctional range can be manufactured from a conventional structural component. The design and integration of the sensor system is based on the specific requirements of the Resin-Transfer-Moulding (RTM) process as an established manufacturing process for CFRP components as well as specific functional requirements of a sensor-integrated component in automotive engineering.

The integration of sensor systems into CFRP enables a multitude of new functions, which in turn can have a positive effect on the cost-benefit ratio of the product. Process monitoring for quality improvement during production or predictive maintenance of the composite part but also of the surrounding parts and components in the usage phase are obvious use-case examples. The cost-benefit ratio of this technology is shown on the basis of a new approach for the evaluation of economic efficiency of sensor-integrated CFRPs.

Keywords: automotive composites, functional integration, sensorintegration, wireless sensorsystem, resin-transfer-moulding, process-monitoring, cost-benefit analysis

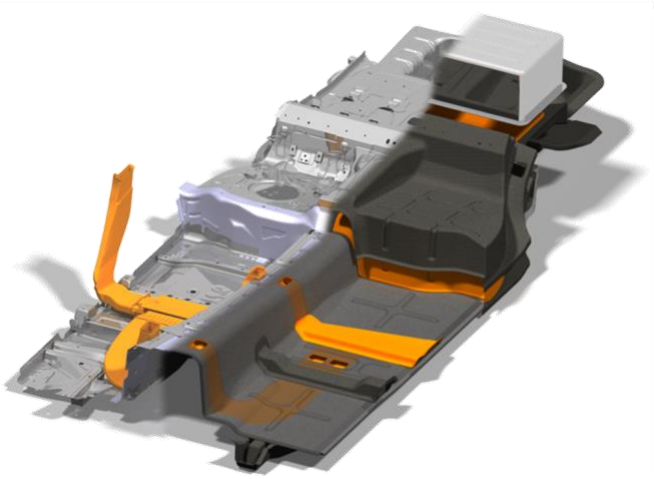


Figure 1: LeiFu (Leightweight with integrated functionalities) - Automotive CFRP underbody structure

References:

1. W. Fleming, “New Automotive Sensors – A Review,” IEEE Sensors J., vol.8, no. 11, pp. 1900-1921, Nov. 2008.
2. K. Moghaddam, et al., “Sensor Integration in Fiber-Reinforced Polymers: Technology and Applications”, Material-Integrated Intelligent Systems - Technology and Applications, pp. 159-200, 2018, Wiley-VCH.
3. B. Fox, et al., „Smarte Kunststoff-Bauteile für Automotive Innovation und Industrie 4.0“, ZWF - Zeitschrift für wirtschatflichen Fabrikbetrieb 112 (7/8), pp 522-525, 2017, Carl Hanser Verlag.

SMS 2019- Session Optically Engineered Surfaces Manufacturing of 3D nanostructured optics (H2020 project PHENOMENON)

Direct Laser Writing: Materials and Applications

Maria Farsari
IESL-FORTH, N. Plastira 100, 70013, Heraklion, Crete, Greece.
*mfarsari@iesl.forth.gr

Abstract

Direct Laser Writing (DLW) is a technique that allows the fabrication of three-dimensional structures with sub-100 nm resolution. It is based on multi-photon absorption; when the beam of an ultra-fast laser is tightly focused into the volume of a transparent, photosensitive material, polymerization can be initiated by non-linear absorption within the focal volume. By moving the laser focus three-dimensionally through the material, 3D structures can be fabricated. The technique has been implemented with a variety of materials and several components and devices have been fabricated such as photonic crystals (Fig. 1a), biomedical devices (Fig. 1b), and microscopic models (Fig. 1c).

The unique capability of DLW lies in that it allows the fabrication of computer-designed, fully functional 3D devices. Here, we summarize the principles of microfabrication, and present our recent work in materials processing and functionalization of 3D structures. Finally, we discuss the future applications and prospects for the technology.

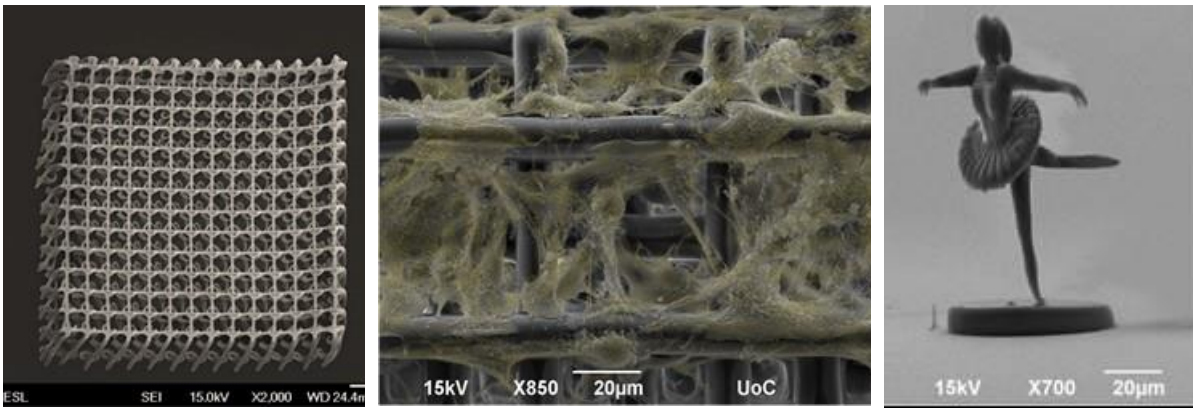


Fig. 1: (a) A spiral photonic crystal. (b) Scaffold for cell growth (c) A micro-dancer

Massively parallel multiphoton photoplotting: rationale, techniques and implementation obstacles

K. Heggarty, L. Perez-Covarrubias, A. Khalidi,

IMT Atlantique, Departement Optique, Technopole Brest-Iroise, 29238 Brest, France

Abstract:
Multiphoton (MPP) – nano/microfabrication is now a mature technology with commercial systems now available from a number of manufacturers (e.g. Nanoscribe, Multiphoton Optics, Microlight … The technique's unrivalled combination of resolution (~10nn) and flexibility (full 3D) has resulted in the use of these systems as a tool by numerous industrial and academic R&D teams across the world for several years: see, for example [1].
However the remaining main practical drawback or weakness of the technique are the very long write times for high resolution structures with areas/volumes greater than 1mm^3 (write times up several hours or days). This has greatly restricted the application of these techniques in the fabrication of large dimension (>cm) structures such as photonic surfaces, particularly in a production environment.
High repetition rate lasers and high speed galvo scanning have enabled plot rates to increase but the fundamental limitation results from the use of a single write beam. A similar problem in conventional "single-photon" laser writers has largely been solved through the use of massive parallelization: dividing a laser beam into up to millions of independent beams [2][3].
Some attempts have been made to apply these parallelization techniques to MPP photoplotting mainly in academic laboratories [4]. They generally use either fixed microoptical structures – such as microlens arrays in an imaging configuration or diffractive optical elements (DOEs) to gereate an array of write spots – or spatial light modulators (SLM) to generate a real-time reconfigurable array of light beams in either a Fourier domain configureation (phase-modulation SLM) or an imaging configuration (amplitude modulation SLM).
We will review these techniques and different approaches, highlighting their advantages and drawbacks and the specific difficulties involved in applying each of these techniques to MPP photoplotting. In particular, we will present the knowledge gained and recent results in our consortium has obtained in the EU H2020 Phenomenon project which aims specifically to study and implement massively parallel MPP photoplotting based on these approaches.

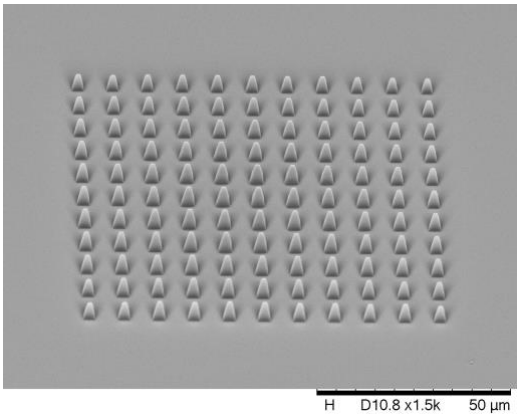


Figure 1. Array of pyramids obtained by parallel MPP with a DOE generated 11x11 array of DOE write beams in the Phenomenon project by partner Multiphoton Optics GmbH.

References:

1. T.Baldacchini, "3D microfabrication using two-photon polymerisation", Elsevier 2016.
2. M. Kessels et al., "Versatile stepper based maskless microlithography using a liquid crystal display for direct-write of binary and multi-level microstructures", Journal of Micro/Nanolithography, MEMS, and MOEMS (JM3), July 2007
3. H. Martinsson et al, "Current status of optical maskless lithography," Journal of Micro/Nanolithography, MEMS, and MOEMS 4(1), 011003 (1 January 2005).
4. S. Gittard et al, "Fabrication of microscale medical devices by two-photon polymerization with multiple foci via a spatial light modulator," Biomed. Opt. Express 2, 3167-3178 (2011)

Acknowledgements
The Phenomenon project received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No.780278.

Tiny Fiber Sensors by Laser Processing

José Miguel López-Higuera[1,2,3],
Pablo Roldan-Varona[1], David Pallarés Aldeiturriaga[1,2], Luis Rodriguez Cobo[2]

Grupo de Ingeneiería Fotónica
[1]Universidad de Cantabria,
[2]Centro de Investigación Biomédica en Red de Bioingeniería, Biomateriales y Na-nomedicia (CIBER-BBN)
[3]Instituto de Investigación Sanitaria Valdecilla (IDIVAL);
Edificio I+D+I de Telecomunicación, planta -3, Avda. Los Castros s/n, 39005 Santander, Spain

Abstract
Sensors are the devices or systems developed to offer the capacity to capture, quantify and trans-late physical and chemical magnitudes to another domain, normally electrical. When the mentioned sensor system uses light-based technologies in their key sensing part/s, then, they can be recognized as Light based Sensors [1] or Pho-tonic Sensors, PS. If any of the processes or parts use fiber-optic technology, a subdivision of PS known as Fiber/Fibre Optic Sensors (FOS), or Optical Fiber/Fibre Sensors (OFS), is then created [2]. When the optoelectronic unit of an Optical Fiber Sensor is equipped with some kind of intelligence and the sensing system is capable to give an actuation signal, then the PS is transformed into a smart optical fiber sensor [2].
By using appropriately laser light-transparent matter interaction concepts, today, it is possible to write optical structures on or inside the optical substrates, using laser beams [3]. Tiny sensing structures can be fabricated on/in optical fibers enabling optical fiber tiny transducers [4]. They could be used in a wide set of applications. It could, for instance, be y placed on/in at a given structure, becoming a key part of a Structural Health Monitoring System (SHM).
In this invited talk, after address some comments concerning the basics of laser light interaction with transparent materials such optical fibers, comments on the key laser parameters and how they could be measured, will also delivered. Then, we will do a "flight" over several cases of tiny transducers written in/on fibers able to be used in very different applications. Challenges to face in the near future will be also addressed and discussed. Finally, according to one of the aims of the PHENOMENON special session, a brief comment con-corning our R&D&I group and ISLIST will be, also addressed.

Keywords: Photonic sensors, Optical sensors, Smart sensors, tiny fiber transducers, tiny optical fiber sensors, lasers processed fiber sensors.

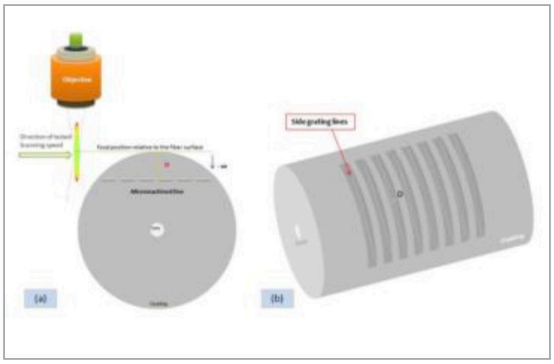


Figure 1. Illustration of a optical fiber micromacrined to write an external sensing structure.

ACKNOWLEDGMENTS

The State Research Agency (AEI) of Spain is support-ing this work under the project SENSA TEC2016-76021-C2-2-R.

References:

1. J.M. Lopez-Higuera et al. 'Fiber Optic Sensors in Structural Health Monitoring (Tutorial Invited)'; Journal of Lightwave Technology, Vol.29, Nº 4, pp. 587-608; 2011.
2. JM López-Higuera,"Smart Light based sensors", In-vited ISLIST/UIMP, June 27, 2018, Santander, Spain
3. R.R Gattass and Eric Mazur, "Fentosecond laser micromachining in transparent materials", Nature Photonics, Vol 2, April 2008.
4. Pallarés-Aldeiturriaga, David, et al. "Curvature sensor based on in-fiber Mach–Zehnder interferometer in-scribed with femtosecond laser." Journal of Light-wave Technology 35.21,4624-4628; 2017.

Novel methods to prepare photoelectrodes for solar fuels

Dr. Salvador Eslava
Senior Lecturer in the Dept. of Chemical Engineering, Imperial College London
s.eslava@bath.ac.uk

Abstract

Photoelectrochemical solar water splitting offers a clean solution to the world energy requirements of a sustainable future. Achieving its full potential depends on developing inexpensive photoanodes that can efficiently evolve oxygen from aqueous electrolytes, the most kinetically demanding step in water splitting. Here I present recent developments we have achieved in the preparation of inexpensive photoanodes: a nanostructured TiO_2 with exposed {0 1 0} facets, an α-Fe_2O_3 self-coated with FeOx electrocatalyst and with an electrodeposited $CoFeO_x$, and a novel all-inorganic halide perovskite $CsPbBr_3$.[1-4] The nanostructured TiO_2 photoanodes are prepared using $Ti_7O_4(OEt)_{20}$ clusters as a precursor and resulting photoanodes show a unique morphology resembling desert roses, pure anatase phase and high exposure of the very active {0 1 0} facet, achieving remarkable ~100% IPCE efficiency at 350 nm wavelength.[1] α-Fe_2O_3 photoanodes simultaneously coated with FeO_x electrocatalyst are prepared using precursors whose morphology and crystallinity is tuned with lactic acid additive, boosting photoanode photocurrents from 0.32 to 1.39 mA cm^{-2} at 1.23 V_{RHE}.[2] An extended electrochemical characterisation also shows that the charge transfer to electrolyte at α-Fe_2O_3 interfaces can be boosted by an extremely thin layer of $CoFeO_x$, unlike less thin $CoFeO_x$ layers that just reduces surface recombination due to self-oxidation.[3] Finally, all-inorganic halide perovskite $CsPbBr_3$ photoanodes are prepared using carbon as a hole transport layer.[4] This type of semiconductor is revolutionising the field of solar cells due to their high efficiencies and inexpensive preparation but remain practically unexplored in applications using aqueous electrolytes. However, our developed inexpensive carbon layers effectively protect the halide perovskite for more than 30 h directly immersed in water, evolving oxygen with a Faradaic efficiency of 82% and achieving photocurrents above 2 mA cm^{-2} at 1.23 V_{RHE}.

References

1. M. Regue, S. Sibby, I. Y. Ahmet, D. Friedrich, F.F. Abdi, A. L. Johnson, S. Eslava, *J. Mater. Chem. A* 2019, 7, 19161-19172.
2. D. Walsh, J. Zhang, M. Regue, R. Dassanayake, S. Eslava, *ACS Appl. Energy Mater*. 2019, 2, 2043–2052
3. J. Zhang, R. García-Rodríguez, P. Cameron, S. Eslava, *Energy Environ. Sci.* 2018,11, 2972-2984
4. I. Poli, U. Hintermair, M. Regue, S. Kumar, E.V. Sackville, J. Baker, T.M. Watson, S. Eslava, P.J. Cameron, *Nature Communications* 2019, 10, 2097

EGF 2019 - Session I
Graphene Synthesis, Growth, Functionalization and Characterization

NanoSonic - Graphenest NanoSonication Technology

Clean graphene nanoparticles production for application across electronics, aerospace and textile industries

A. Bernardes[1], R. Silva[1], B. Figueiredo[1], J. França[1], V. Abrantes[1]

[1] Graphenest S.A., Aveiro, Portugal

Abstract:
In order to meet the demand for a highly profitable, versatile and environmentally friendly graphene production method, Graphenest (GPN) developed a methodology based on liquid phase exfoliation (Figure 1) that tested using a panoply of mineral graphites.

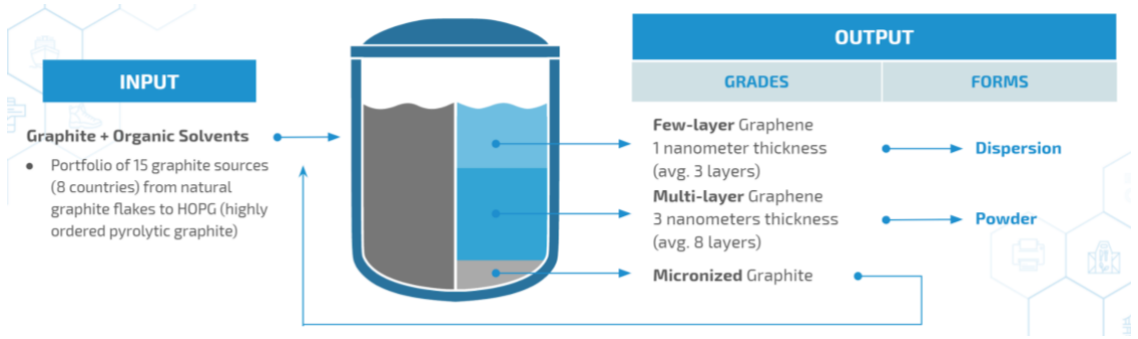


Figure 1. Graphenest's NanoSonicatin Technology – NanoSonic

Since 2010, graphene suppliers took advantage of the novelty of this nanomaterial and wide range of potential applications by overselling it as a wonder material or a magic dust that would suddenly transform any industry. Naturally, and with time, hype faded away and realism has finally set in. Today, is possible to affirm that the industry is finding some focus and converging to specific applications due to the accumulated market feedback. Therefore, graphene nanoplatelets are increasingly, and in the right way, viewed as part of the expansive continuum of carbon additive materials. Nonetheless, in terms of applications, the opportunities for graphene are endless. Since late 2018, and apart from the graphene nanoparticles production, GPN also develops relevant R&D initiatives, within the functional inks/coatings and advanced composites markets, where two end-products pop-up:

1. A conductive ink/coating: **HexaShield**TM is an innovative graphene-based EMI shielding paintable coating system that offers customized electrical resistance and wave attenuation levels. It was developed to solve problems such as temporary disturbances, data loss, and system failure of electronic devices, equipment, and systems caused by Man-made and natural EMI sources. Graphene's conductive properties make it possible to replace metallic coatings, foils, meshes, and enclosures, with a lighter, flexible coating that can be easily applied using a straightforward approach; and

2. An advanced epoxy system: **HexaMatrix**TM is a graphene-based epoxy resin system that can be applied in any fibre reinforced to improve mechanical strength, fibre wetting properties, moisture absorption, flow properties, durability, and chemical resistance. Graphene nanoplatelets upgrades these properties by taking advantage of its aspect ratio, as well as of its intrinsic mechanical strength..

However, GPN is still developing other relevant graphene-based application within the following markets: automotive, electronics, aerospace, marine/industrial and textile.

Bias-controlled doping of graphene with thin ice: a theoretical DFT study

E. Rauls[1], U. Gerstmann[2], A. Jaadouni[2], W.G. Schmidt[2]

[1] Institutt for Matematikk og Fysikk, University of Stavanger, 4036 Stavanger, Norway
[2] Department of Physics, University of Paderborn, 33098 Paderborn, Germany

Abstract:
Since the discovery of graphene the adsorption of water has been discussed as a promising possibility for doping [1], while changing the electron mobility surprisingly little. Theoretical studies have shown however, that the electronic properties of the resulting system strongly depends on the microscopic details of the substrate [2]. On the other hand, in particular if adsorbed on surfaces, water can occur in many crystalline ice phases [3]. In this theoretical work we investigate the influence of the different ice phases on water absoption on graphene using density functional theory (DFT).

Taking into account van-der-Waals interaction, we demonstrate that adsorption of a few layers of ice on graphene, free standing as well as adsorbed on silicon carbide, can indeed result in a charge transfer between the ice and the graphene layers. In principle, it thus can lead to a doping of graphene. The sign of the charge transfer and by this the type of doping, however, essentially depends on the orientation of the water molecules, whereby the respective differences in total energy are almost negligible. As a consequence, in thermal equilibrium a mixture of different phases is expected, resulting in a cancellation of the doping effect. We demonstrate how external electric fields can be used to discriminate between different ice phases. Depending on the sign of the bias voltage an electric field component parallel to the surface normal proposes a well-defined control of the doping covering both types of doping, *n*-type as well as *p*-type.

Keywords: graphene doping, ice, water, DFT, simulation, electric field

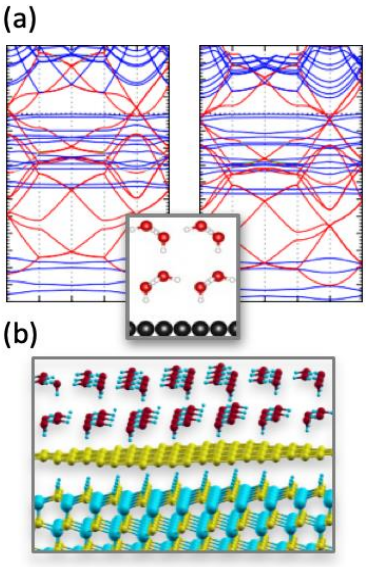


Figure 1: (a) bandstructures of 2ML ice on graphene. Adsorbate orientation and application of static electric fields lead to p-type and n-type doping. (b) substrates with different lattice mismatches affect doping. On SiC, water mediated n-type doping survives, while p-type doping is suppressed.

References:

1. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Science **306**, 666 (2004).
2. T.O. Wehling, A.I. Lichtenstein, and M.I. Katsnelson, Appl. Phys. Lett. **93**, 202110 (2008).
3. G. Algara-Siller, O. Lehtinen, F.C. Wang, R.R. Nair, U. Kaiser, H.A. Wu, A.K. Geim, and I.V. Grigorieva, Nature **519**, 443 (2015).

Soliton fractional charges in graphene nanoribbon and polyacetylene: similarities and differences

S.-R. Eric Yang
Department of Physics, Korea University, Seoul, Korea

Abstract:
An introductory overview of current research developments regarding solitons and fractional boundary charges in graphene nanoribbons is presented. Graphene nanoribbons and polyacetylene have chiral symmetry and share numerous similar properties, e.g., the bulk-edge correspondence between the Zak phase and the existence of edge states, along with the presence of chiral boundary states, which are important for charge fractionalization. In polyacetylene, a fermion mass potential in the Dirac equation produces an excitation gap, and a twist in this scalar potential produces a zero-energy chiral soliton. Similarly, in a gapful armchair graphene nanoribbon, a distortion in the chiral gauge field can produce soliton states [1]. In polyacetylene, a soliton is bound to a domain wall connecting two different dimerized phases and display spin-charge separation [2]. In graphene nanoribbons, a domain-wall soliton connects two topological zigzag edges with different chiralities. However, such a soliton does not display spin-charge separation. The existence of a soliton in finite-length polyacetylene can induce formation of fractional charges on the opposite ends (there is as yet no conclusive experimental evidence for this). In contrast, for gapful graphene nanoribbons, the antiferromagnetic coupling between the opposite zigzag edges induces integer boundary charges. The presence of disorder in graphene nanoribbons partly mitigates antiferromagnetic coupling effect (see Fig.1). Hence, the average edge charge of gap states within a small energy interval is e/2, with significant charge fluctuations. However, midgap states exhibit a well-defined charge fractionalization between the opposite zigzag edges in the weak-disorder regime (see Fig.2) [3]. An excellent opportunity to observe these boundary charges has recently arisen, as rapid progress has been made in the fabrication of atomically precise graphene nanoribbons (GNRs) [4].

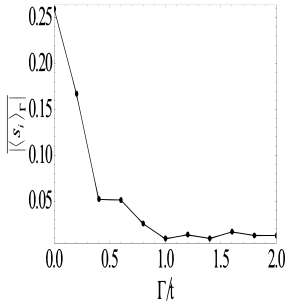


Figure 1 Disorder-averaged spin value per edge site vs. strength of disorder Γ. Range of impurity potential, ratio between numbers of impurities and carbon atoms, length of ribbon, width of ribbon are, respectively, $\mathbf{d = 0}$, $\boldsymbol{n_{imp}} = \mathbf{0.1}$, $\boldsymbol{L = 125.4, w = 7.1}$. The number of disorder realization is $N_D = 10$.

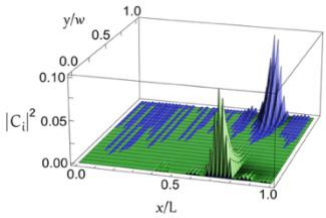


Figure 2 Probability density of a midgap state with fractional charges of 1/2 residing on the opposite zigzag edges.

References

1. Y. H. Jeong, S.C. Kim and S.-R. Eric Yang, Topological gap states of semiconducting armchair graphene ribbons, *Phys. Rev. B* **91**, 205441 (2015).
2. T. C. Chung, F. Moraes, J. D. Flood, A. J. Heeger, Solitons at high density in trans-(CH)x: Collective transport by mobile, spinless charged solitons. Phys. Rev. B **29**, 2341 (1984).
3. Y. H. Jeong, S.-R. Eric Yang, and M. C. Cha, Soliton fractional charge of disordered graphene nanoribbon. J. Phys.: Condens. Matter **31**, 26560 (2019).
4. P. Ruffieux, S. Wang , B. Yang , C. Sanchez-Sanchez , J. Liu, T. Dienel, L. Talirz , P. Shinde, C. A. Pignedoli, D. Passerone, T. Dumslaff , X. Feng, K. Mullen and G. Fasel R, On-surface synthesis of graphene nanoribbons with zigzag edge topology, *Nature* **531**, 489 (2016).

Simulation and Growth of Graphene for Silicon Microeletronic Applications

G. Lippert,[1*] J. Dabrowski,[1] A. Becker, [1] M. Lisker,[1] Ch. Wenger,[1,2] A.Mai,[1,3] M. Lukosius[1]

[1] IHP - Leibniz-Institut für innovative Mikroelektronik, 15236 Frankfurt (Oder), Germany
[2] Brandenburg Medical School Theodor Fontane, 16816 Neuruppin, Germany
[3]Technical University of Applied Science Wildau, Hochschulring 1, 15745 Wildau, Germany

Abstract:
As graphene is expected to complement the existing technologies, notably the mainstream CMOS, its deposition on substrates compatible with Si CMOS is of high importance. Transfer of graphene onto the target wafer might be an option, but is associated with cost and risks [1], so graphene should best be grown directly on the same substrate, on which it will be used.
One of a potential substrates is an epitaxial Ge film deposited on Si(001) [2-4]. C is then delivered from solid source molecular beam epitaxy (MBE) or in hydrocarbons by chemical vapour deposition (CVD). The growth physics is thus not obvious from common experience and the need for process optimization calls for advanced knowledge on the mechanism involved [3,4].
We report on experimental and theoretical study of graphene synthesis on Ge(001)/Si(001) from CH_4 and also from atomic carbon (Fig.1). The effect of the growth parameters was investigated by μ-Raman, secondary electron microscopy (SEM), scanning tunneling microscopy (STM), atomic force microscopy (AFM), and by transmission electron microscopy (TEM); ab-initio density functional theory (DFT) was used to get insight into the atomistic details of the nucleation and growth. The chemical interaction of C atoms with the Ge substrate plays an important role in the process. This interaction can be addressed experimentally by growing graphene from atomic carbon [2,4].
We also discuss the attempts to integrate the grown graphene into the 200mm silicon technology platform. We investigated the processes of graphene synthesis, cleaning, patterning, a non-destructive deposition of dielectric materials on the graphene sheet as well as the combinations of these processes for various concepts of contacting graphene (Fig.2).

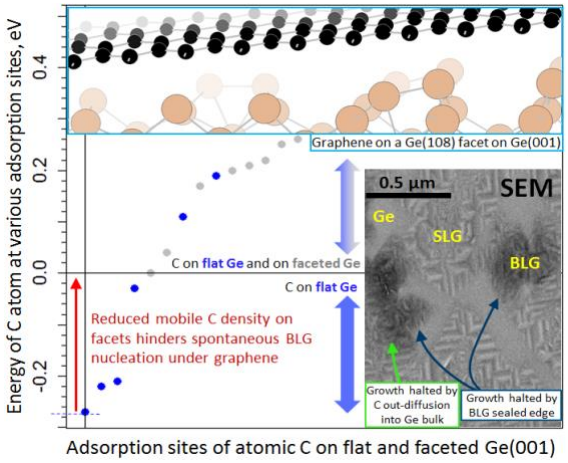
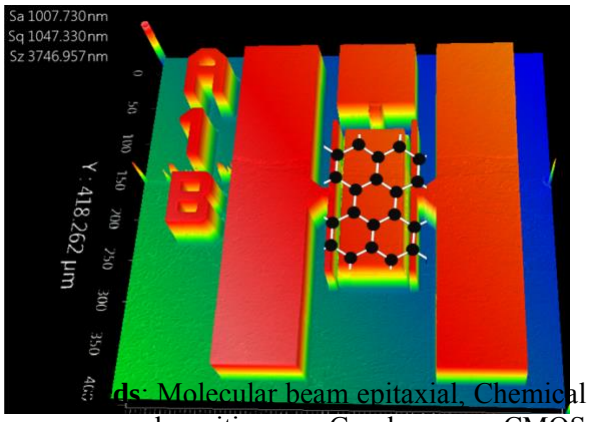


Figure 1: Growth-induced faceting of Ge(001). **Plot**: C atom energy at various sites on flat (blue) and faceted (gray) surface. **SEM**: Single-layer graphene (SLG) with parasitic bi-layer (BLG) islands; flat area is uncovered Ge. Faceting and BLG formation are explained by DFT results.



ds: Molecular beam epitaxial, Chemical vapour deposition, Graphene, CMOS technology, DFT simulations.

Figure 2: Optical profilometry of a processed graphene device (graphene base transistor [5]).

References:

1. G. Lupina et al., ACS Nano, 9, 4776 (2015).
2. G. Lippert et al, Carbon 75 (2014) 104.
3. M. Lukosius et al., ACS Appl. Mater. Interfaces 8, 33786 (2016).
4. J. Dabrowski et al, Sci. Rep. 6, 31639 (2016).
5. W. Mehr et al, EDL 33, 691 (2012)

Graphene Oxide as the Catalyst of Ethane Dehydrogenation

A.A. Abakumov, I.B. Bychko, P.E. Strizhak

L.V. Pisarzhevsky Institute of Physical Chemistry of the National Academy of Sciences of Ukraine
Nauky Ave. 31, 03028 Kyiv, Ukraine

Abstract:
Direct dehydrogenation (DDH) of alkanes is a perspective pathway for producing olefins. Most of the dehydrogenation catalysts are presented by metal-based materials. The exploiting of metal-containing catalysts is interfered with intense coke formation and metal particles agglomeration at high temperatures. Therefore, the DDH process requires the design of novel catalysts. Reduced graphene oxide (RGO) is characterized by high thermal stability and coke-formation resistivity. Also, it was shown that RGO shows catalytic activity in the hydrogenation reaction of unsaturated hydrocarbons [1,2]. Therefore, RGO may be a perspective candidate for catalyzing the DDH of alkanes. This report describes the catalytic activity of RGO and N-doped RGO (N-RGO) in DDH of ethane. Initial graphene oxide was synthesized according to the improved procedure [3]. Both solids are characterized by similar lamellar morphology. The distance between defects does not exceed 3 nm for both materials. The thickness (L_c) and lateral size (L_a) of the structures formed by graphene region overlapping are up to 3 and 10nm, respectively, for both catalysts. The molar ratios C/O are 12 and 3 for N-RGO and RGO, respectively. The nitrogen content in N-RGO corresponds to 1 nitrogen atom per 18 carbon atoms. The specific surface areas are 250 and 140m_2/g for N-RGO and RGO, respectively. Functional groups are presented by carbonyls, hydroxyls, ethers and carboxyls. Also, the N-RGO sample contains pyrazole cycles, graphitic and N-oxide prirdinic nitrogen atoms. Figure 1 illustrates the catalytic activity of RGO and N-RGO in DDH of ethane. Major hydrocarbon products of ethane DDH are presented by methane and ethylene. The main product of ethane DDH is ethylene. The productivity values for RGO sample are higher compared to N-RGO. Smaller catalytic activity of N-RGO may be caused by nitrogen doping graphene lattice with nitrogen resulting in transfer of electron density from graphene area to nitrogen atoms. Additional possible reason of lower catalytic activity may be the smaller oxygen functional group content.

Keywords: ethane, dehydrogenation, reduced graphene oxide, graphene

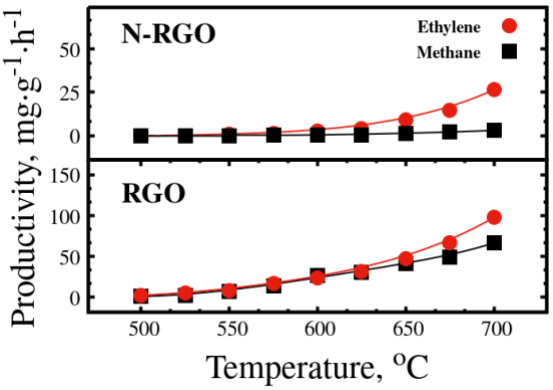


Figure 1: Dependences of ethylene and methane formation productivity on temperature for N-RGO and RGO. Productivity dimensionality is mass of products in “mg” per 1g of the catalyst per 1 hour. Catalyst load is 500mg. The inlet gas mixture flow rate is 10 ml/min with helium-to-ethane ratio of 1:1.

References:

1. A. Primo, F. Neatu, M. Florea, V. Parvulescu, H. Garcia. Graphenes in the absence of metals as carbocatalysts for selective acetylene hydrogenation and alkene hydrogenation. *Nat. Comm*. 2014, 5:5291.
2. T. I. Perhun, I. B. Bychko, A. I. Trypolsky, P. E. Strizhak. Catalytic Properties of Graphene Material in the Hydrogenation of Ethylene. *Theor. Exp. Chem*. 2013, 48, 367–370.
3. D. C. Marcano, D. V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J.M. Tour. Improved Graphene Oxide Synthesis. *ACS Nano*. 2010, 4, 4806–4814.

Catalytic activity of carbon nanomaterials in the ethylene and acetylene hydrogenation

I. Bychko,[1*] P. Strizhak[1]

[1]L. V. Pisarzhevsky Institute of Physical Chemistry of the National Academy of Sciences of Ukraine, Kyiv, Ukraine.

Abstract:
Transparent
In the last 7 years several studies dedicated to the carbon nanomaterials such as multi-walled carbon nanotubes (CNTs) and reduced graphene oxide (rGO) catalytic activity in the hydrogenation reactions have been reported. Particularly, in our group for the first time it was shown that rGO and CNTs are active in the gas-phase hydrogenation reactions on the example of ethylene hydrogenation. Our experiments indicate that than the ethylene and acetylene hydrogenation rate reaches $2.1 \cdot 10^{-7}$ mol•s^{-1}•m^{-2} and $1,4 \cdot 10^{-6}$ mol•s^{-1}•m^{-2} respectively for CNTs and $8 \cdot 10^{-8}$ mol•s^{-1}•m^{-2} and $1,5 \cdot 10^{-7}$ mol•s^{-1}•m^{-2} respectively for rGO.
The structure of catalytic active sites on the surface of the carbon nanomaterials in the hydrogenation reaction is still an open problem. It was shown that H_2 activation can take place at the carbon atom vacancies. A possibility of H_2 activation by frustrated Lewis pairs on the carbons surface has been also discussed. Recently, it has been indicated an activation via the π-π interaction for aromatic compounds.
Our experiments indicate a fairly high stability of CNT in a comparison with the typical hydrogenation catalysts in both, hydrogen-rich and ethylene-rich, atmospheres. This offers new opportunities for the CNT-based catalysts application in the hydrogenation reaction at high temperatures, in particular, under conditions when the metal-containing catalysts deactivate due to the carbonaceous deposits formation.

Keywords: reduced graphene oxide, gas-phase hydrogenation, carbocatalysis, selective hydrogenation.

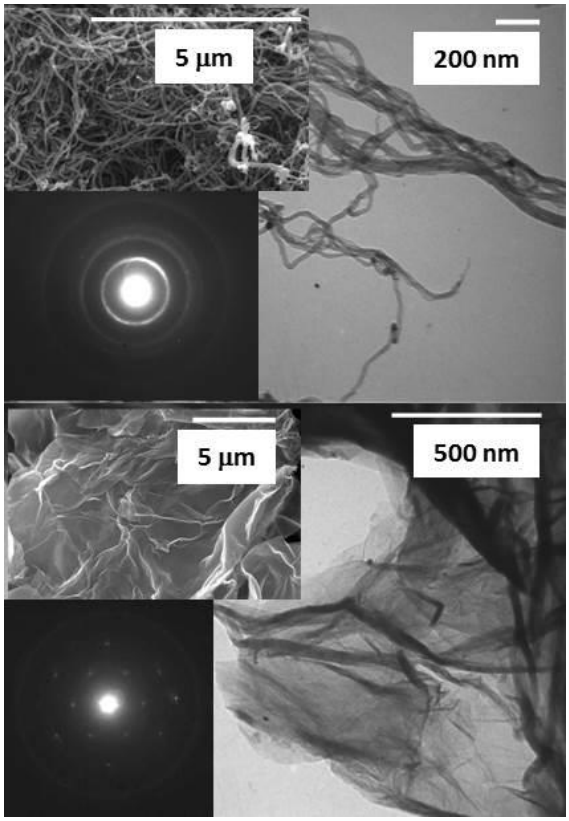


Figure 1: Figure shows typical TEM, SEM images, and electron diffraction patterns (EDP) of MWCNT and rGO.

References:

1. Abakumov A.A., Bychko I.B., Selyshchev O.V., Zahn D.R.T., Xiaohua Q., Tang J., Strizhak P.E. Catalytic properties of reduced graphene oxide in acetylene hydrogenation, In Press.
2. Bychko I. Strizhak P. (2018) Carbon nanotubes catalytic activity in the ethylene hydrogenation, *Fullerenes, Nanotubes and Carbon Nanostructures*, 26, 804-809.

Improving Mechanical Properties of Carbon Fiber Reinforced Epoxy Polymer Composite with Carbon Nanotubes

K. Yüceer,[1,2,*] D. Çöker,[1]

[1] Middle East Technical University, Department of Aerospace Engineering, Ankara, Turkey
[2] Turkish Aerospace Company, Ankara, Turkey

Abstract:

Increasing usage preference of composite material over metallic in the aerospace industry brings the requirement of improving mechanical properties of the material. Composite materials in complex structural shape, especially at curved region, can be improved in case of mechanical properties with reinforcement materials. Nanocomposite materials are winner due to their filling mechanism in nanoscale with better bridging mechanism between matrix and reinforcement where porosity is inaccessible to be reached by traditional filler materials. In this study, it is suggested that carbon nanotube (CNT) utilization is settlement of the stronger, tougher and stiffer composite structures. The first visual of nanomaterial is demonstrated in figure 1 from Iijima's research in years of 20th century. Because of the nano-scale, the macro-scale mechanical properties of composite material containing randomly distributed nanomaterials are effectually isotropic and nanocomposites can be agreed as homogeneous materials; that is critical point of their excellent mechanical properties.

Mechanical improvement of composite materials is analyzed with contribution of functionalized multi-walled CNT (MWCNT) with carboxy group (-COOH) and non-functionalized MWCNT by calendering mixing method using three roll milling machine in figure 2. Five different weight fractions of each type of nanomaterial is dispersed into epoxy resin with cycle number of 7.

Functionalization of CNT provides a better wetting of the reinforcement with epoxy matrix due to additional chemical bonding. Relatedly, better mechanical properties are observed for the weight fraction of 0.8; however, in the weight fraction of 1.0 for both chemical structure of CNT, the situation is different. For further study, the mechanical properties are investigated for different fractions to optimize. The weight fraction is optimized by mechanical tests and composite laminates are going to be manufactured with optimal fraction.

Keywords: Composite, Nanomaterial, Calendering, Funtionalization

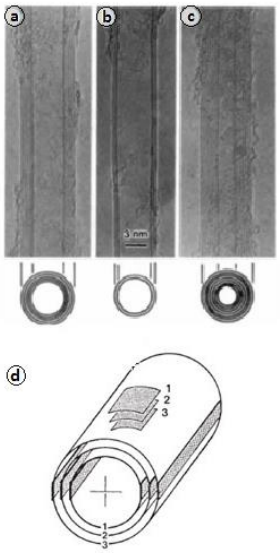


Figure 1: Electron micrographs of microtubules of graphitic carbon a) 5-wall tube with diameter of 6.7 nm; b) 2-walled tube with diameter of 5.5 nm; c) 7-walled tube with diameter of 6.5 nm in largest, 2.2 nm in smallest; d) clinographic view of possible structural model for a graphitic tubule [1]

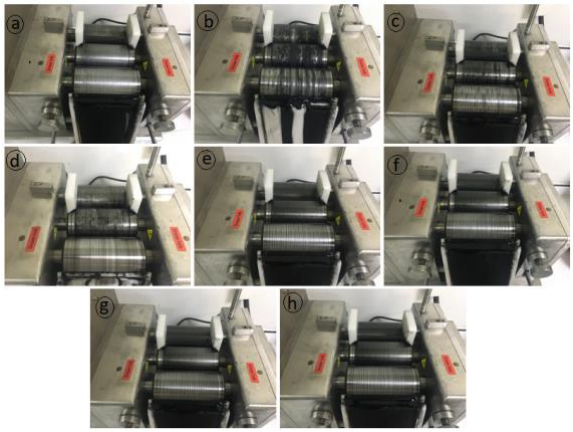


Figure 2: Three roll mixing process of 1.2 wt. % MWCNT-COOH and 400 g epoxy; a) first cycle-beginning at 3 min of endurance at 20 rpm, b) first cycle-finish with 23 min endurance at 20 rpm, c) second cycle with 23 min endurance at 20 rpm, d) third cycle with 16 min endurance at 25 rpm, e) fourth cycle with 16 min endurance at 25 rpm, f) fifth cycle with 13 min endurance at 28 rpm, g) sixth cycle with 12 min endurance at 30 rpm, h) seventh cycle with 10 min endurance at 35 rpm

References:

1. Iijima, S. (1991). Helical microtubules of graphitic carbon. Nature, 354, 56–58.
2. Xu, L. R., Bhamidipati, V., Zhong, W. H., Li, J., Lukehart, C. M., Lara-Curzio, E., … Lance, M. J. (2004). Mechanical property characterization of a polymeric nanocomposite reinforced by graphitic nanofibers with reactive linkers. Journal of Composite Materials, 38(18), 1563–1582. https://doi.org/10.1177/0021998304043758

Analytical approach for nonlinear optical selection rules of excitons in monolayer transition metal dichalcogenides

A. Taghizadeh,[1,2,*] T. G. Pedersen,[1,2]

[1] Department of Physics and Nanotechnology, Aalborg University, Aalborg East, Denmark
[2] Center for Nanostructured Graphene (CNG), Aalborg East, Denmark

Abstract:
Recently, there has been a great interest in the nonlinear optical (NLO) response of two-dimensional (2D) materials such as graphene and monolayer transition metal dichalcogenides (TMDs) due to their large nonlinear coefficients in comparison with the bulk semiconductors [1]. In particular, huge spin-orbit coupling combined with strong excitonic effects in monolayer TMDs make their NLO response unique.
We present our novel analytical approach for calculating the NLO response of monolayer TMDs by using an effective Hamiltonian with the trigonal warping (TW) term [2]. Employing the TW Hamiltonian, we derive elegant analytical expressions for excitonic matrix elements (or oscillator strengths), which provide the guidelines for determining the optical selection rules. By utilizing the analogy with the Hydrogen atom orbitals, a novel informative diagram encompassing the excitonic selection rules is then suggested as shown in Figure 1(a). This diagram is used to identify the fundamental transitions for the first-, second-, and third-order optical processes. For instance, the main transitions for the second-order nonlinear processes are shown in Figure 1(b). The diagram clearly demonstrates the importance of the *s* excitons in the NLO responses and the crucial role of the trigonal warping in the even-order nonlinearities.
For comparison purposes, we compute the optical conductivity, second harmonic generation and third harmonic generation (THG) spectra of monolayer MoS_2 using the numerically demanding Bethe-Salpeter equation (BSE). In particular, our results for the THG of monolayer MoS_2 are reported for the first time, to the best of our knowledge. The analytical results are in excellent agreement with the full BSE calculations using considerably less numerical efforts, while also providing valuable physical insights into the nature of the spectral resonances. For instance, it is shown that the fundamental resonance in the THG spectrum appears at the frequency of the *1s* exciton and, remarkably, originates from three distinct transition paths including *p* and *d* excitons. Our analytical approach can readily be extended to any other nonlinearities and, hence, provides a simple but accurate tool for analyzing experimental NLO spectra of monolayer TMDs.

Keywords: exciton, nonlinear optical response, monolayer transition metal dichalcogenides, selection rules, analytical model, second harmonic generation, third harmonic generation, Bethe-Salpeter equation.

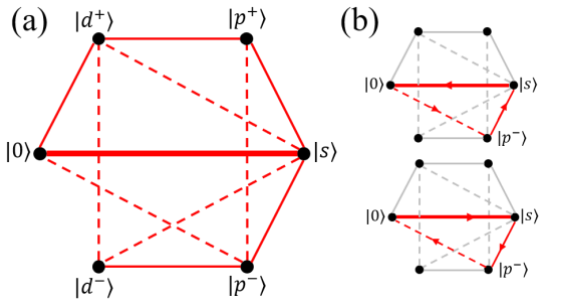


Figure 1: (a) Schematic diagram of optical selection rules at the K valley. Black dots represent the ground state, 0, and excited states, *s*, *p* and *d*. Solid/dashed lines represent the possible transitions between the states, which are allowed without/with the TW. (b) The dominant transition paths for a second-order process are shown in red.

References:

1. A. Autere, H. Jussila, Y. Dai, Y. Wang, H. Lipsanen, and Z. Sun, *Adv. Mater.* 30, 1705963, 2018.
2. A. Taghizadeh, and T. G. Pedersen, *Phys. Rev. B* 99, 235433, 2019.

Exploration of Graphene for the Improvement of Plasma Facing Components in Fusion Plasmas

M. Navarro [1], M. Zamiri [2], K. Hall [1], R. Doerner [3], O. Schmitz [1], M. Lagally [1], J. Santarius [1], G. Kulcinski[1]

[1] University of Wisconsin-Madison, Department of Nuclear Engineering, Wisconsin, USA
[2] Universtiy of Ottawa, Department of Electrical Engineering and Computer Science, Ottawa, Canada
[3] University of California-San Diego, Department of Nuclear Engineering, Wisconsin, USA

Abstract:
This research explores the performance of graphene as a coating for plasma facing components (PFC's). A few studies have shown that graphene can act as a protective layer against sputtering due to energetic ions. In the presence of such irradiation, PFC's tend to develop surface morphologies that lead to mass loss of the wall material, potentially diminishing their lifetime and plasma performance.
We have shown that graphene can reduce and slow down changes of surface morphology due to energetic helium over a wide range of energies, as tested in the MITE-E facility at UW-Madison and PISCES at UC-San Diego. We have also gained insight into the interaction of graphene with high and low energy ions using Raman Spectroscopy as a diagnostic for determining the damage and lifetime of the membrane. In addition, heating tests were performed of graphene on tungsten in a variable pressure deuterium environment to determine its survivability and chemical stability. Although, the deuterium appears to etch some of the carbon atoms, the increase in vacancies is minor enough that the graphene still retains its structure, and at pressures expected in the plasma edge, the deuterium seems to have little effect on damage in W. Half-coated tungsten samples were exposed in the PISCES facility, and through surface analysis techniques it was found that the tungsten fuzz growth can be reduced by about 30% for high fluences (10^{20}-10^{21} He-D/cm^2). In addition, data shows that graphene does not perform as well at ion bombarding energies close to the carbon binding energy, as seen across the different exposures. This research hopes to expand on candidates for plasma facing components in a nuclear fusion environment.

Keywords: Graphene, tungsten, helium, deuterium, plasma facing components.

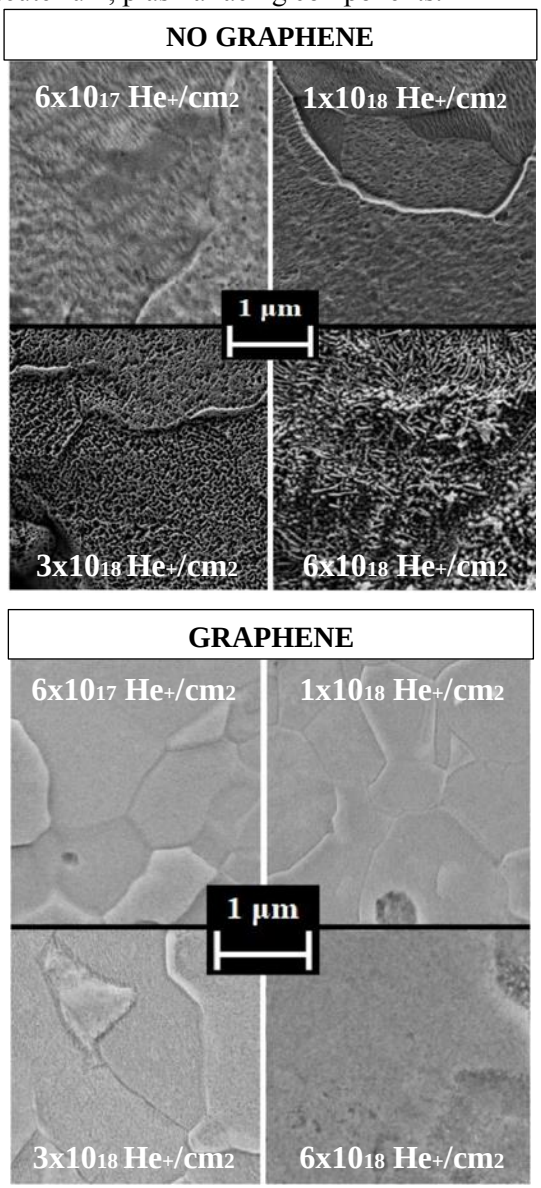


Figure 1: Surface morphology changes to the tungsten under intense helium irradiation at 30 keV, 900 °C.

Graphene properties from curved space Dirac equation

A. Gallerati [1,2], F. Laviano [1,2]

[1] Politecnico di Torino, Dep. of Applied Science and Technology (DISAT), Torino, Italy

[2] INFN Sez. TO, Torino, Italy

Abstract:

From the perspective of high energy physics, graphene can provide us a real framework to study what is believed to be (as close as possible) a quantum field in a curved space-time, with measurable effects pertaining to the electronic properties of the sample itself. The peculiar structure of a graphene sheet determines a natural description of its properties in terms of massless, relativistic Dirac pseudoparticles, giving the possibility to study quasi-relativistic particle behaviour at sub-light speed regime. The charge carriers' behaviour at Dirac points in curved graphene can be thus obtained exploiting a massless Dirac spectrum description for particles living in a curved bidimensional background in the large wavelength approximation [1].

The study of particular curved configurations, together with the quantization of some physical quantities due to the particular geometry of the manifold, can lead to characteristic observable effects. In particular, some optical responses of the graphene sheet can be obtained in peculiar ranges of energy including the visible light energy spectrum [2].

Keywords: Dirac equation, optical conductivity, curved geometry, QFT in curved spaces.

References:

1. O. Boada, A. Celi, J.I. Latorre, M. Lewenstein, New J. Phys. 13, 035002 (2011).
2. Antonio Gallerati, Eur. Phys. J. Plus 134, 202 (2019).

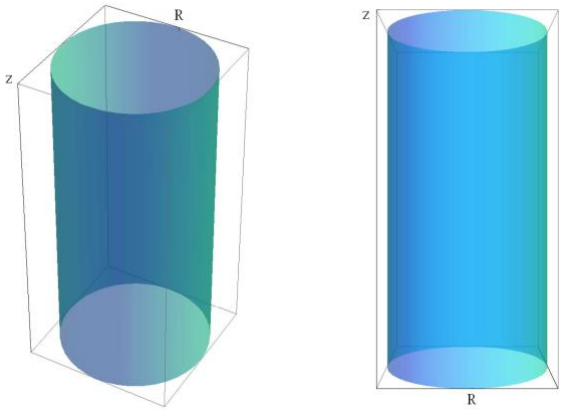


Figure 1: Graphene cylindrical sheet.

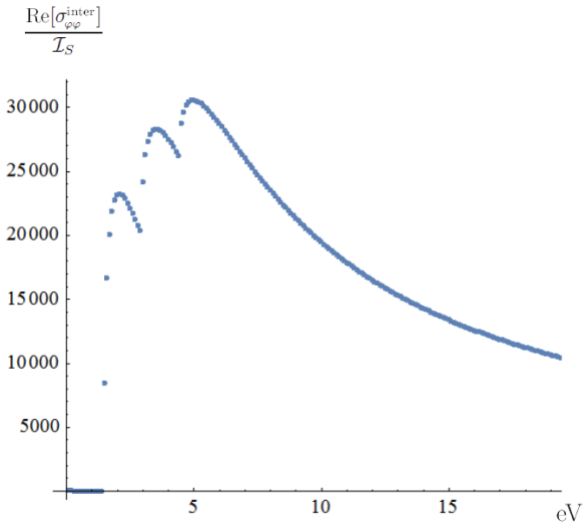


Figure 2: Real part of the transverse interband Kubo optical conductivity for a graphene cylindrical layer wrapped around itself 3 times (nanoscroll).

Identification of Active Electrocatalytic Sites Using Electrochemical Scanning Tunneling Microscopy

R.M. Kluge[1*], R.W. Haid[1], A.S. Bandarenka[1]

[1] Physics of Energy Conversion and Storage, Department of Physics, Technical University of Munich James-Franck-Str. 1, 85748 Garching, Germany

Abstract:

In order to economize the resources of our world, research should focus on the use of widely abundant and environmentally friendly materials and techniques. In the field of energy conversion and storage, a so-called "hydrogen economy" would provide such a sustainable and worldwide accessible energy system. Here, hydrogen can be produced as a fuel, from water and electicity, and converted back without any exhaust other than water vapor. However, in order for such electrochemical energy provision devices to become competitive in contributing to new environmentally friendly energy production schemes, suitable catalysts have to be developed. The performance of such a heterogeneous catalyst is highly dependent on the electronic structure of specific surface sites, so-called active sites, that offer optimal binding of reaction intermediates.

Here, we study the properties of highly oriented pyrolytic graphite (HOPG) for the hydrogen evolution reaction (HER), the reaction taking place at the cathode side of an electrolyzer.

For the first time, we can spatially map and in-situ identify the active sites of HOPG with down to atomic resolution using a conventional scanning tunneling microscope (STM). In general, the recorded tunneling current depends on several factors such as tip-sample distance, surface electronic structure and tunneling medium.[1] As shown in Figure 1a), reactants and products ad- and desorbing on and from the surface present in the tunneling gap, change the composition of the medium, and thus have an influence on the tunneling current. By monitoring relative changes in the tunneling current, an increased noise level was detected over active centers, confirming electrochemical STM (EC-STM) as a powerful tool to determine the position of active sites.

Figure 1b) resolves the typically honeycomb-like structure of the HOPG. During operation of the HER, certain sites appear brighter than others. This indicates a higher noise level and thus the presence of active sites. Thus, active sites can be ascribed being located rather at step or defect sites than at terraces. This knowledge allows for further optimization of carbon-based catalytic materials paving the path towards reduced used of precious transition metals such as platinum.

Keywords: scanning tunneling microscopy, HOPG, hydrogen evolution reaction, non-precious catalyst

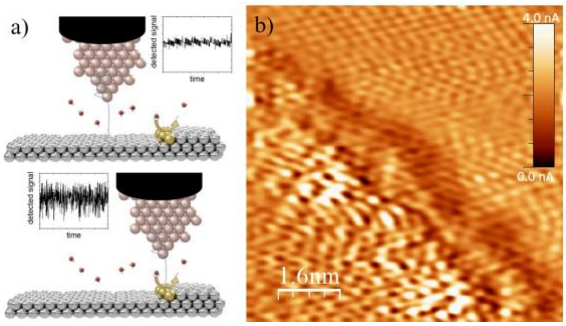


Figure 1: a) Illustration of the concept of EC-STM. An increased noise level in the recorded signal is detected over an active site (down) in comparison to a non-active site (top). Active sites are highlighted in gold. b) EC-STM image of HOPG for the HER in 0.1 M $HClO_4$. The typical honeycomb-like crystal structure of graphite can be identified. Some sites expose an increased level of tunnelling current *i.e.* noise and can therefore be identified as being active. Therefore, sites near steps or defects can be assumed to be more active than terrace sites. With this measurement we are able to resolve active sites in-situ with down to atomic resolution.

References:

1. Pfisterer, J.H.K., Liang Y., Schneider O., Bandarenka A.S. (2017) Direct instrumental identification of catalytically active surface sites, *Nature*, 549, 74-77.

Monitoring Folds and Strain Localization in 2D Transition Metal Chalcogenides (TMDCs) using Second Harmonic Generation

A. R. Khan,[1,2,*] Y. Lu,[1]

[1] Research School of Engineering, College of Engineering and Computer Science, Australian National University, Canberra ACT, 2601, Australia
[2] Department of Industrial and Manufacturing Engineering, (Rachna College), University of Engineering and Technology, Lahore 54700, Pakistan

Abstract:
Folding and local strain engineering are extensively applied to alter the optoelectronic properties of 2D materials such as interlayer coupling, bandgap, etc. Optical techniques such as PL, Raman were used in the past to probe the folds and strain localization. Here, we show that optical second harmonic generation (SHG), which is sensitive to the crystalline symmetry of 2D materials is a powerful tool to monitor the folds and strain localization in 2D Transition Metal Dichalcogenids (TMDCs). 2D TMDCs are well-suited for thi purpose because of their mechanical properties suitable for straining and folding suc as 2D TMDCs can be folded due to their high flexibility, in addition, they have good rupture strength. Our study includes the fabrication process of clean folds and strained wrinkles on ultra-thin layers of TMDCs and then their optical characterization using SHG imaging. The SHG from a fold is a coherent superposition of the SHG from the individual layers of the fold, whereas, strain results in the distortion of the SHG polar plot. We explain our results using superposition and photo-elastic principles. Our results show SHG as a powerful approach to investigate folds and local strain localization in 2D materials.

Keywords: 2D TMDCs, SHG, Folding, Strain, Photoelastic

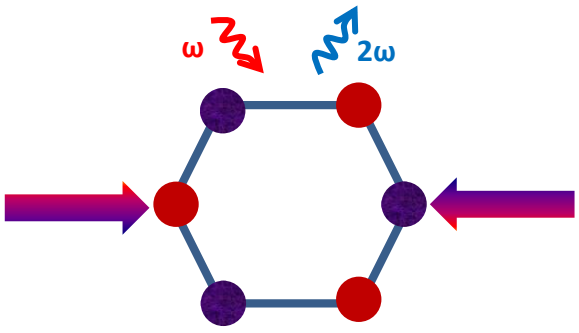


Figure 1: Figure illustrating strain effect on the 2D TMDC structure and resultant Second Harmonic Generation (SHG). Second Harmonic Generation (SHG) is a nonlinear optical process in which two photons of same frequency ω merge into a single photon with double frequency 2ω.

References:

1. Jiang, T.; Liu, H.; Huang, D.; Zhang, S.; Li, Y.; Gong, X.; Shen, Y. R.; Liu, W. T.; Wu, S. (2014), Valley and Band Structure Engineering of Folded MoS 2 Bilayers. Nat. Nanotechnoly.
2. Castellanos-Gomez, A.; Roldán, R.; Cappelluti, E.; Buscema, M.; Guinea, F.; Van Der Zant, H. S. J.; Steele, G. A. (2013) Local Strain Engineering in Atomically Thin MoS2. Nano Letters.

Novel Economic Simple Strategy for Mass Synthesis of Nitrogen-doped Graphene: Controllable Growth Mechanism and Structure

M. A. A. Mohamed[1,*], F. Carrasco-Marín[2], N. A. Elessawy[3] and H. A. F. Hamad[1,2]

[1] City of Scientific Research and Technological Applications, Advanced Technology and New Materials Research Institute, Alexandria, Egypt
[2] University of Granada, Inorganic Chemistry Department, Carbon Materials Research Group, Granada, Spain

Abstract:
Nitrogen-doped graphene (NG) is known with novel superb electronic properties compared to pristine graphene. For instance, N doping of graphene enables realization of desirable semiconducting properties. Thus, NG represents a promising candidate for variety of electronic applications such as electrochemical sensing, field-effect transistors, electrocatalysis in fuel cells, lithium batteries and supercapacitors [1]. Therefore, development of high-quality NG via easty-to-operate scalable synthesis strategy is tremendously worldwide desirable. Recently, NG nanosheets (NGs) have been synthesized through a novel one-pot single-step process, involving hydrothermal treatment of glucose under mild conditions, using Cetyltrimethyl-ammonium bromide (CTAB) and Ammonia as structure-directing agents. The merit of this novel proposed strategy for NGs industrial production resides in its simplicity, cost-effectivness and eco-friendly along with the high yield and good structural features of the produced NGs. The study also provided deep insights regarding the NGs growth mechanism [2]. The present research focuses on understanding how the synthesis conditions can control the growth mechanism of NG and subsequently its characteristic structural features. This will enable design of NG with tunable and tailored electronic properties via simple production route, which will broaden its application base in electronic industry. Hydrothermal synthesis temperature and CTAB dose have been manipulated and the evoloved NG structure has been explored regarding the oxidation level, N-doping configuration, crystalline structural order and morphology. The results are impressive. Thus, the manipulation of processing parameters interstingly lead to product transfer from oxygenated graphitic carbon with agglomerated microsized spherical-sheet morphology to extensevily exfoliated graphene nanosheets of slight oxygen content. N-doping configuration and crystalline structural order are also signficantly influenced. Hydrothermal synthesis temperature has the major effect compared to CTAB dose. Modulations in the NG growth mechanism accompanied the variation of processing parameters are investigated in depth to understand the origin of evolved structural features.

Keywords: N-doped graphene, Hydrothermal synthesis, CTAB, Processing parameters-growing structure relationship, Structure tuning.

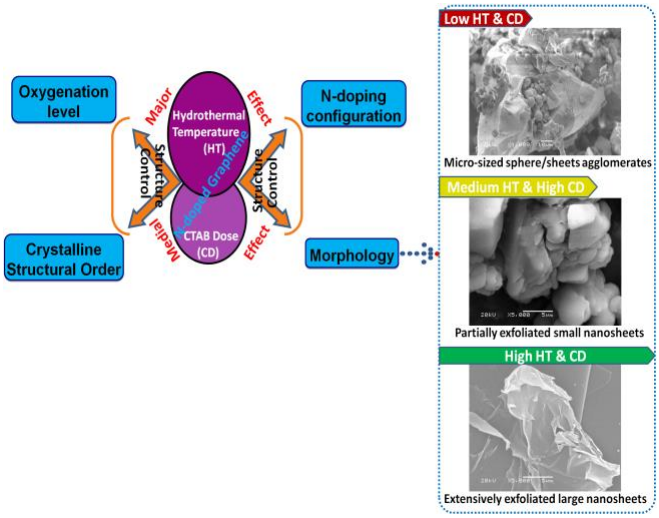


Figure 1: Controlled synthesis of NG with tuned structural features.

References:

1. Usachov, D., Vilkov, O., Gruneis, A. (2011), Nitrogen-Doped Graphene: Efficient Growth, Structure, and Electronic Properties, Nano Lett., 11, 5401-5407.
2. Mohamed, M., Elessawy, N., Carrasco-Marín, F., Hamad, H. (2019), Novel One-Pot Facile Economic Approach for Mass Synthesis of Exfoliated Multilayered Nitrogen-doped Graphene-like Nanosheets: New insights into the Mechanistic Study, Phys. Chem. Chem. Phys., 21, 13611-13622.

Homogeneous Anti Corrosion Coating of Spontaneously Dissolved Defect Free Graphene

M. Bin Subhan,[1*] P. Cullen,[2] C. Howard[1]

[1] University College London, Department of Physics & Astronomy, London, UK
[2] University College London, Department of Chemical Engineering, London, UK

Abstract:
A recent study by the World Corrosion Organization estimated that corrosion related damage causes $2.5tr worth of damage every year. As such, a low cost and easily scalable solution is required to the corrosion problem which is economically viable. Graphene is an ideal anti-corrosion barrier layer material due to its excellent barrier properties and chemical stability which makes it impermeable to all molecules. However, attempts to employ graphene as a barrier layer has been hampered by the fact that defect sites in graphene accelerate corrosion due to the inert nature of graphene which promotes galvanic corrosion at the expense of the metal. The recent discovery of spontaneous dissolution of charged graphite intercalation compounds in aprotic solvents enables defect free graphene platelets to be employed for anti-corrosion applications[1]. These 'inks' of defect-free charged graphene platelets in solution can be coated onto a metallic surfaces via electroplating to form a homogeneous barrier layer. In this paper, initial data showing homogeneous coatings of graphene barrier layers on steel coupons via electroplating will be presented. This easily scalable technique also provides a controllable method for applying different barrier thicknesses from ultra thin layers to thick opaque coatings making it useful for a wide range of applications.

Keywords: Anti-corrosion, coating, defect-free, electroplating, graphene, intercalation

References:

1. Cullen, P., Cox, K., Bin Subhan, M., et al. (2017), Ionic solutions of two-dimensional materials, *Nature Chemistry* volume 9, pages 244–249

SMS 2019 - Session I
Smart coatings and surfaces

Supported lipid monolayers as sensing and selective layers for ISFET sensors

V. Kilinc[1], T. Nguy[2], A. Kenaan[1], S. Lamant[1], C. Henry-de-Villeneuve[3], G. Monier[4], M. Petit[1], Y. Wakayama[2], J. M. Raimundo[1], A. Charrier*[1]

[1] CINaM, Aix Marseille Université, CNRS, Marseille, France
[2]NIMS, Tsukuba, Japan
[3]PMC, Ecole Polytechnique, Palaiseau, France
[4]Institut Pascal, Aubière, France

Abstract:
We present an original platform constituted of an engineered lipid monolayer which is used as the active sensitive layer and as ultra-thin gate dielectric in field effect transistor sensors. Supported lipid layers, with thicknesses of a few nanometers indeed constitute good candidates. In living cells lipid membranes are known to constitute natural insulators which play an efficient role as barrier to both ionic and electronic transport across the membrane, associated with an electrical resistance of the order of several giga-Ohms in magnitude. However, despite excellent insulating properties, lipid bilayers and even more lipid monolayers have been poorly exploited in devices due to their inherent instability under application of an electric field, leading to damages caused mainly by an electroporation process occurring at low electric field. Furthermore a lack of mechanical stability is often observed.
We show that the mechanical and chemical stability of lipid layers as well as their dielectric performances can be improved by changing the molecular structure of the lipids and by achieving intra-chain reticulations within the layer, and that surprisingly both these properties are correlated. In fact such reticulated layers with a thickness of 2.5 nm only present low leakage current even at high electric field, and a direct dielectric breakdown occurring at ~30 MV/cm, i.e. much higher than for a silicon oxide layer of similar thickness or other high-□ dielectrics.
We show that ones the lipid monolayer on the transistor channel the specificity of the sensor given by the grafting of probes to the lipids can be tuned using simple procedure making our sensor extremely versatile.
As a proof of concept, we present here different sensors that were developed for the detection of Fe3+, Cu2+ and Cs+ ions using different materials, inorganic transistors with silicon channel and organic transistors with a Poly(3-hethyl)thiophen as channel, and different types of probes.
Our sensors present good specificities with exceptional low limit of detection down to the sub-femtomolar range, high sensitivity and a linear response over several decades.

Keywords: lipid monolayers, mechanical and dielectric properties, ISFET sensors

Acknowledgments: We would like to acknowledge the French National Research Agency (ANR) and the SATT Sud-Est for supporting our project under contract numbers *ANR-16-JTIC-0003-01 and N°147680 respectively.*

References:

1. Charrier A. et al., Langmuir 26, 2538 (2010)
2. Charrier at al., Patent: FR2983637/WO2013083490A1 (2013)
3. Dumas C. Et al., Langmuir 27, 13643 (2011)
4. Nguyen T.D. et al., J. Phys. Chem. B 116, 7190 (2012)
5. El Zein R. et al., J. Mat. Chem. B 1, 443 (2013)
6. Nguyen T.D. et al., Biosens. Bioelect. 54, 571 (2014)
7. Kenaan A. Et al., Anal. Chem.(88) 3804 (2016)
8. Charrier A. et al., Patent: PCT/EP2016/074569 (2016)
9. Kenaan et al., Adv. Func. Mat. 1801024 (2018)

Polyvinyl alcohol / barium titanate composite films: filler content, particle size and surface modification effects on dielectric-electrical properties

K. Gille, C. Lapeyronie, S. Scheffler, M. Rajaoarivelo, W. Neri, A. Bentaleb, I. Ly, A. Derré, J. Yuan, P. Poulin, C. Jaillet*
University of Bordeaux, Centre de Recherche Paul Pascal (CRPP), UMR 5031, Pessac, France

Abstract:
Barium titanate (BT) is known for its good piezoelectric properties however it is fragile. On the other hand, the polyvinyl alcohol (PVA) has low electrical properties but high mechanical strength. So, combining these two materials should result in a flexible ceramic/polymer composite with interesting piezoelectric properties.
For this purpose, barium titanate particles (cubic and tetragonal form, 60 and 200 nm size, respectively) have been dispersed and stabilized in water by surfactant absorption. Then, adequate quantities of BT dispersion were mixed with a PVA solution to fabricate PVA-based composites films containing various amounts of BT fillers (from 2.5 to 10 vol%). After structural characterization of the films, dielectric and electrical properties have been investigated. The scanning electron microscopy images (**Figure 1**) demonstrated that we can obtain flexible PVA-based BT composites films, with particles uniformly dispersed even at 10 vol% filler content. As expected, at same BT content, better results have been obtained using tetragonal form particles. The dielectric constant of the composites films increase with increasing the filler content and reached a high value of 15 (10^4 Hz) at only 10 vol% BT which is encouraging for the targeted properties. Indeed, similar values of dielectric constants have been recently obtained in the litterature from PVDF/BT composite films but for higher BT volume fraction (30 vol%).[1] Currently, the effect of surface modification of the BT particles is investigate to try to enhance the piezoelectric performances of the composite films and, mechanical and thermal experiments are performed on these promising composites.

Keywords: barium titanate particules, polyvinyl alcohol, composite films, filler content, dielectric constant, electrical properties, mechanical properties, piezoelectric performances.

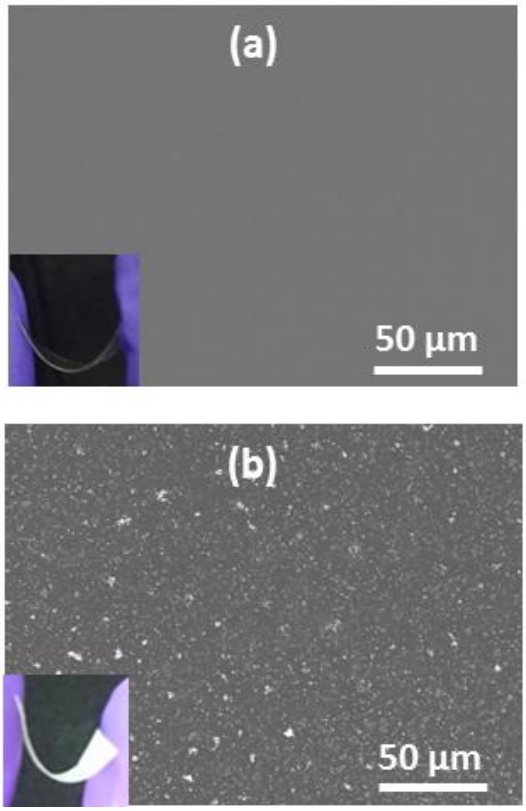


Figure 1: SEM images of surfaces of **(a)** neat PVA film and **(b)** composite film with 10 vol% BT 200 nm content. Insets: photographies of the films highlighting their flexibility.

References:

1. Jiao, Y.Q., Deng, L.M., Yang, S.Y., Zhang, P. (2019), Cleaner preparation of poly(vinylidene fluoride)/barium titanate composites: Thermal, mechanical, and dielectric properties and relaxation dynamics *Journal of Applied Polymer Science,* 136(13), 47254-47263.

Smart corrosion inhibition and structural effect of lithium in PMMA-silica coatings

A. Trentin,[1,2] K. Marcoen,[2] S. V. Harb,[1] M. C. Uvida,[1] C. V. Santilli,[1] H. Terryn,[2] T. Hauffman,[2] P. Hammer[1]

[1] São Paulo State University, Institute of Chemistry - UNESP, Araraquara, Brazil
[2] Vrije Universiteit Brussel, VUB, Department of Materials and Chemistry, Brussels, Belgium

Abstract:
Organic-inorganic sol-gel coatings based on polymethyl methacrylate (PMMA)-silica hybrids provide efficient corrosion protection for metallic surfaces [1]. Although high performance hybrid coatings have been developed to protect aluminum alloys, corrosion in form of pitting can severely affect their service lifetime. The addition of increasing amounts of lithium carbonate (0, 500, 1000 and 2000 ppm) to the inorganic precursor (tetraethoxysilane - TEOS) yielded hybrid coatings with enhanced connectivity of nanometric silica cross-link nodes, uniformly distributed in a highly polymerized PMMA matrix, and improved adhesion to the aluminum substrate (AA7075). Results of electrochemical impedance spectroscopy (EIS) in 3.5% NaCl, showed that the improved coating structure at higher lithium loadings leads to an increase of the corrosion resistance, with a low frequency impedance modulus up to 50 GΩ cm2, and revealed that the lithium induced self-healing ability significantly improves their lifespan. Time of flight secondary ion mass spectrometry and X-ray photoelectron spectroscopy proved that the regeneration occurs by means of lithium ions leaching from the coating surface towards the pit, which is restored by a protective layer of precipitated Li containing aluminum hydroxide species [2]. An analogous mechanism was found for scratched coatings presenting a recovery of the impedance modulus after 7 days of salt spray test. The obtained results evidence the dual role of lithium ions in improving the connectivity of the hybrid network and extending through the self-healing ability the lifetime of metallic components.

Keywords: PMMA-silica hybrid, corrosion inhibition, lithium carbonate, self-healing, aluminum alloy

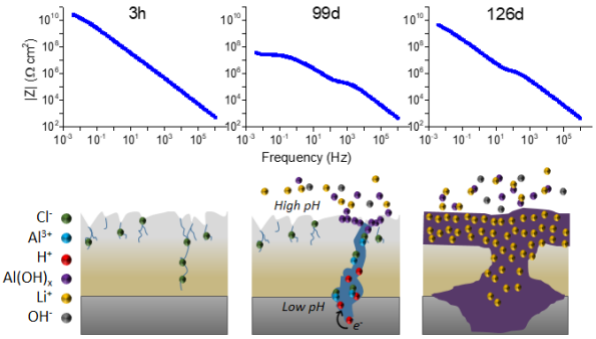


Figure 1: Time evolution of the impedance modulus of the PMMA-silica coating containing 1000 ppm of Li immersed in 3.5% NaCl along with the proposed self-healing mechanism for the formation a protective barrier.

References:

1. Dos Santos, F.C., Harb, S.V., Menu, M.J., Turq, V., Pulcinelli, S.H., Santilli, C.V., Hammer, P. (2015), On the structure of high performance anticorrosive PMMA-siloxane-silica hybrid coatings, *RSC. Adv.* 5, 106754-106763.
2. Visser, P., Marcoen, K., Trindade, G.F., Abel, M.-L., Watts, J.F., Hauffman, T., Mol, J.M.C., Terryn, H. (2019), The chemical throwing power of lithium-based inhibitors from organic coatings, *Corr. Sci.*, 150, 194-206.

High-rate deposition of high-quality oxide layers using reactive high-power impulse magnetron sputtering

J. Rezek, J. Houška, J. Vlček

Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia, Plzen, Czech Republic

Abstract:
High-power impulse magnetron sputtering (HiPIMS) is a very suitable and progressive method for preparing high-quality oxide layer. This is mainly because of a high degree of ionization of target material particles in the discharge plasma and the associated high ion-to-atom ratio in particles flux going toward a substrate. These could result in formation of very dense films structure. Moreover, enhanced kinetic energy of particles impacted onto growing film could substitute thermal heating of the substrate which is very important in the case of deposition on heat sensitive substrates. In this work, we carried out high-rate reactive depositions of densified stoichiometric ZrO_2, HfO_2 and Ta_2O_5 films on a floating substrate[1]. The depositions were performed using a strongly unbalanced magnetron with a planar Zr, Hf and Ta target of 100 mm diameter in argon-oxygen gas mixture. The target-to-substrate distance was 100 mm. For the same duty cycle of 10 %, the deposition rates were up to 120 nm/min for the ZrO_2 films, up to 125 nm/min for the Ta_2O_5 films and even up to 345 nm/min for the HfO_2 films. Moreover, results obtained during low-temperature, high-rate reactive deposition of transparent conductive oxides, namely In-Ga-Zn-O and ZnO:Al will be also reported.

Keywords: reactive high-power impulse magnetron sputtering, HfO_2, ZrO_2, Ta_2O_5, IGZO, AZO, TCO, high-rate deposition.

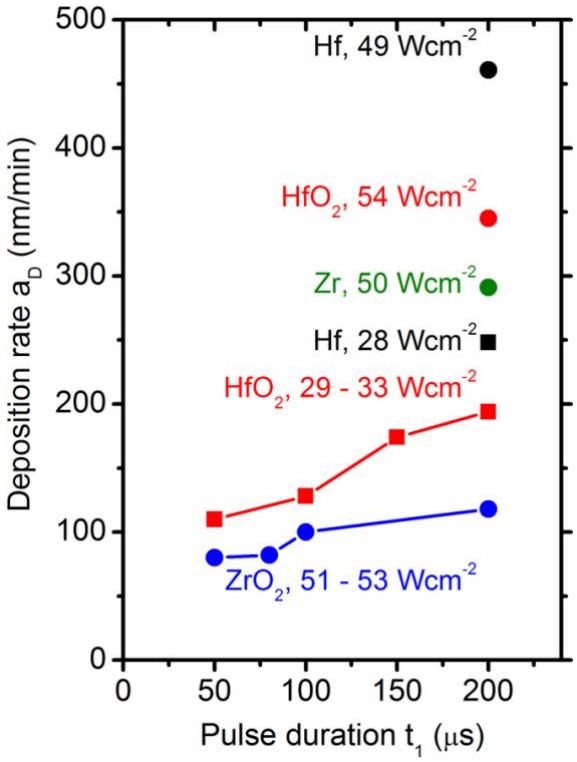


Figure 1: The figure illustrates very high deposition rates reached during reactive HiPIMS of ZrO_2 and HfO_2 thin films. All films were highly optically transparent (value of an extinction coefficient at the wavelength of 550 nm, k_{550}, below 0.001 for all films) and densified (mass density reached bulk mass density).

References:

1. J. Vlček, J. Rezek, J. Houška, R. Čerstvý, R. Bugyi, Process stabilization and a significant enhancement of the deposition rate in reactive high-power impulse magnetron sputtering of ZrO2 and Ta2O5 films, Surf. Coat. Technol. 236 (2013) 550–556.

Multifucnctional Smart Materials for the Corrosion Inhibition of Metal Artefacts

C. Giuliani, [1*] G. Di Carlo, [1] Cristina. Riccucci, [1] M. Pascucci, [1] E. Messina, [1] G. M. Ingo. [1]
[1] Istituto per lo Studio dei Materiali Nanostrutturati - CNR, Rome (Italy)

Abstract:
Corrosion is a natural process that leads to the gradual loss of the structural, functional and aesthetic properties of metal objects due to chemical reactions with the surrounding environment. In particular, in the field of Cultural Heritage the effects of corrosion becomes invaluable. At present, the most commonly used protective materials are based on toxic corrosion inhibitors, petrochemical-derived polymers and large amounts of harmful organic solvents for their application and removal. Therefore, the development of high-performance materials that fulfill the protective, aesthetic and safety requirements is a serious challenge for the scientific community.
In this context we propose an innovative approach to achieve a long-lasting, sustainable and safe preservation of Cultural Heritage. In particular, within the EU H2020 Nanorestart project "NANOmaterials for the REStoration of works of ART", we developed stimuli responsive nanostructured coatings able to provide an active, smart and safe protection of modern metal works of art exposed to indoor environment conditions. These innovative systems are based on environmentally friendly chitosan polymer[1] and stimuli responsive nanocontainers[2] for a controlled release of the corrosion inhibitors. It is also worth noting that, according to the mandatory aesthetic and ethical requirements in the field of Cultural Heritage, these smart coatings were developed in order to be optically transparent, preserving the appearance of the artifact, and easily removable without compromising the integrity of the underlying metallic surface (Figure 1). Moreover, the new water-based formulations are more sustainable and safe than commercial products since they can be applied avoiding harmful organic solvents. To assess the efficacy of the protective polymer layers, accelerated corrosion tests were performed on the coated and bare bronze substrates. The surface properties of Cu-based alloy with and without protective coatings were investigated before and after the accelerated corrosion treatments. Thanks to their superior performance with respect to commercial benchmark, the developed multifunctional materials have been applied on real works of art in collaboration with Peggy Guggenheim conservators.

Keywords: chitosan, stimuli responsive nanocarriers, corrosion protection, Cu-based alloys, green polymer, smart coatings, Cultural Heritage.

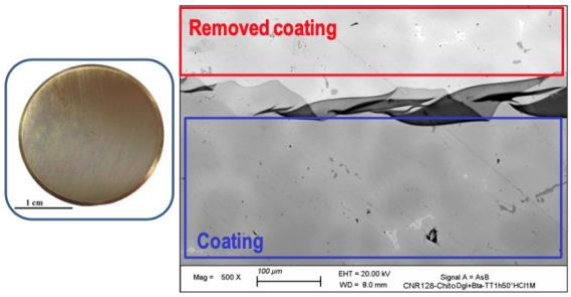


Figure 1: Optical and SEM images of Cu-based alloy substrate coated with chitosan-based protective coating after thermal treatment (1 h, 50 °C) with acid vapours. In the SEM image the boundary between the film and the bare alloy after film removal can be appreciated.

References:

1. Giuliani*, C., Pascucci, M., Riccucci, C., Messina, E., Salzano de Luna, M., Lavorgna, M., Ingo, G. M., Di Carlo, G. (2018), Chitosan-based coatings for corrosion protection of copper-based alloys: A promising more sustainable approach for cultural heritage applications, Progress in Organic Coatings, 122, 138-146.
2. Salzano de Luna, M., Buonocore, G., Giuliani, C., Messina, E., Di Carlo, G., Lavorgna, M., Ambrosio, L., Ingo, G. M. (2018), Long-Lasting Efficacy of Coatings for Bronze Artwork Conservation: The Key Role of Layered Double Hydroxide Nanocarriers in Protecting Corrosion Inhibitors from Photodegradation, Angew. Chem. Int Ed, 57, 7380 –7384.

Electrochromic thin films – methods of preparation and properties

M. Wałęsa-Chorab

Adam Mickiewicz University in Poznan, Department of Chemistry, Poznan, Poland

Abstract:

One of the most important class of plastic electronics are electrochromic devices consisting active layers made of compounds which are able to change their optical properties, especially color, in response to an external electric stimulus.[1] The most interesting classes of electrochromic materials are conjugated polymers or metallopolymers, which can show the wide range of colors which can be tuned by chemical structure modifications.[1] Using of polymers as active materials in electrochromic devices has an advantage that such compounds are not miscible with electrolyte gel, what results in good device lifetime and color contrast, but it is disadvantage in terms of the processability. The best way to obtain non soluble electrochromic layers is formation of the thin film by polymerization of solution processable monomers directly on an electrode or substrate surface.[2-4] Obtained films exhibit different electrochromic propertied depending on the structure of monomers, polymerization method or the morphology of the layer.
Different on-substrate polymerization methods will be presented and the electrochromic properties of obtained thin films will be discussed.

Keywords: electrochromism, on substrate polymerization, electroactive polymers, photopolymerization, thermal polymerization, electropolymerization

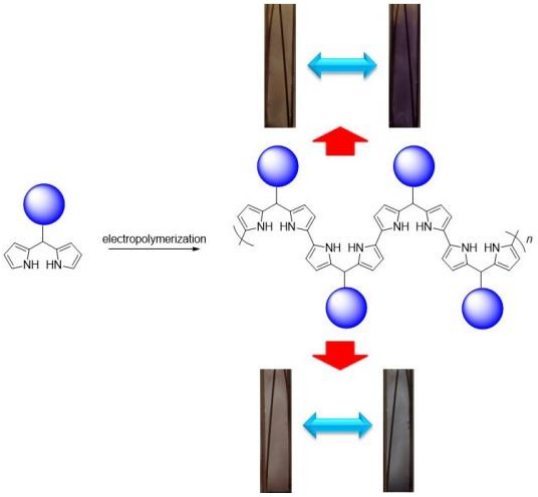


Figure 1: Figure illustrating the electropolymerization of dipyrromethane functionalized monomers and their electrochromic properties dependent on the structure of monomers.

Acknowledgements:

Project supported by: grant 2016/21/D/ST5/01631 from the National Science Centre, Poland.

References:

1. Beaujuge, P.M., Reynolds, J.R. (2010) Color Control in π-Conjugated Organic Polymers for Use in Electrochromic Devices, *Chem. Rev*., 110, 268-320.
2. Wałęsa-Chorab, M.; Skene, W. G. (2017) Visible-to-NIR electrochromic device prepared from a thermally polymerizable electroactive organic monomer, *ACS Appl. Mater. Interfaces*, 9, 21524-21531.
3. Wałęsa-Chorab, M.; Banasz, R.; Kubicki, M.; Patroniak, V. (2017) Dipyrromethane functionalized monomers as precursors of electrochromic polymers *Electrochim. Acta*, 258, 571-581.
4. Wałęsa-Chorab, M.; Skene, W. G. (2014) On-substrate polymerization – a versatile approach for preparing conjugated polymers suitable as electrochromes and for metal ion sensing, RSC Advances, 4, 19053-19060.

Robust and versatile grafted bacteriostatic polymer surfaces based on ionenes

S. Bernardi,[1*] M.N. Bellon-Fontaine,[2] G. Carrot[1]

[1] NIMBE UMR CEA-CNRS 3685, Université Paris-Saclay, CEA – Saclay, 91191 Gif-sur-Yvette, France

[2] GMPA, EcoMic UMR AgroParisTech-INRA 782, Université Paris-Saclay, 1 avenue des Olympiades, 91300 Massy, France

Abstract:

Microbial contamination are of great concern for many environmental, industrial and medical applications. Contact-active coatings with immobilized antimicrobial agents provide an efficient approach to limit the residual toxicity while maintaining efficient antibacterial properties. Antimicrobial polymers are of particular interest, as they generally possess long-term activity with a strong chemical stability. Among them, polycations with a proportionate amphiphilic character efficiently disrupt the outer and the cytoplasmic membrane which affords lysis of the bacteria.

In the present research work, we covalently grafted ionenes onto different surfaces using a robust and efficient method based on polydopamine coatings and diazonium salt induced polymerisation[1]. Ionenes are particularly good candidates since they possess quaternary ammoniums separated by hydrophobic fragments (PI x,y). Moreover, lack of toxicity[2] and ability to mitigate resistance development[3] has been demonstrated.

We tested the adhesion and antibacterial properties of the grafted surfaces in aqueous media using *Staphylococcus aureus* (Gram+) and *Escherichia coli* (Gram-). Detailed characterizations of the grafted surfaces have been performed (XPS, FTIR spectroscopy, surface energy measurements). Results obtained from microbiology tests demonstrated the bacteriostatic and pro-adhesive properties of the ionene grafted surfaces. We clearly showed that our treated surfaces with ionenes led to an important reduction of bacteria, depending on the length of the hydrophobic spacer in the ionene (Figure 1). Finally, these modular polymer coatings would be particularly attractive as inhibition traps, leading to tremendous potential application in medical and insdustrial field.

Keywords: antibacterial polymers, polyionenes, bacteriostatic surfaces, bacterial adhesion, *Staphylococcus aureus*, *Escherichia coli*.

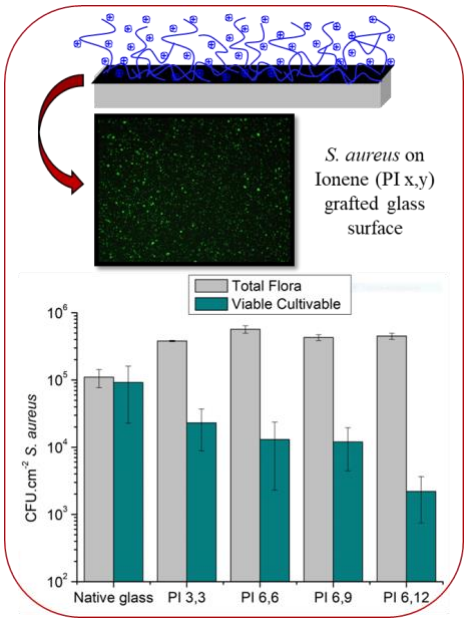


Figure 1: Upper : Epifluorescence microscopy of fluorescent *S. aureus* strains (total flora) on ionene surfaces. Lower : Enumeration of viable cultivable bacteria and total adherent bacteria of *S. aureus* strains in the presence of initial glass substrate and ionene surfaces.

References:

1. Bernardi, S., et al. (2019), Robust and versatile grafted bacteriostatic polymer surfaces based on ionenes, *ACS Appl. Mater. Interfaces*, submitted.
2. Lou, W., et al. (2018), Antimicrobial polymers as therapeutics for treatment of multidrugresistant Klebsiella pneumoniae lung infection, *Acta Biomateriala*, 78, 78-88.
3. Liu, S., et al. (2017), Highly potent antimicrobial polyionenes with rapid killing kinetics, skin biocompatibility and in vivo bactericidal activity, *Biomaterials*, 127, 36-48.

Environ. Sci, Toxicology and Food Technology (IOSR-JESTFT), 8, 1–7.

Innovative polymer coatings for packaging

V. Beghetto,[1,2,*] V. Gatto,[2] S. Conca[1,2], N. Bardella[1], R. Samiolo,[2]

[1] University Ca' Foscari of Venice, DSMN (Department of Molecular Sciences and Nanosystems), Via Torino 155, 30172 Mestre (VE), Italy
[2] Crossing Ltd., Viale della Repubblica 193/b, 31100 Treviso, Italy

Abstract:
Food waste is a major problem for society. Approximately 89 million of tones are wasted in the EU every year. The most common causes of perishable food waste at retailers are inappropriate quality control, product handling, overstocking and consumer behavior. Microbiological concern is associated with extended shelf life and control measures for ensuring microbiological quality and safety is demanding. Many solutions exist today for preserving and extending food shelf's life such as for example, active packaging which foresees incorporation of additives into packaging systems with the aim of maintaining or extending food product quality and shelf-life. Active packaging systems include oxygen scavengers, ethylene scavengers, flavor and odor absorber/releaser, antimicrobial and antioxidant packaging technologies. Nonetheless, these packaging systems are devised so that the "active" component is gradually released into the food or drink stored inside.
We will report a highly sustainable and innovative solution which has been developed in order to deliberately and irreversibly attach an antimicrobial agent to packaging surfaces of different nature (plastic, paper, steal, etc.) in order to prolong shelf life and reduce or avoid the use of preservatives in food improving food safety. Usually preservatives are added to food and drinks and are ingested by the consumer; this will not be the case if they are anchored to the surface of the packaging.
A different set of antimicrobial agents have been devised which may be anchored to commercially available polymers. Different reaction parameters have been studied and all products have been fully characterized by ^{1}H, ^{13}C NMR.
The antimicrobial polymers have been formulated in order to be used for the coating of different materials employed for packaging applications. A perfectly transparent film is produced which has been testes with AATCC 147 test against different bacteria such as *Straphylococcus aureus* (gram+), *Klebsiella pneumoniae* (gram-), etc. (Figure 1). Release tests in food simulants confirm that there is no leaching of the antimicrobial agent even after 10gg at 40°C in different test solutions such as Ethanol 10 % (v/v), Acetic Acid 3 % (w/v), Ethanol 20 % (v/v), Ethanol 50 % (v/v), Olive oil.
In addition, we will present some preliminary tests of the use of these coatings for the antimicrobial treatment of textile fibers.

Keywords: coating, active packaging, antimicrobial treatment, polymer, surface modification, green chemistry, food safety, shelf life.

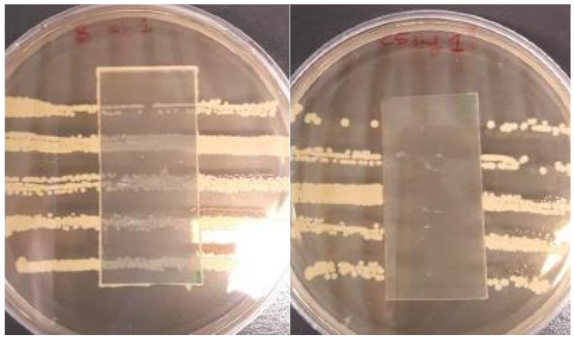


Figure 1: Figure illustrating the result of AATCC 147 test against *Klebsiella pneumoniae* (gram-).

References:

1. Monier, V., Mudgal, S., Escalon, V., O'Connor, C., Anderson, G., Montoux, H., Reisinger, H., Dolley, P., Oglivie, S., Morton, G. (2011), Preparatory Study on Food Waste across EU 27. European Commission.
2. Buisman, M.E., Haijema, R., Bloemhof-Ruwaard, J.M. (2019), Discounting and dynamic shelf life to reduce fresh food waste at retailers, *Int. J. Prod. Econ.*, 209, 274–284.
3. Prasad, P., Kochhar, A. (2014), Active Packaging in Food Industry: A Review, *J. Environ. Sci, Toxicology and Food Technology* (IOSR-JESTFT), 8, 1–7.

Development of repellent surfaces

Ana Antelava[1,2] *, Anna Wojdyła-Cieślak[3], Geraldine Durand[1,3], Achilleas Constantinou[1], Alan Taylor[3]

[1]London South Bank University, 103 Borough Rd, London SE1 0AA, United Kingdom
[2]National Structural Integrity Research Centre (NSIRC Ltd.), Granta Park, Great Abington, Cambridge, CB21 6AL, United Kingdom
[3]TWI Ltd, Granta Park, Great Abington, Cambridge, CB21 6AL, UK

Abstract:

Surface contamination is an important industrial problem that leads to loss of performance and increased operational costs. Various methods have been developed to prepare a super-repellent surface but the retention of high levels of repellence has not been achieved yet[1]. The development of surfaces that repel liquids has attracted lots of interest due to variety of possible applications in industry. There are many examples in the literature of highly repellent and even omniphobic coatings. A deeper understanding of the key chemical and topographic characteristics that dictate this behaviour would provide the enabler for the engineering of anti-contamination, anti-sticking and self-cleaning materials[2]. The purpose of this research is to better understand the conditions that dictate super repellence, specifically in terms of decoupling the effect of surface chemistry from surface roughness and to develop a new methodology for assessing wettability.

To deconvolute the effects of surface chemistry from topographic contributions, planar glass slides with minimal surface roughness were used as substrates. The surface of these slides were treated with a range of different chemical functionalities known to promote low surface energies[3]. This included silanes, silicones, silazanes, fluorinated and non-fluorinated treatments.

Static contact angle measurements were undertaken with both water and diiodomethane, but little difference between various surface treatments was observed.

To provide a more discriminating test to enable the selection of the most repellent surface chemistry, an examination of advancing-receding contact angle as a function of tilt was undertaken. In addition, an evaluation of the droplet location as a function of tilt was carried out to determine when the droplet moves and whether it exhibits film-forming behavior.

The outlined approach forms the basis of a new methodology for assessing repellence that accounts for a wider range of behaviours other than simple static sessile drop assessments.

Keywords: Super Repellence, Wetting, Surface Roughness, Surface Chemistry

References:

1. Wojdyła A., Durand G, Taylor A., and Boyd I. (2014) Advanced low-energy durable coatings. *International Journal of Energy Research*, 39(2), 165-171.
2. Hsieh C., Wu F., and Chen W. (2009) Super water- and oil-repellencies from silica-based nanocoatings. *Surface and Coatings Technology*, 203(22), 3377-3384.
3. Li L., Li B., Dong J., and Zhang J. (2016) Roles of silanes and silicones in forming superhydrophobic and superoleophobic materials. *Journal of Materials Chemistry*, 4(36), 13677-13725.

Photochemically Initiated Conversion of Coordination Compounds – A Low Temperature Route to Metal Oxide Thin Films

P. With,[1]* J. Lehnert,[1] L. Seifert,[1] S. Dietrich,[2] H. Krautscheid,[2] S. Naumov,[1] A. Prager,[1] G. Mirschel,[1] L. Prager,[1] U. Helmstedt[1]

[1] Leibniz Institute of Surface Engineering (IOM), Leipzig, Germany

[2] Institut für Anorganische Chemie, Universität Leipzig, Leipzig, Germany

Abstract:

Considering the steadily increasing demand for large-area and flexible metal oxide thin films from electronic industries we thus developed an attractive low-cost alternative to conventional preparation techniques. Those require either high processing temperatures >350 °C, e.g. in sol-gel methods and atmospheric pressure CVD, or low pressures, e.g. in most CVD, ALD and PVD methods. Processes involving photochemically initiated reactions offer the potential to overcome these drawbacks. They can comprise the 'wet' coating of a substrate with precursor solutions followed by UV-light initiated oxidative conversion and thin film formation close to room temperature and at normal pressure.[1]

Photochemical conversion of coordination compounds as precursors, e.g. of metal alkoxides ($[Ti(OEt)]_4$,[2] $[Fe(O_tBu)_3]_2$, $[Nb(OEt)_5]_2$, or metal hexanoates ($[Al(OH)\{O_2C(CH_2)_4CH_3\}]_n$[1]), using VUV light and under oxidative conditions is a viable method to prepare oxide thin films <100 nm close to room temperature and atmospheric pressure (Figure 1, a). Chemically pure metal oxide films were obtained as demonstrated by XPS measurements combined with depth sputtering. Apart from detailed kinetics studies and contemplation of organic and inorganic conversion products based on ATR-FTIR spectroscopy and gas chromatography, density functional theory (DFT) calculations were carried out to gain insight into the photochemical reaction pathway. The kinetics of thin film conversion strongly depends on the initial precursor film thicknesses. Moreover, by FTIR measurements together with DFT calculations it has been assumed that for Fe-, Nb- and Ti-alkoxides, M(OCO)-ring structures have been formed as intermediates (Figure 1, b). Metal oxide thin films prepared by VUV irradiation were crack free as shown by SEM. Photochemical conversion of Fe-, Nb-, and Ti-alkoxides resulted in a higher degree of oxide densification than achieved by simple hydrolysis at the same reaction temperature. By GIXRD and Raman analysis the amorphous state of the oxide thin films could be verified. Furthermore, due to the high structural disorder in the amorphous oxides network, photochemically prepared thin films showed higher transparency and band gaps as compared to crystalline materials. Thus, the shown photochemical synthesis approach represents an attractive alternative in achieving dense metal oxide coatings at low temperatures, e.g. for coating onto flexible and thermally sensitive polymeric substrates (Figure 1,c).

Keywords: metal oxide semiconductor, low temperature synthesis, photochemical, thin film.

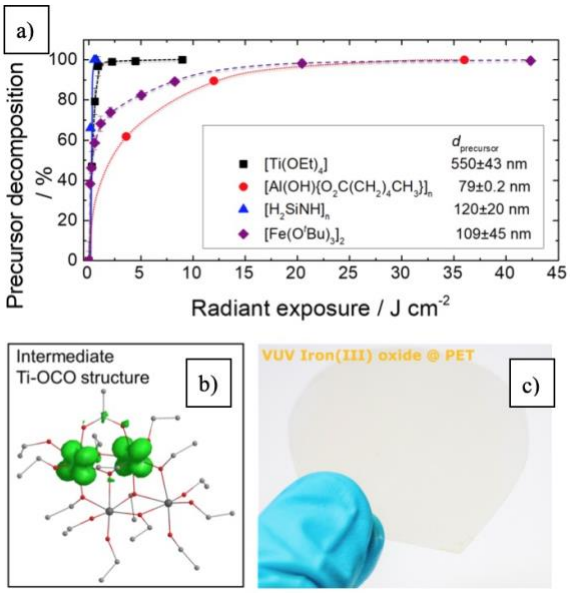


Figure 1: a) Comparison of VUV-induced (Xe-excimer irradiation; $E_{Photon} \approx 7.2$ eV) decomposition of different coordination compound thin films on Si-wafers depending on the applied radiant exposure (H_e) at ambient conditions. b) Structure of an intermediate Ti(OCO) ring structure from DFT calculations.

c) Photo of an iron(III) oxide thin film on a PET film.

References:

1. Prager, L., Dierdorf, A., Liebe, H., Naumov, S., Stojanovic, S., Heller, R., Wennrich, L., Buchmeiser, M.R., *Chemistry Eur. J.* (2007), 13, 8522-8529.
2. With, P.C., Helmstedt, U., Naumov, S., Sobottka, A., Prager, A., Decker, U., Heller, R., Abel, B., Prager, L., *Chem. Mater.* (2016), 28, 7715-7724.
3. Wennrich, L., Khalil, H., Bundesmann, C., Decker, U., Gerlach. J.W., Helmstedt, U., Manova, D., Naumov, S., Prager, L., *Mater. Chem. Phys.* (2013), 137, 1046-1052.

SMS 2019 / EGF 2019
Joint Plenary Session

Applications in Nanotechnology of Focused Electron and Ion Beam Induced Deposition

José M. De Teresa,[1,2,*]

[1] Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Univ. of Zaragoza, Zaragoza, Spain.
[2] Laboratorio de Microscopías Avanzadas (LMA), Univ. of Zaragoza, Zaragoza, Spain.
*email address: deteresa@unizar.es

Abstract:
In this talk I will summarize our recent work on the use of focused electron and ion beams in combination with gas and condensed precursors to grow functional nanostructures. Advantages of this set of direct nanomaterials growth techniques are the avoidance of resists, the high resolution attainable, the capability for growth of three-dimensional structures, their use on non-flat substrates and the functionality of the deposited materials. More specifically, I will focus on three types of functionalities.

Metallic deposits grown by Focused Ion Beam Induced Deposition (FIBID) are of interest in circuit editing and for making electrical contacts on nano-objects, with Pt-based or W-based precursors in the gas phase being used in these applications. We have recently succeeded in the growth of metallic deposits by Ga^+-FIBID using a condensed layer of $W(CO)_6$ formed on the substrate under cryogenic conditions (Cryo-FIBID), with obvious advantages due to the low ion irradiation dose required (~ 50 $\mu C/cm^2$) [1].

Magnetic deposits grown by Focused Electron Beam Induced Deposition (FEBID) are of interest to grow magnetic tips on cantilevers, with applications in magnetic sensing. We have used $Co_2(CO)_8$ and $Fe_2(CO)_9$ gas precursors to grow magnetic nanospheres and nanowires on various types of cantilevers, with application in Magnetic Force Microscopy [2].

Superconducting deposits grown by Ga^+-FIBID using $W(CO)_6$ gas precursor have been found to be of interest to investigate the physics of vortices [3]. We have recently succeeded in the growth of superconducting nanowires, nanotubes and nanohelixes by He^+-FIBID using $W(CO)_6$ gas precursor [4]. The capability of FIBID for the growth of three-dimensional superconducting nanostructures opens new perspectives in the field.

Keywords: Focused Ion Beam, FEBID, FIBID, Nanolithography, Circuit Edit, Magnetic Nanowires, MFM, Nano-superconductivity, three-dimensional nanoprinting

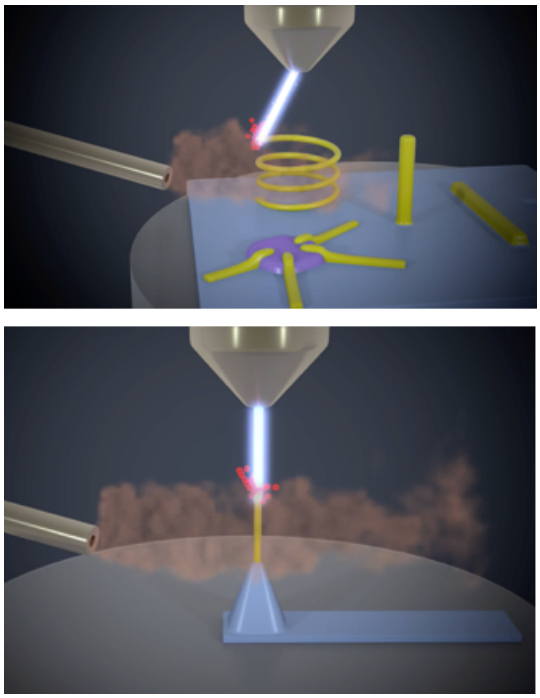


Figure 1: Figure illustrating the growth of nanostructures by FEBID and FIBID

References:

1. Córdoba, R. et al. (2019) Ultra-fast growth of W-C metal nanostructures by FIBID under cryogenic conditions (Cryo-FIBID); manuscript submitted
2. De Teresa J. M. et al. (2016) Review on magnetic nanostructures grown by Focused Electron Beam Induced Deposition; J. Phys. D: Appl. Phys. 49, 243003
3. Córdoba, R. et al. (2013) Magnetic field induced dissipation free state in superconducting nanostructures; Nature Communications 4, 1437
4. Córdoba R. et al. (2018) Vertical growth of superconducting crystalline hollow nanowires grown by He^+ focused ion beam induced deposition; Nano Letters 18, 1379

Multifunctional Adaptive Sandwich Structures: Modeling and Optimization

A.L. Araújo

IDMEC, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

Abstract:
The sandwich construction is an effective way of minimizing structural weight while simultaneously maximizing the bending stiffness of a composite. It has been widely applied in the transportation industries, namely in automotive, naval and aerospace structures, as well as in buildings. Allied to its excellent structural stiffness and strength performance, when vibration and noise reduction and thermal transfer or insulation are also a concern, the sandwich construction proves its superiority when compared to other structural composite solutions. The modeling of composite sandwich structures has been an active research field in the last years and when combined with viscoelastic, piezoelectric and functionally graded materials, the need for special purpose models becomes a concern [1]. This lecture presents a state of the art review of the modeling and design optimization formulations of multifunctional adaptive sandwich structures, including the work developed by the authors and his research group in the past decade. Some modeling approaches will be presented for linear and nonlinear static, buckling and dynamic analysis. Optimization formulations will also be described concerning the design of these structures for vibration and noise reduction [2], using active and passive damping technologies. As an example, Figure 1 shows the results obtained for the optimal placement of piezoelectric sensors and actuators on the surfaces of a viscoelastic sandwich plate. The objective was to minimize sound radiation, added mass and the number of controllers needed for the active negative velocity feedback control.

Keywords: composite laminates, sandwich structures, viscoelastic materials, piezoelectric materials, numerical modelling, active control, optimization, vibration and noise attenuation.

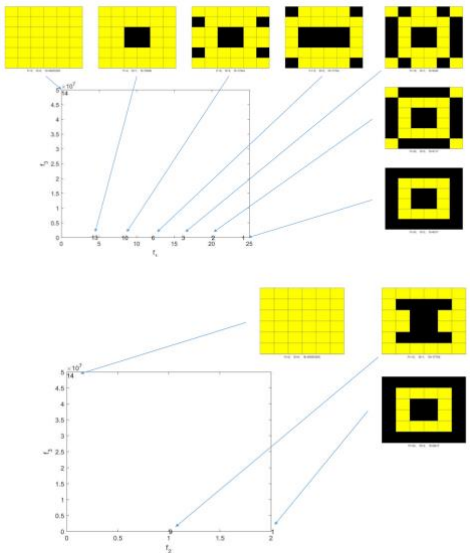


Figure 1: Figure illustrating the multiobjective solutions for optimal placement of sensors and actuators on the surface of a viscoelastic sandwich plate in order to minimize sound radiation, added mass and number of controllers.

References:

1. Araújo, A.L., Carvalho, V.S., Mota Soares, C.M., Belinha, J., Ferreira, A.J.M. (2016), Vibration analysis of laminated soft core sandwich plates with piezoelectric sensors and actuators, *Composite Structures*, 151, 91-98.
2. Madeira, J.F.A, Araújo, A.L., Mota Soares, C.M., Mota Soares, C.A., Ferreira, A.J.M. (2015), Multiobjective design of viscoelastic laminated composite sandwich panels, *Composites Part B: Engineering*, 77, 391-401.

Novel Power Generator using Dielectric Elastomers

S. Chiba,[1,*] M. Waki,[2] K. Fujita[3]

[1] Chiba Science Institute, Tokyo, Japan
[2] Wits Inc., Tochiji, Japan
[3] Tohoku University, Miyagi, Japan

Abstract:

Increase in world population and the acompanying surge in demand for energy, food and water, as well as the sudden increase in energy consumption caused by recent industrial development and betterment of life standards in newly developing countries will accelerate global warming. Among the diverse measures proposed to meet our energy needs, the use of renewable energy is receiving increasing attention. Especially, the wave power generation has attracted attention as one of useful utilization methods for ocean energy. However, the conventional wave generators are large, expensive, and unable to efficiently generate electric power with small amplitude waves, limiting their widespread usage. To solve these problems, this article discusses the possibilities for a wave power generator using dielectric elastomer (DE) artificial muscle recently developed as a novel method for harvesting renewable energy.

DEs are a new transducer technology that has been began an investigation by SRI International (R. Perline, S. Chiba et al) in 1991. DE is based on a very simple structure comprising an elastomer sandwiched between two stretchable electrodes. As the term "artificial muscle" implies, DE is often used in the actuator mode, which utilizes the coulombic attraction forces that occur between the electrodes to deform the elastomer. More recently, the use of DE in the reverse mode, in which deformation of the elastomer by external mechanical work is used to generate electrical energy, has been gaining more attention. These DEs enable electric power generation by their expansion and contraction.

As DE is very light, inexpensive, and easily formed into multiple layered structures, it can make a very simple and robust direct drive wave power system that is economically viable. The use of significantly larger amounts of DE material to produce generator modules with outputs in the Megawatt at range is being investigated for application to ocean wave power system. Figure 1 summarizes sites where power generation using DEs is possible and conceptual rendering of the generation systems. They are a) Wind Power Generators on tops of buildings, b) Water Mill Generators, c) Waste energy Generators, d) Drain Generators, e) Wind Power Generators for Personal Houses, f) Solar Heat Generators, g) Wave Generators, and h) Water Flow Generators, i) Wave Generators in Ocean, and, j) Hydrogen Production Plant.

Keywords: Dielectric elastomer, Power-generator, Sensor, Actuator, EAP, Artificial Muscle, Soft Actuator, Marine Energy, Renewable energy

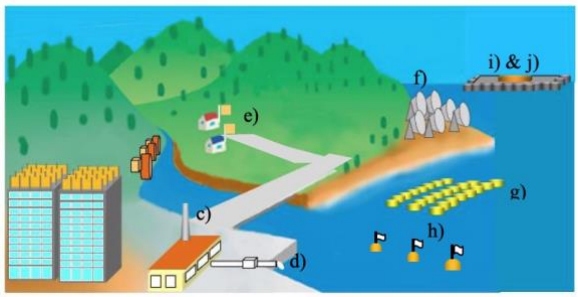


Figure 2: Sites where power generation using DE is possible and conceptual rendering of the generation systems.

References:

1. Pelrine, R., Chiba, S., (1992), Review of Artificial Muscle Approaches," Proc. Third International Symposium on Micromachine and Human Science, Japan, pp 1–9, October.
2. Chiba, S., et al., 2013, Consistent OceanWave Energy Harvesting Using Electroactive (Dielectric Elastomer) Artificial Muscle Generators, *Applied Energy*, 104, 497-502, ISSN 0306-2619
3. Chiba, S., et al., (2019), Recent Progress on Soft Transducers for Sensor Networks, Chapter 23, Technologies and Eco-innovation towards Sastainability II, *Springer Nature*, Doi.org/10.1007/978-981-13-1196-3_23.

Active Composite Materials for 4D-printed Structures

M. Sinapius,[1,2,*] R. Mitkus,[1]

[1] Technische Universität Braunschweig, Institute of Adaptronics and Function Integration, Braunschweig, Germany
[2] German Aerospace Center, Institute of Composite Structures and Adaptive Systems), Braunschweig, Germany

Abstract:
4D printing combines additive manufacturing (AM) processes with intelligent materials to create structures that are able to change shape or properties over time under the influence of environmental stimuli. Fused Deposition Modelling (FDM) fits well with the concept of 4D printing by providing the ability to pre-program structures during the printing process. As a possible approach, multimaterial shape-variable structures representing a hinge are presented in the lecture. The structures are printed in multiple layers with PLA and TPU and remain in a temporary shape after printing until they are exposed to a deformation stimulus due to temperature change. The main objective of this presentation is to show the parameters of the pre-programming step, which can be adapted by variation of printing process and design parameters. Experimental results are presented that investigate the influence of printing speed, temperature of the building panel and the number of layers in the structure. Furthermore, the repeatability of deformations after a small number of cycles is investigated. Approaches for the introduction of the activation energy are shown. Additionally, a new approach is presented as a perspective of printing sensory structures, in which a layered component based on a printable thermoplastic is realized by adding a second phase. The goal is a printed fiber-reinforced carrier structure with printed electrodes and printed sensor layer. All layers are based on the same base material to which an adapted second phase (fibers, conductive additives, energy converting particles) is added. This approach will lead to an optimal functional conformity.

Keywords: 4D printing, Active Composite Materials

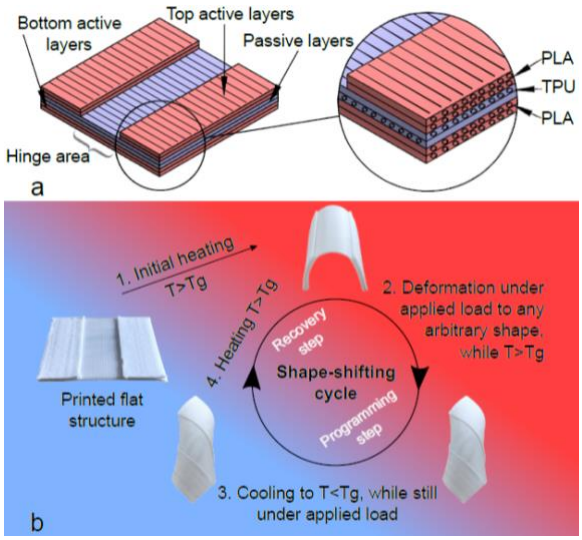


Figure 1: Figure illustrating the fundamental principle of 4D-printed, morphing structures

References:

1. Kačergis, Lukas; Mitkus, Rytis; Sinapius, Michael: Influence of Fused Deposition Modeling Process Parameters on the Transformation of 4D printed morphing structures, Smart Materials and Structures, accepted, (2019)

Free-standing nanostructures at Atomic Scale: from growth mechanisms to properties

Sara Martí-Sánchez,[1] Marc Botifoll,[1] Christian Koch,[1] Jordi Arbiol[1,2,*]
[1].Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Catalonia, Spain
[2].ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Catalonia, Spain

Abstract:
The lack of mirror symmetry in binary semiconductor compounds turns them into polar materials, where two opposite orientations of the same crystallographic direction are possible. Interestingly, their physical properties (e.g.: electronic or photonic) and morphological features (e.g.: shape, growth direction, etc.) also strongly depend on the polarity. It has been observed that nanoscale materials tend to grow with a specific polarity, which can eventually be reversed for very specific growth conditions. In addition, polar-directed growth affects the defect density and topology and might induce eventually the formation of undesirable polarity inversion domains in the nanostructure, which in turn will affect the photonic and electronic final device performance.
Here, we present a review on the polarity-driven growth mechanism at the nanoscale, highlighting suitable future possibilities of polarity engineering of semiconductor nanostructures from VLS vertical complex heterostructures to the newest selected area growth hybrid quantum networks. The present study has been extended over a wide range of semiconductor compounds, covering the most commonly synthesized III-V (GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb) and II-VI (ZnO, ZnTe, CdS, CdSe, CdTe) nanowires and other free-standing nanostructures (tripods, tetrapods, belts and membranes). This systematic study allowed us to explore the parameters that may induce polarity-dependent and polarity-driven growth mechanisms, as well as the polarity related consequences on the physical properties of the nanostructures.

References

1. M. de la Mata, et al., Nano Letters, **12**, 2579 (2012)
2. M. de la Mata, et al., Nano Letters, **14**, 6614 (2014)
3. M. de la Mata, et al., Nano Letters, **16**, 825 (2016).
4. M. de la Mata, et al., Nano Letters, **19**, 3396 (2019).
5. M. Heiss, et al., Nature Mater., **12**, 439 (2013).
6. M. de la Mata, et al., J. Mat. Chem. C, **1**, 4300 (2013).
7. S. Vaitiekėnas, et al., Physical Review Letters, 121, (2018) 147701.
8. F. Krizek, et al., Physical Review Materials, 2, (2018) 093401.
9. P. Aseev, et al., Nano Letters, 19, (2019) 218.
10. G. Tutuncuoglu, et al., Nanoscale, 7, (2015) 19453.
11. M. Friedl, et al., Nano Letters, 18, (2018) 2666.

*Corresponding author: Prof. Jordi Arbiol, Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Catalonia, Spain, e-mail: arbiol@icrea.cat

SMS 2019 / EGF 2019
Joint Session II:
Novel Materials / Graphene for Energy and Environment applications

Engineering photoanodes for photoelectrochemical solar water splitting

Dr. Salvador Eslava[1]

[1] Department of Chemical Engineering, University of Bath

Abstract:
Photoelectrochemical solar water splitting offers a clean solution to the world energy requirements of a sustainable future. Achieving its full potential depends on developing inexpensive photoanodes that can efficiently evolve oxygen from aqueous electrolytes, the most kinetically demanding step in water splitting. Here I present recent developments we have achieved in the preparation of inexpensive photoanodes: a nanostructured TiO_2 with exposed {0 1 0} facets [1], an α-Fe_2O3 self-coated with FeOx electrocatalyst [2] and with an electrodeposited $CoFeO_x$ [3] (Figure 1), and a novel all-inorganic halide perovskite $CsPbBr_3$ [4]. The nanostructured TiO_2 photoanodes are prepared using $Ti_7O_4(OEt)_{20}$ clusters as a precursor and resulting photoanodes show a unique morphology resembling desert roses, pure anatase phase and high exposure of the very active {0 1 0} facet, achieving remarkable ~100% IPCE efficiency at 350 nm wavelength [1]. α-Fe_2O_3 photoanodes simultaneously coated with FeO_x electrocatalyst are prepared using precursors whose morphology and crystallinity is tuned with lactic acid additive, boosting photoanode photocurrents from 0.32 to 1.39 mA cm^{-2} at 1.23 V_{RHE} [2]. An extended electrochemical characterisation also shows that the charge transfer to electrolyte at α-Fe_2O_3 interfaces can be boosted by an extremely thin layer of $CoFeO_x$, unlike less thin $CoFeO_x$ layers that just reduces surface recombination due to self-oxidation [3]. Finally, all-inorganic halide perovskite $CsPbBr_3$ photoanodes are prepared using carbon as a hole transport layer [4]. This type of semiconductor is revolutionising the field of solar cells due to their high efficiencies and inexpensive preparation but remain practically unexplored in applications using aqueous electrolytes. However, our developed inexpensive carbon layers effectively protect the halide perovskite for more than 30 h directly immersed in water, evolving oxygen with a Faradaic efficiency of 82% and achieving photocurrents above 2 mA cm^{-2} at 1.23 V_{RHE}.

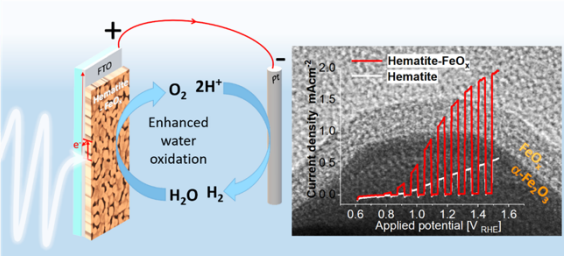


Figure 1: (left) Diagram illustrating the use of photoanodes for water oxidation, the bottleneck reaction in water splitting for hydrogen generation. (right) TEM image of α-Fe_2O_3 and FeO_x amorphous coating and photocurrent results.

Keywords: solar fuels, photoanodes, TiO2, hematite, CsPbBr3, perovskite, water splitting, hydrogen production.

References:

1. M. Regue, S. Sibby, I. Y. Ahmet, D. Friedrich, F.F. Abdi, A. L. Johnson, S. Eslava, submitted, 2019
2. D. Walsh, J. Zhang, M. Regue, R. Dassanayake, S. Eslava, ACS Appl. Energy Mater. 2019, 2, 2043–2052
3. J. Zhang, R. García-Rodríguez, P. Cameron, S. Eslava, Energy Environ. Sci. 2018,11, 2972-2984
4. I. Poli, U. Hintermair, M. Regue, S. Kumar, E.V. Sackville, J. Baker, T.M. Watson, S. Eslava, P.J. Cameron, Nature Communications 2019, 10, 2097

European Research Council session

Adela I. Carrillo Gomez[1]

[1] European Research Council Executive Agency, Brussels, BE
adela-isabel.carrillo-gomez@ec.europa.eu

Abstract:
The European Research Council (ERC) is an european funding agency looking for supporting the excellent ideas that have not happened yet and the scientists who are dreaming them up.
ERC grants are awarded on the sole criterion of scientific excellence. The ERC awards are flexible and provide funding for a period of up to five years.
The grant budgets for a single Principal Investigator varies from 1.5 - 3.5 million euros. Independent researchers of any age and career stage and from all over the world can apply, provided that their host institution is located in a European Member State or in a Country associated to the European research funding programmes.
Since 2007, ERC has funded more than 9000 scientific projects, ERC grantees have won prestigious prizes, including 6 Nobel Prizes, 4 Fields Medals and 5 Wolf Prizes.
In this informative session, the main features of the ERC individual grants (i.e. Starting, Consolidator and Advanced grants) as well as information on the applications and evaluation process will be presented.
Outstanding scientists in the Physical Sciences & Engineering domain will describe their experience as ERC evaluators, providing some tips to write a successful proposal and, explaining the most common mistakes/faults they observed when reviewing the projects.
In addition, some of our grantees will give their own insights on how to present a project to convince the evaluators that their idea is an 'excellent idea' that will contribute to the future of science. Moreover, we will see how the ERC grant has help them to establish and/or consolidate their independence scientific career.
Should you have a brilliant idea that you really wish to make real, don't miss this session; you will see what the European Research Council can do to make your dreams come true.

Keywords: funding, Europe, career development.

Better in Vacuum - how vacuum can improve investigation of 2D materials using conductive Atomic Force Microscopy (AFM)

Romain Bourrelier[4], Jonathan Ludwig[1,2], Marco Mascaro[1,2], Umberto Celano[1], Ilka M. Hermes,[3,A] Wilfried Vandervorst[1,2], Kristof Paredis[1]

[1] IMEC, Leuven, Belgium
[2] Department of Physics and Astronomy, University of Leuven, Leuven, Belgium
[3] Park Systems Europe GmbH, Mannheim, Germany
A. Corresponding author: Ilka M. Hermes, ihermes@parksystems.com
4. Park Systems France SARL, Orsay, France

Abstract

In the last years, the aim of semiconductor industry to produce nanoscale-sized devices determined an increasing interest for a series of 2D materials. Among them, transition metal dichalcogenides (TMDs) are under investigation due to some promising electrical characteristics, such as an inherent band gap and a relatively high mobility of charge carriers, exhibited at nanoscale on single grains or islands.

Atomic Force Microscopy (AFM) offers a platform for the simultaneous characterization of multiple properties of 2D materials. AFM allows to determine the structural conformation and growth of 2D materials and probe their local electrical response. We used AFM to perform this kind of correlative microscopy on MoS_2 layers grown onto sapphire via Metal Organic Chemical Vapor Deposition (MO-CVD). The morphological and electrical properties of samples with different thickness were studied and compared by using Conductive AFM.

t is known that water contamination strongly affects the properties of MoS_2, because it leads to a p-doping of the material. In order to assess the effect of water on the conductive properties of MoS_2, AFM measurements were done both in air and in high vacuum using a Park HiVac AFM system. The vacuum allows to get rid of the water layer naturally present on the top of the sample in ambient conditions. Results showed a larger local conductivity in vacuum with respect to air. Moreover, conductivity maps in vacuum showed an increased sensitivity with respect to measurements in air, allowing to determine boundaries between different conductive grains.

The ability of AFM to resolve electrical properties at nanoscale and the current advancement of the AFM technology, which allows integrating these characterization tools into the semiconductor manufacturing process, make AFM the ideal platform for the study of these 2D semiconductor materials.

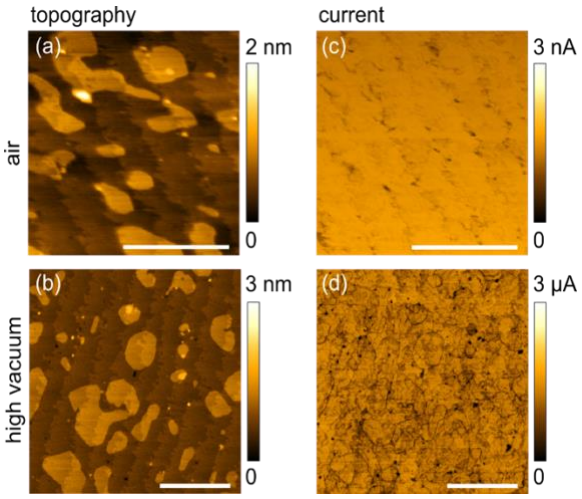


Figure 1: cAFM from the same 3-4 layered MoS_2 sample showing the increased current level and sensitivity under high vacuum. (a) and (b) Topography (c) current images in air at 5 V bias (d) current images taken immediately after pumping to high vacuum at 0.5 V bias. The data taken in air and high vacuum was acquired using identical parameters: same probe with spring constant k of 7 N/m, set point of 10 nN, and 1 Hz scan rate. Scale bar is 500 nm.

Image courtesy: IMEC, Leuven, Belgium

Buckled MoS_2 nanoribbons for bistable vibration energy harvesters

G. Abadal,[1*] R. López,[1] and X. Cartoixà[1]

[1] Departament d'Enginyeria Electrònica, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

Abstract:
Suspended nanomechanical structures based on monolayers of piezoelectric 2D materials have been recently proposed as the transducer element of energy harvesting components for future selfpowered nanodevices[1,2]. In particular, it has been demonstrated that engineering the strain induced buckling of clamped-clamped single atom thick nanoribbons it is possible to maximize the harvested power from mechanical noise sources. In this contribution, we present performance results in terms of mechanical vibration and electrical power of a MoS_2 buckled clamped-clamped nanoribbon predicted by an analytical model based on beam theory. The model has been previously validated using similar structures based on h-BN monolayers, by comparing with the performance results predicted by atomistic models in previous works[1]. Monolayer thickness is used as a fitting parameter. After validation, the model is fed with Young modulus and piezoelectric coefficient values of MoS_2 obtained from atomistic calculations. Then, the static elastic potential energy vs. out-of-plane deflection curves (figure 1) as well as the dynamic response to white gaussian noise (figure 2) are both calculated for different compressive strain values in the pre and post-buckling regimes. From these calculations, we can deduce that the optimum strain value that maximize the dynamic response depends on the intensity of the mechanical noise. Thus, the higher the excitation noise intensity, the larger the optimum compressive strain. The explanation to this fact can be found in the time evolution graphs, that clearly show that at low and high strain levels the ribbon slightly vibrates around the local potential minimum. Instead, when strain is tunned around the optimum value, the ribbon jumps from one potential well to the other symmetric one, leading to an increase of the vibration amplitude of the structure. We acknowledge financial support by the Spanish MINECO under grant TEC2015-67462-C2-1-R (MINECO/FEDER) and the MICINN under grant No. RTI2018-097876-B-C21 (MICINN/FEDER).

Keywords: nanoelectromechanical systems, nonlinear energy harvesting, piezoelectric 2D materials. molybdenum disulphide, noise.

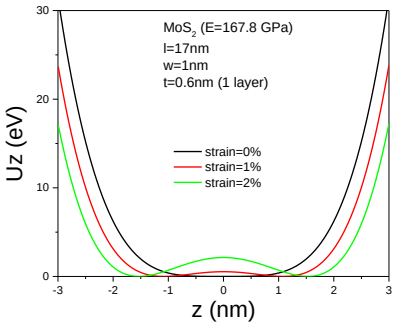


Figure 1: Elastic energy vs. out-of-plane displacement (z) for different compressive strain values of a 17x1x0.35 nm[3] MoS_2 ribbon.

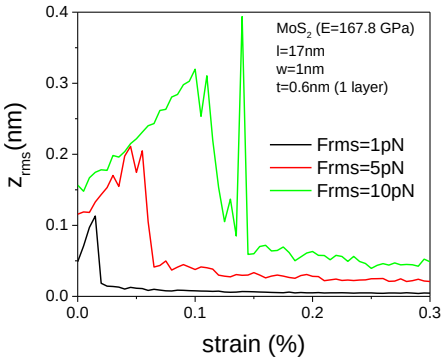


Figure 2: Dynamic response of figure 1 ribbon for different excitation intensities.

References:

1. M. López-Suárez, M. Pruneda, G. Abadal, R. Rurali. "Piezoelectric monolayers as nonlinear energy harvesters". Nanotechnology, 25 (17), 175401 (2014).
2. M. López-Suárez, G. Abadal, L. Gammaitoni, R. Rurali, "Noise energy harvesting in buckled BN nanoribbons from molecular dynamics" Nano Energy 15, 329–334 (2015).

Electric charges recovering from aqueous media using conductor oxides

V. Ledoux, A. Evstratov
Institut Mines-Telecom Mines Alès, Centre des Matériaux Mines d'Alès (C2MA), Alès, France

Abstract:
Nowadays, it's commonly admitted that n-type conductor oxides (≡ MO_x) with large bandgap, as SnO_2:F, can generate hydroxyl radicals from water, according to the reaction below [1]:

$$MO_x + H_2O \rightarrow MO_x(^{\bullet}OH) + H^+ + 1\ e^- \quad \textbf{(1)}$$

In electrocatalytic conditions, in the field of waste water treatment for example, this behavior at metal oxides was studied by numerous authors [2,3]. However, the mechanism of hydroxyl radical generation on the oxide surfaces was not studied in details. Unfortunately no mention exists in literature on the opportunity to recover the elementary electric charges derived from the hydroxyl radical generation process. It's important to underline the effect of complementary charge generation by the surfaces of conductor oxide anodes was already outlined by the previous research works [4].
Despite some recent contributions demonstrating the existence of an oxide layer on the noble metal surfaces [5], the last are not able to form hydroxyl radicals in aqueous media contrary to the semi-conductor metal oxides. In our study we propose a detailed reaction cycle for the hydroxyl radical general by a conductor oxide surface (Figure 1). The proposal approach allows to consider that the radical formation occurs before the water splitting (≡ water electrolysis). The key steps of this mechanism, underlined by brown circles on Figure 1, were verified with independente methods. The hydroxyl radical formation on the SnO_2:F surface was tested directly by the oxidation reaction $Pb^{2+} \rightarrow PbO_2$ that doesn't occur at the metal surfaces, and undirectly by the oxidation reaction $C_6H_6O_2 \rightarrow C_6H_4O_2$. Futhermore, benefits of organic compounds (Hydroxyl radical scavengers, HRS) in the water for the recovering of electric charges was highlighted. To conclude, according with this new reaction schema between water and an oxide surface, the recovering at elementary electric charges becomes available.

Keywords: Electric charges, conductor metal oxides, tin dioxide, energy generation, hydroxyl radicals.

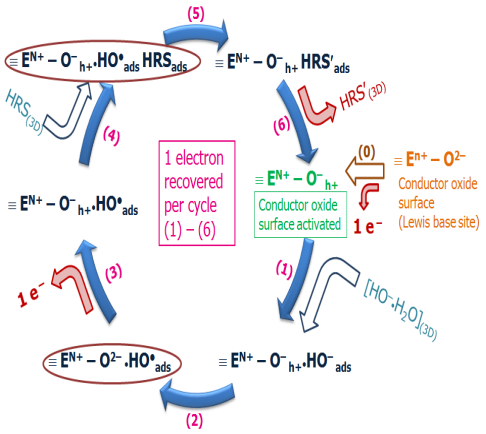


Figure 1: Principal steps of an electrocatalytic reaction cycle explaining the hydroxyl radical generation and the recovering of elementary electric charges from water by a conductor oxide surface.

Acknowledgements:
This research was financially supported by the European Commission (project H2020 MSCA-RISE-2015 n°691010 "HUNTER", 2016 – 2019).

References:

1. Comninelis, C. (1994), Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment, *Electrochim. Acta*, 39, 1858-1862.
2. Rao, A. N. S., Venkatarangaiah, V.T. (2014), Metal oxide-coated anodes in wastewater treatment, *Environ. Sci. Pollut. Res.*, 21, 3197-3217.
3. Martínez-Huitle, C. A., Andrade, L. S. (2011) Electrocatalysis in wastewater treatment: recent mechanism advances, *Quim. Nova*, 34, 850-858.
4. Panizza, M.; Cerisola, G. (2009), Direct and mediated anodic oxidation of organic pollutants, *Chem. Rev.*, 109, 6541-6569.
5. Reier, T., Oezaslan, M., Strasser, P. (2012), Electrocatalytic Oxygen Evolution Reaction (OER) on Ru, Ir, and Pt catalysts: A comparative study of nanoparticles and bulk materials, *ACS Catal.*, 2, 1765-1772.

Bio-inspired microshapes converted to functional materials for catalysis and photovoltaics

H.C. Hendrikse,[1*] L. Helmbrecht,[1] A. van der Weijden,[1] M. Ronda Llorett,[2] W.L. Noorduin[1]

[1] AMOLF, Self-Organizing Matter, Amsterdam, The Netherlands
[2] University of Amsterdam, Van 't Hoff Institute for Molecular Sciences, Amsterdam, The Nethelands

Abstract:
Bio-inspired microshapes are nanocrystal assemblies, where the reaction conditions decide the shape of the structure. These microshapes can form complex, but controlled, morphologies like vases or corals among many others (for examples see the attached figure) by rational modulations of the reaction conditions.
The nanocrystals of these microshapes exist of calcium, strontium or barium salts. Unfortunately, these chemical compositions are unused in fields like catalysis or photovoltaics, even though these fields could benefit from the complex 3D structures found in nature[1]. In this talk I will show how we can use bio-inspired self-assembly to shape materials in 3D and use ion exchange convert these materials into a wide variety of compositions, while maintaining their 3D shape[2].
Based on this control, we also will explore the functionalities of the newly made material by synthesizing forms with catalytic and photovoltaic performance.[3]

Keywords: Self-Assembly, Coprecipitation, Ion Exchange, Hierarchical Ordering, Syngas Production, Catalysis applications, 3D Perovskite, Photovoltaic Applications.

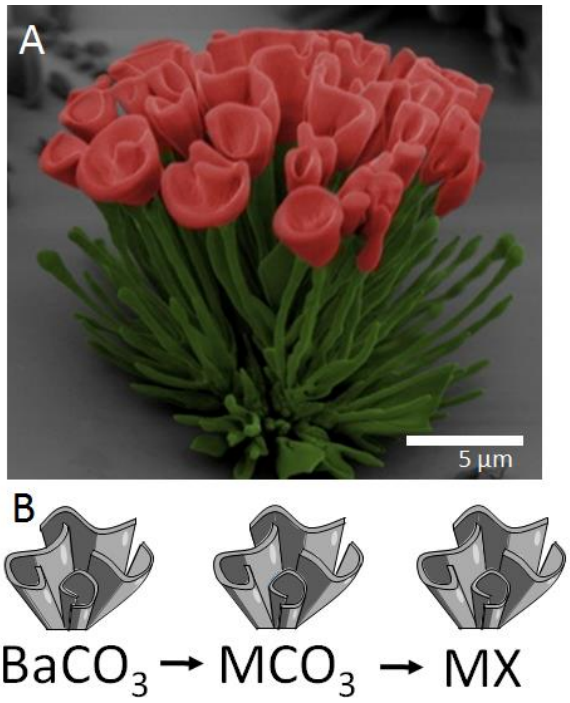


Figure 1: A. Example of a microshape. B. Schematic showing how microshapes can be transformed from their original composition towards a large variety of compositions.

References:

1. Chen K., Tüysüz H., (2015), Morphology-Controlled Synthesis of Organometal Halide Perovskite Inverse Opals, *Angew. Chem*, 54,13806–13810
2. Nooduin W.L., Grinthal A., Mahadevan L., Aizenberg, J. Rationally Designed Complex, Hierarchical Microarchitectures, *Science*, 340, 6134, 832-837
3. Holtus T., Helmbrecht L., Hendrikse H.C. *et al.*, (2018), Shape-preserving transformation of carbonate minerals into lead halide perovskite semiconductors based in ion exchange/insertion reactions, *Nature Chemistry*, 10, 740-745

Size-dependent Electronic Properties of Strongly Confined Graphene Quantum Dots and their Application in Electrochromic and Photovoltaic Devics

Z. Ji,[1] E. Dervishi,[1] S. K. Doorn,[1] M. Sykora,[1,2]

[1] Los Alamos National Laboratory, Los Alamos, NM 87544, USA
[2] Laboratory for Advanced Materials, Comenius University, 842 15 Bratislava, Slovakia

Abstract:
The absence of an electronic band gap in graphene presents a significant barrier to its effective utilization in optoelectronic applications. One way an electronic bandgap can be introduced into graphene is through exploitation of reduced dimensionality effects. Nanometer-size graphene fragments called Graphene Quantum Dots (GQDs) retain many of the remarkable properties of graphene, but unlike bulk graphene, due to quantum confinement (QC) effects, they possess a size-dependent, non-zero electronic bandgap. In spite of many exciting theoretical predictions and important practical implications, *quantitative experimental* studies of QC effects in GQDs have so far been limited. This is, in part, due to the difficulties with reproducible preparation of structurally uniform GQDs and challenges with their experimental characterization.
Recently, we developed a surface-assisted bottom-up synthesis approach that addresses the challenges with preparation of uniform ensembles of GQDs.[1-3] Using this approach we prepared series of uniform ensembles of GQDs with sizes less than 2 nm (≤ 204 carbon atoms) and experimentaly characterized, using newly developed characterization method, the effects of QC on their electronic structre. Our results show that the standard Dirac fermion model does not adequately describe the electronic properties of GQDs in the strongly confined regime. We also show experimentally (for the first time) how exciton binding energies and absolute energies of conduction and valence band offsets vary with GQD size. This information is essential for effective exploitation of GQDs in applications. Finally, we show how our approach and insights can be exploited in practical applications, such electrochromic and photovoltaic devices.

Keywords: graphene quantum dots, quantum confinement, size-dependence, bottom-up, synthesis, spectro-electrochemistry, electrochromism, displays, solar cells, photovoltaics.

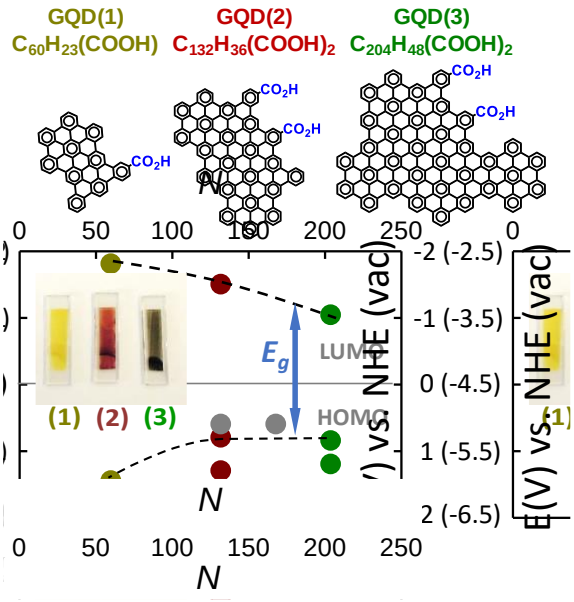


Figure 1: Examples of GQDs prepared by a "bottom up" surface-assisted synthesis approach and the experimentally determined dependence of the electronic structure on their size. The inset shows a photograph of the films with GQDs adsorbed on a transparent glass substrate.

References:

1. Ji, Z.; Dervishi, E.; Doorn, S. K.; Sykora, M. Size-Dependent Electronic Properties of Uniform Ensembles of Strongly Confined Graphene Quantum Dots. *J. Phys. Chem. Lett.* **2019**, *10*, 953-959.
2. Ji, Z.; Wu, R.; Adamska, L.; Velizhanin, K. A.; Doorn, S. K.; Sykora, M. In-Situ Synthesis of Graphene Molecules on TiO_2: Application in Sensitized Solar Cells. *ACS Appl. Mater. Interfaces*, **2014**, *6*, 20473-20478.
3. Ji, Z.; Doorn, S. K.; Sykora, M. Electrochromic Graphene Molecules. *ACS Nano*, **2015**, *9*, 4043-4049.

PRINTED ELECTROLYTE-GATED FIELD-EFFECT TRANSISTORS FROM GRAPHENE OXIDE FORMULATIONS: ELECTROCHEMICAL TUNING OF CHARGE TRANSPORT

S. Vasilijević[1], N. Battaglini[1,*], G. Mattana[1], G. Anquetin[1] and B. Piro[1]

[1] ITODYS, Université Paris Diderot, Sorbonne Paris Cité, Paris, FRANCE

Abstract:
Graphene-based field-effect transistors (GFETs) offer interesting perspectives due to their high sensitivity, especially for biosensing applications.[1] By applying the appropriate potential to the gate, it is possible to modulate the charge carriers' concentration in the graphene-based channel of the GFET.[2] Among the different fabrication techniques, inkjet-printing is particularly interesting as it permits the fabrication of this kind of devices outside the clean room in a timely and cost-effective manner.
In this work, we have formulated a home-made graphene oxide (GO) suspension and deposited it by inkjet-printing in the channel of a transistor architecture made by photolithography. Among the different ways to turn GO into a material suitable for charge transport, we have chosen to develop an in situ electrochemical approach to obtain conductive reduced GO (rGO) directly on the device.[3] The morphology of the printed rGO layer as well as its electrical properties as conductive channel in the electrolyte-gated transistor configuration (Figure 1) have been investigated. Our transfer curves show a strongly marked Dirac point and an ambipolar behavior as previously described.[2] In the first place, we demonstrate the fact that the charge transport phenomenon inside the GFET channel, gated by the electric double layer formed at the electrolyte/rGO interface, exhibits a drastic evolution with the reduction degree of GO, which allows an electrochemical control over charge carriers mobility and doping level into rGO.[4] In a second step, we show that the functionalization of the rGO channel's interface with adsorbed π-conjugated organic molecules acting as dopants, leads to an additional tuning of the Dirac Point. Our results pave the way for the electrochemical and chemical tuning of charge carrier transport in rGO-based materials.

Keywords: reduced graphene oxide, GFET, Electrolyte-gated field-effect transistor.

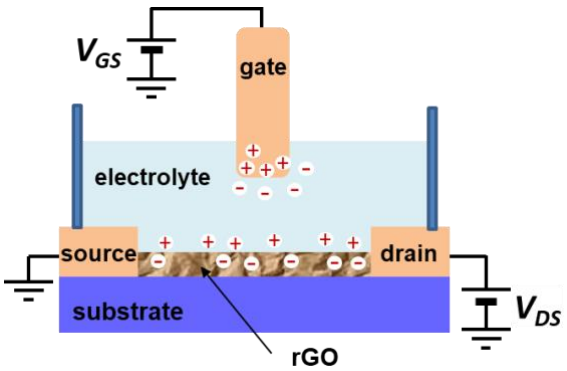


Figure 1: Scheme of the GFET setup in the electrolyte-gated configuration (EGFET). The channel is made of rGO obtained from the *in situ* electro-reduction of inkjet printed GO.

References:

1. Zhan, B., Li, C., Jenkins, G., Huang, W., Dong, X. (2014), Graphene Field-Effect Transistor and Its Application for Electronic Sensing, *Small*, 10, 4042-4065.
2. Meric, I., Han, M. Y., Young, A. F., Ozyilmaz, B., Kim, P., Shepard, K.L. (2008), Current saturation in zero-bandgap, top-gated graphene field-effect transistors, *Nature*, 3, 654-659
3. Mativetsky, J.M., Liscio, A., Treossi, E., Orgiu, E., Zanelli, A., Samori, P., Palermo, V. (2011), Graphene Transistors via in Situ Voltage-Induced Reduction of Graphene-Oxide under Ambient Conditions, *J. Am. Chem. Soc.*, 133, 14320-14326.
4. Vasilijević, S., Mattana, G., Anquetin, G., Battaglini, N., Piro, B. (2019), Electrochemical tuning of reduced graphene oxide in printed electrolyte-gated transistors. Impact on charge transport properties. *Carbon*, submitted.

Soft Transducers having Stretchable & Flexible CNT Electorodes

M. Takeshita[1*], S. Chiba[2], M. Waki,[3] M. Uejima[1], K. Arakawa[1]

[1]Zeon Corporation, Tokyo, Japan, [2]Chiba Science Institute, Tokyo, Japan
[3] Wits Inc., Tochigi, Japan

Abstract:
Soft transducers have many features that are desirable for various devices. An especially attractive of soft transducers is dielectric elastomer (DE). DEs are a new transducer technology that has been began an investigation by S. Chiba et al in 1991(1). The basic element of DE is a very simple structure comprised of a thin elastomer sandwiched by stretchable and flexible electrodes (2). When a voltage difference is applied between the electrodes, they are attracted to each other by Coulomb forces leading to a thickness-wise contraction and plane-wise expansion of the elastomer. The typical thickness of the elastomers is about 400 nm to 500 microns. The electrode uses carbon black, SWCNT (ZEONANO®SG101*), or nano-sized metal. At the material level, DE actuator has fast speed of response (over 100,000 Hz), with a high strain rate (up to 630% as shown in Fig. 1), high pressure, and power density of 1 W/g (2). They can be used for pressure-sensors and 3D position-sensors. Furthermore, we have developed DE transparent diaphragm-speakers for the first time in the world. Recently, DE actuator having only 0.15 g of DE material can lift the weight of 41N easily using SWCNT electrodes.
The use of DE actuator in the reverse mode, in which deformation of the elastomer by external mechanical work is used to generate electrical energy, has been gaining more attention. The amount of electricity generation is 0.284J/1g. The energy conversion efficiency is more than 70%(3).
We are challenging micro-nano fluidic devices using DE. The films of 10-100 nm thickness can be fabricated. We have fabricated a pump with the diameter of 900 nm using DE nano sheets. It can be also acting as sensors.

* ZEONANO®SG101 is Single-Wall carbon nanotube synthesized by Super Growth method.

Keywords: Dielectric elastomer, Power-generator, Sensor, Actuator, EAP, Artificial Muscle, Soft Actuator, Marine Energy, Renewable ene

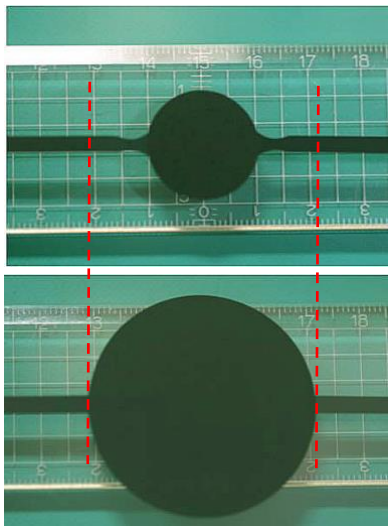


Figure 1: Expanding Circular Actuator up to 630%

References:

1. Pelrine, R., Chiba, S., (1992), Review of Artificial Muscle Approaches," Proc. Third International Symposium on Micromachine and Human Science, Japan, pp 1–9, October.
2. Chiba, S., et al., (2019), Recent Progress on Soft Transducers for Sensor Networks, Chapter 23, Technologies and Eco-innovation towards Sastainability II, *Springer Nature*, Doi.org/10.1007/978-981-13-1196-3_23.
3. Waki, M., et al, 2017. "Experimental Investigation on the Power Generation Performance of Dielectric Elastomer Water Power Generation mounted on a Square Type Floating Body", Journal of Material Science and Engineering B7, (9-10), 2017, 179-186, DOI:10.17265/2161-6221/2017.9-10.001

Graphene flake with an adatom illuminated by an optical pulse

M. Kosik[1*], M. Pelc[2], M. Müller[3], C. Rockstuhl[3,4], K. Słowik[1], A. Ayuela[2]

[1] Institute of Physics, Faculty of Physics Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland
[2] Donostia International Physics Center (DIPC) and Centro de Física de Materiales, CFM-MPC CSIC-UPV/EHU, 20018 San Sebastián / Donostia, Spain
[3] Institute of Theoretical Solid State Physics, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany
[4] Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany

Abstract:
We develop a set of analytical and numerical tools to describe dynamics, spectral and optical properties of hybrid systems made of graphene nanoflakes coupled to adatoms in the presence of an external electromagnetic field. An adatom is an atomic system described by a small number of energy levels, localized near the flake, which can exchange electrons with a selected carbon site at the flake. The method combines the tight-binding model to characterize eigenstates and eigenenergies of the system with the master equation approach to trace the time evolution of charge density under external illumination, similarly to as it has been proposed in Ref. 1. Here, we additionally exploit the Anderson impurity model [2] and integrate it in the temporal picture to account for the adatom's influence on the dynamics of the graphene flake, as well as the back-action from the latter.
The method is applied to two-level adatoms at graphene flakes of size below 10 nm of various shapes and edge types. Due to the presence of the adatom, the spectral, plasmonic and transport properties of the system can be notably modified. We study this influence in function of various system parameters, in particular of the Fermi energy and external field properties which provide knobs to eventually fully control the dynamics with external means.

Keywords: graphene flake, adatom, dynamics, Anderson impurity model, tight-binding model, master equation.

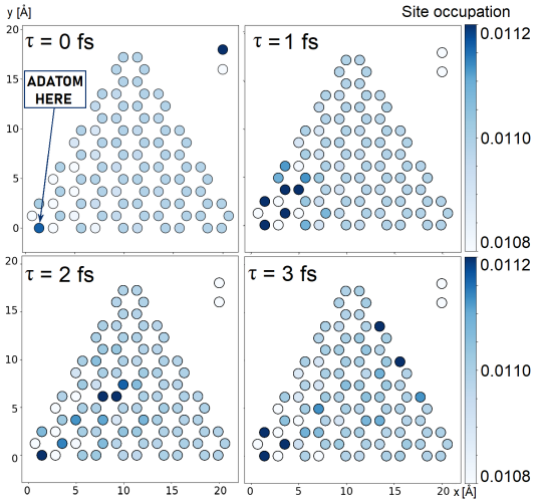


Figure 1: Transfer of the population from a two-level adatom into an armchair graphene flake of size 2 nm. Charge propagating from the lower-left corner towards the opposite edge is clearly seen. The two circles in the upper-right corner indicate the population of the adatom states. The adatom levels have energies ±0.5 eV. At time $\tau = 0$ the adatom's entire population is in the excited state. The coupling parameter between the selected graphene site and excited (ground) adatom level is $t_e = 2t$ ($t_g = t$), where $t = 2.66$ eV is the tight-binding hopping parameter.

References:

1. Cox, J. D., García de Abajo, F. J. (2014), Electrically tunable nonlinear plasmonics in graphene nanoislands, *Nat. Commun.* 5, 5725.
2. Castro Neto, A.H. et al. (2009), Adatoms in graphene, *Solid State Commun.* 149, 1094.

Graphene Radio-Frequency Transistors with Self-Aligned Channel and Core-Shell Nanowire Gate

V. Silva,[1,2,*] L. Baptista,[1,2] J. Borme,[1] C.-D. Liao,[1] P. Mendes[2] and P. Alpuim[1,3]

[1]International Iberian Nanotechnology Laboratory, INL, Braga, Portugal
[2]Universidade do Minho, CMEMS, Guimarães, Portugal
[3]Universidade do Minho, CFUM, Braga, Portugal

Abstract:
Graphene has attracted an immense amount of attention due to its amazing properties, among which a huge carrier mobility, making it a high-potential candidate for radio-frequency electronics. Transistors fabricated with graphene have reached intrinsic cut-off frequencies of 300 GHz but can only reach tens of GHz when it comes to extrinsic cut off frequencies. The fabrication of graphene RF transistors is challenging as most of the standard CMOS technologies can not be employed in their current state to this new material. In this work, a physical deposition of the gate and gate oxide (Ni/NiO manowires) were chosen to minimize the damages to the graphene lattice and a self-aligned process to reduce the contact resistance.
In order to obtain the maximum extrinsic cut-off frequency, simulations were made for the intended structures which pointed towards a critical parameter, the parasitic capacitance of the gate and drain pads. To lower this capacitance, the device was fabricated on top of a highly resistive silicon substrate (>10kΩ.cm) covered with a 1 micron thick layer of silicon dioxide (SiO_2) and the area of the gate and drain contact pads was greatly reduced.
Graphene was grown by CVD on a copper foil, in conditions yielding a high quality, with millimeter crystal size over large area samples, and was transferred onto the insulating substrate. Nickel nanowires were grown by eletrochemical deposition using an anodized aluminum oxide (AAO) template with a gold seed layer and a mixture of $NiSO_4$, $NiCl_2$ and H_3BO_3, resulting in nanowires with diameters ranging from 200 to 400 nm. The template was removed with a solution of NaOH creating free standing nanowires. These were then thermally oxidized in an oven at 250ºC for 1 hour to create a 5 nm thick shell of nickel oxide (Figure 1a) so that the core acts as the gate and the shell as the gate dielectric. The core-shell nanowires were realesed from the seed layer with a solution of KI and I_2 and subsequently randomly placed on top of the graphene. High resolution images of the nanowires precise position were taken and with the aid of titanium-tungsten (TiW) markers previously deposited, masks for a lithographic process were designed, setting the channel width to 3 µm (Figure 1b and 1c). A dielectrophoretic method is under development to perfectly position the nanowires on the substrate as an ordered array, and in turn scale up the device fabrication process. A self-aligned process was lastly employed to deposit the drain-source contacts (Cr/Pd) using the NW as mask, which self-aligns the gate and channel, greatly reducing the acess resistance. Currently, the fabricated devices are under tests (Figure 1d).

Keywords: graphene RF transistors, cut-off frequency, core-shell nanowire, electrochemical deposition, self-aligned contacts.

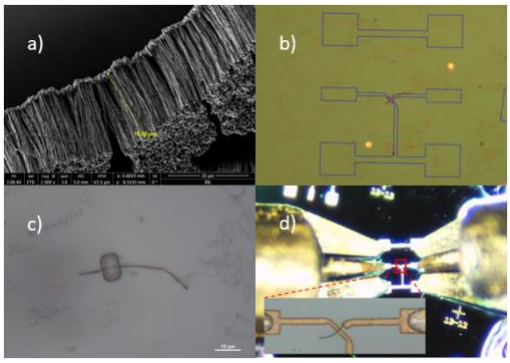


Figure 1: a) Grown nanowires attached to the seed layer. Scale bar: 20µm. b) AutoCAD masks for the devices. c) Lithography of the graphene channel. Scale bar: 10µm. d) Contact between the RF probes and the pads of the RF device. Inset showing a close view of the core-shell Ni/NiO nanowire and the self-aligned Drain-Source contacts.

References:

1. L. Liao et al., "High-speed graphene transistors with a self-aligned nanowire gate," Nature 467 (7313) 305–308 (2010).

SMS 2019 Session II
Smart sensors, smart Textiles, wearables & Internet of things

Smart Sensors using Light technologies: a comprehensive vision

José Miguel López-Higuera[1,2,3]

Grupo de Ingeneiería Fotónica
[1] Universidad de Cantabria, [2]Centro de Investigación Biomédica en Red de Bioingeniería, Biomateriales y Nanomedicia (CIBER-BBN), [3]Instituto de Investigación Sanitaria Valdecilla (IDIVAL);
Edificio I+D+I de Telecomunicación, planta -3, Avda. Los Castros s/n, 39005 Santander, Spain

Abstract:
In the current modern times, it is necessary to develop the capacity to capture, quantify and translate physical and chemical magnitudes to another domain, normally electrical. Sensors, in general, are the devices or systems developed for carrying out these tasks. When the mentioned sensor system uses light based technologies in their key sensing part/s then they can be recognized as Light based Sensors or Photonic Sensors [1].
If it is possible to pick-up data that enables the determination of their "state" from light coming from a target or object (left side of figure 1). The light from the target can be produced by the object itself or could be consequence of their excitation with an optical radiation or any other source of excitation energy. The whole device/system designed to carry out this detection/measurement function is considering a Photonic Sensor, PS, that can be understood as a photonic system in which the measured object magnitude, measurand, or input signal ($\boldsymbol{i}_{SX}$), introduces modifications or modulations in some of the characteristics of light in an optical system. After being detected, processed and conditioned, the system will deliver an output signal ($\boldsymbol{o}_{SX}$), usually in the electric domain, which will be a valid reproduction of the object variable [1]. The light from the target includes information (modulated by the measurand or modulating signal) in some of several of its main characteristics (in its amplitude, phase, frequency, polarization or any other behaviour of the light). In accordance with this concept, if any of the processes or parts use fiber-optic technology, a subdivision of PS known as Fiber/Fibre Optic Sensors (FOS), or Optical Fiber/Fibre Sensors (OFS), is created [2].
When a PS is equipped with some kind of intelligence and the sensing system is capable to give an actuation signal, then the PS is transformed into a Smart Photonic Sensor or Smart Light based Sensor (SLS) [2]. So, a SLS can be understood as the photonic sensor system that includes some kind of intelligence (algorithms, programs, etc.) that offer actuation signals to allow further actuations concerning the place or structure in which the SFS is installed. For instance, if the SPS is placed on/in/or looking at a given structure, it could offer information concerning some loading and damaging conditions and supply warning or and actuation signals to protect the structure integrity. By using these signals, the material, the structure state can be deducted and decisions (and even predictions) could also be taken being, in cases the SLS, an integral part of the materials or of the structure that in both cases are dotted with Smartness. A SLS can be, for example, a key part of a Structural Health Monitoring System (SHM) or can play a relevant role in the supervision or monitoring of a civil or a geotechnical structure [3].
In the keynote, after a mention of what it must be understood, in wide sense, as Smart Light based Sensors, just to justify this coomprehensive or inclusive vision, we will do a "flight" over several significant cases of SLS used in real applications inside very diferrent sector appliactions. The main challenges to face in the near future will be also addressed and discussed.

Keywords: Light based sensors, Photonic sensors, Optical sensors, Smart sensors, Smart Light based sensors, Smart Photonic sensors.

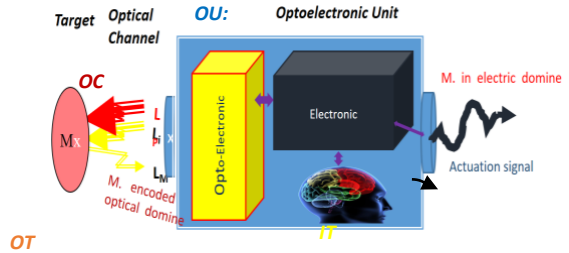


Figure 1: **.-** Illustration of a general Smart Light based Sensor system architecture: optical transducer on the target (OT); optical channel(OC); optoelectronic unit (OU); intelligence (IT).

Acknowledgments

The State Research Agency (AEI) os Spain is supporting this work under the project SENSA TEC2016-76021-C2-2-R.

References:

1. JM López-Higuera,“Handbook of Optical Fiber Sensing Technology”, John Wiley & Sons Inc., 2002.
2. JM López-Higuera,”Smart Light based sensors”, Invited ISLIST/UIMP, June 27, 2018, Santander, Spain
3. J.M. Lopez-Higuera et al. 'Fiber Optic Sensors in Structural Health Monitoring (Tutorial Invited)'; Journal of Lightwave Technology, Vol.29, Nº 4, pp. 587-608; 2011.

Engineering Photonic Structures and Functional Materials Towards Smart Physical and Chemical Sensors

C. Riziotis*

National Hellenic Research Foundation, Theoretical & Physical Chemistry Institute, Athens, Greece

Abstract:
Photonics engineering has been widely recognised as a Key Enabling Technology-KET with applications in many technological areas. Advances in materials research have driven the development of new exotic optical material platforms such as multicomponent glasses and metamaterials with customizable properties that could enable in turn the further development of tailored photonic devices. However, further to the fundamental research on those platforms the applicability in real applications is still rather limited as is required considerable amount of research for the development of reliable components required to follow strict operational specifications and standards. In parallel the need for low cost customizable photonic devices, structures and sensors for specific applications requires the efficient exploitation of well established platforms. Employment of efficient material processing techniques and use of specially designed functional materials provides a route that allows the rapid prototyping of customized devices. Within this frame we present recent and characteristic activities of photonics engineering (at NHRF) towards the development of customized structures and devices for a wide range of demanding and emerging applications. Theoretical design & modeling issues together with experimental implementations of structures by direct laser writing, micromachining, and thermal processing will be covered. Photonic platforms such as polymer optical fibers, silica or specialty hybrid fibers, silica-based integrated optics, plasmonic and resonating structures, will be considered towards smart sensors development. A broad range of customized solutions covering application areas from Structural Health Monitoring-SHM, industrial monitoring & predictive maintenance, to defence systems and biomedical applications will be presented.

Keywords: photonics, optical fibers, optical materials, Laser, micropatterning, devices, physical sensing, chemical sensing, structural health monitoring, biomedical applications.

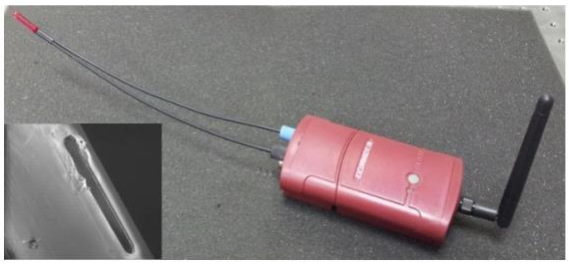


Figure 1: Polymer fiber optic sensor integrated in an autonomous wireless sensing node. Inset, presents a micromachined optical sensing head.

References:

1. Athanasekos, L., Vasileiadis, M., El Sachat, A., Vainos, N.A., C. Riziotis. (2014), ArF excimer laser microprocessing of polymer optical fibers for photonic sensor applications, *J. Optics*,17, 015402.
2. Riziotis, C., Eineder, L., Bancallari, L., Tussiwand G. (2013), Fiber optic architectures for strain monitoring of solid rocket motors' propellant, *Sensor Letters*, 11, 1403-1407.
3. El Sachat A., Meristoudi, A., Markos, C., Sakellariou, A., Katsikas, S., Riziotis, C. (2017), Characterization of industrial coolant fluids and continuous ageing monitoring by wireless node-enabled fiber optic sensors, *Sensors,*17, 568-20.
4. Athanasekos, L., El Sachat, A., Pispas, S., Riziotis, C. (2014), Amphiphilic diblock copolymer based multi-agent photonic sensing scheme, *J. Pol. Sci. Part B: Pol. Phys.,* 52, 46-54
5. Petropoulou, A., Antonopoulos, G., Bastock, P., Kakarantzas, G., Craig, C., Hewak, D.W., Zervas, M.N., Riziotis C. (2018), All-fiber plasmonic platform based on hybrid composite metal/glass microwires, *J. Phys. Chem. C*, 22, 26169-26176.
6. Tsiambas, E., Riziotis C. (2017), Implementation of a real-time reference and calibration grid platform for improved screening- mapping in Pap Test slides, *Pathology International,* 67, 24-31.

Printed Electrodes for Hot Electron Electrochemistry Applications

S. Kulmala,* Päivi Grönroos, Kalle Salminen, Nur-E-Habiba

Aalto University, Department of Chemistry and Material Sciences, Espoo, Finland

Abstract:
This paper reports utilization of printed hot electron emission electrodes for hot electron-induced electrochemiluminescence (HECL) and other hot electron electrochemistry applications. Hot electron-induced electrochemiluminescence (HECL) is typically a method utilizing luminophores as labels in sensitive bioaffinityassays such as in immunoassays. Method normally applies hot electrons generated by tunnel emission from thin insulating film-coated cathodes such as oxide-coated silicon electrodes [1] or presently also organic polymers doped with conductive particles. If the energy of tunnel-emitted hot electrons into the aqueous solution is above the conduction band edge of water, electrons may enter the conduction band of water and are likely to become hydrated (e_{aq}-) after thermalization and solvation [1, 2]. When these hot or hydrated electrons react with dissolved oxygen and added co-reactants, such as electron scavengers producing highly oxidizing radicals (peroxodisulphate, peroxodiphosphate or hydrogen peroxide), both extremely strong oxidants and reductants are simultaneously available, and difficult redox reactions e.g. excitation of label compounds are enabled.
Present electrode chips were fabricated by printing first all the electrode areas with silver ink (Fig. 1, grey), and then the working electrode area was made by printing either polystyrene or ethyl cellulose layer doped with conducting particles (Fig. 1, black) and finally the cell area was fabricated by printing a hydropohobic ring (Fig. 1, blue) exposing the working electrode and counter electrode to the aqueous sample solution.
C-reactive protein immunoassays were carried out on these printed electrode chips utilizing either a Tb(III) chelate label or a fluorescein label.

Keywords: Hot electron electrochemistry; electrochemiluminescence; screen printed electrodes; bioaffinity assays; Tb(III) labels, C-reactive protein;

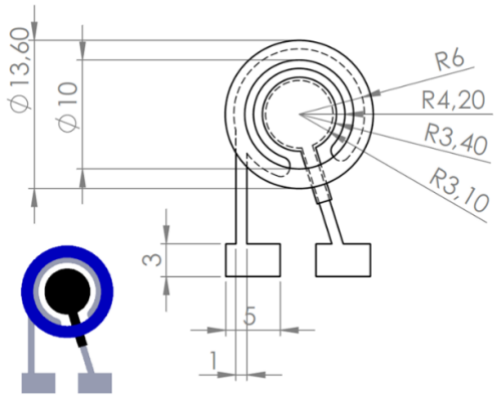


Figure 1: Printed electrolysis cell design. Working electrode (black), counter electrode (grey) and hydrophobic plastic ring (blue).

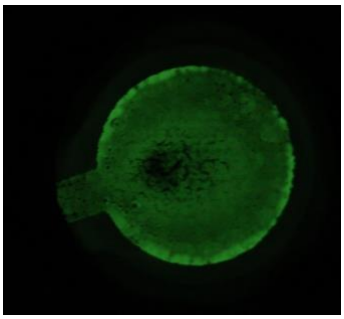


Figure 2: Tb(III) chelate label HECL emission under excitation by cathodic voltage pulses at ethyl cellulose-carbon black electrode. Conditions: pulse voltage −46 V, pulse charge 31.5 µC, frequency 50 Hz, 0.01 NaN_3 in 0.05 M $Na_2B_4O_7$, 0.1 M Na_2SO_4.

References:

1. J. Suomi, S. Kulmala. Hot electron-induced electrogenerated chemiluminescence, Reviews in Fluorescence (2011), Volume Date 2009, 6, 47-73
2. S. Kulmala, A. Kulmala, T. Ala-Kleme and J. Pihlaja, 1998, Primary Cathodic Steps of Electrogenerated Chemiluminescence of Lanthanide(III) Chelates at Oxide-covered Aluminum Electrodes in Aqueous Solution, Anal. Chim. Acta 367: 17–31.

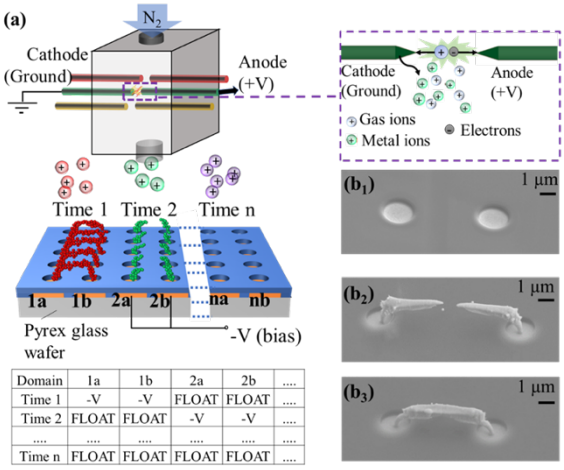
Combinatorial Gas Phase Electrodeposition for Fabricating Multimodal Three Dimensional Nano-Bridge Gas Sensors

N. A. Isaac[1], L. Schlag[1], J. Reiprich[1], S. Katzer[1], H. Nahrstedt[1], J. Pezoldt[1], T. Stauden[1], H. O. Jacobs[1*]

[1] Technische Universität Ilmenau, Department of Nanotechnology, 98693, Ilmenau, Germany

Combinatorial approaches for three dimensional (3D) morphologies have potential to overcome technological/economic challenges faced in 2D planar homogenous film applications. Gas phase electrodeposition concept can guide charged nanoparticles to predetermined locations on a surface with sub micrometer resolution. Sequential shutter free deposition is possible, preventing use of additional steps for lift-off and improving material yield. This generic and relatively new process enables parallel growth of multiple material 3D self aligning nanoparticulate bridges on the substrate. Earlier, such self aligning structures have been demonstrated as interconnects for nanoelectronics (1). In this study, the process is applied to fabricate a multimodal conductometric gas sensor array. The application requires the programmable deposition of more than one material type at predetermined locations to accomplish a single chip "electronic nose" like sensor array with orthogonal sensing capabilities and multi gas sensitivity and selectivity. This particular design uses an array containing 1080 locally grown nanobridges of platinum, nickel oxide and gold to accomplish a stable multi sensor response vector. From an experimental point of view, the method uses a spark discharge-based nanoparticle source in combination with sequentially biased surface electrodes and charged photoresist patterns to accomplish the required programmable site selective 3D deposition and growth (***Figure 1***). In this study, a trimodal sensor array will be demonstrated to detect three different concentrations of Ammonia (NH_3), Carbon Monoxide (CO) and Hydrogen Sulfide (H_2S). The sensor chip operates at room temperature. Additionally, this study lays down challenges which need to be systematically studied to realise the full potential of combinatorial gas phase electrodeposition.

Keywords: nanomaterials, nanosynthesis, surface science, interfacial studies, nanosensors, gas sensing, surface patterning, combinatorial nanofabrication.



Domain	1a	1b	2a	2b	....
Time 1	-V	-V	FLOAT	FLOAT	....
Time 2	FLOAT	FLOAT	-V	-V	....
....	....	....	....	....	....
Time n	FLOAT	FLOAT	FLOAT	FLOAT	....

Figure 1: Programmable electrodeposition procedure, spark discharge and bridge growth example: (a) Electrodeposition procedure with programmable domain electrodes in (orange). Two neighboring electrodes form a domain pair (e.g. 1a and 1b). During time 1, domain pair 1 is switched ON (biased) and material 1 (red) is synthesized and collected on this electrode until a bridge forms; all other domain pairs have a floating potential. This process is repeated n times to produce an array of n different nanoparticle composed bridges on a single chip. An insert shows spark discharge-based nanoparticle synthesis through cathode erosion. (b) SEM micrographs of the bridge formation process starting with a blank substrate with openings in the photoresist to a charge dissipating domain pair (top). Continued collection of nanoparticles (middle) leads to the growth and eventual formation of a nanoparticle composed bridge through nearest neighbor coulombic interaction.

References:

1. Fang, J.; Schlag, L.; Park, S. C.; Stauden, T.; Pezoldt, J.; Schaaf, P.; Jacobs, H. O., Approaching Gas Phase Electrodeposition: Process and Optimization to Enable the Self-Aligned Growth of 3D Nanobridge-Based Interconnects, Adv. Mater. 2016, 28 (9), 1770–1779

Challenges and Opportunities in Reproducible Electrochemical Ink Formulation and Processing for Multiplexed Designs

N. Broughton,[1,*] D Barwick, [1] R. Kadara,[2,3] B. Bender,[3]

[1] Centre for Process Innovation, Wilton, Redcar, United Kingdom
[2] JE Solutions Consultancy, Manchester, United Kingdom
[3] Bender Tech, Raleigh, North Carolina, United States of America

Abstract:
Multiplexing of electrochemical sensors provides opportunities for point-of-care biomedical screening and diagnostic applications that require fast results, a simple user experience, and the simultaneous quantification of multiple biomarkers [1]. Sensitive and specific quantification of biomarkers in complex biological fluids requires development of new, highly engineered materials with reproducible and scalable manufacturing processes to achieve their promise of low-cost and widespread adoption. However, traditional manufacturing processes for existing electrode ink formulations to necessarily transfer to newly developed ink formulations that incorporate nanomaterials with unique mixing properties [2]. It is important to identify flexible processes that can accommodate varying ink properties for multiplexed designs and to identify failure mechanisms for different classes of ink formulations. We report the use and testing of electrochemical sensor processing techniques for multiplexed sensor designs with different metal oxide ink formulations. The electrochemical response to various processing techniques and ink formulations were assessed to identify prospective manufacturing techniques that deliver reproducible results that can scale. In addition, we have identified challenges and failure mechanisms regarding processing timing and material selection. The identification of these challenges and optimization of these processing techniques provides and understanding needed for moving applications in electrochemical sensors from the lab to the clinical setting.

Keywords: electrochemistry, materials processing, chemical sensors, multiplexing, nanomaterials, manufacturing, biomedical applications.

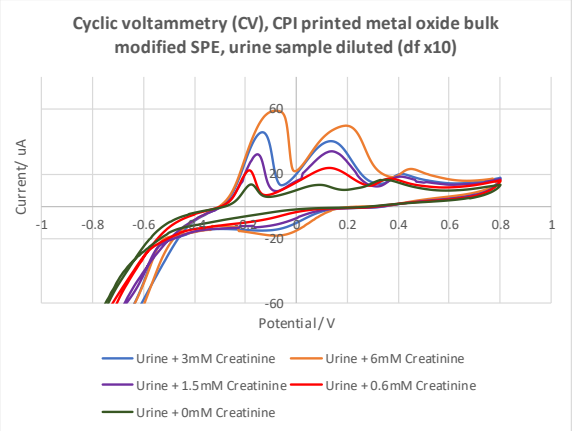


Figure 1: Voltammograms demonstrating a robust and sensitive electrochemical response in real-world biological conditions of bulk processed metal-oxide inks.

References:

1. Patel, S., Nanda, R., Sahoo, S., Mohapatra, E. (2016) Biosensors in Health Care: The Milestones Achieved in Their Development towards Lab-on-Chip-Analysis, *Biochem. Res. Intern.*, 2016(3130469), 1-12.
2. Martin-Yerga, D. (2019), Electrochemical Detection and Characterization of Nanoparticles with Printed Devices, *Biosens.*, 9(47), 1-24.

Incorporating Functionalized Polydiacetylene in Alginate Beads For Bacterial Detection

A. Al Choueiry,[1,*] M. Bassil,[1] E. El Kaady, [1] G. Moarbess,[2] M. El Tahchi,[1]

[1] LBMI -Department of Physic- Lebanese University- Faculty of sciences- PoBox: 90656, Jdeideh, Lebanon

[2] TMPAC Department of Chemistry and Biochemistry, Lebanese University, Faculty of Sciences 2, Fanar, Lebanon

Abstract:

Polydiacetylene (PDA) is a conjugated polymer intensively studied to detect different targets like proteins, bacteria and viruses due to its unique colorimetric properties [1]. PDA can be easily synthesized by polymerization of diacetylenic monomers under photo-irradiation, without the need for chemical initiators, and functionalized with various recognition elements [2] to act as a sensing device (figure 1). The application of PDA in the field of biosensor is still at early stage due to stability and selectivity problems. PDA may undergo a color change from bleu to red in response to several external stimuli such as pH, temperature and solvent. The multiplicity of facors influencing the color transition is a major factor limiting the use of PDA-based sensors for the detection of bacteria. Our work focuses on the developement of a selective and sensitive sensor to detect Escherichia coli (E. Coli) bacteria. To achieve this objective we incorporated functionalized PDA with a specific phospho-glyco-lipid receptor into an alginate host matrix. The role of the host matrix is to avoid the agglomeration problems of PDA encounter in solution leading to a deacrease in the sensitivity to bacteria. We report the importance of the optimization of alginate porosity to enhance interaction between E. Coli and functionalized PDA. Moreover, colorimetric responses evoked by enviremental factors are quantified. Finally, we present some strategies to improve the performance of PDA based biosensors.

Keywords: Bacterial detection, polydiacetylene, colorimetric transition, Alginate beads, Biosensor applications

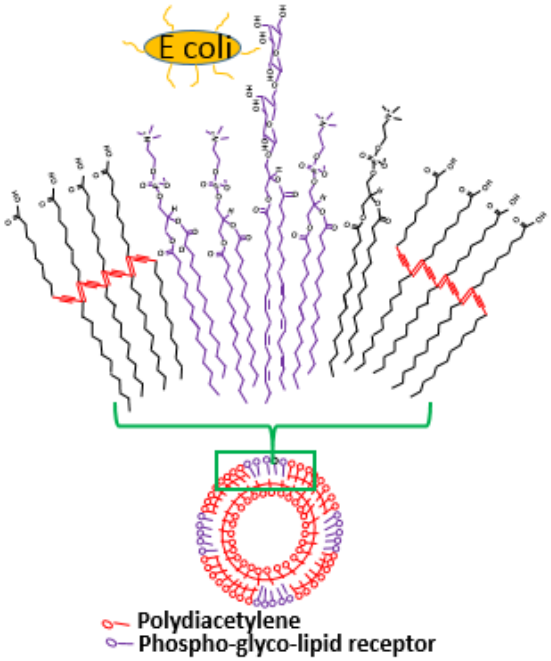


Figure 1: Schematic diagram of a polymerized vesicle composed of polydiacetylene and a specific phosphor-glyco-lipid recognition receptor for E.coli. Once the E. Coli is attached to the receptor, a color transition from blue to red is observed.

References:

1. Lebègue, E., Farre, C., Jose, C,. Saulnier, J., Lagarde, F., Chevalier, Y., Chaix, C., Jaffrezic-Renault, N. (2018), Responsive Polydiacetylene Vesicles for Biosensing Microorganisms, Sensors ,18, 599;
2. Cho, E., Jung, S., (2017), Biomolecule-Functionalized Smart Polydiacetylene for Biomedical and Environmental Sensing, Molecules, 23, 107

Smart sensors based on structural embossing and supramolecular controlled order loss

Y. Foelen[1]*, D.A.C. Van Der Heijden, A.P.H.J. Schenning[1]

[1] Eindhoven University of Technology, Stimuli-responsive Functional Materials & Devices, Department of Chemical Engineering and Chemistry, Eindhoven, The Netherlands

Abstract:
An efficient approach to reduce food waste is the incorporation of temperature exposure sensors to individual products, providing visual feedback that shows if the consumable has been exposed to jeopardous temperatures. Recently within our group[1], thermal sensors based on cholesteric liquid crystal coatings have been developed using a printable fabrication method, showing battery free and user-friendly properties. By using the purposefully designed shape memory feature of these polymer coatings, we demonstrate that it is possible to program various functional responses through embossing the surface with microsized topographies that cause light scattering, making the coating appear opaque and colorless. The simple procedure of activating this surface scattering that camouflages the printed features of the coating allows for the activation of time temperature tracking of individual products down the chain from retailer to consumer (Figure 1).

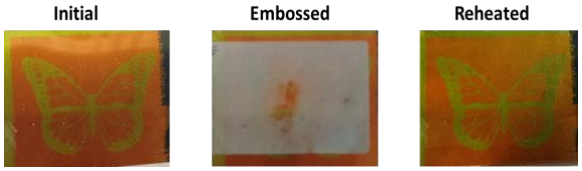


Figure 1: Example of time-temperature dependent camouflage of a printed pattern.

Also, a different mechanism[2] for coatable time-temperature sensors was studied. A complete loss of color is achieved by making use of supramolecular dynamic interaction freedom for applications that require high temperature monitoring such as steam sterilization verification. A coating in which acid-functionalized groups provide physical interactions without any covalent crosslinks is prone to gradually lose the color reflection when exposed to temperatures that grant for enough freedom through the dynamic H-bond monomer-dimer equilibrium shift (Figure 2a). Furthermore, this system is sensitive to humidity due to the interaction between water and the dynamic H-bonds, as a result an even higher scattering state is obtained due to the increased surface roughness due to the surface interaction with water (Figure 2b).

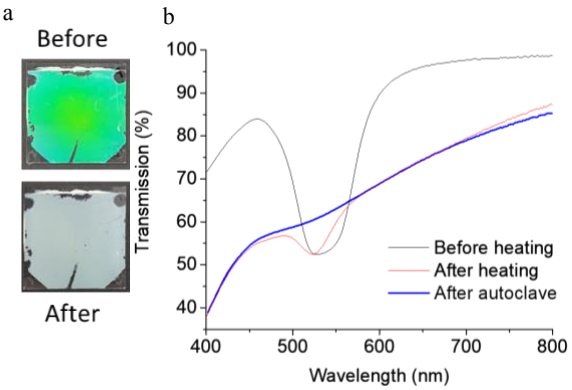


Figure 2: Supramolecular Humidity Temperature Time Integrator as a steam sterilization sensor. a: Sensor before and after steam sterilization procedure. b: UV-VIS spectrum comparing only heating the coating to the spectrum after steam sterilization to illustrate the contribution of humidity to the scattering effect.

Keywords: Thermoresponsive, photonic coatings, shape memory, liquid crystal, chiral nematic, cholesteric, smart sensor, supramolecular crosslinks.

References:

1. K. Nickmans, D. A. C. Van Der Heijden, A. P. H. J. Schenning, Photonic shape memory chiral nematic polymer coatings with changing surface topography and color. (Submitted)
2. Y. Foelen, D. A. C. Van Der Heijden, A. P. H. J. Schenning, 2019, Effect of crosslinking on H-bonded supramolecular cholesteric liquid crystal coatings. (In preparation)

The next generation of Smart Textiles

K.M.B. Jansen

Delft University of Technology, Department of Design Engineering, Delft, The Netherlands

Abstract:
The era of smart textiles has begun. Sensors become smaller, more reliable and require less power and the market of garments for health monitoring increases exponentially. Smart Textiles are studied in many research labs all over the world for many years and yet they are not yet available in the shops nextdoor. The challenges still are in the seamless integration, robustness and ease of use. In addition to that, to allow large scale production an intensive cooperation between the electronics industry developing the sensors and the classical textile industry will be required.
In this paper we will discuss the developments and trends, list the challenges and propose a strategy to come to the next generation of Smart Textiles.
Keywords: Smart Textiles, wearables, sensors, flexible electronics, energy harvesting
Introduction:
According to the IdTechEx report [1] the market for e-textiles is currently close to the $100m in annual wholesale revenue and is expected to grow towards the $5 bn in 2027. The key market sectors include Sports & Fitness, Medical & Healthcare, Wellness, Home & Lifestyle, Military, Fashion and Automotive. This rapid growth and spreading over the different market sectors is quite fascinating and calls for a more in depth study on how the sectors of electronics and textiles could merge towards a novel market field.
Design of a modular smart textile system:
In order to improve the comfort and facilitate manufacturing it would be desirable to be able to replace the electrical wiring system with a textile layer which replaces all the copper wires and onto which the sensors and actuators can be mounted. Such a textile layer will then have a function similar to a Printed Circuit Board and in analogy can be called a "Fabric Circuit Board, as suggested in Li and Tao's paper [2].

Figure 1: Examples of Smart Textile prototypes develop at the TU Delft

Further, we need to simplify the production and assembly costs. This can be done by adapting a modular system which consists of a textile part with integrated wiring circuit (the Fabric Circuit Board) and separate sensing and data processing nodes which can be added to the base garment by clicking or snap fitting. In this way the garment with wiring system can be mass produced using well known and mostly already proven textile manufacturing technologies and equipment. Using computer controlled methods for the knitting, printing or embroidery of the conductive circuitry, also different shapes and sizes of the base garment can be readily manufactured. The main problem that then remains is of course the interconnection between the active nodes and the passive Fabric Circuit Board. Such interconnections need to be robust, reliable and above all, standardized. This will not be easy but is in principle possible considering the experience and expertise with interconnect technology that is available in the microelectronics domain.
A modular electronic garment as proposed here will have several additional advantages. Sensor nodes which are malfunctioning or outdated can be simply replaced individually without the need to discard the entire garment. Changing, updating or adding sensors can then be done in a similar way as we currently work with apps on our mobile phones. Moreover, with such a garment the electronic components can be

easily separated from the textile part at the end-of-life.

References:

1. https://www.idtechex.com/research/reports/e-textiles-2017-2027-technologies-markets-players-000522.asp
2. Q. Li and X.M. Tao (2014), Three-dimensionally deformable, highly stretchable, permeable, durable and washable Fabric Circuit Boards, *Proc.R.Soc. A 470: 20140472*

Development of Flexible Textile Aluminium-Air Battery Prototype

Aleksandrs Vališevskis,[1] Uģis Briedis,[1] Miguel Carvalho,[2] Fernando Ferreira,[2]

[1] Riga Technical University, Institute of Design Technologies, Riga, Latvia
[2] University of Minho, Textile Engineering Department, Guimaraes, Portugal

Abstract:
There is one component that virtually any embedded wearable needs – a power source. This paper proposes an energy source, which contains no harmful substances, can be stored in a stand-by dry state for indefinite time period, is flexible and has tactile characteristics similar to that of textile. The battery design is based on aluminium-air electrochemical process (Figure 1). The paper focuses on the choice of textile materials for the main battery components – aluminium anode, current collector, oxygen storage etc. The new materials show promising results and performance that is equivalent to that of pure metal elements, which were used in the original design of the battery and had caused various issues. The new design includes only textile-based materials, which ensure greater flexibility and better fusion with textile materials, where the battery is intended to be integrated.
Besides that, results of first experiments with multiple elements are presented, which show that the arrangement of the elements in a multi-element pack should be horizontal rather than vertical. These batteries can be integrated into smart textiles or smart sensors and have no expiration date (before liquid is introduced, which activates the battery). It expands their potential use to storage solutions and healthcare/health monitoring solutions, because the design of the battery allows it to be used as an active sensor, which generates electric current, when it detects liquid.
In order to test the actual characteristics of the newly designed battery, a multi-cell flexible textile aluminium-air battery prototype was developed (Figure 2), which consists of four sealed cells. The battery is capable of producing 3V upon activation, which enables it to power semiconductors without the need of additional voltage conversion or energy accumulation.

Keywords: aluminium-air battery, flexible battery, smart textiles, embroidery

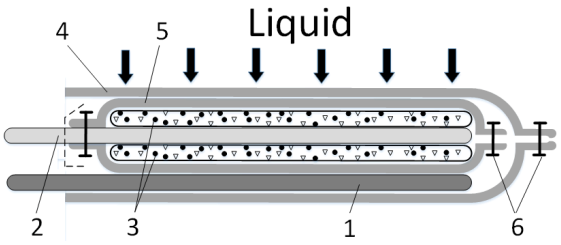


Figure 1: . Flexible textile Al-Air battery cell
1 – aluminium anode, Mtex® aluminium-textile composite material; 2 – cathode current collector, Shieldex® Budapest conductive textile; 3 – carbon granule and optional NaCl mixture; 4 – cotton enclosure of the element; 5 – cotton enclosure of the cathode; 6 – sewn joints.

Figure 2: Prototype of a multi-cell flexible textile Al-Air battery with cells arranged on a plane.

References:

1. Briedis, U., Vališevskis, A., Zelča, Z. Flexible Aluminium-Air Battery for Enuresis Alarm System. In: 16th International Scientific Conference "Engineering for Rural Development": Proceedings. Vol.16, Latvia, Jelgava, 24-26 May, 2017. Jelgava: 2017, pp.619-624. ISSN 1691-3043. Available from: doi:10.22616/ERDev2017.16.N123.
2. Li, Q., Bjerrum, N.J. Aluminum as anode for energy storage and conversion: a review. Journal of Power Sources 110 (2), pp. 1-10, 2002. ISSN: 03787753.
3. Yang, S., Knickle, H. Design and analysis of aluminum/air battery system for electric vehicles. Journal of Power Sources 112 (1), pp. 162-173, 2002. ISSN: 03787753.

Connecting the world to garments – capturing, filtering, defining, translating, mapping and actuating in, on and off the textile

E. Lindell[1,*], L. Guo[1], R. Holt[2], Z. Ling[2], E Kontopoulos[3], N-K. Persson[1]

[1] University of Borås, Smart Textiles, Polymeric E-textiles, Borås, Sweden
[2] University of Leeds, School of Mechanical Engineering, Leeds, UK
[3] Center for Research & Technology Hellas (CERTH), Greece

Abstract:
Smart textiles has been around as a concept for some decades. Often defined as materials that can sense stimuli as input and give off some output, response, they are interesting multi- and cross disciplinary items with versatile use. In spite of the vast potential for so disperse fields as health monitoring and automotive composites the complexity of fulfilling the definition in reality has been found to be pronounced. Presently, a solution is to take use of the on-going technology shift manifested in ubiquitous wireless communication, and the Cloud and the Fog. Then part of the computing including semantic classification of the surrounding in stored databases of visual, audial and digital (social media) information is performed outside of the textile, "the off textile domain". By this, degrees of freedom are released for the textile domain enabling better production, comfort, use and waste performance.
We here show the need for systemic perspective for a truly "smart" textile. Such a one need capability to capture data from the surroundings. Here we use visual information from RGB camera and audial information from ultrasound detector. This generates large data volumes and we identify the need for filtering this at different levels. Not until then it is possible to define and classify the entity detected. Here we use image analysis in the off textile domain to identify physical artefacts in the neighborhood of the textile. Here the problem of what is relevant to convey as information to the user is shown to be highly problematic. This Relevance problem is multidimensional shown embracing a) textile engineering, b) haptic sensorial, c) ethical d) linguistically e) perceptual and f) customization related questions. We then show the construction of a bodily matrix for integration of actuating elements. This is then clearly in the on-textile domain. We discuss pro- and cons of using different actuating mechanisms (1).
Currently there is an interest expanding the senses such as for assistive wearable technologies for sight or hearing impaired persons. The present study is part of larger activities of sense switching, here focusing on mapping the world to haptic modalities. This study shows the complexity of creating a real smart textile fulfilling often counteracting demands.

Keywords: smart textiles, integration in, integration on, assistive devices, biomedical applications.

References:

1. Persson, N-K., Martinez, J., Zhong, Y., Maziz, A., Jager, E.W.H. Actuating Textiles - next generation of smart textiles (2018) *Advanced Materials Technologies* 1700397

Towards responding fabrics – textile processing of thin threadlike pneumatic actuators

C. Backe[1,*], L. Guo[1], E.W.H. Jager[2], N-K. Persson[1]

[1] University of Borås, Smart Textiles, Polymeric E-textiles, Borås, Sweden
[2] Linköping University, Department of Physics, Chemistry and Biology (IFM), Sensor and Actuator Systems, Linköping, Sweden

Abstract:
With few exceptions (such as 1) textiles have not been considered as means for obtaining actuation. This is surprising as textiles have many advantageous characteristics such as the D=M property, which stands for Doing Devices while Making the Material. This means that functions are introduced simultaneously as the material, such as in a weave, is built up tread by tread. Traditionally a tread could have a certain colour so in total an aesthetical pattern is formed. Now we take a step beyond this working with threads having more advanced functions. Included are fiber formed structures showing actuation behavior.
This we employ here. We make fiber formed actuating structures (FAS) following the McKibben principle (2) with braided mesh sleeves surrounding a prolonged inflatable tube. Here we worked with relatively large diameters in the relaxed state but show that there is prospect for obtaining relaxed diameters of less than 1 mm approaching the range of large scale weaving manufacturing.
We study the behavior of these fibre formed actuating structures individually. Length changes obtained are -20%. We then make textile constructions by integrating several of these FASes with textile processing. By this, we build simple models of fabrics showing actuating behavior.
This study shows how textile constructions can support or hinder overall movement. It is a first logical step in order to get an understanding of actuating fabrics based also on other actuating mechanisms (3).

Keywords: smart textiles, soft robotics, actuating textiles, artificial muscles, wearables, assistive devices, exoskeletons,

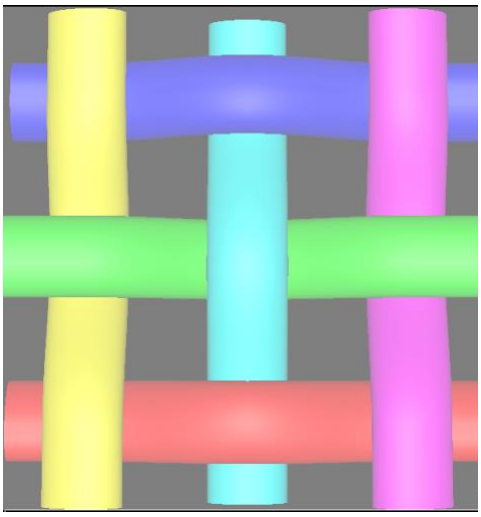


Figure 1: 3D model of a woven structure with different colours indicating yarns with different properties, for example actuation ability. Locking certain yarns and letting others move freely for example by open yarn spacing enables overall movement of the so formed fabric.

References:

1. Maziz, A., Concas, A., Khaldi, A., Stålhand, J., Persson, N-K., Jager, E.W.H. (2017) Knitting and weaving artificial muscles *Science Advances* 3(1) 25 January 2017 doi: 10.1126/sciadv.1600327
2. Daerden, F., Lefeber, D. (2002), Pneumatic Artificial Muscles: actuators for robotics and automation, *European Journal of Mechanical Engineering*., 11-22.
3. Persson, N-K., Martinez, J., Zhong, Y., Maziz, A., Jager, E.W.H. Actuating Textiles - next generation of smart textiles (2018) *Advanced Materials Technologies* 1700397

Towards the development of smart textile wound dressings using temperature an pH responsive hydrogel

D. Štular[1], I. Jerman[2], B. Simončič[1], B. Tomšič[1]

[1] University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Ljubljana, Slovenia
[2] National Institute of Chemistry, Ljubljana, Slovenia

Abstract:
Due to the new insights on complex wound healing conditions, the quest of new pro-actively-adaptable textile materials arises. Among others, wound care systems should be biocompatible and have an ability to adapt to individual wound healing conditions, protect the damaged tissue from bacterial infections, promote healing by allowing gas exchange, create moist environment and deliver active substances to the wound [1, 2]. In this research, smart textile materials with great potential for the use in the field of wound dressings were developed by functionalization of textile substrates with temperature and pH responsive hydrogel based on poly-N-isopropylacrylamide) and chitosan (PNCS hydrogel). The PNCS hydrogel exists in swollen and hydrophilic state when temperature is below 32 °C and pH is below 6.5 and undergoes phase change transition to shrunken and hydrophobic state when the temperature and/or pH level rise above this values. On textile fibers, PNCS hydrogel particles can be used as carriers of different active substances, thus the swelling and shrinking of their structure effects the breathability and moisture management of the textile material [3]. Therefore, antimicrobials with different action mechanisms were incorporated into the PNCS hydrogel particle structure for the purpose of their pro-active release upon the shrinking of PNCS hydrogel particles, i.e. when conditions indicate the infection of the wound. The developed functionalized textile materials showed no cytotoxicity, furthermore the pro-active breathability, moisture management and antimicrobial activity in accordance with the changes in the temperature and pH of the environment were achieved.

Keywords: smart textiles, wound dressings, stimuli-responsive hydrogel, pro-active release, poly-NiPAAm, chitosan, antimicrobial activity, moisture management.

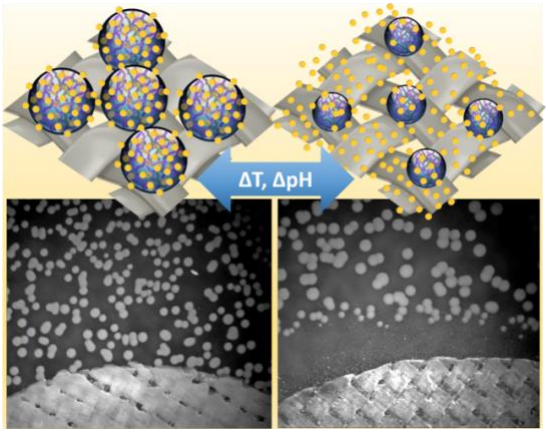


Figure 1: Pro-active release of antimicrobials from the poly-(N-isopropylacrylamide) / chitosan (PNCS) hydrogel functionalised textile substrate upon the shrinking of the hydrogel particles.

References:

1. Derakhshandeh, H., Saheb Kashaf, S., Aghabaglou, F., Ghanavati, I. O., Tamayol, A. (2018) Smart Bandages: The Future of Wound Care, *Trends Biotechnol*, 36, 1259-1274.
2. Gupta, B. (2010), Textile-based smart wound dressings, *Indian J Fibre Text., 35, 174-187.*
3. Štular, D., Šobak, M., Mihelčič, M., Šest, E., German Ilić, I., Jerman, I., Simončič, B., Tomšič, B. (2019), Proactive release of antimicrobial essential oil from a "Smart" cotton fabric. *Coatings*, 9, 1-18.

Untethered stimuli-responsive liquid crystal polymer actuators

M. Pilz da Cunha,[1] M. G. Debije,[1] A.P.H.J. Schenning,[1,]

[1] Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, Eindhoven, The Netherlands

Abstract:
Natural biological systems use environmental stimuli as triggers for functional actuation, aiding in tasks including locomotion, proliferation or defense. Scientific fascination for nature's demonstration of functional organisms has fueled the development of synthetic soft materials that incorporate stimuli-responsive behaviour expanding the archetype of material functionality. These biologically inspired soft materials are of great interest in the fields of medicine, sensors, energy generation, microfluidics and soft robotics. A present endeavor in the field of soft actuators is the elimination of wire connectivity between the functional material and the external control, allowing for lighter and more versatile designs. Furthermore, incorporation of multi-stimuli response into smart polymers will expand their functionality and versatility. Present state-of-the-art aspires towards development of materials for soft robots with untethered locomotive freedom and the ability to perform multiple complex movements to also execute advanced tasks such as cargo transportation.
Liquid crystal networks (LCNs) are popularly employed as active materials in soft actuators since they can operate in dry environment and can show programmed stimuli response. When considering untethered stimuli, light is popularly employed for a high degree of control and temporal resolution. Photo responsive behaviour in LCNs is achieved through inclusion of light sensitive molecules, commonly azobenzene derivatives, and specific design of mesogenic alignment in the network. LCN actuators have obtained considerable attention due their promising integration in light driven soft robots. In our studies we innovate the state-of-the-art for soft actuators, presenting a facile method for the integration of multi-stimuli responsive behaviour, demonstrating a light and magneto-responsive LCN based soft robot, capable of wireless multitasking.
The robot integrates magnetic polydimethylsiloxane (PDMS) with an LCN actuator containing light-responsive azobenzene dyes in a bilayer architecture. The bilayer device orchestrates locomotion and rotation via magnetic guidance and light-driven deformation for manipulation of a soft gripper used to perform cargo pick up, transport and delivery. We explore and clarify the mechanism for light driven deformation of LCN bilayer actuators, shedding light on important mechanistic contributions to control deformation amplitude and speed of such devices. This study also permits us to discuss limitations and improvements in light responsive liquid crystal-based smart materials, considering the development of next generation amphibious functional actuators.

Keywords: Stimuli-responsive materials, untethered actuators, light and magnetic responsive materials, liquid crystal actuators, soft robotics.

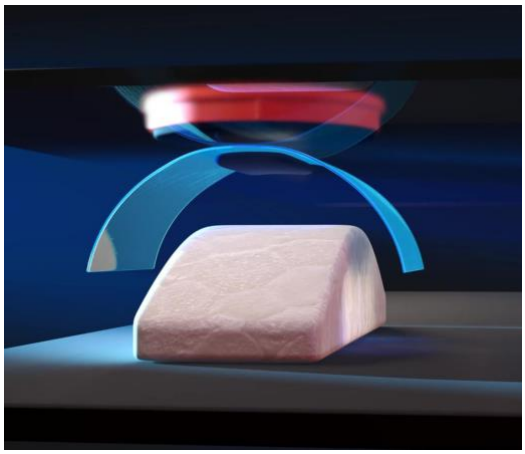


Figure 1: Figure illustrating our novel light- and magneto-responsive gripper device, showing ability to perform untethered locomotion and cargo handling activities.

Towards measuring flexoelectric coefficient of single carbon nanotubes

R. El Beainou,* J.-Y. Rauch, S. Dembélé, O. Lehmann, L. Hirsinger, M. Devel
FEMTO-ST Institute, UBFC, CNRS, ENSMM, 15B avenue des Montboucons, 25030 Besançon CEDEX, FRANCE

Abstract:
Unlike piezoelectricity (proportionality between a uniform stress and the electric polarization of a material), flexoelectricity (proportionality between stress gradient and electric polarization of a material) was rarely considered for electromechanical transduction because of its small relative importance for macrosystems. However, flexoelectricity can be obtained from any material, unlike piezoelectricity which requires that the material unit cell be non centro-symmetric[1]. Furthermore, the flexoelectric effect increases as the scale of the system goes down, hence the idea to use this effect in a nanosystem that would harvest energy for a micro-device (see e.g. [2,3]).
Since multi-wall carbon nanotubes (MWCNTs) are quite flexible, very stable and possess interesting electric properties, we would like to study their potential for the generation of flexoelectricity from mechanical deformations. A first study of this kind,[4] presents experimental results on a thin film filled with MWCNTs bearing PZT microparticles. This PZT-MWCNT nanogenerator was found to produce a peak output voltage of 8.6 V and an output current of 47 nA when a force of 20 N was applied.

Following this line of thought, we have started exploring the flexoelectric capabilities of single MWCNTs through their manipulation with a SEM-FIB based microrobotic system [5] along with computer vision tools. We managed to grip and bend single MWCNTs of about 30 nm diameter (Fig. 1), while tracking the region of bending over successive images and computing its brightness. Preliminary experiments showed an increase of brightness with respect to an increase of bending (Fig. 2), possibly related to the excess charges due to the polarization of the MWCNT as a result of the imposed strain gradient (flexoelectric effect). Our ultimate goal is to transform these measurements of brightness into measurements of local charges so as to be able to compute the effective flexoelectric coefficient of the bent MWCNT.

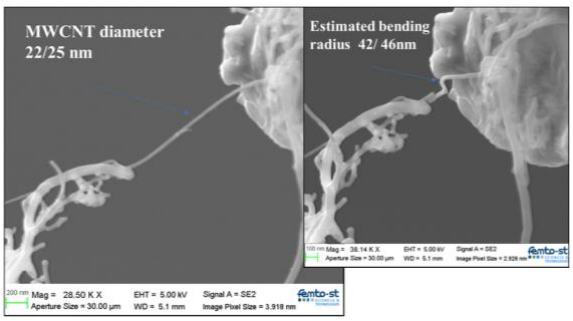


Figure 1: Illustration of the gripping and bending of a single 30 nm diameter MWCNT, in the µRobotex facility of the FEMTO-ST institute.

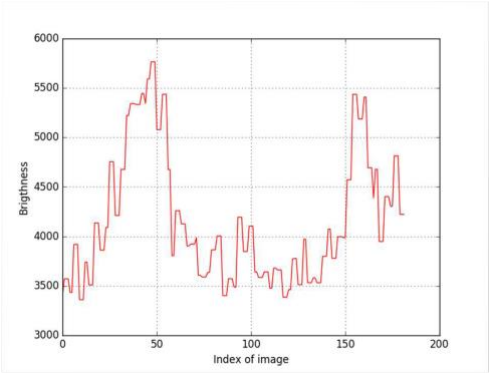


Figure 2: Brightness of the region of bending with respect to the index of image in the sequence of images: peaks of brightness correspond to maximum of bending.

Keywords: flexoelectricity, nanomanipulation, carbon nanotubes, energy harvesting.

References:

1. P. Zubko et al., Annu. Rev. Mater. Res., **43**, 387–421 (2013)
2. Majdoub et al., Phys. Rev. B., **78**, 121407 (2008)
3. Yurkov et al., Int. J. Sol. Str., **162**, 96-104 (2019)
4. Han et al., Scientific reports, **6**, 29562 (2016)
5. Rauch et al., JVSTA, **36**, 41601 (2018)

NanoMed 2019 / EGF 2019 Joint Plenary session Bioinspired materials / Nanotechnology in Therapy / Pharmaceutical Nanotechnology

Graphene surfaces for detection of biomolecules

P. Alpuim,[1,2]

[1]INL - International Iberian Nanotechnology Laboratory, 4715-330, Braga, Portugal
[2] Department of Physics, University of Minho, 4710-057, Braga, Portugal

Abstract:
The importance of biosensors in biomedical research keeps increasing at a fast pace, as they are routinely used in a wider range of applications. Biomolecular sensing is crucial for areas like Biomedicine, Food safety, Environmental monitoring and other areas where the detection of traces of biomolecules or DNA can be used for early-stage diagnosis, food quality and authenticity control, or contaminant detection. Graphene low-dimensionality, as well as its high carrier mobility and chemical stability, allows to fabricate relatively simple label free, highly sensitive biosensors, based on different types of devices. Here, we propose the development of a miniaturized biosensing platform based on liquid-gate graphene field-effect transistors (GFETs) that achieve detection of DNA hybridization down to attomolar concentration, while being able to discriminate a single nucleotide polymorphism (SNP). The platform comprises 3 modules: target extraction and purification, isothermal target amplification, and detection. The sensor readout consists of a home-made electronic platform, with the size of a credit card, to ensure portability. In this communication I will focus on the detection module: the GFET sensor chip and a PDMS flow cell fitting the sensor layout are assembled and then inserted in the portable platform (Figure 1). This system, connected to a syringe pump and a multiposition valve, allows for automation, improving the precision over manually operated ones.
Another type of graphene biosensor that we propose is an electrochemical chip consisting of 6 independent gold microelectrode arrays covered with a patterned graphene layer serving as working electrodes, and platinum reference and counter electrodes. The devices are fabricated at the wafer scale and are used in the detection of DNA hybridization.
Finally, we use the z^{-4} nanoscale distance-dependence of the fluorescence lifetime for fluorophores located in the vicinity of graphene to track the hybridization of fluorescently labelled DNA beacons attached to CVD grown graphene with complementary (target) DNA added in solution. We follow the conformational changes of the beacons by determining the fluorescence lifetimes of the labelling dye and converting them into nanoscale distances from the graphene. In this way, we are able to monitor the vertical displacement of the label during DNA-beacon unfolding with an axial resolution reaching down to 1 nm.

Keywords: graphene, biosensor, immunoassay, DNA, electrolyte-gated field-effect transistor, planar technology, surface functionalization, near-field sensing, fluorescence quenching.

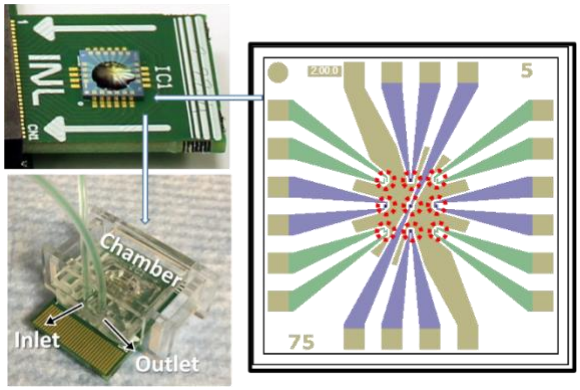


Figure 1: (counterclockwise from right to left) The sensor chip containing 9 GFETs (highlighted in red) is wire bonded to a PCB that is inserted in the control board. A PDMS flow cell, fitting the sensor layout, can be assembled to the chip prior to insertion in the board.

References:

1. Campos, R., Borme, J., Guerreiro, J.R., Machado Jr, G.L., Cerqueira, M.F., Petrovykh, D.Y., Alpuim, P. (2019) Attomolar label-free detection of DNA hybridization with electrolyte-gated graphene field-effect transistors, *ACS Sensors* 4, 286-293.
2. Adão, R.R.M., Campos, R., Figueiras, E., Alpuim, P., Nieder, J.B. (2019) Graphene setting the stage: tracking DNA hybridization with nanoscale resolution, *2D Materials*, In Press (doi.org/10.1088/2053-1583/ab41e0).

Graphene-based sheets for biomedical applications: case studies.

Paula A. A. P. Marques[1]

[1] University of Aveiro, Department of Mechanical Engineering, Aveiro, Portugal

Abstract:
From a functional point of view, the 2D arrangement in graphene guarantees a notably high specific surface area that can be used to establish suitable cell-material interactions6 and to provide multiple attachment spots for biomolecules [1]. The remarkable electronic and optical properties of graphene are deeply linked with its singular electronic band which, by combining both metallic and semiconducting characteristics, allows the π electrons to behave like ultrarelativistic particles able to move with a speed close to the speed of light. Indeed, this nanomaterial is a bioactive and transparent zero-gap semiconductor capable of significantly upgrading the selectivity and sensitivity of both electrochemical, field-effect transistor (FET) and optical biosensors [2, 3] in the road to more efficient enzymatic biosensing, DNA sensing, and immunosensing.

Complementary to graphene, graphene oxide (GO) presents a highly reactive surface, with hydrophobic sp^2 carbon regions intercalated by sp^3 regions where the carbons are linked with oxygen functional groups (carboxyl, epoxy and hydroxyl) that guarantee the presence of hydrophilic zones able to promote good water dispensability, a near infrared (NIR) to visible fluorescence and also covalent and/or non-covalent attachment points for biomolecules, metals and polymers [4]. This singular mix of features is receiving increased attention from biomedical engineers, who look to GO as the central building block for versatile strategies capable of combining imaging, sensing and therapy [5, 6]. For instance, GO can be simultaneously used for drug delivery and live cellular imaging by diffusing its oxygen moieties via a mild thermal annealing procedure able to maintain their availability to be conjugated with cancer drugs while inducing blue fluorescence [7].

The inclusion of graphene-related materials (GRM) in natural or synthetic polymers to produce biomimetic 3D tissue engineering (TE) scaffolds is being explored with interesting added properties, like mechanical reinforcement, cell-adhesion enhacement capability, between others.

Despite the innovative and extensive results provided by GRM in biomedical applications, including revolutionary diagnosis, monitoring and therapeutic approaches, there is still a long road ahead until some important concerns related to production processes and biological interactions including toxicity are irrefutably solved. However, it is quite possible that this road will be covered more quickly than expected based on the vertiginously rapid growth of the field and the enthusiasm of the scientific community, which are helping to overcome the mentioned challenges, leading to real and decisive breakthroughs in a near future.

Keywords: graphene-related materials in therapeutic strategies; graphene-based scaffolds for tissue engineering.

References:

1. D. Li, W. Zhang, X. Yu, Z. Wang, Z. Su and G. Wei, Nanoscale, 2016, 8, 19491-19509.
2. A. T. Lawal, Biosensors and Bioelectronics, 2018, 106, 149-178.
3. E. Morales-Narváez, L. Baptista-Pires, A. Zamora-Gálvez and A. Merkoçi, Advanced Materials, 2016, 29, 1604905.
4. D. P. Singh, C. E. Herrera, B. Singh, S. Singh, R. K. Singh and R. Kumar, Materials Science and Engineering: C, 2018, 86, 173-197.
5. D. W. Hwang, H. Y. Kim, F. Li, J. Y. Park, D. Kim, J. H. Park, H. S. Han, J. W. Byun, Y.-S. Lee, J. M. Jeong, K. Char and D. S. Lee, Biomaterials, 2017, 121, 144-154.
6. K. Muazim and Z. Hussain, Materials Science and Engineering: C, 2017, 76, 1274-1288.
7. S.-J. Cheng, H.-Y. Chiu, P. V. Kumar, K. Y. Hsieh, J.-W. Yang, Y.-R. Lin, Y.-C. Shen and G.-Y. Chen, Biomaterials Science, 2018, 6, 813-819.

Challenges on Graphene-Based Nanomaterials in Nanomedicine

D. Iannazzo

University of Messina, Department of Engineering, Messina, Italy

Abstract:
Graphene and its modified nanostructures have attracted great research interest in recent years, owing to their unique structure and outstanding physicochemical properties.[1] Among the different classes of nanomaterials possessing graphene sheets as building blocks, the one-dimension carbon nanotubes and the next generation of carbon nanomaterials, graphene quantum dots, have been widely investigated in biomedical field. The versatile surface functionalization, ultra-high surface area, photoresponsive properties and the presence of different reactive groups on the graphene surface allow their multimodal conjugation with various functional groups and biologically active molecules, making them ideal candidates for nanomedicine applications.[2-6]
Carbon nanotubes (CNTs) offer potential advantages over the more widely investigated nanoparticle systems, including their ability to cross cell membranes and shuttle drugs, biomolecules, including DNA, siRNA and proteins, into various types of cells such as cancer cells and T cells. Biocompatible drug delivery systems based on CNT have been investigated for their ability to deliver doxorubicin on cancer cells, showing the possibility to tune the amount of drug released, by controlling the functionalization degree of the CNT-based material.[2] Moreover, in order to prove the ability of CNT to form strong interactions with viral enzymes and to act as HIV inhibitors, highly hydrophilic and dispersible CNT have been conjugated with antiretroviral drugs and their antiviral activity was found to be strictly related to the physicochemical properties of the nanomaterials.[3]
Graphene quantum dots (GQD), the next generation of carbon based nanomaterials, due to their outstanding physical, chemical and biological properties, and their strong size-dependent photoluminescence have shown potential in revolutionizing the future of nanomedicine and biotechnology.[4] Biocompatible and cell traceable drug delivery systems, GQD based, were reported for the targeted delivery of anticancer agents to cancer cells. These nanomaterials, conjugated with tumor targeting modules, able to efficiently recognize receptors over-expressed on cancer cells, showed high water dispersibility, great biocompatibility and enhanced anticancer activity.[5] GQD, conjugated with reverse transcriptase inhibitors, have been also investigated as nano-drugs for anti-HIV therapy; some of the synthesized nanosystems revealed to be potential candidates for HIV treatment.[6]

Keywords: Graphene-based materials, carbon nanotubes, graphene quantum dots, anticancer therapy, HIV therapy.

References:

1. D. Iannazzo, A. Pistone, I. Ziccarelli, et al. (2018) *Fullerenes, Graphenes and Nanotubes: A Pharmaceutical Approach*. A. M. Grumezescu Eds. Elsevier, cap. 8, 297-329.
2. A. Pistone, D. Iannazzo, S. Ansari, et al. (2015), Tunable doxorubicin release from polymer-gated multiwalled carbon Nanotubes, *Int. J. Pharm.*, 515, 30–36.
3. D. Iannazzo, A. Pistone, S. Galvagno, et al. (2015), Synthesis and anti-HIV activity of carboxylated and drug-conjugated multi-walled carbon nanotubes, *Carbon*, 82, 548-561.
4. D. Iannazzo, I. Ziccarelli, A. Pistone (2017), Graphene quantum dots: multifunctional nanoplatforms for anticancer therapy, *J. Mat. Chem. B*, 5, 6471–6489.
5. D. Iannazzo, A. Pistone, M. Salamò, et al. (2017), Graphene quantum dots for cancer targeted drug delivery, *Int. J. Pharm*., 518, 185–192.
6. D. Iannazzo, A. Pistone, S. Ferro, et al. (2018), Graphene Quantum Dots Based Systems As HIV Inhibitors. *Bioconjugate Chem*., 29, 3084−3093.

Measuring Forces at the Nanoscale for Cardiovascular Risk Evaluation

Ana Filipa Guedes,[1] Luís Sargento,[2] José Braz-Nogueira,[3] Nuno Lousada,[2] Carlos Moreira,[3] Filomena A. Carvalho,[1] Nuno C. Santos,[1,*]

[1] Instituto de Medicina Molecular, Faculdade de Medicina, Universidade de Lisboa, Lisbon, Portugal
[2] Hospital Pulido Valente, Centro Hospitalar Lisboa Norte, Lisbon, Portugal
[3] Hospital de Santa Maria, Centro Hospitalar Lisboa Norte, Lisbon, Portugal

Abstract:
Erythrocyte aggregation is an indicator of cardiovascular risk, which is influenced by plasma fibrinogen concentration. Fibrinogen levels are elevated during cardiovascular diseases. Our main goals were to understand how fibrinogen-erythrocyte binding influences erythrocyte aggregation and how it constitutes a cardiovascular risk factor in chronic heart failure (CHF) [1] and essential arterial hypertension (EAH) [2,3]. Fibrinogen-erythrocyte and erythrocyte-erythrocyte adhesion measurements were conducted by atomic force microscopy (AFM)-based force spectroscopy (Figure 1). Upon increasing fibrinogen concentration, there was an increase in the work and force necessary for cell-cell detachment, both for healthy donors and EAH patients. Nevertheless, higher values were obtained for the EAH patients at each fibrinogen concentration. Fibrinogen-erythrocyte (un)binding forces were higher in EAH and CHF patients, when compared with the control group, despite a lower binding frequency. Ischemic CHF patients showed increased binding forces compared to non-ischemic patients. Erythrocyte deformability (assessed as elongation index) results show that heart failure patients presented higher erythrocyte deformability than the control group at lower shear stresses, and lower deformability at higher shear stresses. This indicates that patients' erythrocytes are more deformable than those from healthy donors in blood vessels with larger internal diameters; however, in smaller-diameter vessels the opposite trend exists. Importantly, a 12-month clinical follow-up shows that CHF patients with higher fibrinogen-erythrocyte binding forces, probed by AFM at the beginning of the assessment, had a significantly higher probability of being hospitalized due to cardiovascular complications on the subsequent year. Our results show that AFM can be a promising tool for clinical prognosis, pinpointing those patients with increased risk for cardiovascular complications, for which special personalized medicine strategies should be envisaged.

Keywords: cardiovascular diseases, heart failure, hypertension, atomic force microscopy, force spectroscopy.

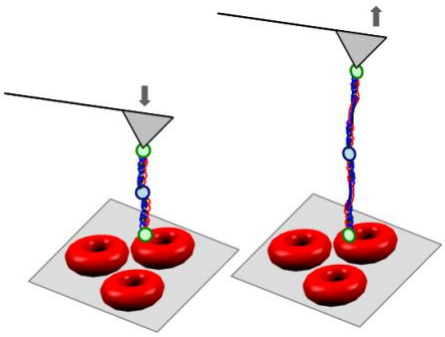


Figure 1: Schematic representation of the measurement by AFM-based force spectroscopy of the force necessary to overcome the fibrinogen-erythrocyte binding.

References:

1. Guedes, A.F., Carvalho, F.A., Malho, I., Lousada, N., Sargento, L., Santos, N.C. (2016), Atomic force microscopy as a tool to evaluate the risk of cardiovascular diseases in patients, *Nature Nanotechnol.*, 11, 687-692.
2. Guedes, A.F., Carvalho, F.A., Moreira, C., Nogueira, J.B., Santos, N.C. (2017), Essential arterial hypertension patients present higher cell adhesion forces, contributing for fibrinogen-dependent cardiovascular risk, *Nanoscale*, 9, 14897-14906.
3. Guedes, A.F., Moreira, C., Nogueira, J.B., Santos, N.C., Carvalho, F.A. (2019), Fibrinogen-erythrocyte binding and hemorheology measurements on the assessment of essential arterial hypertension patients, *Nanoscale*, 11, 2757-2766.

Proton stimulation therapy for iron-oxide mineral forming Alzheimer's disease

J.K. Kim,* Y. Choi, J.-G. Jeon

Catholic University of Daegu, School of Medicine, Department of Biomedical Engineering, Daegu, South Korea

Abstract:
Iron oxide magnetite was identified as redox-toxic mineralization in hallmarks of AD from patient or transgenic AD mice brain (1-3). We have discovered therapeutic effect of proton stimulation in AD plaque targeting magnetite. Our prior works (4-5) as proof-of-concept studies of proton stimulation on iron oxide minerals in Aβ fibril or in a plaque-forming transgenic AD mice model demonstrated disruption of Aβ-magnetite complex and removal of Aβ-plaque burden (60-90% in single treatment) and detoxification of ferrous magnetite into soluble ferric magnetite in dose-dependent manner. Proton stimulation was performed in traversing pristine mode without deposition Bragg peak inside tissue with entrance dose of 1-4 Gy. Therefore, this innovative treatment on AD brain did not damage on normal tissue including microvessel, demonstrating no ischemic damage or inflammation, haemorrhage after treatment. We suggest further study with heavy ion beam to take an advantage of higher peak-to-plateau ratio at higher energy and enhanced electron emission from magnetite via nanoradiator effect in 1-5 Gy compared with proton stimulation.
Since iron-oxide mineral is not only in AD dementia but also Parkinson's disease, we want to investigate this technique in any iron-oxide mineral forming protein aggregates of neurodegenerative diseases under organized international collaborative research group.

Keywords: Iron oxide nanoparticles, protein aggregates, Alzheimer's diseases, redox toxicity, neurodegenerative disease, proton stimulation.

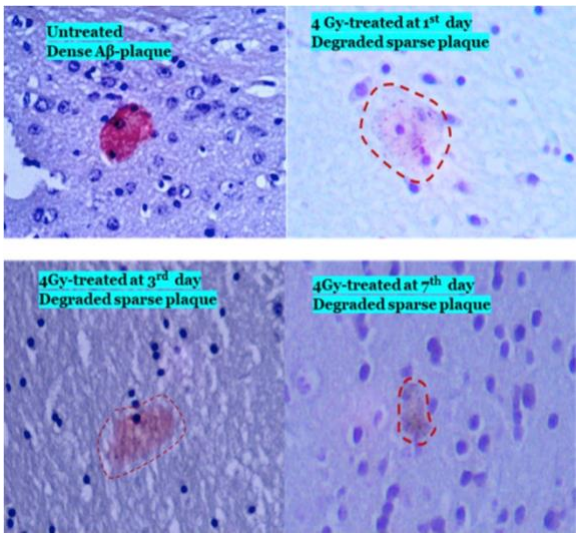


Figure 1: Figure illustrating the results of proton stimulation on AD transgenic mouse model expressing amyloid plaque. Congo Red staining (plaque) were reduced by more than 78-99 % in a dose-dependent and kinetic manner after single dose treatment.

References:

1. B. A. Mahera et al., PNAS 113 (2016) 10799.
2. J Everett et al., Nanoscale 10 (2018) 11782.
3. Telling, N.D. et al., Cell Chemical Biology 24 (2017)1205.
4. Y. Choi et al., MRS Comms 8 (2018) 955.
5. J.K. Kim et al. Manuscript Submission in PNAS (2019).

Radiolabelled Gold Nanoparticles for Image-guided Chemoradiotherapy of Glioblastoma Multiforme

A. Paulo,[1,*] A. Belchior,[1] A. D'Onofrio,[1] C. Mendes,[1] C. Oliveira,[1] F. Marques,[1] F. Silva,[1] M. P. C. Campello,[1] Lurdes Gano,[1] M. Ravera,[2] P. Raposinho[1]

[1]Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10 (km 139,7), 2695-066 Bobadela LRS, Portugal

[2]Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale "Amedeo Avogadro", Alessandria, Italy

Abstract:

Glioblastoma multiforme (GBM) is among the most aggressive cancers and remains essentially an incurable disease. Therefore, there is an urgent need for innovative therapies against GBM. To tackle this goal, we have focused on multifunctional gold nanoparticles (AuNPs) for image-guided GBM chemoradiotherapy, using an unprecedented strategy that relies on the simultaneous delivery of Pt(IV) prodrugs and therapeutic radionuclides. By considering AuNPs for the design of these new theranostic tools, we have took into consideration their appealing properties for medical application, such as, biocompatibility, easy functionalization with molecular vectors and good biological half-life. Additionally, AuNPs can also be explored as multifunctional platforms for targeted-delivery of radionuclides and chemotherapeutic drugs. Herein, we will report on the synthesis, characterization and biological evaluation of AuNPs decorated with Pt(IV) prodrugs, a DOTA-based chelator for coordination of medically relevant trivalent metals (e.g. ^{67}Ga, ^{177}Lu)[1] and a bioactive peptide (substance P derivatives) that recognizes the NK1 receptor overexpressed in GBM cells. Some of the SP-containing AuNPs were also labeled with ^{125}I profiting from the presence of a Tyr residue in the peptide sequence. The studies included the assessment of cellular uptake and (radio)cytotoxic activity in cells for the designed multifunctional nanoparticles, aiming to obtain a first insight on their suitability for targeted chemoradiotherapy of glioblastoma

Keywords: gold nanoparticles, Substance P, radionuclide therapy, Pt(IV) prodrugs, chemoradiotherapy, glioblastoma multiforme.

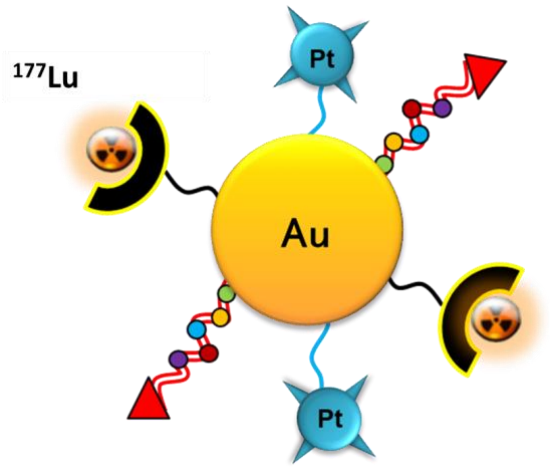


Figure 1: Schematic drawing of the multifunctional AuNPs, decorated with a therapeutic radionuclide (^{117}Lu), Pt(IV) drugs and Substance P peptide to target the NK1 receptor.

References:

1. Silva, F., Zambre, A., Campello, M. P. C., Gano, L., Santos, I., Ferraria, A. M., Ferreira, M. J., Singh, A., Upendran, A., Paulo A., Kannan, R. (2016) *Bioconjugate Chemistry*, 27, 1153-1164.

Acknowledgements: This work is supported by Fundação para a Ciência e Tecnologia (projects PTDC/MED-QUI/29649/2017 and UID/Multi/04349/2013).

NanoMed 2019 - Session II: Nanotechnology in Therapy / Pharmaceutical Nanotechnology

Nanomedicine, Science & Regulation: the translation issues for the next generation of technologies

R. Gaspar [1]

[1] Universidade de Lisboa, Faculdade de Farmácia (FFUL)
& Institute of Bioengineering and Biosciences (iBB), Lisboa, Portugal

Abstract:
Nanomedicine is bringing together new opportunities for healthcare, using the integration of disciplines through Converging Science at the nanoscale. The last decades have seen a profusion of approaches based on modulation of biodistribuition and pharmacokinetics, with significant impact in areas like oncology or infectilous diseases. Meanwhile several challenges are still unmet and the emergence of others strategies (e.g. immunotherapy in cancer) are increasing the barriers for early adoption and clinical translation.
New challenges in Regulatory Science need to be met by better integration between materials science and solution of translational issues, like validation of adequate models (e.g. preclinical human cells and tissues in appropriate setting to foster clinical translation and better outcomes within clinical phase), targeting adequate disease stage and disease evolution conditions, within the current setting and also trying to address appropriate clinical questions in personalized medicine.
The innovation in materials science as to meet clinical standards already established for already approved medicinal products that went through the challenge of regulatory approval for both clinical experiences (under clinical trials) but also for marketing authorization and routine clinical use. Meanwhile the need for adequate standardization and characterization has moved the USA to a specific platform initiative (NCL at NCI) and Europe is moving in different ways looking to a more integrated platform to address it (e.g. EU-NCL within Horizon 2020).
All advances need to be put in context aiming always at improved healthcare, more efficient, with increased rational use of complex therapeutic platforms, optimizing diagnostic and therapeutic functions, delivering affordable technologies capable of really improving healthcare in specific groups or populations of patients. And specifically improving the integration of technologies and the integration of healthcare.
Nanomedicine is bringing converging sciences to an adequate platform of technologies that need to allow better health care but also enable the design and clinical use of innovative solutions aiming at solving still unmet clinical needs.
We envisage a near future where bridging diagnostics and therapeutics through nanotechnology-based tools brings the promise of personalized medicine as an attainable goal at an adequate cost for both society and individual patients.

Keywords: Nanomedicine, nanomedicines, nanopharmaceuticals, translational research, regulatory science, market access, health technologies, biomedical applications.

References:

1. R Duncan and **R Gaspar** - Nanomedicine(s) under the microscope, Molecular Pharmaceutics (2011) 8(6): 2101-2141, doi 10.1021/mp200394t
2. **R Gaspar** – Therapeutic products: regulating drugs and medical devices. Chapter 14 in "**International Handbook on Regulating Nanotechnologies**", editors Graeme Hodge, Diana Bowman and Andrew Maynard, Edward Elgar Publishing, 2010, pp 291- 320, ISBN 978-1-84844-673-1.
3. **R Gaspar**, R. Duncan – Polymeric carriers: Preclinical safety and the regulatory implications for design and development of polymer therapeutics. Advanced Drug Delivery Reviews (2009), 61: 1220-1231, doi 10.1016/j.addr.2009.06.003
4. **R Gaspar**, B Aksu, A Cuine, M Danhof, M Jadrijevic-Mladar Takac, HH Linden, A Link, E-M Muchitsch, CG Wilson, P Öhrngren, L Dencker - Towards a European Strategy for Medicines Research (2014-2020): The EUFEPS Position Paper on Horizon 2020. European Journal of Pharmaceutical Sciences 47 (2012): 979-987, doi 10.1016/j.ejps.2012.09.020

Ceramic biomaterials instruct cell behavior in regenerative medicine

S. Panseri

Institute of Science and Technology for Ceramics, National Research Council of Italy – Faenza (RA), Italy

Abstract: The ever increasing need of more effective and targeted therapies for the treatment of various pathologies is pushing scientists to develop new solutions associating enhanced safety with smart functionality, also permitting the establishment of personalized therapeutic approaches. Regenerative medicine often requires the use of scaffolds acting as an instructing guide for cells, so that substantial mimicry of compositional, morphological and structural features of natural tissue is highly desired. However, this target is very hard to achieve, when human tissues with high compositional and structural complexity. An emerging concept in material science is to draw inspiration from natural processes and products, which we may consider as the most advanced examples of smart nanotechnology. Ceramic-based nanomaterials represent very versatile biomaterials offering promising examples, and here two successful studies were reported. Natural structures such as woods and plants exhibit multi-scale hierarchic organization that is the source of smart and anisotropic mechanical properties associated with high porosity and lightness. Porous woods (rattan) were recently transformed into hydroxyapatite (HA) scaffolds with hierarchic organization focusing on long bone critical defect. Biomorphic 3-D hierarchically organized porous ceramics consisted in highly biomimetic, multi-substituted nanocrystalline apatite phase, directly nucleated in the 3-D state to form a scaffold exhibiting bone-mimicking structure with open and interconnected porosity and hierarchical organization at the multiscale. Such features determined very high mechanical strength and damage-tolerant mechanical behaviour, thus resulting into high mimicry of bone tissue.We have proved the cellular cross-talk between human mesenchymal stem cells and human endothelial cells in a perfusion bioreactor system as a predictive *in vitro* model for bone regeneration. These results confirm that the adoption of nature-inspired processes is an elective approach to obtain highly bioactive materials with innate cell-instruction ability, thanks to biomimetic features that are not achievable by the traditional ceramic processing.

Another example of the great potential of ceramic nanomaterials is related the cell therapy.

Cell therapy is one of the most exciting and promising areas for disease treatment and regenerative medicine. However the success rate of cell-based therapies, despite their great potential, is limited mainly due the ineffective delivery and retention of therapeutic cells in the specific organ. Magnetic targeting has emerged as a method to overcome these limitations. So far these attempts have used superparamagnetic iron oxide nanoparticles (SPIONs), only clinically approved metal oxide nanoparticles. Nevertheless the exposure to SPIONs has always been associated with significant toxic effects such as inflammation, apoptosis and generation of ROS. Our group, by doping HA, the mineral component of bone, with Fe^{2+}/Fe^{3+} ions, had obtained novel biocompatible and fully bioresorbable superparamagnetic nanoparticles (FeHA). This work demonstrates the opportunity of FeHA in Mesenchymal Stem Cells (MSCs) labeling. MSCs easily internalized the FeHA, and they became magnetic enough to be guided and retained to specific site by a magnet. Magnetic MSCs maintained their morphology and cell viability was not negatively affected. Due the well-known osteoinductive feature of HA, magnetic MSCs overexpress osteogenic genes. We are also investigating the possibility to combine these above-mentioned results with the contrast ability of FeHA for a real time imaging of the magnetic MSCs *in vivo* by magnetic resonance imaging.

In conclusion, these new approaches promise to be a breakthrough in the synthesis of bioceramics with boosted bioactivity,

potentially opening to frontier applications in regenerative medicine.

Keywords: regenerative medicine, nanomaterial, ceramic, cell therapy, tissue engineering, 3D scaffold, co-culture.

Nanomaterials for and from immune cells: nanoparticles and extracellular vesicles

S. G. Santos[1,2]

[1]i3S - Instituto de Investigação e Inovação em Saúde and INEB - Instituto de Engenharia Biomédica, Universidade do Porto, Portugal;
[2]ICBAS - Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Portugal
Susana.santos@ineb.up.pt

Abstract:
Nanomaterials are being incorporated in a wide range of products, but their safe use requires that interactions with the immune system are better understood.
To defend the host against pathogens immune cells, like macrophages and Dendritic cells (DCs), surveil peripheral tissues, engulphing pathogens and foreing materials. Nanomaterial development strategies that avoid, but also that take advantage of immune cells, are being actively pursued. DCs roles in immune surveillance and antigen-presentation, linking the innate and adaptive immunity, grant them center stage in immunomodulatory strategies, both for promoting immunity, in fighting cancer or infection, and for promoting tolerance in autoimmunity. Herein, results on evaluating nanomaterials to deliver drugs to DC will be presented, and the use of Extracellular Vesicles (EV) for the delivery of molecules and drugs will be discussed.
Using nanostructured lipid carriers (NLC) as delivery systems for human primary DC, we could reduce the dose of resveratrol required to inhibit DC response to TNF-α at the phenotypic and functional levels, including cytokine secretion and T cell activation. Both immature and mature DCs internalized NLC, without cytotoxicity (Figure 1A), making them suitable carriers for fluorescent labels or bioactive molecules for human DCs [1].
EV, which include exosomes and microvesicles, work as cell communication and molecular delivery mediators. These vesicles are secreted by virtually all cells, loaded with potentially active molecules, from nucleic acids to proteins, including enzymes, and are amenable to modifications, before and after secretion [2]. Our results show that EV produced by primary human and rat DC have a cup-like morphology (Figure 1B), and other characteristics akin to exosomes. DC-EV are internalized by Mesenchymal Stem/Stromal Cells (MSC) (Figure 1C), and are able to promote their recruitment, containing potentially chemotactic molecules [3]. EV as nanocarriers will also be discussed [2].

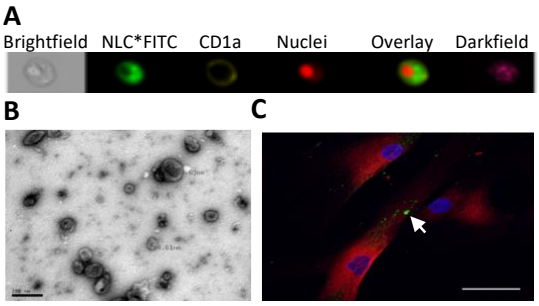


Figure 1: **A.** Human primary DC (CD1a+) showing internalized FITC-labelled NLC, by imaging flow cytometry; **B.** Transmission electron microscopy of EV secreted by DC; **C.** DC-secreted EV (green,white arrow), internalized by MSC, with endoplastic reticulum protein calnexin labelled in red.

Keywords: nanoparticles, dendritic cells, tissue repair, exracellular vesicles

Acknowledgements: Work funded by project NORTE-01-0145-FEDER-000012, Norte Portugal Regional Operational Programme (NORTE 2020), under PORTUGAL 2020 Partnership Agreement, through European Regional Development Fund (ERDF); UP and Santander (PP_IJUP2011_220), AO Foundation, Switzerland (S-15-83S); and Portuguese funds through FCT, including PhD and Post-Doc fellowships.

References:
1. Barbosa, J.P., et al., Nanostructured lipid carriers loaded with resveratrol modulate human dendritic cells. Int J Nanomedicine, 2016. **11**: p. 3501-16.
2. Pinheiro, A., et al., Extracellular vesicles: intelligent delivery strategies for therapeutic applications. J Control Release, 2018. **289**: p. 56-69.

3. Silva, A.M., et al., Dendritic Cell-derived Extracellular Vesicles mediate Mesenchymal Stem/Stromal Cell recruitment. Sci Rep, 2017. **7**(1): p. 1667.

Gellan Gum-based *In-situ* Gelling Systems containing Self-Assembling Mixed Nanomicelles: A Novel combined system for the Ocular Delivery of Cyclosporine-A

E. Terreni[1], E. Zucchetti[1], D. Monti[1], S. Burgalassi[1], S. Tampucci[1], P. Chetoni[1]
[1] University of Pisa, Department of Pharmacy, Pisa, Italy

Abstract: Cyclosporine-A (CyA) is an important anti-inflammatory agent for the treatment of Dry Eye Syndrome (DES). CyA has very poor water solubility and a hight molecular weight, which makes its ocular delivery a real challenge. An additional issue consists in the safety and tolerability of the ophthalmic product for direct ocular application that must be considered. This study aimed to obtain an eye-drop formulation able to increase CyA bioavailability and prolong drug resident time in the application site. A combination of a) nanomicellar system, that can raise CyA solubility, and b) in situ gelling system to prolong CyA resident time in the pre-corneal area was adopted.
Nanomicelles with different non-ionic surfactants were prepared. One nanomicellar system was selected and associated with different gellan-gum concentrations, and the final nano-gelling systems characterized by: critical micellar concentration (CMC), size, entrapment/loading efficiency, pH, osmolality, thermal stability, nanomicelles regeneration time, chemical stability, rheological measurements, cytotoxicity assays, in vivo tolerability and pharmacokinetic (PK) studies.
Mixed Nanomicellar system containing Vit-E TPGS and Kolliphor® RH-40 (1:1, molar ratio) showed best results in terms of size, thermal stability and CyA entrapment/loading efficiency. Then, it was combined with three aqueous dispersions containing different amount of gellan gum (0.1, 0.15 and 0.2%) and added of mono- and bivalent salts to give a sol-gel transition when in contact with the tear fluid. The presence of gellan gum allowed the self-formation of nanomicelles with a small particle size (< 20 nm) and a narrow distribution (PI < 0.3). Entrapment and loading efficiencies were higher than 90% and 7%, respectively. A short-term stability was performed and no significant changes in term of drug content and particle sizes were found at the tested storage temperature (4°C and 20°C). Cytotoxicity assays on the combined nano-gelling systems using Rabbit Cornea Epithelial cells confirmed the ocular safety of the components used in the formulation. Finally, PK studies in the rabbits' tear fluid were performed on the nanomicelles aqueous dispersion, the nano-gelling systems and a commercial product (Ikervis®), used as reference. In all cases, the drug concentration in tear fluid decreased rapidly after administration but the elimination of CyA was slowed down in presence of gellan gum, confirming the in vivo gelling ability of the combined system. The nano-gelling systems containing higher concentrations of gellan gum showed better PK parameters than marketed Ikervis® as well as a good tolerability. In conclusion, the combination of nanomicelle and in situ gelling system can improve both CyA bioavailability and resident time in the tear fluid and ocular tolerability with respect of the marketed Ikervis®.

Keywords: *in-situ* gelling system, self-assembling mixed nanomicelles, Vit E-TPGS, RH-40, Cyclosporine-A, dry eye syndrome, gellan gum, Ikervis.

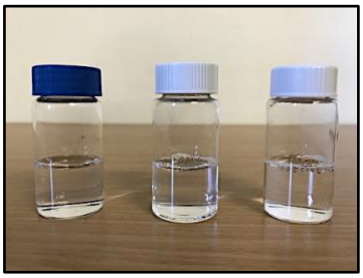


Figure 1: Figure illustrating three combined systems obtained from this study: clear water eye-drop solutions containing the poorly soluble Cyclosporine-A, which are able to pass from sol to gel when in contact with the physiological tear fluid.

References:

1. F. Lallemand, M. Schmitt, J. Bourges, R. Gurny, S. Benita, J. Garrigue (2017), Cyclosporine A Delivery to the Eye: A Comprehensive Review of Academic and Industrial. *Eur J Pharmand Biopharm*, 117, 14-28.

Development of bio-based hybrid microparticles as poorly water-soluble drug delivery systems

Koceïla Doufène*, Vincent Lapinte, Jean-Jacques Robin, Joël Chopineau, Jean-Marie Devoisselle, Corine Tourné-Péteilh and Anne Aubert-Pouëssel.

ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France.

Abstract:
Nowadays, the development of new Active Pharmaceutical Ingredients (API)s is in great demand. However, the vast majority of these APIs have solubility issues and their "drug-like" profiles are compromised during early stages of the development. Herein, we report a novel drug delivery system of poorly water-soluble APIs: the "castor oil / silica" hybrid microparticles (HMPs) (Figure 1). Castor oil was selected for its solubilizing properties and the ease of its functionalization. Green chemistries were used to functionnalize the oil with a silylated agent, and further to cross-link it into solid microparticles by sol-gel reaction in soft conditions (aqueous medium and mild temperature). Silylated castor oils at various silylation ratios were prepared and allowed the solubilization of ibuprofen at several concentrations up to 16 %.
In a first approach, the HMPs were formulated by thermostabilized emulsion process which permits to "freeze" the oil-in-water emulsion while the sol-gel reaction occurs[1]. The hybrid mineral / organic composition and the morphology (spherical shape and micrometric size) of these HMPs were determined by complementary technics. The HMPs reached a good ibuprofen loading efficiency regardless to the formulation used while the release kinetics in simulated oral administration exhibited a tunable release according to the silylation ratio. For subcutaneous conditions, ibuprofen release took place over 15 days. Finally, biodegradability assays suggested a surface-limited digestion of the particles and cytocompatibility studies on demonstrated an excellent cellular viability.
In a second approach, a microfluidic protocol has been set up in order to produce monodisperse microparticles with controlled structures.

Keywords: vegetable oil, microfluidics, emulsion, sol-gel, hybrid microparticles, lipid-based drug delivery system.

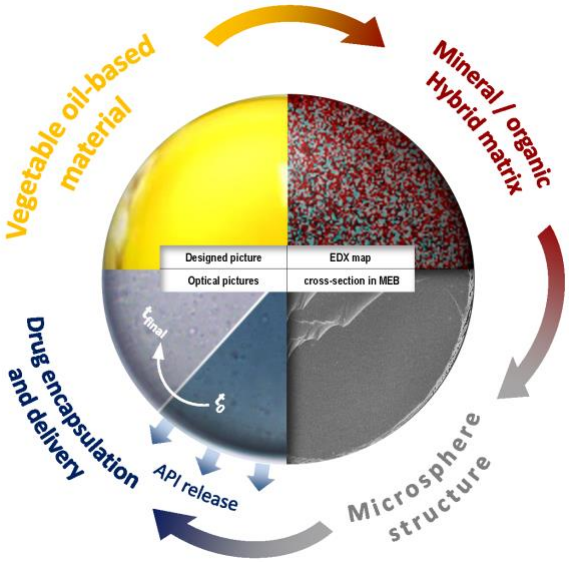


Figure 1: Figure illustrating the concept of bio-based hybrid microparticles as drug delivery system for poorly water-soluble APIs.

References:

1. Gallon, G. *et al.* Cross-Linked Castor Oil-Based Hybrid Microparticles as Drug Delivery Systems. *ACS Sustainable Chemistry & Engineering* **5**, 4311–4319 (2017).

* *: corresponding author*

Carbon nanotubes as a scaffold for hESC differentiation toward photoreceptor precursor cells

Y.Chemla[1,2] , E.Shawat[2,3] , A. Markus[1,2] , Y. Kostikov[2,3], F. Nairouz[1] , S. Aviad.slotky[1], D.Nessim[2,3] , Y.Mandel[1,2]

[1] Bar Ilan University, Faculty of Life Sciences, School of Optometry and Vision Science, Ramat Gan, Israel

[2] Bar Ilan University, Bar-Ilan Institute for Nanotechnology & Advanced Materials (BINA), Ramat Gan, Israel

[3] Bar Ilan University, Department of Chemistry, Ramat Gan, Israel

Abstract:

Carbon Nanotubes (CNTs) have been introduced as an efficient scaffold and interface in various biological applications due to their physical (mechanical and thermal) and electrical properties[1]. Their physical properties are known to influence stem cell proliferation and differentiation, and are therefore used as a scaffold for in vitro differentiation studies [2] and as scaffold for implantation in vivo [3]. Here we introduce our approach of utilizing CNTs as a scaffold for the differentiation of human embryonic stem cells (hESCs) into photoreceptor precursor cells (PRPs) and report preliminary results of the investigation of cell morphology and cell-surface interface and the effect of the CNT direction (aligned vs random-CNF) on the differentiation process (Figure 1).

Our results reveal that the substrate affected the migration of the cells from the embryoid bodies, and had no toxic effect on the differentiating cells. Interestingly, horizontally aligned CNT (HACNT) also affected the migration directionality and morphology of the differentiating cells.

Finally, we found that there was no significant effect of the various substrates on the differentiation toward PRP cells compared with the control substrate.

In summary, these results demonstrate the potential of these nanostructure to be used for the generation of new platforms that will allow the precise control of hESC differentiation by tuning the characteristics of their physical and chemical microenvironment.

Keywords: Carbon Nanotubes (CNTs), photoreceptor precursor, biomaterials.

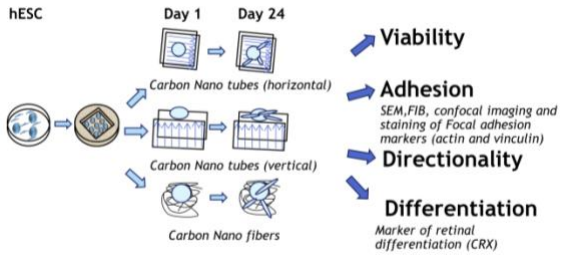


Figure 1. Schematic illustration of the study design for investigating the effect of nanostructure substrates, CNT (aligned) and CNF, on hESC differentiation towards PRPs. At the end of the differentiation process we studied viability, adhesion, directionality and differentiation markers.

References:

1. Zhu, Y., L. Wang, and C. Xu, "Carbon Nanotubes in Biomedicine and Biosensing," in *Carbon Nanotubes - Growth and Applications*, InTech, 2011.
2. Li, X. *et al.*, "The use of carbon nanotubes to induce osteogenic differentiation of human adipose-derived MSCs in vitro and ectopic bone formation in vivo," *Biomaterials*, vol. 33, no. 19, pp. 4818–4827, Jun. 2012.
3. Li, X. *et al.*, "The use of carbon nanotubes to induce osteogenic differentiation of human adipose-derived MSCs in vitro and ectopic bone formation in vivo," *Biomaterials*, vol. 33, no. 19, pp. 4818–4827, Jun. 2012.

Synthesis and preliminary biological evaluations of PSMA-targeted NIR upconverting nanoparticles for optical/scintigraphic imaging of prostate cancer

A. Cordonnier[1,2,*], D. Boyer[2], S. Besse[1], A. Briat[1], F. Degoul[1], R. Mahiou[2], A. Maisonial-Besset[1], B. Maunit[1], L. Mazuel[1], M. Quintana[1], M. Vivier[1], E. Miot-Noirault[1], J-M. Chezal,[1]

[1] Université Clermont Auvergne, INSERM, UMR 1240 IMoST, Clermont-Ferrand, France
[2] Université Clermont Auvergne, CNRS, SIGMA Clermont, UMR 6296 ICCF, Clermont-Ferrand, France

Abstract:
Over the last few years, upconversion nanoparticles (UCNPs) have been widely investigated in nanomedicine due to their high potential as imaging agents in the near infra-red optical window of biological samples and tissues. In this project, we develop and evaluate active targeted UCNPs for dual fluorescence and scintigraphy-guided surgery of PSMA-expressing prostate cancers.
The β-$NaYF_4$-based core-shell UCNPs co-doped with Yb^{3+} and Tm^{3+} ions were designed to provide a 800 nm emission upon excitation at 980 nm. A one-pot thermolysis synthesis was performed to obtain UCNPs with a mean diameter of 32±2 nm, confirmed by both DLS and TEM measurements.
Then, hydrophilization and surface functionalization of UCNPs were performed by a multi-step process. Several phosphate, bis and tetraphosphonate-based polyethylene glycol (PEG) ligands were synthesized and an exchange method was used to make UCNPs water-soluble. In order to select the optimal coating agent, the stability of the hydrophilized UCNPs was assessed by DLS in different media (water, NaCl 0.9%, PBS, culture media). An azide analogue of the most efficient PEG used for surface passivation was then synthesized in order to conjugate both PSMA targeting ligands (i.e. glutamate-urea-lysine derivatives called KuEs) and radiolabeled prosthetic groups to UCNPs by bio-orthogonal chemistry.
In competition binding assays in LNCaP cell lines, KuEs showed a good affinity towards their target, as well as fully functionalized KuE-UCNPs. These results were also confirmed by flow cytometry and confocal imaging using PSMA-negative (*i.e.* PC3) and PSMA positive (*i.e.* LNCaP) human prostate cancer cells. Intravenous injections of KuE-UCNPs in healthy mice were well tolerated (up to 1 mg *per* mouse) and allowed the detection of injected UCNPs *in vivo* using fluorescence optical imaging (see figure). These results encourage us to radiolabel and evaluate the biodistribution and optical/scintigraphic imaging potential of KuE-UCNPs in PSMA-expressing prostate cancer xenograft models.

Keywords: upconverting nanoparticles, prostate cancer, PSMA, bio-orthogonal chemistry, fluorescence imaging, scintigraphy.

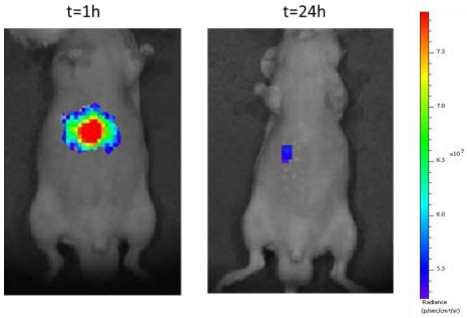


Figure : Images illustrating the up-conversion fluorescence in a healthy mouse after iv injection of KuE-UCNPs (centered on the liver, 1 mg) upon 980 nm laser excitation (laser power 300 mW/cm^2 at 1 h and 24 h post injection).

References:

1. Francolon, N., Boyer, D., Leccia, F., Jouberton, et *al.* (2016), Preparation of core/shell $NaYF_4$:Yb,Tm@dendrons nanoparticles with enhanced upconversion luminescence for *in vivo* imaging, *Nanomedicine*, 12, 2107-2113.
2. Shi, Y., Shi, B., Everest-Dass, A.V., Lu, Y., Sayyadi, N., Kautto, L., Willows, R.D., Chung, R., Piper, J., Nevalainen, H., Walsh, B., Jin, D., Packer, N.H. (2016), Stable upconversion nanohybrid particles for specific prostate cancer cell immunodetection, *Sci. Rep.*, 6, 37533.

A RATIONAL APPROACH TOWARDS BREAST CANCER TREATMENT

Eduardo Costa*[1,2], Catarina O. Silva[3], Miguel Cardoso[4], Pedro Faísca[5], Catarina Pinto Reis[6, 7], A. Silvério Cabrita[2], Isabel Vitória Figueiredo[1,8]

[1]Pharmacology and Pharmaceutical Care Laboratory, Faculty of Pharmacy – University of Coimbra, Coimbra;
[2]Experimental Pathology Service, Faculty of Medicine – University of Coimbra, Coimbra;
[3]Department of Biomedical Sciences, Faculty of Pharmacy, University of Alcalá, Ctra. A2 Km 33,600, Campus Universitario, 28871 Alcalá de Henares, Spain;
[4]Dentistry Area, Faculty of Medicine – University of Coimbra, Portugal;
[5]IGC, Portugal;
[6]iMed.ULisboa - Faculty of Pharmacy – University of Lisboa, Lisboa;
[7]IBEB, Faculty de Sciences, University of Lisboa, Lisboa;
[8]Coimbra Institute for Clinical and Biomedical Research (iCBR), Coimbra, Portugal
*e-mail: eduardo.leitao.costa@gmail.com

Abstract:
Breast cancer is a global public health issue mainly due it is one of the most frequently diagnosed malignancy in women in the Western world and commonest cause of cancer death. 7,12 Dimethylbenzanthracene (DMBA) is considered to be one of the ethiologic factors of malignant neoplasms in humans. DMBA is present in cigarette smoke, coal, burned wood, coal tar and gasoline and diesel engines. It has been assigned various toxicological, immunotoxic, mutagenic, teratogenic and carcinogenic effects.
Novel approaches aiming a targeted and more efficient breast tumors treatment are being developed. In the case of photothermal therapy, gold core nanoparticles (NPs) have shown great flexibility for obtaining multifunctional systems due to their plasmonic tunable properties and surface functionalization (1).
In the present study, efficiency and safety assessments of Epidermal Growth Factor (EGF) conjugated gold core NPs in breast tumors were performed.
Gold (III) chloride trihydrate was supplied from Sigma-Aldrich and EGF was purchased from Life Technologies. Gold core NPs were produced based on the modified seed-mediated growth (1,2). Mean particle size, polydispersity index (PI) and Zeta potential was measured with a Coulter Nanosizer Delsa NanoTMC (Fullerton, CA, USA).
Cell viability studies were conducted in human immortalized keratinocytes (HaCaT, Epplheim, Germany) using the MTT assay. EGF-conjugated gold core NPs were tested at different concentrations 0-80μM. Cells were exposed to NPs for 24h. After this period, the cells were incubated with MTT solution. DMSO was added to dissolve the formazan crystals and absorvance was read at 595nm (Thermo ScientificMultiskan Shanghai, China).
To conduct the *in vivo* preliminary assays, Sprague-Dawley female rats with 55-57 days of age were purchased from Charles-River laboratories and were orally administered by gavage of DMBA (65 mg/kg diluted in olive oil) for breast tumors induction. This protocol was approved by the competent national authority Direção-Geral de Alimentação e Veterinária (DGAV) and in accordance with the EU Directive (2010/63/UE) and Portuguese laws (DR 113/2013, 2880/2015 and 260/2016). Rats were randomly chosen to integrate the different treatment groups: 1) only laser exposure; 2) intra-tumoral injection of EGF-conjugated gold core NPs and 3) control group, i.e., with no manipulation. For histological evaluation, 24h after each treatment, animals were sacrificed according to animal welfare principles. Tumors and organs were excised, weighed and measured. Then, organs were fixed in 10% formalin, paraffin embedded, and cut into micrometer sections for hematoxylin-eosin staining.
As results, multifunctional NPs showed small size (<450nm) and PI<0.12. EGF-conjugated gold core NPs showed a maximum absorbance wavelength in the near infrared range (650-900nm) in contrast to commercial gold NPs.
Without laser irradiation, EGF-conjugated gold core NPs showed a cell viability of around 75% at the highest concentration 80μM.
Gold NPs treatment allowed a tumor reduction in volume and, in some cases, they showed very promising histopathological alterations.
Organs removed for analysis after necropsy showed no morphological changes of these tissues.
The study of molecular mechanisms on human breast cancer is still ongoing.

Keywords: Gold nanoparticles, Breast tumors, DMBA, Nanothecnology applications.

References:
1. Silva CO et al. Ther Deliv. 2016, 7(5) 287-304.

2. Silva CO et al. PLoS One. 2016, 11(10):e0165419.

Magnetic microparticles for magneto-mechanical treatment of glioblastoma cells

C. Thébault[1], C. Naud[1,2], E. Billiet[1], H. Joisten[1,4], M. Carrière[3], B. Dieny[1], Y. Hou[3,§], R. Morel[1, §]
1 Univ. Grenoble Alpes, CEA, CNRS, Grenoble INP*, IRIG-Spintec, 38000 Grenoble, France
2 Brain Tech Lab, UMR-1205, INSERM / UGA / CHU, F-38000 Grenoble, France
3 Uni. Grenoble Alpes, CEA, CNRS, INAC-SyMMES, 17 Rue des Martyrs, 38000 Grenoble, France
4 Univ. Grenoble Alpes, CEA, LETI, 38000 Grenoble, France
* Institute of Engineering Univ. Grenoble Alpes
§ These authors contributed equally to this work

Abstract:
In nanomedicine, treatments based on physical mechanisms are more and more investigated and are promising for challenging therapy of tumors. In particular, magnetic nanoparticles have been widely studied for imaging and for hyperthermia treatment, showing great potentials. Herein, we used a different strategy by inducing cell death via the vibration of anisotropic magnetic particles, triggered by a magnetic field rotating at a low frequency (about 20 Hz). Previous studies showed that this method may activate the cell apoptosis. [1,2]
We prepared anisotropic magnetite particles by liquid-phase ball milling of a magnetite powder. Then, they were functionalized by a 2-step silanization, the first one for obtaining an intermediate silica coating (Fe_3O_4@SiO_2), the second one for offering diverse physicochemical surface properties. Magnetic particles with different surface properties were studied to compare their influence on the treatment efficiency.
The intrinsic cytotoxicity of the particles with silica coating was evaluated *in vitro,* demonstrating a low toxicity on human glioblastoma U87-MG cells. The mechanical treatment was investigated *in vitro* on the U87-MG cells using magnetic particles with different surface properties to determine the optimum conditions of magnetic field application. For each type of particle, the viability was measured by LDH test to evaluate the membrane permeability and by WST-1 test to observe the metabolic activity of the cell. As shown in Figure 1, the efficiency of the magneto-mechanical treatment is highly dependent of the physicochemical surface properties of the magnetic particles. To further investigate the mechanism of the treatment, we studied the percentage of apoptotic cells after treatment, which showed also a dependence on the surface properties of particles.
To conclude, we validated *in vitro* the efficiency of the magneto-mechanical treatment of U87-MG cells with the functionlized magnetite particles.

Keywords: magnetic particle; mechanical treatment; rotating magnetic field; glioblastoma; cancer

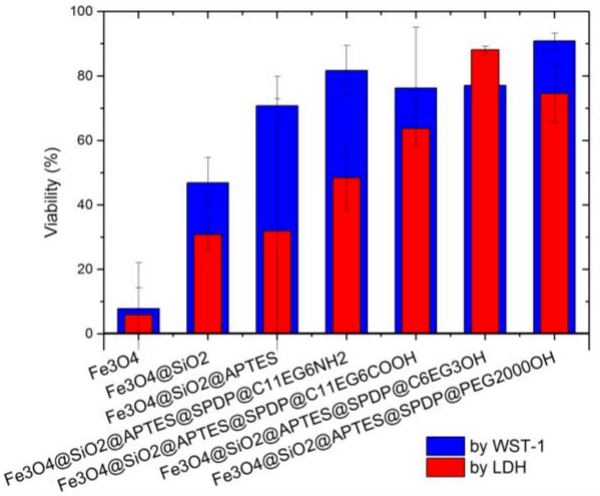


Figure 1: Percentage of viability of U87-MG cells with 50 mg/L of particles 18 h after a treatment of 40 min in a magnetic field rotating at 20 Hz. The viability was measured by WST-1 and LDH test.

References:

[1] Kim, D.H., Rozhkova, E.A., Ulasov, I. V., Bader, S.D., Rajh, T., Lesniak, M.S., Novosad, V. (2010) Biofunctionalized magnetic-vortex microdiscs for targeted cancer-cell destruction, *Nat. Mater.* 9, 165–171.
[2] Leulmi, S., Chauchet, X., Morcrette, M., Ortiz, G., Joisten, H., Sabon, P., Livache, T., Hou Y., Carrière, M., Lequien, S., Dieny, B. (2015) Triggering the apoptosis

of targeted human renal cancer cells by the vibration of anisotropic magnetic particles attached to the cell membrane, *Nanoscale*, 7, 15904–15914.

Active Pulmonary Targeting against Tuberculosis (TB) via Triple–Encapsulation of Q203, Bedaquiline and SPIOs in Nanoparticle Aggregates

Wilson POH[a], Nurlilah AB RAHMAN[b], Yan OSTROVSKI[c], Josué SZNITMAN[c], Kevin PETHE[b], Say Chye Joachim LOO[a,d*]

[a]School of Material Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798.
[b]Lee Kong Chian School of Medicine and School of Biological Sciences, Nanyang Technological University, 59 Nanyang Dr, Singapore 636921.
[c]Department of Biomedical Engineering, Technion, Israel Institute of Technology, 32000 Haifa, Israel.
[d]Singapore Centre for Environmental Life Sciences Engineering (SCELSE), Nanyang Technological University, 60 Nanyang Drive, Singapore 637551.

Abstract:
Tuberculosis (TB) has gained attention over the past few decades by becoming one of the top ten leading causes of death worldwide. This infectious disease of the lungs is orally treated with a medicinal armamentarium. However, this route of administration passes through the body's first-pass metabolism which reduces the drugs' bioavailability and taxes the liver and kidneys. Inhalation therapy represents an alternative to the oral route, but low deposition efficiencies of delivery devices such as nebulizers and dry powder inhalers render it challenging as a favourable therapy. It is hypothesized that by encapsulating two potent TB-agents, i.e. Q203 and Bedaquiline, that inhibit the oxidative phosphorylation of the bacteria together with a magnetic targeting component, Superparamagnetic Iron Oxides (SPIOs), into a PDLG carrier using a single emulsion technique, the treatment of TB can be a better therapeutic alternative. This simple fabrication method achieved a homogenous distribution of 500 nm particles with a magnetic saturation of 28 emu/g. Such particles are shown to be magnetically susceptible in an *in-vitro* assessment, viable against A549 epithelial cells, and are able to reduce two log bacteria counts of the BCG organism. Furthermore, through the use of an external magnet, our *in-silico* Computational Fluid Dynamics (CFD) simulations support the notion of yielding 100% deposition in the deep lungs. Our proposed inhalation therapy circumvents challenges related to oral and respiratory treatments and embodies a highly favourable new treatment regime.

Keywords: Tuberculosis, Pulmonary Delivery, Magnetic Targeting, Superparamagnetic Iron Oxides, PDLG, Q203, Bedaquiline

References:

1. M. M. Mehanna, S. M. Mohyeldin, and N. A. Elgindy, "Respirable nanocarriers as a promising strategy for antitubercular drug delivery," *Journal of Controlled Release,* vol. 187, pp. 183-197, 2014.
2. W. H. Organization, *Global tuberculosis report 2018*: World Health Organization, 2018.
3. K. Hirota, T. Hasegawa, H. Hinata, F. Ito, H. Inagawa, C. Kochi, *et al.*, "Optimum conditions for efficient phagocytosis of rifampicin-loaded PLGA microspheres by alveolar macrophages," *Journal of controlled release,* vol. 119, pp. 69-76, 2007.
4. D.-D. Pham, E. Fattal, and N. Tsapis, "Pulmonary drug delivery systems for tuberculosis treatment," *International journal of pharmaceutics,* vol. 478, pp. 517-529, 2015.

Novel Strategies Towards Surface Modification of Polymeric Biomedical Devices Based on Nylon 6 and Polycaprolactone

S. Swar[1], V. Máková[2]*, B. Holubová[2], P. Šubrtová[1] and J. Horáková[3]

[1]Institute for Nanomaterials, Advanced Technologies and Innovation, Technical University of Liberec, Czech Republic
[2]Department of Chemistry, Faculty of Science, Humanities and Education, Technical University of Liberec
[3]Department of Nonwovens and Nanofibrous Materials, Faculty of Textile, Technical University of Liberec

Abstract:
With the aid of surface chemistry, the modern biomedical polymer devices may be made biocompatible, non-cytotoxic, antibacterial and resistant to pathogenic bacteria. Hence, a proper choice of surface modification of polymeric nanomaterials used in various biomedicine applications gained nowadays a very close attention. Further modification of polymeric surface by introducing specific functional groups may improve performance of polymeric implants or implant devices as half of all nosocomial infections are now device related.[1]
Newly developed man-made synthetic polymers like polyamides or polyesters rapidly entered medical application field already during the second half of the 20th century. The biomedical applications include suture material, wound dressing, catheters, bone tissue scaffolds and dialysis membranes. But the modification of their surface is crucial as a bare polymers represent a high risk for patients (i.e.: thrombogenesis etc.).
In our study, the chemical method was used to modify the surface of one polyamide (Nylon 6) and one polyester (polycaprolactone (PCL)) material in order to create a resistant surface against the formation of a harmful biofilm caused by pathogenic bacteria. On Nylon 6 surface, the amide functional groups were successfully converted into secondary amine. Modified Nylon 6 has been found to be antibacterial particularly due to the presence of hydrophilic poly(ethylene glycol) methyl ether (H_3C-PEG) chains, and moreover, due to the subsequent physical deposition of copper nanoparticles among the PEG chains (Figure 1).[2] In the second case, tannin coating on PCL (polycaprolactone) nanofibrous membrane was applied and the antibacterial tests focused on the gram negative bacterial strain confirmed the significant effect on the bacterial adhesion to the modified surface as well.

Keywords: nylon 6, polycaprolactone, functionalisation, pathogenic bacteria, staphylococcus aureus, pseudomonas aeruginosa

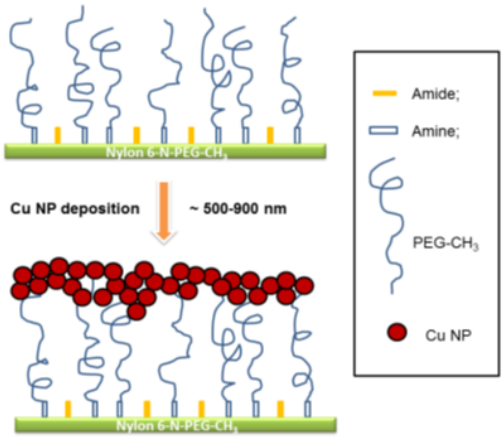


Figure 1: The conversion of Nylon 6 into Nylon 6-NH, followed by grafting on Nylon 6-NH via H_3C-PEG-OTs and Cu NPs to form Nylon 6-N-PEG-CH_3-Cu.

References:

1. Maitz, M.F. (2015) Applications of synthetic polymers in clinical medicine, *Biosurface and Biotribology*, 1, 161–176.

2. Swar, S., Zajícová V., Mullerova, J., et al. (2018) Effective poly(ethylene glycol) methyl ether grafting technique onto Nylon 6 surface to achieve resistance against pathogenic bacteria Staphylococcus aureus and Pseudomonas aeruginosa *J. Mater. Sci.* 53(20), 14104-14120.

Characterization and Modeling of Local Electronic Properties of Native Bone Tissue in Intact and Damaged Areas

A.A. Pavlychev[1*], X.O. Brykalova[1], D.O. Samoilenko[1]

[1] St.Petetersburg State University, Department of Physics, Peterhof, Saint Petersburg, RF

Abstract:
Hierarchical organization in life science is extended from atoms to ecological spheres. This organization is regarded as a platform for application of various physical and chemical models to scientific research in diseases and body functions [1]. Applying quantum mechanics to study chronobiological and osteochondral processes as well as for diagnosis of native bone in subcellular levels we encounter with great difficulties because the major morphological models are mainly developed for qualitative description of structure-functional organization of the skeleton whereas quantitative characterizations of bone tissue in nanoscale are poorly investigated. Development at the beginning of ex- and then in-vivo quantitative approaches to hierarchical nanostructures in combination with the novel 3D superlattice of "black-nanoboxes-in-muddy-waters" (3DSL) model [2] is a pathway in medical, material and life sciences. In addition to changes in elemental composition the 3DSL model takes into account both the structure-functional organization of the skeleton and the peculiarities of electron wave propagation through the 3D superlattice assembled from nanocrystallites of hydroxyapatite (HAP) $Ca_{10}(PO_4)_6(OH)_2$ (see, Figure 1).

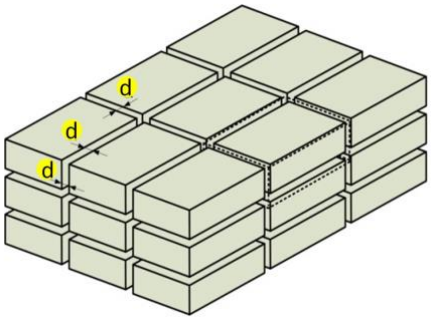


Figure 1: Figure illustrating the coplanar assembling of HAP-nanocrystallites separated by the hydrated nanolayers with the thickness ***d***.

Distinct HAP-to-bone spectral changes in core-to-valence transitions are predicted and confirmed by the recent X-ray absorption spectra-scopic measurements of young, adult and mature bone and HAP [2]. The 3DSL approach is applied to model the thermal and age related changes in electronic and atomic structure of mineralized bone.

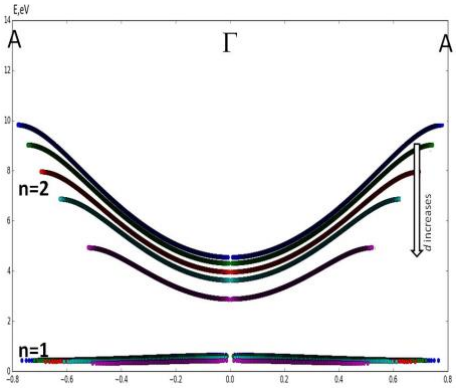


Figure 2: Figure presents model changes in dispersion $E(k)$ of band energy in the superlattice as a function of ***d***. Heine equation:

$$e^{2ikr} - 2Re[T^{-1}(E, \langle d \rangle, \langle L \rangle)]e^{2ikr} + 1 = 0$$

is used to model the band dispersion and to assign the certain energy E with the electron wave number k. T is the amplitude of electron transmission through the cell of the superlattice and $\langle d \rangle$ and $\langle L \rangle$ are the mean sizes of the hydrated nanolayers and nanocrystallites.

Keywords: hierarchical organization, bone tissue, superlattice, electronic and atomic structure

References:

1. Pumain D., Hierarchy in Natural and Social Sciences, (2006) New York, New York: Springer-Verlag
2. Pavlychev A.A. *et al.* (2016) Local electronic structure and nanolevel hierarchical organization of bone tissue: theory and NEXAFS study, *Nanotechnology*, 27, 504002-1-8
3. Konashuk A.S. *et al.* (2018) Thermal changes in young and mature bone nanostructure probed with Ca 2p excitations, *BPEX*, 4 035031

SMS 2019 - Session III: Novel Materials Biomaterials Properties and Applications

Challenges and opportunities for x-ray spectro-microscopies in magnetism and spintronics

P. Fischer[1,2,*]

[1] Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA, USA
[2]Physics Department, University of California, Santa Cruz, CA, USA

Abstract:
Nanomagnetism research aims to understand and control magnetic properties and behavior on the nanoscale through proximity and confinement. Recently, there has been a shift in focus to emerging phenomena occurring on mesoscopic scales. New avenues to control magnetic materials open up through enhanced complexity and new functionalities, which can impact the speed, size and energy efficiency of spin driven applications in spintronics.

Advanced characterization tools that provide magnetic sensitivity to spin textures at high spatial resolution, ultimately at buried interfaces and in all three dimensions [1], and at high temporal resolution to capture the spin dynamics across scales, are therefore of large scientific interest.

Magnetic soft X-ray spectro-microscopies [2] provide unique characterization opportunities to study the statics and dynamics of spin textures in magnetic materials combining X-ray magnetic circular dichroism (X-MCD) as element specific, quantifiable magnetic contrast mechanism with spatial and temporal resolutions down to fundamental magnetic length, time, and energy scales.

Current developments of x-ray sources aim to increase dramatically the coherence of x-rays opening the path to new techniques, such as ptychography [3] or x-ray photo-correlation spectroscopy (XPCS) [4] that allow unprecedented studies of nanoscale heterogeneity, complexity, and fluctuations.

I will review recent achievements and future opportunities with magnetic x-ray spectro-microscopies. Examples will include the static properties and dynamic behavior of magnetic skyrmions [5,6] textures with potential application to novel magnetic logic and storage devices, as well as results from an XPCS study at LCLS with a novel 2-pulse scheme that allowed to discover an unexpected and drastic change of the correlation times in nanoscale spin fluctuations near phase boundaries, i.e., in the skyrmion phase, and near the boundary with the stripe phase of a multilayered Fe/Gd system [4]. Finally, I will present a study on ferromagnetic liquid droplets, which could establish a complete paradigm shift in magnetic materials, that combine characteristics of liquid, such as reconfigurability and short range spatial and temporal correlations with ferromagnetism, which so far has been confined to condensed matter [7].

Acknowledgement: This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division Contract No. DE-AC02-05-CH1123 in the Non-Equilibrium Magnetic Materials Program (MSMAG)

Keywords: X-ray magnetic circular dichroism, magnetic x-ray spectromicroscopy, spin dynamics, chiral spin textures.

References:

1. A. Fernandez-Pacheco, et al., Nature Comm 8 15756 (2017)
2. P. Fischer and H. Ohldag, Report on Progress in Physics 78 094501 (2015)
3. X. Shi, et al, Appl Phys Letter 108, 094103 (2016)
4. M. H. Seaberg, et al, Phys Rev Lett 119 067403 (2017)
5. S. Woo, et al., Nature Materials 15 501 (2016)
6. N. Kent et al, Appl Phys Lett (2019) under review
7. X. Liu et al, Science Science 365 264 (2019)

From the Atomic Structure to the Optoelectronic Properties Studies of Carbon and Related Nanostructures via TEM

R. Arenal[1,2,3,*]

[1] Laboratorio Microscopias Avanzadas, INA, U. Zaragoza, 50018 Zaragoza – Spain
[2] Fundacion ARAID, 50018 Zaragoza – Spain
[3] Instituto de Ciencias de Materiales de Aragon, CSIC-U. Zaragoza, 50009 Zaragoza – Spain

Abstract:
The recent advances in transmission electron microscopes (TEM) bring access to electron probes of one angstrom within energy resolutions of <100 meV even working at low acceleration voltages (40-80 kV) [1-2]. These performances offer new possibilities for probing the optical, dielectric and electronic properties of nanomaterials with unprecedented spatial information, as well as for studying the atomic configuration of nanostructures [1-15]. In this contribution, I will present a selection of recent works involving all these matters. These works will concern the study of the atomic structure & configuration of 1D and 2D atomically thin nanostructures (including nanotubes & graphene/graphene-like materials, nanodiamonds in pristine and hybrid forms) as well as the opto-electronic properties studies carried out via EELS measurements [2-15]. These works will illustrate the excellent capabilities offered by the use of a Cs probe-corrected (S)TEM, combined with the use of a monochromator, to study these properties within a very good spatial resolution. In summary, these studies elucidate critical questions concerning the local chemistry and the structure of these materials. This detailed knowledge is essential for better understanding the outstanding properties of such nano-structures.

Keywords: 1D-2D nanomaterials, transmission electron microscopy, plasmonic nanostructures, HR(S)TEM, EELS, electron tomography.

References:

1. "Advanced Transmission Electron Microscopy: Applications to Nanomaterials", Eds. L. Francis, A. Mayoral and R. Arenal. Springer (2015).
2. M. Serra, R. Arenal, R. Tenne, Nanoscale 11, 8073-8090 (2019).
3. R. Arenal, L. Henrard, L. Roiban, et al., J. Phys. Chem. C 118, 25643–25650 (2014).
4. P. Torruella, R. Arenal, F. de la Peña, et al., Nano Lett. (2016).
5. R. Canton-Vitoria, Y. Ahmed, M. Pelaez-Fernandez, R. Arenal, C. Bittenrcourt, C.P. Ewels, N. Tagmatarchis, NPJ 2D Materials and Applications (2017).
6. H.Y. Feng, F. Luo, R. Arenal, F. Garcia, G. Armelles, A. Cebollada, Nanoscale 9, 37 (2017).
7. L. Lajaunie, C. Padannaud, C. Martin, P. Puech, C. Hu, M.J. Biggs, R. Arenal, Carbon 112, 149-161 (2017).
8. L. Liu, U. Diaz, R. Arenal, G. Agostini, P. Concepcion, A. Corma, Nature Materials 16 (2017).
9. L. Liu, D. Zakharov, R. Arenal, et al., Nat Comm., (2018).
10. L. Lajaunie, G. Radovsky, R. Tenne, R. Arenal, Inorganic Chemistry (2018).
11. L. Lajaunie, A. Ramasubramaniam, L. Panchakarla, R. Arenal, Appl. Phys. Lett. 113, 031102 (2018).
12. R. Arenal, Microscopy and Microanalysis 23 (S1), 2274-2275 (2017).
13. L. Vallan, R. Canton-Vitoria, H. Gobeze, Y. Jang, R. Arenal, A. Benito, W. Maser, F. D'Souza, N. Tagmatarchis, J. Amer. Chem. Soc., 140, 13488-13496 (2018).
14. R. Arenal, et al. to be submitted.
15. Research supported by the Spanish MINECO (MAT2016-79776-P, AEI/FEDER, EU), Government of Aragon through project DGA E13_17R (FEDER, EU) and European Union H2020 programs "Graphene Flagship" (785219), "ESTEEM3" (823717) and Flag-ERA GATES (JTC 2017).

Mussel-inspired injectable hydrogel glue for Tissue Repair

Kongchang Wei,[1,*] Berna Senturk,[2] Martin T. Matter,[3,4,5] Xi Wu,[6] Inge Katrin Herrmann,[3,4] Markus Rottmar,[2] Claudio Toncelli[1]

[1]Laboratory for Biomimetic Membranes and Textiles, [2]Laboratory for Biointerfaces, [3]Laboratory for Particles-Biology Interactions, Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland;
[4]Nanoparticle Systems Engineering Laboratory, Department of Mechanical and Process Engineering, [5]Particle Technology Laboratory, Institute of Process Engineering, Department of Mechanical and Process Engineering, ETH Zurich, Sonneggstrasse 3, 8092 Zurich, Switzerland; [6]Institute for Mechanical Systems, ETH Zürich, Leonhardstrasse 21, 8092 Zürich Switzerland.
* Wei, K. kongchang.wei@empa.ch

Abstract:
Injectable hydrogels are desirable biomaterials with great potential in many biomedical appli-cations, especially in regenerative medicine that usually requires targeted delivery of therapeu-tic agents such as drugs, bioactive proteins and living cells for tissue repair. However, a low retention ratio of the delivered therapeutic agents at the targeted locations often leads to poor outcomes of such applications. To improve the efficacy of the delivered therapeutic agents, injectable hydrogel glues that can prevent early leakage and post-gelation loss of the delivered therapeutic agents are in acute demand. An ideal injectable hydrogel glue for this purpose should have a com-bined material properties, including but not limited to: 1) cytocompatible but fast gelating mechanism; 2) proper mechanical property close to the targeted tissues; 3) appreciable adhe-siveness to both tissues and cells; 4) cell-instructive degradability that allows the delivered cells to function properly. However, it is still challenging to integrate all these material proper-ties into one injectable hydrogel. Herein we report the development of a bio-inspired injectable hydrogel glue that meets this requirement. Inspired by the excellent wet adhesion of mussels where different mussel foot proteins (Mfps) function cooperatively, gelatin biopolymer (Gel) was molecularly engineered with thiourea-catechol (TU-Cat) groups to mimic Mfps and their gelating pathway. The molecularly engineered gelatin biopolymers (Gel-TU-Cat) obtain the collective new properties that do not exist in the parental polymer. The injectable hydrogel glue could be a promising platform for many biomedical applications including tissue repair.

Keywords: bioinspired materials, injectable hydrogels, tissue glue; tissue repair, biomedical applications.

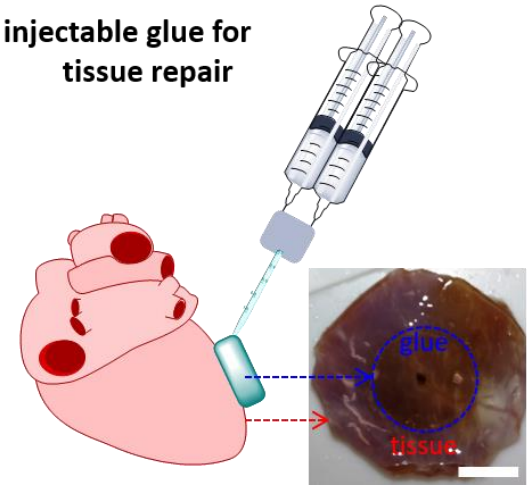


Figure 1: Figure illustrating the the application of the injectable hydrogel glue to a porcine pericardium tissue surface (scale bar: 10 mm).

References:

1. Ko, D. Y.; Shinde, U. P.; Yeon, B.; Jeong, B. (2013) Recent progress of in situ formed gels for biomedical applications. *Progress in Polymer Science*, 38 (3-4), 672-701.
2. Zhu, W. Z.; Chuah, Y. J.; Wang, D. A. (2018) Bioadhesives for internal medical applications: A review. *Acta Biomaterialia*, 74, 1-16.
3. Brubaker, C. E.; Messersmith, P. B. (2011) Enzymatically Degradable Mussel-Inspired Adhesive Hydrogel. *Biomacromolecules* **2011,** *12* (12), 4326-4334.
4. Lu, M.; Yu, J. S. (2018) Mussel-Inspired Biomaterials for Cell and Tissue Engineering. *Novel Biomaterials for Regenerative Medicine*, 1077, 451-474.
5. Xu, Y. J.; Wei, K.; Zhao, P.; Feng, Q.; Choi, C. K. K.; Bian, L. (2016) Preserving the adhesion of catechol-conjugated hydrogels by thiourea-quinone coupling. *Biomaterials Science*, 4 (12), 1726-1730.

Ca 2p Photoelectron Spectroscopy of Surfaces of Cortex and Subchondral Femoral Bone in Intact and Damaged Areas

X.O. Brykalova[1], N.N. Kornilov[2] , A.A. Pavlychev[1*]

[1] St.Petersburg State University, Department of Physics, Peterhof, Saint Petersburg, RF
[2] Vreden Russian Research Institute of Traumatology and Orthopedics, Saint Petersburg, RF

Abstract:
Bone is one of the most complicated hierarchically organized nanostructured material in nature. Material science, biological and medical research discloses the complex hierarchy of the skeleton designs from macro- to nanolevels. Specifically, nanolevel studies of bones encounter great difficulty mainly because electronic and atomic structure as well as molecular architecture of their nanoblocks are not fully understood. This gap prevents from successful solution of many fundamental and clinically relevant problems such as the development of new methods of medical imaging at subcellular levels and medical diagnosis of skeletal pathology at early stage too. X-ray absorption spectroscopy, as it was shown [1], provides a sensitive evaluation of relationships between hierarchical organization of bone and its local electronic and atomic structure. In this study we used X-ray photoelectron spectroscopy to investigate surface of cortex and subchondral bone in intact and degeneratively damaged by osteoarthritis areas. The tibia cortex medial and lateral condyles of the femur resected during total knee arthroplasty in patients with medial compartmental knee osteoarthritis were used as samples. Their preparation is discussed [2]. Table 1 demonstrates the spectroscopic characteristics such as the Ca $2p_{1/2}$ binding energy (BE) and full-width-half-maximum (FWHM), measured for the samples from their proximal sides of rat cortex and femur bone cuts. The characteristics of the distal side surface of the cuts are also examined. The difference between the Ca^{2+} surface states of healthy and arthritic areas is revealed. It is discussed within the 3DSL model [1]. Perspectives for development of novel methods of medical imaging of the subhondral bone at the subcellular level are discussed too.

Keywords: bone tissue, hierarchical nanostructures, photoelectron spectroscopy, knee joint, subchondral bone, surface states, osteoarthritis.

Phase	Ca 2p½ BE/eV	FWHM/eV
Hydroxyapatite	350.75	1.6
Cortex (mature rat)	350.65	1.8
Subchondral, intact area, sample 1	350.55	2.2
Subchondral, sclerotic area, sample 2,	A-comp 350.55 B-comp 350.05 C-comp 351.95	1.9 2.0 2.0
Subchondral, intact area, sample 2	350.45	1.7
Subchondral, Sclerotic area, sample 2.	A-comp 350.45 B-comp 350.05	1.6 1.6

Table 1: The spectroscopic parameters of the Ca 2p½-1 surface states of cortex and damaged (sclerotic) and healthy areas of femoral condyles in knee osteoarthritis patient. The error of the measured data is ±1% or ±0.1 eV, respectively.

Acknowledgements:
The experiments were carried out with the support of the SPbSU Resource Centers "Centre for Physical Methods of Surface Investigation" and "Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics". This work is supported by RFBR grant 19-02-00891.

Reference:

1. Pavlychev A.A. *et al*. (2016) Local electronic structure and nanolevel hierarchical organization of bone tissue: theory and NEXAFS study, *Nanotechnology*, 27, 504002-1-8
2. Brykalova X.O. *et al.* (2019) Electronic and atomic structure of femoral bone in intact and osteoarthritic damaged knee compartments, *Eur. Phys. J. D*. 73: 113

A new design of a petal valve designed for pulsatile heart assist pumps application, presents and future development

Roman Major[1], Maciej Gawlikowski[2], Aldona Mzyk[1], Sachiro Kakinoki[3] Juergen M. Lackner[4]

[1] Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Reymonta St. 25, Cracow, Poland.
[2] Heart Prosthesis Institute, Artificial Heart Laboratory, Wolnosci 345A, 41-800 Zabrze, Poland.
[3] Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering Kansai University 3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan
[4] Joanneum Research Forschungs-GmbH, Materials – Functional Surfaces, Leoben, Austria

Abstract:
The work concerns biocompatibility tests of material used for manufacturing new design of petal valve intended for pulsatile blood pumps. Numerous variants of biomaterial which differ from one another in technology of manufacturing have been developed. The PVD and PECVD technology has been utilized in order to coat the titanium-based substrate by hydrogenated tetrahedral amorphous carbon (ta-C:H) as well as amorphous hydrogenated carbon (a-C:H and a-C:H:N). The indentation test and tests have been conducted in order to assess the mechanical features of material. For all variants of material the hemocompatibility examination have been performed.
Experiments were carried out on whole human blood under arterial shear stress conditions in cone-plate type analyzer (ap. 1800 1/s). Platelets activation have been investigated by means of determination the ratio of p-selectin positive cells (CD-62P monoclonal antibody) and fibrinogen active binding (PAC-1) to the total amount of platelets, marked by CD-61 monoclonal antibody. According to P-selectin activation analysis, most coatings had little effect on activation processes, without using the platelets that remained in the blood.
In most cases, the tested coatings showed good or very good haemopoietic properties. The tested materials did not cause blood hemolysis under shear conditions in direct contact with blood. In terms of activation, the risk of aggregation and the impact of generating microparticles of apoptotic origin, the coatings type a-C: H: N proved to be the best. Materials of this type also showed very good mechanical properties. These coatings have been selected for in vivo studies.
For best prognostic materials the in-vivo animal trials have been carried out according to ISO 10993 standard. Intradermal reactivity have been assessed on 3 rabbits. Examination of sub-acute toxicity and local effects after implantation have been performed on 12 rabbits. In one case the minor general health problem of animal appeared (glomerulopathy not related to the experiment). After requires period of observation no organ failure as well as wound tissue damage have been recognized in post-mortem examination. However in the first week after implantation slight inflammatory changes were found at the wound related to the implant. Summarizing – performed investigation demonstrated high biocompatibility of tested biomaterial with reference to thrombogenicity, toxicity and influence of wound tissue. Prototypes of petal valves have been manufactured, mounted as a parts of pulsating blood pumps and examined on blood in order to assess their hydrodynamic features and impact on red blood cells (hemolysis) as well as coagulation system (systemic thrombogenicity).

ACKNOWLEGEMENT:
The research was financially supported by the Project no. DZP/M-ERA.NET-2014/291/2015 “Nonthrombogenic metal-polymer composites with adaptable micro and macro flexibility for the next generation heart valves in artificial heart devices” of the Polish National Centre of Research and Development. The preliminary work dealing with the future perspectives financially supported by the Project no. DWM/M-ERA.NET-2017/16/2018 “4 Dimensional Single Piece Miniaturized Blood Rotor” of the Polish National Centre of Research and Development.

Advanced micromanufacturing strategies for the production of biomimetic and bioresorbable vascular stents and peripheral nerve implants

I.Quintana, R.Ortiz, X.Mendibil, R.Diez, S.Merino[1]

[1] IK4-TEKNIKER, Eibar, Spain

Abstract:
In this work, advanced micromanufacturing strategies including surface micropatterning, microextrusion and micromoulding are presented for the production of biomimetic tubular implantable devices. Such strategies were demonstrated using novel bioresorbable materials and considering two medical applications: The development of Bioresorbable Vascular Stents (BVS) with enhanced biocompatibility and Peripheral Nerve Implants (nerve guidance conduits: NGCs) mimicking the native tissue architecture.
Biocompatibility enhacenment in terms of endothelialization potential and hemocompatibility is considered one of the main challenge to face in **BVS development**. In this work we consider a laser ablation technology as a high-throughput manufacturing method for surface micropatterning and cutting of a bioresorbable polymer used in stent production (PEGylated PLLA).The technology is applied to generate parallel microgrooves with varying geometries, which significantly enhanced human cardiac microvascular endothelial cell (HCMEC) adhesion and orientation, in comparation to smooth, non-patterned surfaces. This results demonstrate that a biomimetic interface can be produced, emulating in some extent the effects that the blood flow has *in vivo*.
Implantable nerve guidance conduits offer a promising alternative to conventional treatments for post-traumatic peripheral nerve repair, supporting and guiding the axons during their growth. Fundamental requirements for effective nerve tissue regeneration demands a biomimetic tubular scaffold that should be biocompatible, biodegradable and flexible. Additionally, inner microstructures are desired to mimic the guiding basal lamina microchannels in nerve autografts. We develop a novel biomimetic nerve implant paying special attention to device structure, biomaterials and their combination with high-throughput manufacturing methods, overcoming the current limitations of commercially available hollow tubes. Poly(ε-caprolactone) biomaterial was considered in combination with microextrusion and micromoulding for the external porous tubular scaffold and microchanneled inner structure fabrication, respectively. Those technologies allow us to manufacture NGCs where inner diameter and wall thickness can be tuned as well as microchannel dimensions and density. Nerve regeneration enhancement was demonstrated by considering those approaches, showing the presence of Schwann cells, myelinated regenerated axons and fibrin protein inside the microchannels.

Keywords: bio-resorbable tubular scaffolds, surface patterning, microextrusion, endothelialization, peripheral nerve regeneration.

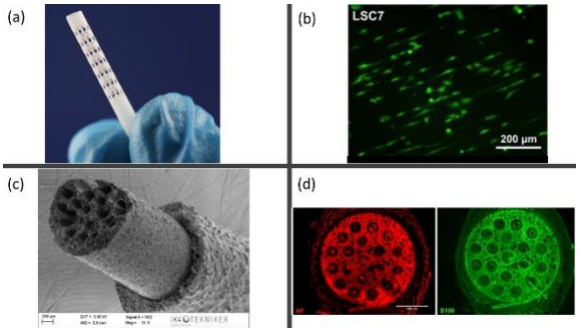


Figure 1: (a) BVS produced in this work. (b) HCMECs 24 h after seeding onto micropatterned surface and stained using live/dead staining. (c) Porous NGC produced in this work. (d) Myelinated regenerated Axons (red) and Schwann cells (green) on the inner part of the tubular device

References:

1. S. Pacharra, R. Ortiz, S. McMahon, W. Wang, R. Viegahn, J. Salver, **I. Quintana**. Surface patterning of a novel PEG-functionalizaed poly-L-lactide polymer to improve its biocompatibility: Applications to bioresorbable vascular stents. *J Biomed Mater Res Part B* 2019:107B:624-634.
2. S.Merino, **I. Quintana**, et al., Implantable nerve guidance conduit for nerve repair. PCT/EP2018/054984.

EGF 2019 / NanoMed 2019
Joint Session III

Graphene and graphene/drug conjugates for cancer phototherapy

D. Bogas[1,*], R. Costa-Almeida[2,3,*], C. Couto[1], J.R. Fernandes[4], M.C.L. Martins[2,3], I.C. Gonçalves[2,3], F.D. Magalhães[1,*], A.M. Pinto[1,2,3,*] (*- equal contribution)

[1]LEPABE, Faculdade de Engenharia, Universidade do Porto, Porto, Portugal; [2]i3S - Instituto de Investigação e Inovação em Saúde, Universidade do Porto, Portugal; [3]INEB - Instituto de Engenharia Biomédica, Universidade do Porto, Rua Alfredo Allen, 208, 4200-180 Porto, Portugal; [4]CQVR – Centro de Química Vila Real, Universidade de Trás-os-Montes e Alto Douro, Portugal.

Abstract:
Basal cell carcinoma (BCC) is the most common form of human cancer, and its clinical management usually involves surgical treatment. However, several nonsurgical alternatives can be employed, as topical therapy, radiation therapy or photodynamic therapy (PDT).[1] Despite PDT being well described on management guidelines and literature, photothermal therapy (PTT), which can be applied as an effective non-invasive strategy, needs to be further studied. Near-infrared (NIR) light energy can be used to induce mild temperature increases (43-50 °C), that can lead to tumor cells apoptosis. Graphene-based materials (GBMs) are able to absorb radiation and possess large surface area. Both features can be explored for synergetic biologic and drug release hyperthermia triggered effects.[2] In this study, we propose the use of GBMs and GBMs loaded with an anti-cancer drug, as platforms for PTT treatment of BCC. For this purpose, GO was produced through the modified Hummer's method,[3] and further sonicated and centrifuged to obtain nano-sized GO (GOn). GOn was thermally reduced and functionalized with poly(ethylene) glycol (PEG) to obtain stable aqueous dispersions (rGOn-PEG).[4] Particle size was determined by transmission electron microscopy and dynamic light scattering. Surface charge was measured using a zetasizer. Oxidation degree was characterized by X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR). GOn and rGOn-PEG (0.125 mg mL^{-1}) were sonicated for 30 min and mixed with 5-FU dispersions (0.25-5 mg mL^{-1}), in water (RT). Aliquots were collected from 0 min to 72h, centrifuged (13000 rpm), and the difference in free 5-FU quantified by measuring its absorbance (265 nm). GBMs and drug absorbance spectra (200-850 nm) were obtained using a UV-Vis spectrophotometer. GBMs water dispersions were irradiated with a custom-built LED based light source with peak emission at 812.8 nm, FWHM of 29.9 nm, and irradiance of 150 mW cm^{-2}. The temperature increase was recorded using a K-type thermocouple. GOn was obtained with mean lateral dimensions of 248 nm (size range: 50-250 nm). GOn dispersion showed colloidal stability with zeta potential values around -50 mV (neutral pH). XPS analysis revealed that GOn O at.% was 28.5%, also a typical FTIR spectra was obtained, confirming that desired chemical functionalities were obtained. GOn reduction was confirmed by a redshift in the characteristic absorbance peak. Maximum drug loading efficiency was achieved almost immediately after mixing GBMs with 5-FU, regardless of concentrations tested. Drug loading efficiency (5 mg mL^{-1} 5-FU) at rGOn-PEG was 129 %, while for GOn it was about 4-times higher. This can be explained by favorable interaction between GOn oxygen-containing groups and hydrophilic 5-FU, and also by PEG hinderance of drug adsorption. NIR irradiation increased rGOn-PEG temperature with time, with an increase of 11.7 °C compared to GOn being obtained at the end of 30 min. The maximum temperature measured for rGOn-PEG was of 47 °C, which is within temperature ranges of hyperthermia. For that reason, this study opens new avenues for the development of GBM-based platforms for transcutaneous drug delivery and PTT of skin cancer.

Keywords: graphene-based materials, phototherapy, cancer therapy, drug delivery.

References:

1. Kim, J., *et al.* (2018), *J Am Acad Dermatol*, 78, 540-559;
2. Zhang, B., *et al.* (2017), *Curr Med Chem*, 24, 268-291;
3. Pinto, A.M., *et al.* (2015) *Carbon*, 2015, 99, 318-329;
4. Chen, J., *et al.* (2014) *Biomaterials*, 35, 4986-4995.

Acknowledgements: This work was financed by FEDER - Fundo Europeu de

Desenvolvimento Regional funds through the COMPETE 2020 - Operacional Programme for Competitiveness and Internationalisation (POCI), Portugal 2020, and by Portuguese funds through FCT/MCTES in the framework of the project NovaDerma POCI-01-0145-FEDER-031143; PTDC/BTM-MAT/31143/2017, and Unidade de Investigação UID/EQU/00511/2019 - Laboratório de Engenharia de Processos, Ambiente, Biotecnologia e Energia – LEPABE.

Graphene Quantum Dots for Multiphoton Imaging: Myths and Facts

E. Maçôas,[1*] C. Santos,[1,2] C. Correia,[1] I. Mariz,[1] S. Pinto, and J. G. Martinho[1]

[1] Institute of Nanosciences and Nanotechnology (IN), Centro de Química Estrutural (CQE), Institute of Bioengineering and Bioscience (IBB) of Instituto Superior Técnico
[2] QOPNA, Chemistry Department, University of Aveiro

Abstract:
Molecular materials with efficient nonlinear absorption have found application in imaging and sensing in biological media and photodynamic therapy. Recent progress in nanoscience has enabled new kinds of nanostructured materials with improve nonlinear response that can have a real impact in society, among them lanthanide nanoparticle, metal nanoclusters and carbon-based dots.[1] Due to their optical properties, water solubility and ease of functionalization graphene quantum dots (GQDs) became especially attractive as a platform for biomedical applications (imaging, sensing, drug-delivery).[2] Nevertheless, the largely ignored origin of their emission has precluded an insightful approach to their practical applications, which remains mostly driven by empirical evidence and curiosity.
In this presentation, our latest study on graphene quantum dots as nonlinear fluorophores for multiphoton imaging is discussed.[3] We have prepared bottom-up and top-down graphene quantum dots. We found that the two-photon absorption cross-section can be large (≈1000 GM), but quite modest when compared to literature data for other nanomaterials. In general, we observed a slow cellular uptake and a sub-cellular disribution that resembles vesicles suggesting an uptake mediated by endocytic pathways (Figure 1).[3] Most interestingly, we found that the emission spectrum is dependent on the excitation mode. Linear excitation at 350-750 nm introduces the same energy in the system than two-photon excitation in the 700-900 nm range, but the emission that follows is significantly different (Figure 1). We will discuss the origin of the excitation mode dependence of the emission and possible applications of the phenomena.

Keywords: graphene quantum dots, carbon dots, fluorescence imaging, multiphoton imaging, two-photon absorption.

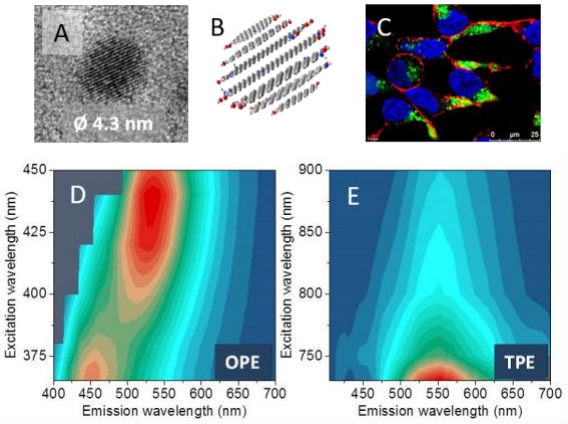


Figure 1: Illustrative results: A) TEM image of the GQDs, B) representation of the GQD structure, C) microscopy image of MCF-7 cells incubated with GQDs (green), a nuclear stain (in blue) and a membrane stain (in red), D and E are contour plots of the two-photon (TPE) and one-photon (OPE) induced emission in GQDs.

We thanl Fundação para a Ciência e Tecnologia for finantial support (PD/BD/127805/2016, PTDC/NAN-MAT/2931 7/2017, PTDC/QUI-QFI/29319/2017, UID/NA N /50024/2019).

References:

1. Zhu, X., Su, Q., Feng, W., and Li, F. (2017), Anti-Stokes shift luminescent materials for bio-applications, Chem. Soc. Rev., 46. 1025.
2. Gui, R., Jin, H., Wang, Z., Tian, L. (2017) Recent advances in optical properties and applications of colloidal quantum dots under two-photon excitation, Coord. Chem. Rev. 338, 141.
3. Santos, C. M., Mariz, I. F. A., Pinto, S., Gonçalves, G., Bdikin, I., Marques, P. A. A. P., Neves, M. G., Martinho, J. M. G. and Maçôas, E.(2018) Selective two-photon absorption in carbon dots: a piece of the photoluminescence emission puzzle, Nanoscale, 10, 12505-12514.

Graphene coated CMOS ISFETs for pH sensing

C. Panteli[1,*], P. Georgiou[1] , K. Fobelets[1]
[1] Imperial College London, Department of Electrical and Electronic Engineering, London, UK

Abstract:
The Ion-Sensitive Field-Effect Transistor (ISFET) is a derivative of Metal-Oxide-Semiconductor Field-Effect Transistor (MOSFET) with the gate oxide not covered by metal but instead exposed to an electrolyte solution [1]. This gives the abilty to the ISFET to sense the concentration of H+ ions or pH in the solution. ISFETs have seen huge attention by researchers due to the compativility with the Complementary Metal-Oxide-Semicnoductor (CMOS) process. This is done via the extended gate approach so that the gate metal is extened to the very top surface of the CMOS chip and thus the oxide and nitride passivation layers provide pH sensitivity thanks to the site binding [2]. Given the potential of monolithic integration of pH sensor and commercial CMOS electronics, the ISFET is higly applicable in biomedical areas such as DNA sequencing, pH and glucose monitoring, virus and infectious diseases detection, chemical imaging and lab-on-chip systems [3]. However, the commercialization of ISFETs is still under investigation due to several drawbacks that degrade its performance. The drawbacks are a result of: (a) the extended gate approach adds an additional capacitance from the passivation layers that causes signal attenuation; (b) the passivation layer trapped charge during fabrication causes a permanent and random threshold voltage offset; (c) the real-time hydration of the oxide and nitride layers from the electrolyte solution cause dynamic threshold voltage offset during measurements [3]. Here, we aim to block or at least minimize the hydration of the sensing membranes of the ISFET by coating them with monolayer and multilayer graphene sheets that thanks to their mechanical robustness can potentially stop ion diffusion through the passivation layers. Using Polymer-Assisted Graphene Transfer (PAGT) process [4,5] we coat CMOS ISFET arrays with graphene sheets (Fig. 1) and characterize them with Raman spectroscopy, interferometry and microscopy. Subsequently, we perform pH sensing, drift and noise experiments (Fig. 1) and analyse the results. We find that graphene coated ISFETs drift less and slower than the uncoated devices. This, is the first step of proving the potential of minimizing the drawbacks of the CMOS ISFETs using 2D materials that will enable more reliable pH sensing devices.

Keywords: graphene, ISFET, pH sensing

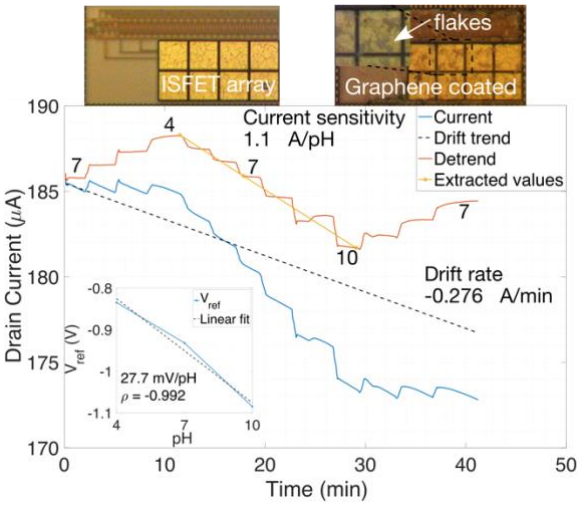


Figure 1: Plain ISFET arrays (top left) and multilayer graphene coated ISFET arrays (top right). The plot shows the real-time effect of drift on the drain current measurement while chaning the pH of the electrolyte solution. The drift can be corrected in software to enable the real calculation of the pH sensitivity. Inset shows the sensitivity in terms of mV/pH. s

References:

1. Bergveld, P. (2003). Thirty years of ISFETOLOGY: What happened in the past 30 years and what may happen in the next 30 years. Sensors and Actuators B: Chemical, 88(1), 1-20.
2. Bausells, J., Carrabina, J., Errachid, A., & Merlos, A. (1999). Ion-sensitive field-effect transistors fabricated in a commercial CMOS technology. Sensors and Actuators B: Chemical, 57(1-3), 56-62.
3. Moser, N., Lande, T. S., Toumazou, C., & Georgiou, P. (2016). ISFETs in CMOS and emergent trends in instrumentation: A review. IEEE Sensors Journal, 16(17), 6496-6514.
4. Panteli, C., Liu, D., Sydoruk, O., & Fobelets, K. (2011). Through graphene etching of porous Si by electroless metal assisted chemical etching.
5. Fobelets, K., Panteli, C., Sydoruk, O., & Li, C. (2018). Ammonia sensing using arrays of silicon nanowires and graphene. Journal of Semiconductors, 39(6), 063001.

Antibacterial activity of polyethersulfone membranes modified with graphene oxide nanosheets

N. C. Homem,[1,2,*] T. D. Tavares,[2] R. Bergamasco,[1] M. T. P. Amorim,[2]

[1] State University of Maringá, UEM, Department of Chemical Engineering, Maringá, Brazil
[2] University of Minho, UMinho, Department of Textile Engineering, Guimarães, Portugal

Abstract:
The importance of antibacterial materials development has increased nowadays. These materials possess a large number of applications, being commonly used in the food industries, as a disinfection step in drinking water treatment, in tissue engineering and also drug delivery systems. In the field of water treatment, the membrane separation processes are one of the most advanced, cost-effective, and sustainable technologies for direct treatment of wastewater containing several types of contaminants. Some researches have pointed out that nanomaterials can be applied in membrane surface modifications, in order to improve its separation properties and also to add specific functionalities as antibacterial performance [1]. Among the techniques used for membrane surface modification we can highlight the layer-by-layer assembly method, which has been proved as a simple and efficient alternative to modify membranes surface. In this method, a positively charged polyelectrolyte (polycation) can be easily electrostaticaly bonded into a negatively charged polyelectrolyte (polyanion) in order to achieve a membrane surface charged according the necessities of the process. The nanomaterials selected play an important role in these cases, being the graphene oxide (GO) nanosheets reported in literature as exhibiting toxicity toward bacterial cells, thereby effectively inhibiting bacterial growth [2]. As GO nanosheets are negatively charged due to the ionization of carboxylate groups in water, they can act as polyanions, and be bonded in a positively charged polymer, as for example the polyethilenimine (PEI), which also has been pointed out as toxic for bacteria. In a previous study, we proved that these two materials can be used to modify the surface of microfiltration membranes, through the layer-by-layer method, in order to improve its performance on the removal of dyes from aqueous solutions [3]. In this study, the goal was to evaluate the antibacterial activity of these membranes. Growth inhibition of Gram-negative *Escherichia coli (E. coli,* ATCC 25922) and Gram-positive *Staphylococcus aureus (S. aureus,* ATCC 6538) bacteria were evaluated. Graphene oxide nanosheets were synthesized by the modified Hummer's method as reported in previous studies [3]. PES microfiltration membranes (47 mm of diameter, average pore size of 0.2 μm) were used as support for the PEI and GO layers (Hexis Científica). The modification of the membranes was performed in a stainless steel stirred cell (HP4750, Sterlitech). Initially, a PEI layer was placed on the surface of the membrane, followed by a GO layer and another layer of PEI. The layers were formed by permeating the PEI and GO solutions through the membranes. Samples were labeled as mPES (bare), mPES/PEI, mPES/PEI+GO and mPES/PEI/GO/PEI, and dried in an oven at 25ºC overnight. The membranes were tested quantitatively using the standard Shake Flask method (ASTM-E2149-01) in which they were cut into 2x1 cm_2, immersed in bacteria solution, and shaken at 100 rpm for 24h at 37ºC. For the mPES membrane, the results showed a bacterial reduction of 57% and 60% for *S. aureus* and *E.coli*, respectively. The modified membranes killed all *S. aureus* bacteria. For the *E. coli*, the bacteria inhibition was superior to 97% for all membranes. In conclusion, the antibacterial properties of the PES membrane were improved by the layer-by-layer assembly of PEI and GO at the surface.

References:

1. J. Li, S. et. al. (2019) High-flux, antibacterial composite membranes via polydopamine-assisted PEI-TiO2/Ag modification for dye removal, *Chem. Eng. J.* 373 (2019).
2. W. Zhang, et. al. (2018) Functionalization of ultrafiltration membrane with polyampholyte hydrogel and graphene oxide to achieve dual antifouling and antibacterial properties, *J. Memb. Sci.* 565, 293–302.
3. N.C. Homem, et. al, (2019) Surface modification of a polyethersulfone microfiltration membrane with graphene oxide for reactive dyes removal, *Appl. Surf. Sci*. In Press.

Influencing Radiosensitizing Properties in Cancer Cells

M. Vetrik,[1,2,*] L. Kobera[1], R. Konefal[1], V. Lobaz[1], M. Hruby[1], G. Pratx[2]

[1] Institute of Macromolecular Chemistry CAS v.v.i, Heyrovsky sq. 2, Prague 6, Czech Republic
[2] Stanford University, Stanford School of Medicine, Stanford, California 94305, USA

Abstract:
Radiation treatment (RT) together with surgery intervention and chemotherapy is one of the most applied cancer therapies nowadays. Greater radi-resistance of cancer cells over normal cells caused by hypoxia is one of the major limiting factor in RT. We developed nanoparticles that are able to alter radiation sensitization of cancer cells in dependence on oxygen saturation. Radiation outcome can be boosted or lowered using self-assembled fluorinated dialkyl diselenide nanoparticles. Highly hydrophobic nature of fluorinated chain gives molecule its self-assembly properties. Amphiphilic character of the nanoparticles is achieved by incorporation of selenocystine linker that can be cleaved during the radiation treatment or when expose to UV light [1]. Radiation initialize the cleavage of selenocystine that act as potent redox-active system. Intracellular generation of reactive oxygen species (ROS) during X-ray application was significantly lowered when 2 Gy and 4 Gy was applied. Fluorinated core that is formed in aqueous environment is able to carry extra oxygen when expose to higher oxygen partial pressure before the irradiaiton [2]. Oxygen saturated nanoparticles are cleaved when radiation is applied. Nanoparticles interact with RT and surrounding radicals (produced by the irradiation causing) and the decomposition occurs followed by oxygen burst release. Presented fluorinated nanoparticles with cleavable selenocystine bond can be utilized during RT as radioprotectants potentially protecting healthy tissues from radiation while allowing delivering higher radiation doses to cancer cells. When saturated with oxygen they can act as radiosensitizers. This project was founded by Czech Academy of Science (# MSMJ200501801) and Czech Ministry of Education, Youth and Sports (grant no. 8J18FR038).

Keywords: radiation oncology, radioprotectives, radiosensitizers, radiosensitizing, oxygen.

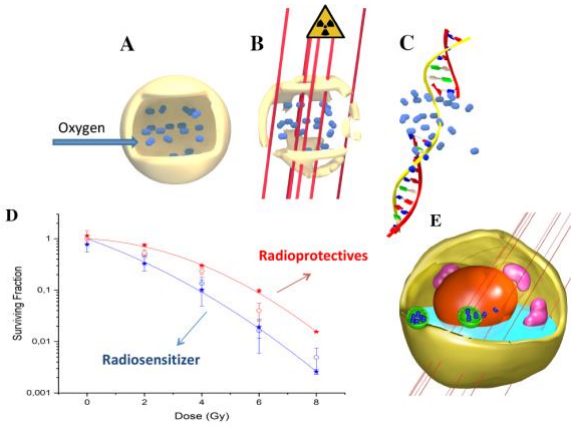


Figure 1: Radiosensitization of nanoparticles under RT. **A.** Nanoparticle (yellow) loaded with oxygen (blue). **B.** Radiation treatment application. Selenocystine bond cleavage and subsequent oxygen **C.** Released oxygen radicals interact DNA double helix causing breaks. **D.** Cell surviving curves shows utilization of nanoparticles as radioprotectives properties and radiosensitizers when particles are loaded with oxygen. **E.** Cancer cell under irradiation with oxygen release.

References:

1. Cao, W., Zhang, X., Yang Z., Xu, H., (2013) γ-Ray-responsive supramolecular hydrogel based on a diselenide-containing polymer and a peptide, *Angew. Chem. In.t Ed. Engl.*
2. Krafft, M.P. (2001) Fluorous and fluorinated amphiphiles in drug delivery and biomedical research, *Adv. Drug. Deliv. Rev.*

pH-responsive ultrasound contrast agents for bio-sensing applications

Julia A. Walker 1, 2*, Kristian Kemp 2, Simon R. Corrie 1.

1 Department of Chemical Engineering, Monash University, Clayton, Victoria, 3800, Australia

2 Monash Institute of Pharmaceutical Sciences, Monash University, Parkville, Victoria, 3052, Australia

ARC Centre of Excellence in Convergent BioNano Science and Technology, QLD and Monash nodes

Abstract:

Ultrasound (US) is one of the most commonly used medical imaging techniques. Contrast agents are admistered to patients to improve fidelity of US images and for theranostic applications. The majority of current research into US contrast agents look to include a gas core, as this leads to high degree of echogenicity. However, this has the disadvatage of 5 minute imaging time in vivo [1]. To our knowledge, the combination of ultrasound technology and contrast agents to create in vivo biosensors has not yet been investigated. This work is aiming to produce a pH-sensitive US contrast agent based on core-shell materials similar to those designed by Zhang et al [2]. Here we use a scaffold of a silica nano particle with Layer-by-Layer (LbL) polymer as the dynamic component (Figure 1). Such biosensors could find application in biomedical research and clinical diagnostics in deep tissue, providing real-time information without relying on laboratory infrastructure or complex imaging systems. In this study, the material synthesis and characterization approces will be outlined, along with proof-of-concept results from *in vitro* and *in vivo* experiments demonstrating a clear pH dependence on US backscatter signal.

Keywords: Ultrasound, sensors, silica-based biomaterials, contrast agents, pH, Layer-by-Layer, biomedical applications.

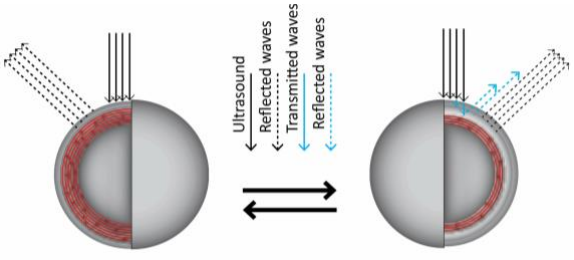


Figure 1: Figure illustrating the question we are looking to answer. Can soild state systems be used as dynamic ultrasound contrast agents.

References:

1. Lin, P. L., Eckersley, R. J., Hall, H, A, E,. (2009) Ultrabubble: A Laminated Ultrasound Contrast Agent with Narrow Size Range. *Adv. Mater.*, 21. 38-39.
2. Zhang, K., Chen, R. H., Guo, X. S., Zhang, D., Zheng, Y. Y., Zheng, R. H., Shi, J. L., (2015) Double-scattering/reflection in a Single Nanoparticle for Intensified Ultrasound Imaging. *Sci Rep.*, 5.

Bactericidal Titania Textiles for Hospital use

J.C. Matos[1] , C. Oliveira[2] and M.C. Gonçalves[1]
[1] CQE, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal
[2]Departamento de Biologia, CESAM, Universidade de Aveiro, Aveiro, Portugal

Abstract:
Healthcare-associated infections (HCAIs), occur worldwide, both in developed and developing countries, affecting approximately 8.7% of all hospitalized patients, causing prolonged hospital stay, disability and extremely high costs to healthcare economies [1].
Daylight bactericidal cotton (100% cotton) textiles are presented and proposed for future hospital use.
Amorphous titania (a-TiO_2) and amorphous titania/chitosan complexes (a-TiO_2//CS) were the selected bactericidal agents. Nanoparticles (NPs) and films were the two paths designed.
Cotton textiles were impregnated with a-TiO_2-based NPs (a-TiO_2, a-TiO_2-NH_2 and a-TiO_2//CS) or coated with a-TiO_2 films. Industrial impregnation/coating will be implemented during the textile finishing treatments. A novel (room temperature and base-catalyzed), green (hydrothermal water as a catalyst), time-saving, and easy scale-up sol-gel process was established to produce the a-TiO_2-based NPs.
Amorphous-TiO_2 films were produced by a dip-in (classic acid catalyzed [2]) sol-gel solution. The bactericidal performance (without the need of an external ultraviolet light source) of TiO_2 NPs, films and impregnated/coated textiles was proven according to AATCC 100 and ASTM E2149 using *Staphylococcus aureus* (*S. aureus* ATCC®6538™) as reference bacterial strain.
A bacterial reduction of 99.99% was achieved for a-TiO_2 films and 99.97% for a-TiO_2//CS NPs Regarding the impregnated textiles, a bacterial reduction of 91.66% was achieved with a-TiO_2//CS NPs, and 99.97% for cotton textiles coated with an a-TiO_2 film.

Keywords: nanoparticles, amorphous titania, chitosan, bactericidal performance, *Staphylococcus aureus*.

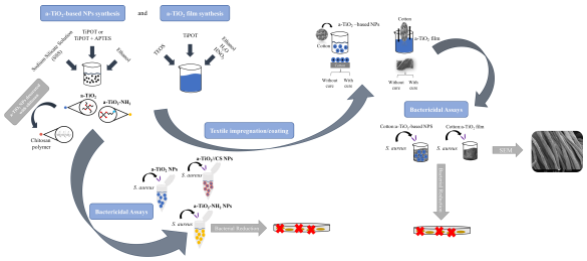


Figure 1: Schematic of a-TiO_2 based nanoparticles synthesis, textiles impregnation/coating and nanoparticles/films/textiles bactericidal performance evaluation.

Acknowledgements:
Financial support for this work was provided by FCT through UID/AMB/50017/2013–POCI-01-0145-FEDER-007638 and UID/QUI/00100/2013 projects. Joana C. Matos acknowledges financial support from FCT, through ChemMat doctoral program (PD/BD/127914/2016).

References:

1. Girard, R., Perraud, M., Prüss, A., Savey, A., Tikhomirov, E., Thuriaux, M., Vanhems, P. (2002) Prevention of Hospital-Acquired Infections: A Practical Guide. World Health Organization, 2nd ed., Ducel, G., Fabry, J., Nicolle, L., Eds., World Health Organization: Geneva, Switzerland.
2. Seco, A.M., Gonçalves, M.C., Almeida, R.M. (2000) Densification of Hybrid Silica–Titania Sol–Gel Films Studied by Ellipsometry and FTIR. *Mater. Sci. Eng. B*, *76*, 193–199.

Prospects and Challenges of Multi-Omics Data Integration in Nanotoxicology

Sebastian Canzler,[1] Jörg Hackermüller,[1,2,*]

[1]Helmholtz Centre for Environmental Research - UFZ, Leipzig, Germany
[2] Bioinformatics Department, University of Leipzig, Leipzig, Germany

Abstract:
Exposure to chemicals or engineered nanomaterials (ENMs) triggers a series of effects at the molecular level. Regulatory pathways involved in such responses exhibit changes of levels, interactions, and feedback loops of biomolecules of different types that are active in complex networks. Different omics techniques are essential for measuring responses in an untargeted manner on the molecular level. Importantly, a single omics technique will detect biomolecules of one type and thus captures changes only for a small subset of the components of a particular pathway. Therefore, applying single omics analyses in response to a toxicant in a non-continuous design led to the identification of biomarkers for certain exposures but not to a systemic understanding of toxicity pathways or adverse outcome pathways (AOPs) in the past. Also, this incomplete representation of pathways in single omics data limits the ability to discriminate adaptive from adverse molecular responses.
We propose that a substantial improvement in detecting the pathway response to ENM exposure can be achieved by using multi-omics data in a time- and concentration-resolved design. We discuss which omics layers to use and how to optimally design studies for multi-omics analyses. Also, we evaluate different approaches for multi-omics data integration including machine learning approaches for dimensionality reduction. Finally, we demonstrate the prospects of multi-omics data integration for the grouping of ENMs.

Keywords: multi-omics, engineered nanomaterials, data integration, omics data integration, machine learning, grouping of engineered nanomaterials.

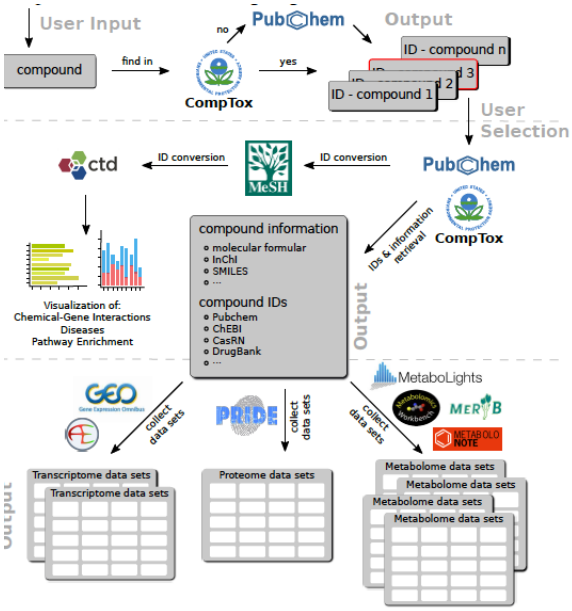


Figure 1: The MOD-Finder workflow for querying related omics data sets for a substance of interest. top) Digital identification and selection of a substance of interest, middle) collection, integration, and visualization of chemical related information and effect annotation, bottom) search of related omics data sets.

References:

1. Canzler S, Hackermüller J, Schor J (2019) MOD-Finder: Identify multi-omics data sets related to defined chemical exposure. bioRxiv 693978;
2. Kämpf C, Specht M, Scholz A, Puppel SH, Doose G, Reiche K, Schor J, Hackermüller J (2019) uap: Reproducible and Robust HTS Data Analysis. bioRxiv 690438; doi: https://doi.org/10.1101/690438

Graphene Oxide Film and Graphene Nanoparticles with Silver Nanoparticles as the Potential Bacteriostatic Ingredient of Food Packaging

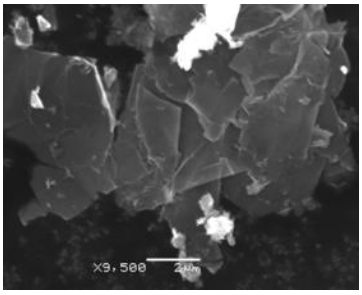
K. Mitura,[1,2] J. Kornacka,[1] J. Kalisz,[1] E.Kopczyńska,[1] E, Czerwińska,[1] L.Volesky,[2] T.Bakalova[2]

[1] Faculty Technology and Education, Koszalin University of Technology, Poland
[2] Department of Materials Science, Technical University of Liberec, Czech Republic

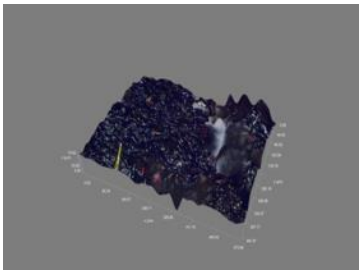
Abstract:
Analysis of the current food and cosmetics market focusing on the identification of foodborne pathogens is one of the most important topics meeting human needs. It covers topics in biology, medicine, biotechnology, food chemistry, molecular biology, genetics and veterinary medicine. Application of films with carbon-based nanomaterials for food packaging gives the possibility to control bacterial infections in food. The selection of graphene family materials is connected with the extended surface of graphene nanoparticles with silver nanoaprticles in comparison with graphene oxide film (1% suspension of graphene oxide in deionized water). Both nanomaterials are commercial products. The surface structure of graphene nanoparticles with silver nanoparticles was inspected in low vacuum by using a JEOL JSM-5500LV Scanning Electron Microscopy (SEM). The structure of the graphene oxide film was examined using 3-D Digital Microscope Leica DVM6.
Four bacterial colonies *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* NCTC 12903 / ATCC 27853, *Staphylococcus aureus* ATCC® 25923, *Streptococcus mutant* ATCC 35668 were examined. Tests were performed on standard strains: *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* NCTC 12903 / ATCC 27853, *Staphylococcus aureus* ATCC® 25923, *Streptococcus mutans* ATCC 35668.
The results indicate that graphene oxide film shows a bacteriostatic effect on colonization of *Pseudomonas aeruginosa* and *Streptococcus mutans* - visible zone of inhibition. Graphene nanoparticles with silver nanoparticles demonstrate bacteriostatic properties for colonization and growth of all pathogens tested. Selective bacteriostaticity of the graphene oxide film is the result of the formation of the so-called *diffusion barrier* and *protective barrier* against the multiplication of foodborne pathogens.

Keywords: graphene, Digital Microscope, bacteriostatic evaluation

A



B



C

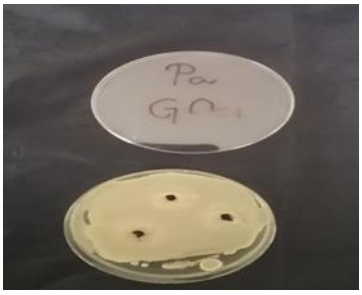


Figure 1. SEM image of graphene nanoparticles with silver nanoparticles (JEOL JSM-5500LV) (**A**). The 3-D image from Digital Microscope of graphene oxide film (1% suspension of graphene oxide in deionized water) (**B**). (Leica DVM6). Bacteriostatic evaluation of the graphene oxide film with *Pseudomonas aeruginosa* (**C**).

References:

1. K.Mitura, P.Zarzycki, (2018), Biocompatibility and toxicity of allotropic forms of carbon in food packaging in A.M. Grumezescu (Eds.), Food Materials Science, Volume 19, chapter 9, ELSEVIER.
2. SN 195920 Textile Fabrics. Determination of the Antibacterial Activity: Agar Diffusion Plate Test.

Challenges on graphene oxide film in the food package system

K. Mitura, [1]E. Kopczyńska[1,3], J. Kornacka[1], J. Kalisz[1], E. Czerwińska[1], E. Ziółkowska[2]

[1]Faculty Technology and Education, Koszalin University of Technology, Poland
[2]The President Stanisław Wojciechowski State University of Applied Sciences in Kalisz
[3] Meden-Inmed Sp. z o. o. Wenedów 2 in Koszalin, Poland

Abstract:
Bioactive packaging covered with graphene oxide film may be an ideal solution in protecting food against harmful microorganisms and extend their shelf life.. Graphene is two-dimensional type of carbon nanomaterials consisting of a single carbon atoms bound with each other by sigma sp^2 hybridization. The active surface of graphene can bind receptor cells in particular placed on the membrane.
The shape and size of graphene sheets were inspected in low vacume by using a JEOL JSM-5500LV Scanning Electron Microscopy (SEM). Adhesion tests were made on a fluorescence microscope(BA 410 E) equipped with an MOTIC camera. Four bacterial colonies (*Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* NCTC 12903 / ATCC 27853, *Staphylococcus aureus* ATCC® 25923, *Streptococcus mutant* ATCC 35668) and four food films: mustard(quadroplex), ice *cream(monoplex), ketchup(duplex),* coffie(triplex) were investigated. Next those foiles were modified by using carbon nanomaterials (i.e. graphen oxide film).
After testing the samples and comparing them with the control group (unmodified films by carbon nanomaterials), it was observed that the modified mustard films show an increase in the adhesion of biological material (bacterial colonies) to the foiles throughout the examined spectrum(e.g. 36,71%.the maximum increase, more living bacteria in field of view in *Pseudomonas aeruginosa* case). On the all modified ice cream food films bacterials adhesion decrease was reported(e.g. 15,38%.the maximum decrease, less living bacteria in field of view in *Streptococcus mutans* case). Similarly, the decrease in adhesion was observed on the all modified coffies films (e.g. 24,3%.the maximum decrease, less living bacteria in field of view in *Pseudomonas eruginosa* case).
Modified ketchup food films depending on type of bacteria, show both increase and decrese bacterials adhesion effect(e.g. 11,35%.the maximum increase, more living bacteria in field of view in Escherichia *coli* case and 14,32% less living bacteria in *Pseudomonas aeruginosa* case-maximum decrease).

Keywords: food packaging, graphene oxide film, SEM, bacteriostatic,

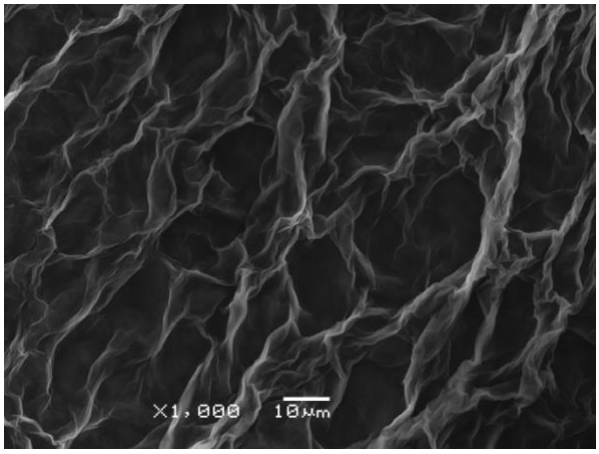


Figure 1. The drawing illustrates layers of graphene oxide film (1 % aqueous emulsion)

References:

1. M. J. Allen, V.C. Tung, R. B. Kaner: Honeycomb carbon: a review of graphene, Chem. Rev., 110, (2009), s. 132.
2. M.Rossi at all, Trends in Food Sciences and Technology, 40, (2014), 127-148.
3. K.Mitura, P. K. Zarzycki, in: A.M. Grumezescu (Eds.), Food Materials Science, 19, (2018), ELSEVIE.
4. N. Kurantowicz at all. Nanoscale Res. Lett. 10:398 (2015) 1-14.
5. E. Sawosz, S. Jaworski, M.Kutwin, Toxicity of pristine graphene in experiments in a chicken embryo model, International Journal of Nanomedicine,2014

Joint Posters Session I Synthesis / Characterization / Propertie

Numerical and experimental validation of SMArt thermography for the control of GFRP composite laminate

M. De Giorgi[1], R. Nobile[1]*, A. Saponaro [1]

[1] University of Salento, Department of Engineering for Innovation, Lecce, Italy

Abstract:
SMArt termography is an innovative and promising technique that could be useful for the detection of damages of large components subjected to in-service loads, like wind blade. This technique requires building traditional carbon or glass fiber reinforced composite laminates adding a regular net of Shape Memory Alloy (SMA) wires in the matrix. These wires confer to the composite material additional features. In particular, the electro-thermal properties of SMA could be used as an internal heat source to be used for the control of the component using the traditional numerical technique used to elaborate the raw thermal data. Despite of other thermography techniques, SMArt Thermography is characterized by a quite reduced amount of heating power, which produces a limited increasing of the temperature of the component subjected to control. On the other hand, the numerical elaboration of thermal data acquired from IR camera is more sensitive and require a deeper comprehension of the phenomena. In this work, a GFRP composite panel containing several artificial defects has been studied both from a numerical and experimental point of view, in order to determine the sensitivity of the technique, the limit of applicability and practical indications about the reliability of the technique.

Keywords: GFRP, Shape Memory Alloy, SMArt thermography, Non-Destructive Technique, FEM analysis.

References:

1. Angioni, S.L., Ciampa, F.,·Pinto, F.,·Scarselli, G., Almond, D.P., Meo, M., (2016), An Analytical Model for Defect Depth Estimation Using Pulsed Thermography, *Experimental Mechanics*, 56, 6, 1111–1122.
2. Pinto, F., Maroun, F.Y., Meo, M., (2014) Material enabled thermography, *NDT&E International*, 67, 1–9.
3. M. De Giorgi, R. Nobile, (2018), A possible use of SMArt thermography for the control of GFRP composite laminate, Proceedings of AIAS 2018 International Conference on Stress Analysis, *Procedia Structural Integrity*, 12, 239-248
4. F. Rizzo, F. Pinto, M. Meo, (2019), Development of multifunctional hybrid metal/carbon composite structures, *Composite Structures*, 222

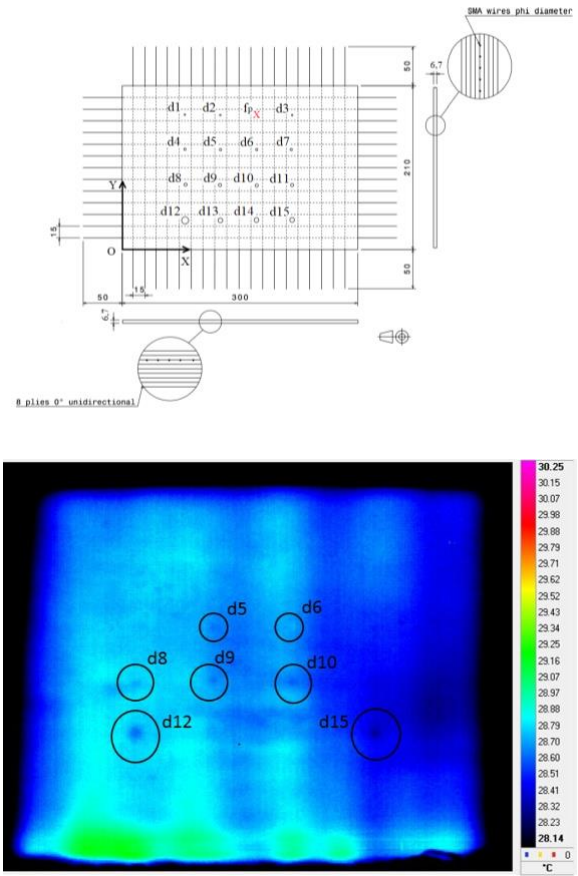


Figure 1: Geometry of the panel containing artificial defects and an example of the thermal map obtained during experimental measurements.

Magnetic and Electrical Properties of postannealed Co_2MnSi Heusler alloy films

G. Grigaliūnaitė-Vonsevičienė[1]*, B. Vengalis[2], A. Maneikis[2] and R. Juškėnas[2]

[1]Vilnius Gediminas Technical University, Saulėtekio al. 11, LT-10223 Vilnius, Lithuania
[2]Center for Physical Sciences and Technology, Saulėtekio al. 3, LT-10223 Vilnius, Lithuania

Abstract:
The Co_2MnSi (CMS) Heusler alloy is known as a strong ferromagnet with high Curie temperature (T_C~985 K) and saturation magnetization M_s of about 5.1 μ_B/f.u. at 4 K. The material provides increasing scientific and technological interest due mainly to full spin polarization of carriers and thus it is promising for the fabrication of magnetic tunneling junctions, spin filters, and other spintronics devices operating at room temperature [1]. In this work, the CMS films (d=100-120 nm) were grown by dc magnetron sputtering of a stoichiometric target on MgO(100) and Si(100) followed by annealing in vacuum at T=T_a=300÷500°C. Formation of nanocrystalline structure with typical grain size 20÷40 nm has been indicated from SEM surface images for the films grown either on Si or MgO. XRD investigations revealed amorphous state for the as prepared films while partially ordered B2 structure and traces of highly ordered $L2_1$ structure have been indicated for the films annealed at T>300°C. The alternating current (AC) magnetic susceptibility (χ~dM/dH) was investigated at RT and 78 K to reveal evolution of magnetic properties of the prepared films with annealing. Increase of saturation magnetisation and reduced electrical resistance have been indicated with T_a increasing from 300 to 400°C. Meanwhile, long term annealing of the films at T≥ 450°C resulted reduced saturation magnetization valus (Figure 1).

Keywords: Co_2MnSi thin films, annealing, magnetic and electrical properties.

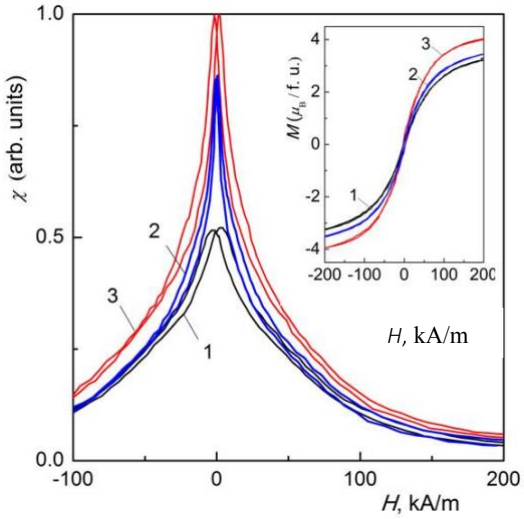


Figure 1: Magnetic field-dependent AC magnetic susceptibility χ~dM/dH and magnetisation, M, measured at RT for Co_2MnSi/Si(001) films annealed in vacuum at 450 °C for 0.5 h (1), 1.5 h (2) and 4.0 h (3)

We point out 3 major competing processes having great influence on magnetic and electrical properties of the films, namely, nucleation of nanometric grains in the beginning of the annealing, diffusion-controled formation of the ordered B2 and $L2_1$ structures and dissociation of highly ordered $L2_1$structure with annealing at T≥ 450°C. Instability of the $L2_1$ structure at the highest annealing temperatures we associate to a possible Si phase segregation at grain boundaries of the prepared nanocrystalline CMS films

References:

1. Felser, C, et al. Basics and prospective of magnetic Heusler compounds, *APL Materials.* 3, 041518 (2015),

Microstructure and mechanical properties of Fe-based amorphous alloy produced using the direct metal deposition method

W. Pilarczyk[1,*]

[1] Silesian University of Technology, Faculty of Mechanical Engineering, Gliwice, Poland

Abstract:
Metallic glasses are potential material for wide application because of their unique physical, chemical and mechanical properties. However, its industrial application is not wide spread because of limited size. From the analysis of obtained data it can be concluded that the production of this type of Fe-based in the form of direct metal deposition coatings can be an interesting technological achievement.
The proposal of using the incremental generation technique to get materials revealing metastable character is innovative in comparison with currently used pressure-die casting method. The possibilities of generating metastable materials with the use of generative technologies have not been fully investigated yet and phenomena accompaning coating of the consecutive layers of amorphous / nanocrystalline alloys have not been explained yet.
The research aimed to design and make specimens having the geometry of a plate using the DMD (Direct Metal Deposition) method as well as to investigate the effect of the number of layers on the structure, hardness and Young modulus of fabricated elements.
In order to measure the size of the discontinuity of the structure and to determine the shape of the revealed defects, metallographic observations were made with the use of the light microscope Axio Observer by Zeiss, scanning electron microscope Supra 35 by Zeiss and stereoscopic microscope. Because of the width of particular additive zone, triboindenter, which enabled the measurement in the scope of between ten to twenty micrometers, was used to examine mechanical properties (nanohardness, reduced Young module).

Keywords: Additive Manufacturing, Direct Metal Deposition, Amorphous Material, Glass Forming Ability, Powder

Acknowledgements

This publication was financed by the Ministry of Science and Higher Education of Poland as the statutory financial grant of the Faculty of Mechanical Engineering SUT and Rector's Grant in the field of research and development, Silesian University of Technology, no.: 10/010/RGJ19/0272.

References:

1. Nong, X.D., Zhou, X.L., Ren, Y.X. (2019) Fabrication and characterization of Fe-based metallic glasses by Selective Laser Melting, *Opt. Laser Technol.*, doi:10.1016/j.optlastec.2018.07.059.
2. Pleass, C., Jothi S. (2018) Influence of powder characteristics and additive manufacturing process parameters on the microstructure and mechanical behaviour of Inconel 625 fabricated by Selective Laser Melting, *Addit. Manuf.*, doi:10.1016/j.addma.2018.09.023.
3. Pilarczyk, W. (2016), The effect of high energy concentration source irradiation on structure and properties of Fe-based bulk metallic glass, *Appl. Surf. Sci.*, doi.org/10.1016/j.apsusc.2015.12.136

Modification and characterization of VACNTs for application as water harvesting surfaces from dew and fog

R.A. Pinheiro,[1] V.J. Trava-Airoldi[1], E.J. Corat,[1*]

[1]National Institute for Space Research, Associated Laboratory of Materials and Sensors, São José dos Campos, Brazil
**Correspondence: evaldo.corat@inpe.br*

Abstract: In some deserts or other isolated planet regions the only water available is dispersed in the air [1]. Overcome the water scarcity in these regions has been a challenging problem. More efficient devices need to be developed because a power source to keep the collecting surface cooled is necessary[2]. Thus, their collecting surfaces must have a high characteristic heat transfer rate to make them viable. As has been shown recently the more efficient surfaces presented specific wettabillity properties which prevents the water films or Wenzel's drops formation[3]. In this work, we discussed how to grow and modify Vertically Aligned Carbon Nanotubes (VACNTs) in order to apply them to this surface type. VACNTs are known for their easily modifiable wettability features. In addition, their nanometric roughness can benefits the process by reducing the solid fraction and breaking the coalesced water drop symmetry[4]. VACNTs growth was carried out by Thermal Chemical Vapor Deposition method in a tubular reactor at 750°C. The catalyst metallic particles were deposited on steel pipes by electroplating method. Ethanol vapor and acetylene supplied carbon to the synthesize step. CO_2 laser treatment performed in air added a second level of roughness on CNTs surfaces by eroding their walls. In addition, we obtained a stable cage-like super-hydrophobic structure, as shown in Fig. 1. These stable structures consist of carbon nanotubes tips joined by laser heating. After the post treatment the nanotubes were coated with a polyethylene (PE) layer aiming them weren't pulled out by water motions. We applied an oxygen plasma into a Micro Wave Plasma Enhanced Chemical Vapor Deposition (MWCVD) technique to change the final composite from super-hydrophobic to super-hydrophilic. The authors investigated the nanotubes changes after each step by X-Ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy, Scanning Electron Microscopy with Field Emission Gun (SEM-FEG), X-Ray Diffraction and Contact Angle (CA) measurements. The authors found that ethanol vapor improved the samples quality and the growth rate. Samples grown without ethanol vapor presented fewer active sites on their surfaces in which oxygen functional groups must be grafted as showed by XPS Spectroscopy. Thus, we concluded that after these modifications VACNTs presented great potential to be applied in water harvesting devices.

Keywords: Water harvesting, Surface modification, Carbon nanotubes, Nanocomposite.

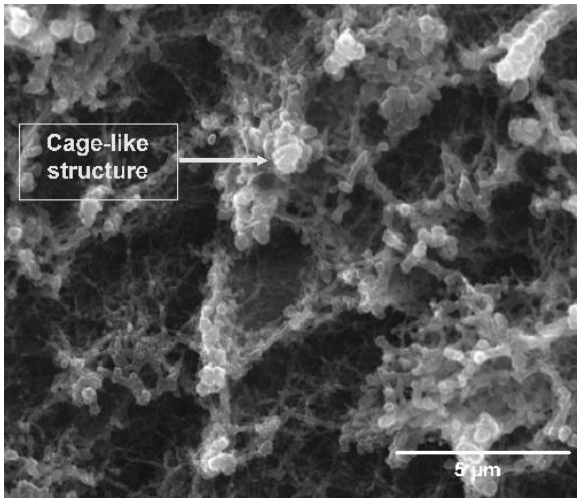


Figure 1: SEM micrographs of PE/modified VACNTs. This SEM micrographs shows the cage-like structure obtained by joining carbon nanotubes tips coated with a polymer layer.

References:

[1] A. Lee, M.W. Moon, H. Lim, W.D. Kim, and H.Y. Kim, Langmuir **28**, 10183 (2012).
[2] N. Miljkovic, R. Enright, Y. Nam, K. Lopez, N. Dou, J. Sack, and E.N. Wang, Nano Lett. **13**, 179 (2013).
[3] K.M. Wisdom, J.A. Watson, X. Qu, F. Liu, G.S. Watson, and C.-H. Chen, Proc. Natl. Acad. Sci. **110**, 7992 (2013).
[4] A. Lafuma and D. Quéré, Nat. Mater. **2**, 457 (2003)

In-pack Ohmic Heating of Packaged Food Using Carbon Black Loaded Polyethylene Films

M. Gratz, H. Jaeger,

University of Natural Resources and Life Sciences (BOKU), Institute of Food Technology, Vienna, Austria

Abstract:
Ohmic Heating (OH) is an uniform and fast heating technology for food. By the application of electrical conductive packaging materials, in-pack heating can be realized. Electrical current is able to overcome the films and is consequently passed directly through the product. As food can be preserved inside the package, recontamination can be avoided and no costly aseptic packaging is necessary.
Physical properties like the geometries and the conductivities of the samples, the packaging material and the surrounding media have a crucial impact on the heating process. In this study two commercial available carbon black loaded polyethylene films are tested. The applicability of the two films for OH in-pack heating is tested using several solid (vegetables, pork, beef) and liquid (salt solution, juice) model food systems. Packaged foods are placed in a batch ohmic heating chamber surrounded by salt water with a defined conductivity. We investigate two concepts: Foods fully wrapped with the conductive films and food products packed in an insulator material where only the sides directed to the electrodes are equipped with the conductive films. We observed higher heating rates in all treated foods packed in conductive films, compared to conventional plastic films. In samples packaged with the conductive films solely, higher heating rates were observed when using the lower conductive film compared to the higher conductive one, the opposite was observed when only the sides were covered by the conductive films. With the results of our study, we will be able to further define setup parameters for in-pack OH applications for specific food products..

Keywords: ohmic heating, electrical conductive, carbon black, food packaging

References:

1. Jaeger, H., Roth, A., Toepfl, S., Holzhauser, T., Engel, K.-H., Knorr, D., Vogel, R.F., Bandick, N., Kulling, S., Heinz, V., Steinberg, P., 2016. Opinion on the use of ohmic heating for the treatment of foods. Trends Food Sci. Technol. 55, 84–97. https://doi.org/10.1016/j.tifs.2016.07.007
2. Kanogchaipramot, K., Tongkhao, K., Sajjaanantakul, T., Kamonpatana, P., 2016. Ohmic Heating of an Electrically Conductive Food Package: Ohmic heating of food package…. J. Food Sci. 81, E2966–E2976. https://doi.org/10.1111/1750-3841.13542
3. Roodenburg, B., 2014. In-pack electrical mild preservation techniques for liquid food products. New Food Mag. 17.

Structural, magnetic and electrochemical properties of AlCoCrFeNiSi high entropy alloys

R. Babilas,[1,*] A. Radoń,[1,2] W. Łoński,[1]

[1] Silesian University of Technology, Institute of Materials Engineering and Biomaterials, Konarskiego 18a, 44-100 Gliwice, Poland
[2] Łukasiewicz Research Network - Institute of Non-Ferrous Metals, Sowińskiego 5, 44-100 Gliwice, Poland

Abstract:
High entropy alloys (HEAs) are multi-component alloys containing at least five different chemical elements mixing with a similar proportions (between 5 and 35 at.%). The same content of the all chemical elements causes the high disordering of the structure in the liquid state. Despite the high entropy these alloys can crystallize in one or few phases. The presence of different phases (fcc and bcc or bcc/B2) in one alloy can has a great impact on their properties. According to the unique crystalline structure HEAs are characterized by improved mechanical strength and corrosion resistance [1-4].
The aim of this work was a preparation of Al-Co-Cr-Fe-Ni-Si HEAs with compositions as follow: AlCoCrFeNiSi, AlCoCrFeNi, AlCoFeNiSi. The samples were prepared by induction melting of pure elements to achieve ingots and by high-pressure casting to prepare plates. The different methods allowed to determine influence of cooling rate on the structure and properties of as-prepared alloys. The structure of alloys was investigated by using X-ray diffraction method and scanning electron microscopy. It can be observed, that the bcc and ordered B2 phases formed in tested alloys. Generally, bcc/B2 phase is treated as a single phase, because B2 is an ordered bcc phase with CsCl-type structure. The magnetic properties were examined using vibrating sample magnetometer and Mössbauer spectroscopy. Additionally, the hardness and corrosion resistance of alloys was investigated. It was noted, that the Al-Co-Cr-Fe-Ni is characterized by the highest corrosion resistance (Figure 1).

Keywords: high entrophy alloys, X-ray diffraction, magnetic properties, Mössbauer spectroscopy, electrochemical measurements, functional materials.

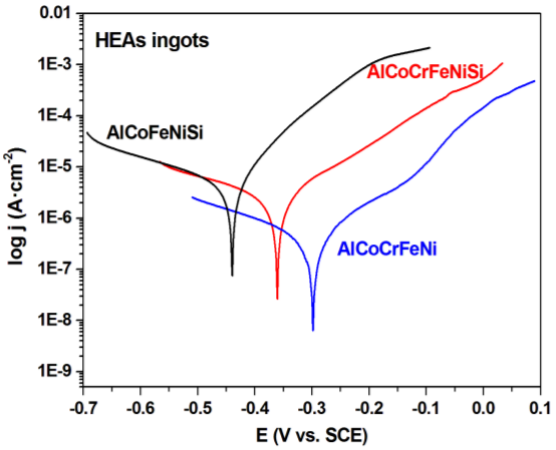


Figure 1: Polariztaion curves of selected HEAs tested in 3.5% NaCl solution at 25°C. The AlCoCrFeNi alloy exhibits the best corrosion potencial which is shifted towards positive values.

References:

1. Kumar, A., Dhekne, P., Swarnakar, A. K., Chopkar, M. K. (2017), Analysis of Si addition on phase formation in AlCoCrCuFeNiSix high entropy alloys, *Mater. Letters*, 188, 73-76.
2. Tang, Z., Yuan, T., Tsai, C.W., Yeh, J.W., Lundin, C.D., Liaw, P.K. (2015), Fatigue behavior of a wrought Al0.5CoCrCuFeNi two-phase high-entropy alloy, *Acta Mater.*, 99, 247-258.
3. Hsu, Y.J., Chiang, W.C., Wu, J.K. (2005), Corrosion behavior of FeCoNiCrCu*x* high-entropy alloys in 3.5% sodium chloride solution, *Mater. Chem. Physics*, 92, 112-117.
4. Tang, Z., Zhang, S., Cai, R., Zhou, Q., Wang, H. (2019) Designing high entropy alloys with dual fcc and bcc solid-solution phases: structures and mechanical properties, *Metall. Mater. Trans. A*, 50, 1888-1901.

Tunable and functionalizable polydopamine thin films by means of electropolymerization.

T. Marchesi D'Alvise,[1] S. Harvey,[1] K. Wunderlich[1], T. Weil[1,2].

[1] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
[2] Institute of Organic Chemistry III/Macromolecular Chemistry Ulm University Albert-Einstein-Allee 11, 89081 Ulm, German
Email (corresponding author): marchesi@mpip-mainz.mpg.de, wunderlich@mpip-mainz.mpg.de

Abstract:
Polydopamine is a biomimetic polymer derived from mussel's adhesive foot proteins and it allows to coat easily every kind of surface. The preparation method leads to the production of very compact and thickness controlled film that can be performed by electropolymerization giving also to the possibility of embedding nanomaterials on it in a very precise way. Polydopamine shows pH responsive and reducing properties together with several functionalization strategies thanks to surface hydroxyl and amine groups. Using the above mentioned characteristics the growth of nanoparticles, like gold ones, was shown can be achieved without using any other reducing or capping agent. The embedding of nanorods for photocatalysis could be controlled through electropolymerization for the preparation of new photoactive material.
Despite all the advantages of electropolymerization one of the disadvantages is the necessity of a conductive substrate to generate the electrons flow needed for the oxidative reaction to occur. In order to avoid this limiting factor we are currently working on the transfer of the polydopamine thin film which can be attached on virtually any substrate and prepared in a very fast and controlled way. The film could be further functionalized with antibodies for sensing tumor markers and by expoiting the semiconductive properties of polydopamine an organic electrochemical transistor could be prepared.This can lead to the synthesis of new biocompatible materials for biosensing devices, advanced catalysis and membrane applications.

Keywords: Polydopamine, mussels inspired material, membranes, electropolymerization, scanning electron microscopy, atomic force microscopy, nanocomposite and functionalized material.

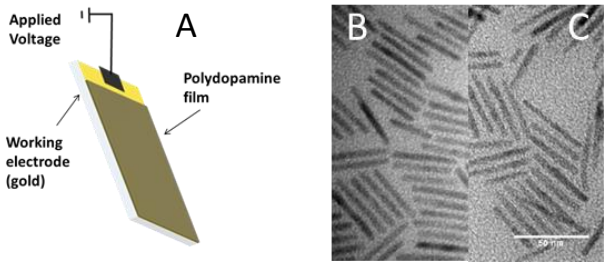


Figure 1: Figure A) showing the schematic prodcedure for polydopamine electropolymerization B) TEM image of NRs and C) TEM image of NRs embedded in polydopamine freestanding film.

References:

1. H. Lee, S. M. Dellatore, W. Miller, and P. Messersmith, *Science Mussel-Inspired Surface Chemistry for Multifunctional Coatings* **318** (5849), 426-430 (2007).
2. B. Stöckle, D. Y. W. Ng, C. Meier, T. Paust, F. Bischoff, T. Diemant, R. J. Behm, K.-E. Gottschalk, U. Ziener, and T. Weil, *ACS Symposium Series Precise Control of Polydopamine Film Formation by Electropolymerization* **346**, 73-81 (2014).

The Effect of Plasma Electrolytic Polishing on the Surface Properties of Steel after Nitrocarburising

S. Kusmanov,[1,*] S. Silkin,[1] I. Tambovskiy,[1]

[1] Kostroma State University, Kostroma, Russia

Abstract:
The effect of anodic plasma electrolytic polishing (PEP) on the characteristics of low carbon steel (0.2% C) after nitrocarburising was investigated. Anodic plasma electrolytic nitrocarburising (PEN/C) is carried out in an aqueous solution of glycerol (8 %), ammonium nitrate (5 %) and ammonium chloride (15 %) followed by quenching, the temperature of a sample reaching 850 °C and electrolyte temperature 20 °C. The formation of the modified layer including a hardened diffusion layer and a surface oxide layer occurs as a result of diffusion saturation. After PEN/C the steel samples were subjected to PEP in an aqueous solution of ammonium sulfate (5%) at a voltage of 300 V and an electrolyte temperature of 90 °C. The PEP time varied from 30 to 300 s. Conducting the PEP of the surface leads to the removal of a loose part of the oxide layer (predominantly FeO), which affects the reduction the surface roughness of 2.0 times (Figure 1). The rate of the weight loss of steel in the PEP process is 0.5 mg/s. The corrosion current density in a 3.5 % sodium chloride solution decreases from 41.0 μA/cm^2 in an untreated sample to 32.6 μA/cm^2 in the steel after PEN/C and PEP during 30 s and to 24.2 μA/cm^2 after PEN/C and PEP during 60 s due to the protective action of the nitride zone and the dense part of the oxide layer. An increase in PEP time of more than 60 s does not change the corrosion current density. Wear test (10 N normal load, 0.4 m/s sliding speed, and 240 m sliding distance, Al_2O_3 ball (6.35 mm in diameter) as an counter-body) shows that wear resistance of steel samples after PEP during 180 s is higher than PEN/C ones of 1.8 times.
This work was financially supported by the Russian Science Foundation (Contract No. 18-79-10094) from Kostroma State University.

Keywords: plasma electrolytic polishing, plasma electrolytic nitrocarburising, steel, surface roughness, corrosion resistance, wear behaviour.

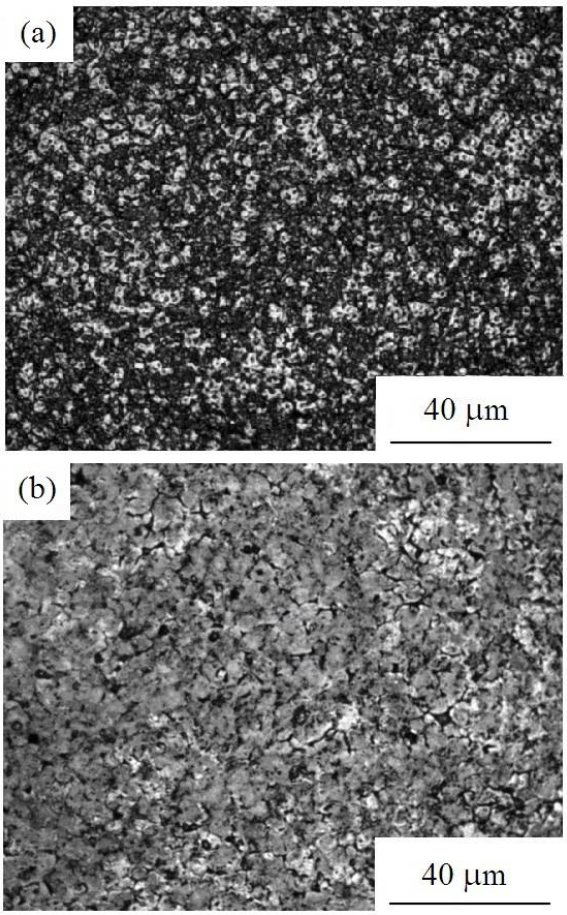


Figure 1: Morphology of steel surface after PEN/C (a) and PEP for 60 s (b).

References:

1. Kusmanov, S., Zhirov, A., Kusmanova, I., Belkin, P. (2019), Aspects of anodic plasma electrolytic polishing of nitrided steel, *Surf. Eng.*, 35, 507–511.
2. Kusmanov, S.A., Silkin, S.A., Smirnov, A.A., Belkin, P.N. (2017), Possibilities of increasing wear resistance of steel surface by plasma electrolytic treatment, *Wear*, 386–387, 239–246.

Microstructure and Corrosion Resistance of Zn-Al-Mg Alloy Coated Steel Product and Its Applications

K. Kim,[1] S. So,[1] I. Park,[1] J. Yoon,[1] M. Oh[1,*] Y. Jang,[2] M. Lee,[2]

[1] Division of Advanced Materials Engineering, Chonbuk National Univerisity, Jeonju, South Korea
[2] Chonbuk National University, School of Dentistry, Department of Dental Biomaterials, Institute of Oral Bioscience and Institute of Biodegradable Material, BK21 plus Program, Jeonju, South Korea

Abstract:
Zn-coated steel products have been widely used in various industries because of their excellent corrosion resistance. We investigated the effects of alloy composition on the coating structure and corrosion resistance of hot-dip Zn-Al-Mg coated steel products. Zn-based alloy coating layers with different Al and Mg compositions were fabricated by using batch-type galvanizing simulator. Various intermetallic compounds such as Zn, Zn/$MgZn_2$ binary eutectic, Zn/Al binary eutectoid and Zn/Al/$MgZn_2$ ternary eutectic phases were formed in the coating layer. The surface and cut-edge corrosion resistance of the Zn-Al-Mg were superior to those of the Zn coating. Corrosion products of Zn-Al-Mg consisted of Simonkolleite ($Zn_5(OH)_8Cl_2•H_2O$), Hydrozincite ($Zn_5(CO_3)_2(OH)$ and zinc oxide (ZnO). The research indicated that molten Mg^{2+} and Al^{2+} cations from the intermetallic compounds containing Mg, such as Zn/$MgZn_2$ and Zn/Al/$MgZn_2$, diffused to the cathodic areas of the coating surface and formed stable corrosion products, which contributed to the improvement of corrosion resistance of the Zn-Al-Mg coated steel products. Al-containing corrosion products, $Zn_2Al(OH)_6Cl_2•H_2O$ and Al_2O_3, were formed with the addition of Al more than 5 wt%. Al-containing corrosion products were formed by corrosion of the Zn/Al eutectoid phases in the coating layer and improved the corrosion resistance of the flat surface of Zn-Al-Mg, but not affected the corrosion resistance at the cut-edge area.

Keywords: hot-dip coating, microstructure, alloy coating, surface treatment, thin-film, corrosion resistance, automotive and construction application.

Acknowledgments: This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MSIT) (No. 2019R1A2C1007552)

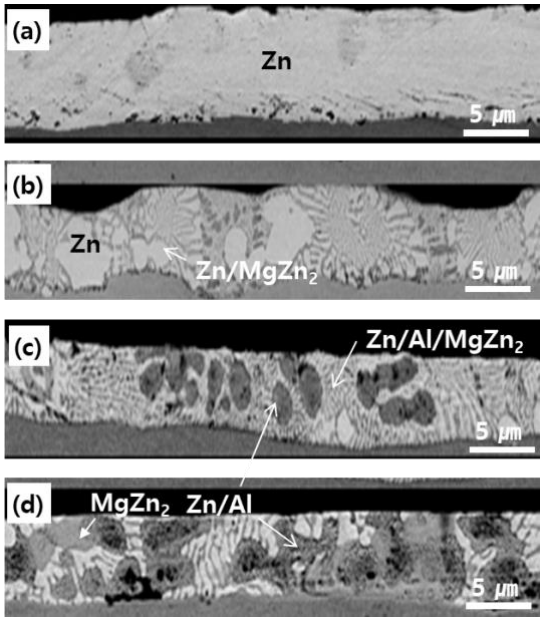


Figure 1: Figure shows a picture of the FE-SEM cross section of the Zn-Al-Mg alloy layer with the variation of Al and Mg composition. Various intermetallic compounds such as $MgZn_2$, Zn/$MgZn_2$, Zn/Al and Zn/Al/$MgZn_2$ were formed within the coating layers.

References:

1. N. Pistofidis, G. Vourlias, S. Konidaris, E. Pavlidou, A. Stergiou and G. Stergioudis (2006) Microstructure of zinc hot-dip galvanized coatings used for corrosion protection, *Mater. Lett.*, 60, 786.
2. S. Maeda (1996) Surface chemistry of galvanized steel sheets relevant to adhesion performance, *Progr. Org. Coating.*, 28, 227.
3. G. M. Song, T. Vystavel, N. van der Pers, J. Th. M. De Hosson and W. G. Sloof (2012) Relation between microstructure and adhesion of hot dip galvanized zinc coatings on dual phase steel, *Acta Mater.*, 60, 2973.

Modified Epoxy Coating with high Efficiency Isocyanate Microcapsules for Corrosion Protection of Steel

M. Attaei[1*], L. M. Calado, M. Taryba A. C. Marques[2], M.F. Montemor[1]

[1] Instituto Superior Técnico, Universidade de Lisboa, Centro de Química Estrutural, Lisbon, Portugal CQE, Lisbon, Portugal
[2] Instituto Superior Técnico, Universidade de Lisboa, CERENA, Lisbon, Portugal

Abstract:
Metals including steel and their alloys are widely used in industrial and engineering structures for their high strength and ductility. However, substantial financial losses have been caused by metal corrosion. Therefore, corrosion protection has become an issue of prime importance to minimize the economic losses. Self-healing coatings for autonomous corrosion protection are at the top of coating research priorities and are considered the next frontier for smart materials.

In this work, highly efficient and long shelf life microcapsules loaded with Isophorone Diisocyanate as polymerisable species were used to modified a commercial epoxy coating used in the Oil&Gas industry.

The barrier properties of a model commercial coating modified with microcapsules were studied using electrochemical impedance spectroscopy. The self-healing potential of the modified coating was assessed using localized electrochemical techniques, namely Scanning Vibrating Electrode Technique, Scanning Ion Selective Electrode Technique, and Localized Electrochemical Impedance Spectroscopy.

Results showed self-healing ability of the modified coating in comparison to the blank reference coating. Enhanced corrosion protection and self-healing of the modified coating is due to polymerization of highly reactive isocyanate in presence of active hydrogen sources, resulting in longer durability of the protective coating.

Keywords: Self-Healing, Microcapsules, Epoxy coating, Isocyanate, Steel, Localized electrochemical techniques.

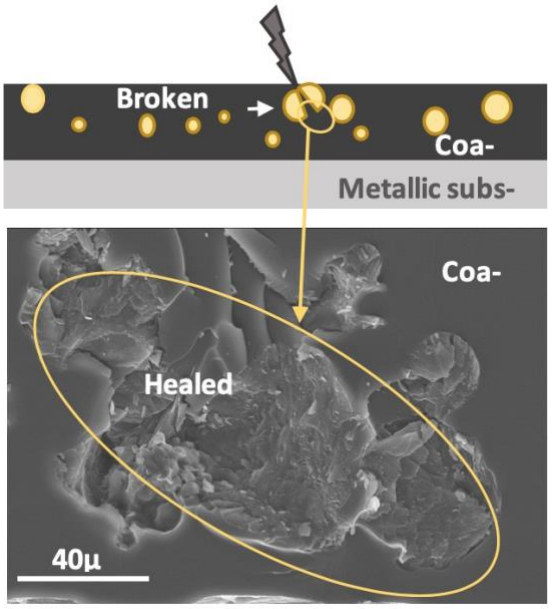


Figure 1: Schematic of coating containing microcapsules, and SEM image of polymerized microcapsules under the damaged zone of the coating.

References:

1. Montemor, M. F. (2014). Functional and smart coating for corrosion protection: A review of recent advances, Surf. Coat. Technol. 258, 17-37.
2. Snihirova, D., Lamaka, S.V., Cardoso, M.M., Condeço, J.A.D., Ferreira, H.E.C.S., Montemor, M.F. (2014). pH-sensitive polymeric particles with increased inhibitor-loading capacity as smart additives for corrosion protective coatings for AA2024, Electrochimica Acta. 145, 123-131.
3. Attaei, M., Loureiro, M. V., Vale, M. D., Condenço, J. A. D., Pinho, I., Bordado, J. C. et al. (2018). Isophorone Diisocyanate (IPDI) Microencapsulation for Mono-Component Adhesives: Effect of the Active H and NCO Sources, Polymers. 10, 825.

Terbium doped calcium germinate (Ca_2GeO_4) as a potential candidate for LED application

I. Koseva[1], P. Tzvetkov[1], P. Ivanov[2], R. Tomova[2]*, A. Yordanova[1], V. Nikolov[1]

[1] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[2] Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Abstract:
These investigations include preparation of luminescent materials based on germanate compound Ca_2GeO_4, doped by rare-earth ion Tb^{3+}. These types of materials are used primarily as fluorescent lamps and modern flat screens and displays due to their low energy consumption, long lifetime, high stability, good brightness, robustness, fast switching, small size and high efficiency. According to some scientists, luminescent materials would reduce the universal electricity consumption up to 50%. Ca_2GeO_4 is orthorhombic, space group Pbmn with crystal lattice parameters a=5.84 Å, b=11.40 Å, c=6.79 Å. Calcium ions occupy two different octahedral crystallographic positions. The ionic radius of terbium (0.93 Å) is closed to that of calcium (0.99 Å), so the terbium ion would prefer the place of calcium. Powder samples of Ca_2GeO_4 doped with 0.5, 1, 2 and 3 at% Tb^{3+} were prepared using conventional solid state synthesis technique. XRD analyses show obtaining of the pure phase at all dopant concentrations. Emission and excitation spectra show the characteristic peaks of Tb^{3+} ion. The Tb^{3+} excitation spectrum in the range from 300 to 500 nm show characteristic transitions of Tb^{3+}, attributed to the f–f transitions. The strongest peak is located at 379 nm corresponding to the $^7F_6 \rightarrow {}^5D_3$ transition. The main emission peak of Tb^{3+} is $^5D_4 \rightarrow {}^7F_5$ transitions at 545 nm, corresponding to green color. Other transitions are located at 416 ($^5D_3 \rightarrow {}^7F_5$), 437 ($^5D_3 \rightarrow {}^7F_4$), 458 ($^5D_3 \rightarrow {}^7F_3$), 488 ($^5D_4 \rightarrow {}^7F_6$), 588 ($^5D_4 \rightarrow {}^7F_4$), 621 ($^5D_4 \rightarrow {}^7F_3$), 651 ($^5D_4 \rightarrow {}^7F_2$) and 675 ($^5D_4 \rightarrow {}^7F_1$) nm. The optimum emission is observed for 2 at% Tb^{3+} ion concentration. At this concentration dominate also ($^5D_4 \rightarrow {}^7F_4$) and ($^5D_4 \rightarrow {}^7F_3$) transitions. CIE coordinates of the samples show different emission colors depending on the active ion concentration (Figure 1). The obtained results confirm that as prepared terbium doped materials could be used as green, yellow and reddish phosphors.

Keywords: Germanate phosphor, Ceramic materials for LED, Rare-earth ions, X-ray, Photoluminescence.

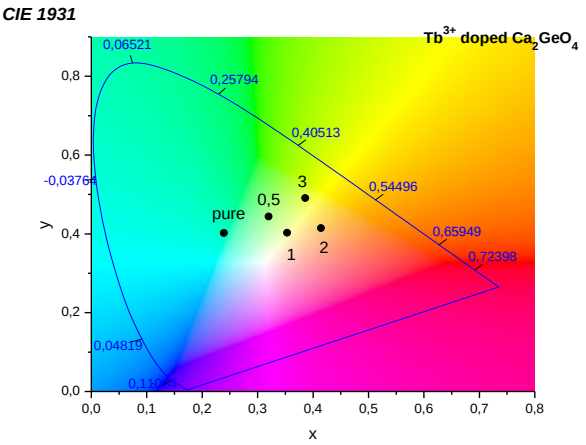


Figure 1: CIE coordinates of the Tb^{3+} doped Ca_2GeO_4 samples with different concentrations of the active ion, illustrating the possibilities to tune colors by changing dopant concentration.

References:

1. Ting Wang et al. (2014), Red phosphor $Ca_2Ge_7O_{16}:Eu^{3+}$ for potential application in field emission displays and white light-emitting diodes, *Mat. Res. Bull.*, 60, 876–881.
2. Lin, C. C., & Liu, R. S. (2011). Advances in phosphors for light-emitting diodes,.*J. Phys.Chem. Lett.*, 2, 1268-1277.
3. Shionoya, S., Yen, W. M., & Yamamoto, H. (Eds.). (2006). *Phosphor handbook*. CRC press.
4. Blasse, George, and B. C. Grabmaier. *Luminescent materials*. Springer Science & Business Media, 2012.
5. Gaft, M., Reisfeld, R., & Panczer, G. (2015). *Modern luminescence spectroscopy of minerals and materials*. Springer.

Structure and luminescent properties of Eu^{3+} doped glass in the system WO_3-La_2O_3-B_2O_3-Nb_2O_5

L. Aleksandrov[1], R. Iordanova[1], M. Milanova[1] P. Ivanov[2], P. Petrova[2], R. Tomova[2]*

[1]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, blvd. Akad. G. Bonchev bl.11, 1113 Sofia, Bulgaria
[2]Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, blvd. Akad. G. Bonchev bl.109, Sofia 1113, Bulgaria

Abstract:
New Eu^{3+} doped multicomponent tungstate glass for optical application was synthesized by melt quenching technique. The obtained glass with composition $35WO_3$-$25B_2O_3$-$15Nb_2O_5$-$(25-x)La_2O_3$-xEu_2O_3, x= 0.5, 1, 2, 3 and 5 (mol%) is colored in light brown and possesses high transparency and high refractive index.
The thermal behavior of the glass was examined by differential thermal analysis (DTA). The observed high value of the glass transition temperature (T_g is about 600^oC), is an indication of the formation of well packed glass structure. The glass crystallization temperature is about 740^oC.
Microstructural and photophysical characterizations were made by IR, Raman, UV-VIS and fluorescence spectroscopies and lifetime measurements. Based on the obtained spectral data short-range order and connectivity in glass network were determined. It was established that WO_6 and WO_4, NbO_6, BO_3 and BO_4 structural units build up the glass network.
Photoluminescence emissions due to the 4f transitions $^5D_0 \rightarrow {}^7F_j$ (j=0-4) of Eu^{3+} ions were observed. Influence of Eu^{3+} content on the emission intensity of the prepared tungstate glass was established.

Keywords

Glass, structure, infrared, Raman spectroscopy, Photoluminescence

Figure 1: Red-orange emission view of the irradiated glass sample with composition $35WO_3$-$25B_2O_3$-$15Nb_2O_5$-$23La_2O_3$-$2Eu_2O_3$ with wavelength λ_{ex}=390 nm.

Acknowledgments
The study was performed with financial support of Bulgarian National Science Fund at the Ministry of Education and Science, Contract КП-06-Н29/7

References

1. Lin, H., Qin, W., Zhang, J., Wu, C. (2007) A study of the luminescence properties of Eu^{3+}-doped borate crystal and glass, *Solid State Commun.,* 141, 436–439.

Dry Transfer of Chemical Vapor Deposition Graphene onto Silicon Wafers Treated by Silane Coupling Agents

M. Ishihara,* M. Hasegawa

National Institute of Advanced Science and Technology (AIST), Nanomaterials Research Institute, Tsukuba, JAPAN

Abstract:
Continuous graphene is potential candidates for transparent conductive films for electrical and optoelectronic devices and various other applications due to its high electrical conductivity, chemical and physical stability. Graphene has been prepared by several methods, including precipitation on a silicon carbide surface, mechanical exfoliation from graphite, reduction of exfoliated graphene oxide, and growth by thermal chemical vapor deposition (CVD) on catalytic metal surfaces [1]. CVD is the most reliable synthesis method and has the advantage of high quality and high productivity on an industrial scale. In order to fabricate the electrical devices, graphene grown on catalytic metal such as copper foil is required to be transferred to the Si substrate. In the typical polymethy methacrylate (PMMA)-supported transfer method, PMMA can cause the local rehybridization of carbons from sp^2 to sp^3 on graphene defects, resulting in the generation of a large number of PMMA residue on the graphene surface. Although thermal release tape was utilized for the large-scale continuous transfer of graphene, the transfer process can cause damage such as large cracks, holes and wrinkles to graphene on the Si substrates. We have synthesized high-quality graphene by plasma treatment of a copper substrate with Joule heating using low concentration carbon source [2]. The copper foil with A4 (211 mm X 297 mm) size was used as substrate. Few-layer graphene was deposited on the copper foil for a few minutes. The transfer of the graphene to a desired target substrate is enabled by the wet-etching of the underlying copper foil. This is carried out by treating the film with an aqueous $(NH_4)_2S_2O_8$ solution after a thermal release tape is covered on the graphene/copper surface. Silicon wafers with heat-oxidizing films (SiO_2/Si) were used for the target substrates. SiO_2/Si wafer was pre-treated with (3-aminopropyl)trimethoxysilane (APTMS) solution. We measured the sheet resistance of the graphene by using four probe method. The sheet resistance of the graphene on the SiO_2/Si substrate with APTMS treatment and without treatment were 600 and 3500 ohm/squqre, respectively. We will discuss the effect of silan coupling agent for dry transfer process of CVD graphene.

Keywords: graphene, transfer process, polymethy methacrylate, thermal release tape, silicon substrate, silan coupling agents, aminosilan, field-effect transistors.

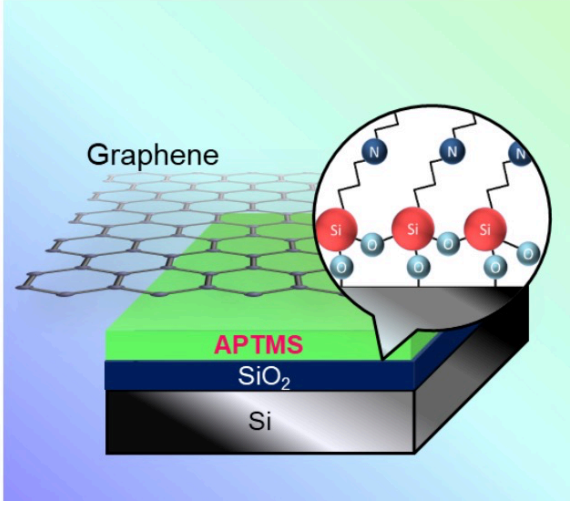


Figure 1: Schematic drawing of graphene on an APTMS-treated SiO_2/Si substrate. APTMS molecules are densely packed on the SiO_2/Si substrate. Inset: the Si atom (red) at the headgroup of the APTMS molecule covalently bonds to an oxygen atom (light blue) of the silanol group on the SiO_2/Si substrate.

References:

1. Li, X. *et al*, (2019) Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils, *Science*, 324, 1312.
2. Kato, R., Tsugawa, K., Ishihara, M., Yamada, T., Okigawa, Y., Hasegawa, M, (2014) Bilayer graphene synthesis by plasma treatment of copper foils without using a carbon-containing gas, *Carbon*, 77, 823.

SnO_x thin films using RF sputtering as transparent conductive materials

Y. Zakaria[1,2,*], A. Slaoui[1], S. Ahzi[2], A. Samara[2], V. Bermudez Benito[2], S. Mansour[2]

[1] Université de Strasbourg, Laboratoire ICUBE UMR 7357-CNRS, Strasbourg, France
[2]Qatar Environment and Energy Research Institute (QEERI), Qatar Foundation, Doha, Qatar

Abstract:
Transparent conductive oxides (TCO) are very useful materials as they combine three main properties of high conductivity, high transparency and chemical stability. They are essential materials in many applications such as solar cells, light emiting diodes and touchscreens. The widely used TCO is Indium Tin Oxide. However, researchers are working on the development of a good alternative to ITO due to the Indium (In) supply challenges in the future. Tin (Sn), instead, is a low-cost material of much higher earth abundance than In. Tin oxides (SnO_x) have two chemical states of Sn^{2+} for SnO and Sn^{4+} for SnO_2. The first is intrinsically n-type semiconductor while the second is a p-type one. In the present work, SnO_x films were synthetized in two steps. First step consists of RF sputtering using high purity (99.99%) SnO target on quartz substrates at 250°C, using six O_2 flow rates: 0, 1, 3, 5, 9 and 15sccm. The second step consists of two different post deposition annealing processes at 400°C, one in air and the other one in a controlled vacuum of $5*10^{-4}$ Torr. Structural properties have been probed using grazing incidence x-ray diffraction to identify the crystal phases. The microstructure was revealed using scanning electron microscopy to define the thin film quality and grain size. Optical properties were investigated using UV-visible spectroscopy to determine the transmittance. Electrical properties were analyzed using four-point probe method to measure resistivity (Figure 1) and hall effect to determine the mobility and the charge carrier concentration. The best conductive thin film was found to have high density without presence of pinholes or cracks and its grain size was relatively larger compared to other samples (Figure 2). Its optical transmittance before and after annealing was above 80% (Figure 3). This was achieved using 3sccm O_2 flow during growth at 250°C and vacuum post annealing. Vacuum annealing provided better conductivity compared to as-deposited and air-annealed samples.

Keywords: transparent conductive oxides; tin oxide; RF sputtering; post deposition annealing.

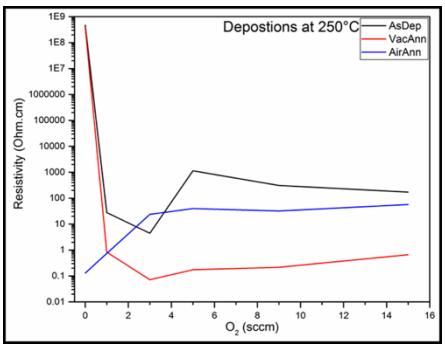


Figure 1: Resistivity as function of O_2 flow rates for the as-deposited, vacuum- annealed and air-annealed samples.

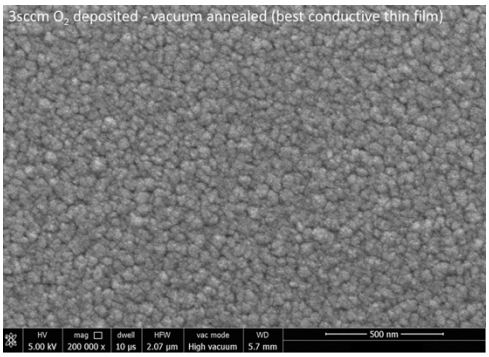


Figure 2: SEM images for the best conductive sample before and after annealing.

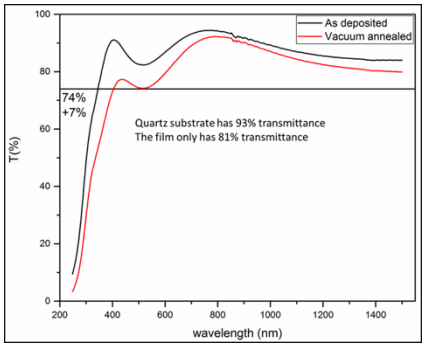


Figure 3: Transmittance spectra for as deposited sample at 250°C vacuum annealed sample at 400°C.

References:

1. D.M. Mukhamedshina, N.B. Beisenkhanov, K.A. Mit', I.V. Valitova, V.A. Botvin - Thin Solid Films 495 (2006) 316 – 320.

The Barrier and Electrochemical Properties of CVD Graphene on Metallic Substrates

P. Ozga *, A. Hara, Z. Świątek, J. Pstruś

Polish Academy of Sciences, Institute of Metallurgy and Material Science, Cracow, Poland

Abstract:
Growth of graphene using CVD method (so-called CVD graphene) on polycrystalline copper surface gives a possibility to obtain large-area, mainly one or two layers graphene coatings [1]. The CVD graphene can be also transferred onto other substrates as zinc, tin etc. The results of many investigations indicate that graphene can provide a barrier substantially reduce the corrosion rate (e.g.[2,3]), however the tightness of real graphene coating is a fundamental feature of a barrier protection. The experimental investigations of barrier properties of graphene layers included the development of methodical bases for characterization of obtained layers in the following working conditions: (i) as a barrier protection against corrosion and protection against processes leading to the loss of solderability (mainly the oxidation processes); (ii) as a barrier to the formation of intermetallic phases; (iii) as a part of the coupling which allows to bond graphene materials with other components. The μ-Raman Spectroscopy (μ-RS) is very sensitive on the properties of graphene layers and this method enable the possibility to characterise the following properties: (i) number of layers of graphene coating; (ii) type and density of defects, (iii) deformation/stresses in graphene coating and (iv) doping charge etc. Simultaneously, this method permits the determination of corrosion products and their changes during corrosion process, as also increase of intermetallic phases in some conditions during formation processes in soldered joint. The relatively large areas of sample can be analysed on the base of set of spectra from the small areas (about 1 μm in used experimental conditions). This allows the formulation of a statistical description, and a graphical representation of the distribution of a heterogeneity of graphene layers in micro-areas simultaneously with description of corrosion products during corrosion process. The surface topography and roughness of the different substrate were examined using atomic force microscopy (AFM, tapping mode). The examinations of the barrier properties in soldering processes were done using tin and tin-zinc alloys on the copper substrate covered by CVD graphene. The processes of the electrodeposition of Sn and Sn-Zn layers from citrate solutions on graphene/copper substrate were investigated and optimal parameters were determined. The barrier properties of selected layers CVD graphene/Zn-Mo alloys were also examined by μ-Raman Spectroscopy, X-ray diffractometry and cross-section microscopy analysis (SEM/EDS). The obtained results indicate a strong influence of defects in CVD graphene materials (types, density), an important role of substrate preparation (topography, roughness, oxidation) and corrosion products as well as an influence of electrodeposition conditions on the barrier properties of graphene layers (damages of graphene coatings by improper electrodeposition conditions). The multilayered graphene coatings (or multilayered areas of coating) have better anti-corrosion performance than a single layer.

Keywords: metallic corrosion, oxidation, barrier protection, graphene CVD, μ-Raman spectroscopy, X-ray diffractometry AFM, SEM.

Acknowledgements: This work was supported by project IMIM PAS Z1 (Environment friendly technologies and materials) and COST Action MP-1407 (e-MINDS).

References:

1. X.Chen, L.Zhang, S.Chena, Large area CVD growth of graphene, Synthetic Metals 210 (2015) 95–108.
2. M.Galbiati, A.C.Stoot, D.M.A.Mackenzie, P.Bøggild, L.Camilli, Real-time oxide evolution of copper protected by graphene and boron nitride barriers, Scientific Reports (2017), DOI: 10.1038/srep39770.
3. N.T. Kirkland, T. Schiller, N. Medhekar, N. Birbilis. Exploring graphene as a corrosion protection barrier, Corrosion Science 56 (2012) 1-4.

Graphene surface analysis and layer counting using scanning low energy electron microscopy

L. Průcha,[1,2,*] J. Piňos,[1] M. Kizovský[3], E. Mikmeková,[1]

[1] Institute of Scientific Instruments of the CAS, Department of Electron Microscopy, Brno, Czech Republic
[2] Brno University of Technology, Institute of Physical Engineering, Brno, Czech Republic
[3]Institute of Scientific Instruments of the CAS, Department of Microphotonics, Brno, Czech Republic

Abstract:
Scanning low energy electron microscopy (SLEEM) can be a very useful tool when it comes to the surface analysis and layer determination of graphene. This approach can be much more precise than conventional methods for the graphene layers determination, such as Raman spectroscopy. In this work, we want to show, that through our SLEEM system MAMOTH, we can easily analyze graphene surface, count the graphene layers and even clean the surface out of air-adsorbed hydrocarbons with the ultra low energy electron beam. Thanks to this approach we are able to optically determine the morphology of layers of graphene flakes. In this study, we also want to show that our approach of the graphene layer analysis has more precise outcome than the conventional Raman analysis. The layer counting is carried out through the change in the reflectivity of the graphene flakes (layers) when low energy electrons (energy less than 50 eV) interact with the surface. As the electron energy goes higher, starting from 0 eV (thanks to the cathode lens system), the reflectivity of graphene layers changes and creates for n-layered graphene n-1 reflectivity minima (Figure 1). The oscillations were predicted by DFT simulations. For this work, all graphene samples were prepared in our prototype CVD furnace on copper foils. Also, graphene samples with different layers (ranging from one layer to FLG) were prepared through the change of the CVD system deposition parameters, so we can analyze and compare various samples.

Keywords: graphene, scanning low energy electron microscopy, layer counting, Raman spectroscopy, electron induced cleaning, DFT.

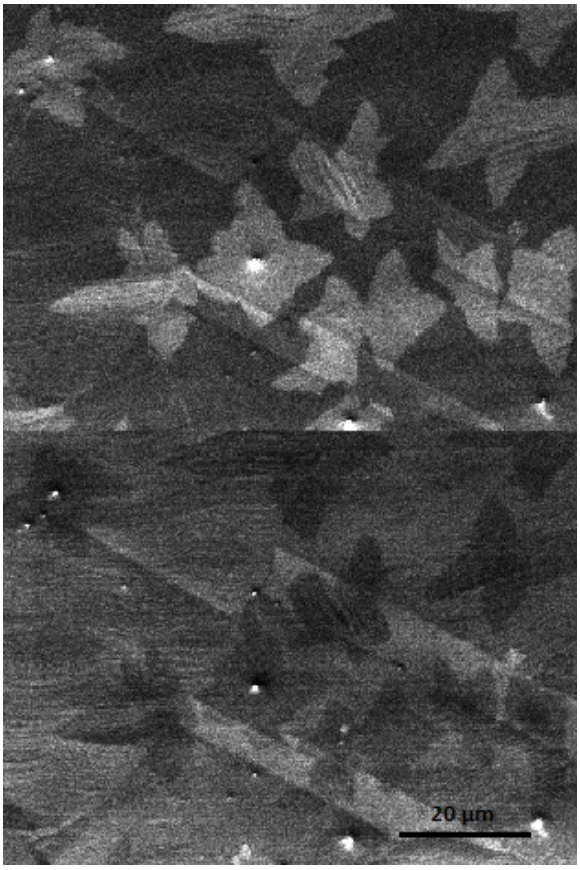


Figure 1: The use of low energy electrons for the determination of the number of graphene layers. Few-layer graphene flakes on Cu foil observed at 7.2 eV (upper) and 12.3 eV and their reflectivity changes caused by different landing energy of the electron beam.

References:

1. Mikmeková, E., Frank, L., Mullerová, I., Li, B. W., Ruoff, R. S., Lejeune, M. (2016) Study of multi-layered graphene by ultra-low energy SEM/STEM. *Diam. Relat. Mater*. 63, 136–142.
2. Frank, L., Mikmekova, E., Lejeune, M. (2017) Treatment of surfaces with low-energy electrons, *Appl. Surf. Sci*. 407, 105–108.

Adjustable Hydrogenation of Monolayer Graphene Depending on Back-Gate Voltage

Harim Choi,[1] Jongil Hong,[1*]

[1] Yonsei University, Matarials Science and Engineering, Seoul 120-749, South of Korea

Abstract:
Graphene is transparent, flexible, high electrical mobility and high carrier mobility.[1] Hence graphene has been actively researched as a transparent electronic device or a field effect transistor device. Despite of these numerous research, opening a band gap of monolayer graphene was a very ideal and challenging study. Our previous study showed that hydrogenated monolayer graphene that can be tunable a band gap up to 4.0 eV by indirect hydrogen plasma at room temperature while preserving the structural of the original graphene.[2] This result reported 25% hydrogen coverages, which other group can not achieve. To figure out how to attatch hydrogen this much without structural damage, we applied various back-gate voltage during hydrogen plasma treatment. First of all, there was no considerable change in the raman spectrum when we didn't do anything to exfoliated monolayer graphene on silicon dioxide(300nm)/Si substrate. But After applying back-gate voltages ranging from -150 V to +150 V during hydrohen plasma treatment, the raman peak linearly increased. (Figure 1). The D and D' peaks became dominant. It means that defects such as sp3 C–H bonds or a disordered carbon sp2 network are induced.[3] In addition, we will find the mechanism of hydrogenated graphene without structural defects by using quadrupole mass analyzer. This study allow us to understand which ion component can effectively affect for the graphene.

Keywords: exfoliated monolayer graphene, defect, back-gate voltage, hydrogen plasma, band gap, raman spectroscopy

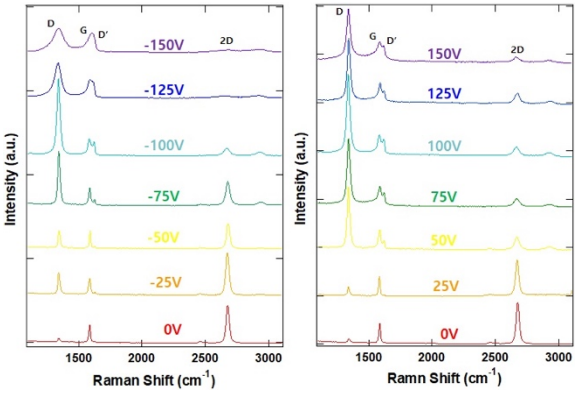


Figure 1: Raman spectrum of Hydrogenated graphene applied back gate voltage from -150 V to +150 V during hydrogen plasma treatment

References:

1. A. K. Geim. (2009), Graphene: Status and Prospects, *Science 324*., 1530-1534.
2. Jangyup son., Soogil Lee. (2016), Hydrogenated monolayer graphene with reversible and tunable wide band gap and its field effect transistor, *Nat. Commun.*, 7, 13261.
3. Elias, D. C. et al. (2009), Control of graphene's properties by reverible hydrogenation: evidence for graphene, *Science 323*., 610–613.

Low contact resistance for graphene on Pt bottom electrode and its effects on device performance

Jongin Cha,[1], Jangyup Son,[1,2] Jongill Hong,[1],

[1] Yonsei University, Department of Materials Science and Engineering, Seoul, Korea
[2] University of Illinois Urbana-Champaign, Department of Mechanical Science and Engineering, Illinois, USA

Abstract:
Graphene has taken center stage as the carbon-based electronics since it was isolated from graphite by means of micromechanical exfoliation.[1] Among various graphene-based electronic devices, field effect transistors (FETs) have been primarily focused to replace the silicon-based FETs. To realize it, one crucial issue is reducing the contact resistance (R_c) between the graphene and metal electrode. R_c could be a dominant factor in nano-scaled devices as the channel length decreased, but reported improved Rc is still high and needs additional process to realize it.[2]
In this letter, we report the extremely low R_c of the graphene overlayer on Pt electrode. In order to reduce the R_c, we used the bottom-electrode contact, and the extremely low R_c and its effect on the device performance will be discussed. We compared electrical transfer characteristic with 2-probe and 4-probe measurement. Even though top-electrode device shows noticeable difference, bottom-electrode device shows similar behaiver with nack gate voltage.
Further, reduction in the R_c will be explored on the basis of edge flow of the current in graphene sheet. These results suggest that the R_c is a crucially important factor for device applications and the bottom-electrode contact will be a new way to reduce the R_c.

Keywords: graphene, contact resistance, field effect transistor, bottom electrode, work function

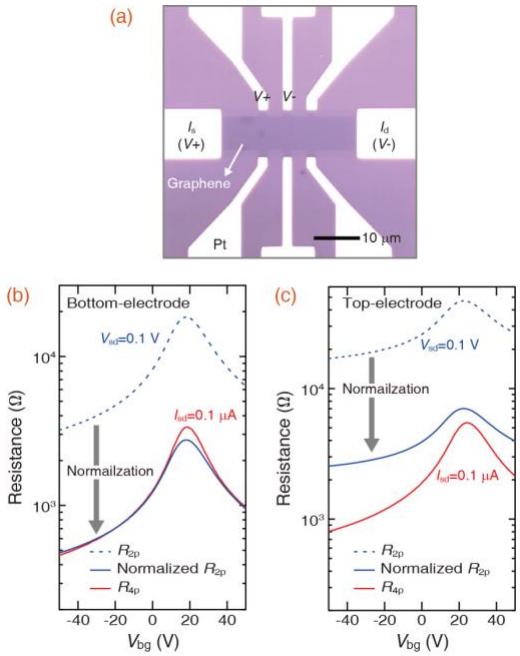


Figure 1: (a) The optical image of the graphene field effect transistors (FETs) using the bottom-electrode contact. (b) Resistance of the bottom-electrode device measure by two- and four-probe (R_{2p} and R_{4p}) as a function of the back-gate voltage. Blue dotted and blue-solid lines are R_{2p} and Normalized R_{2p}, respectively. Normalized R_{2p} was obtained from the R_{2p} divided by the channel length to interval of two voltage probes ratio. (c) R_{2p}, normalized R_{2p} and R_{4p} of the top-electrode device.

References:

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov (2004), Electric Field Effect in Atomically Thin Carbon Films, Science 306, 666.
2. W. S. Leong, H. Gong, and John T. L. Thong (2014), Low-Contact-Resistance Graphene Devices with Nickel-Etched-Graphene Contacts, ACS Nano 8, 994-1001.

Plasmon-enhanced Substrates for the Super-resolution Fluorescence Imaging

Chun-Yu Lin[1], Gerald Abrigo[2], and Fan-Ching Chien[2]*

[1] College of Photonics, National Chiao Tung University, Tainan, 711, Taiwan
[2] Department of Optics and Photonics, National Central University, Taoyuan 32001, Taiwan

Abstract:
We demonstrated the well-designed plasmon-enhanced substrates with appropriate spacing between fluorophores and the metal surface to avoid quenching can significantly increase the excitation rate and fluorescent radiative decay rate by enhancing the local electromagnetic field in the super-resolution fluorescence imaging. The contributions of the local field enhancement, modified quantum yield, emission coupling yield, and relative intensity of detected fluorescence of the fluorophores on the presented plasmon-enhanced substrates were systematically examined to have the optimal signal of the detected fluorescence of the fluorophore. Moreover, the decreasing the fluorescence lifetime also enable the fluorophores on the presented plasmon-enhanced substrates have the better photostability to provide the more number of detected photon. Hence, combined with well-designed plasmon-enhanced substrates in the super-resolution fluorescence imaging, the distribution of the fluorophore-labeled proteins in the cancer cells can be revealed with the better spatial accuracy.

Keywords: plasmon-enhanced substrates, local field enhancement, super-resolution fluorescence imaging, quantum yield, emission coupling yield, fluorophore, photostability, cancer cells

References:

1. Sengupta, P., Engelenburg, S. B. Van, Lippincott-Schwartz, J. (2014), Superresolution imaging of biological systems using photoactivated localization microscopy, *Chem. Rev.*, 114, 3189-3202.
2. Huang, B., Babcock, H., Zhuang, X. (2010), Breaking the diffraction barrier: super-resolution imaging of cells, *Cell*, 143, 1047-1058.
3. Sahl, S. J., Hell, S. W., Jakobs, S. (2017), Fluorescence nanoscopy in cell biology, *Nat. Rev. Mol. Cell Biol.*, 18, 685-701.
4. Jones, S. A., Shim, S.-H., He, J., Zhuang, X. (2011), Fast, three-dimensional super-resolution imaging of live cells, *Nat. Methods*, 8, 499-508.
5. Anger, P., Bharadwaj, P., Novotny, L. (2006), Enhancement and quenching of single-molecule fluorescence, *Phys. Rev. Lett.*, 96, 113002.
6. Benisty, H., Stanley, R., Mayer, M. (1998), Method of source terms for dipole emission modification in modes of arbitrary planar structures, *J. Opt. Soc. Am. A*, 15, 1192-1201.

Synthesis of silver nanoparticles and nanocomposites with unique structure and optical properties by UV-irradiation method

A.Radoń [1]

[1] Silesian University of Technology, Faculty of Mechanical Engineering, Gliwice, Poland

Abstract:
Recently, different methods synthesis of silver nanoparticles (Ag NPs) and nanostructures such as core-shell nanoparticles and nanocomposites with graphene were proposed. One of the most common approaches is the reduction of Ag^+ ions to metallic nanoparticles. For this purpose different reducing agents such as hydrazine or saccharides can be used.
The UV-irradiation method is not a popular method, however very interesting ones. This is associated with the possibility of up-scaling to industry applications. It was confirmed, that reduction by UV light can be succesfully used to synthesize Ag NPs with unique optical and catalytic activity as well as different nanostructures as nanofibers decorated by Ag NPs. Moreover, reduction assistated by UV light has been used to synthesize other noble metal nanoparticles such as palladium and gold nanoparticles.
In this studies UV-irradiation method was used to synthesize different nanostructures (Figure 1). It was confirmed, that the organic modifiers such as chloramine T and sodium laureth sulfate can be used to modify the structure and optical properties of Ag NPs. Additionally, the same method can be used to synthesize AgCl nanocubes decorated by ultrafine silver nanoparticles, Ag-Au nanoalloy and graphene decorated by Ag NPs.
The UV-irradiation method is a very fast and cost-effective method synthesis of nanoparticles. Therefore, the synthesized nanostructures can find applications in catalysis, as electrochemical sensors, drug delivery platforms, and as gas sensors.

Keywords: silver nanoparticles, UV-irradiation, optical properties, graphene oxide, organic modifiers

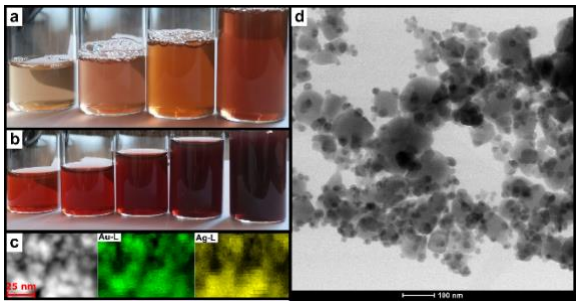


Figure 1: Results of synthesis of different silver based nanostructures by UV-irradiation method: (a) macroscopic image of Ag NPs synthesized using sodium laureth sulfate, (b) macroscopic image of Ag NPs synthesized in presence of chloramine T, (c) 2D EDX maps of Ag-Au nanoalloy, (d) STEM image of AgCl-Ag nanoparticles.

References:

1. Radoń, A., Łukowiec, D. (2018) Silver nanoparticles synthesized by UV-irradiation method using chloramine T as modifier: structure, formation mechanism and catalytic activity. *CrystEngComm,* 20, 7130-7136.
2. Ritthichai, T., Pimpan, V. (2019) Ammonia sensing of silver nanoparticles synthesized using tannic acid combined with UV radiation: Effect of UV exposure time. *J. King Saud Univ. - Sci.*, 31, 277-284.
3. Filip, G. A. et al. (2019) UV-light mediated green synthesis of silver and gold nanoparticles using Cornelian cherry fruit extract and their comparative effects in experimental inflammation. *J. Photochem. Photobiol. B Biol.* 191, 6-37

SbSI nanowires composites for energy harvesting and sensors

B. Toroń[1]*. P. Szperlich[1], M. Jesionek[1], M. Kozioł[2], M. Nowak[1]

[1] Silesian University of Technology, Institute of Physics – Center for Science and Education, Katowice, Poland
[2] Silesian University of Technology Faculty of Materials Engineering and Metallurgy, Katowice, Poland

Abstract:
Composites containing antimony sulfoiodide (SbSI) nanowires have found application in the production of nanogenerators and nanosensors.
Due to high values of electromechanical coefficient (k_{33}=0.9) and piezoelectric coefficient ($d_{33}=1\cdot10^{-9}$ C/N), SbSI is a very attractive material for such devices. SbSI nanowires have lateral dimensions 10–100 nm and length up to several micrometers. They are sonochemically produced. This work presents a few various nanocomposites: production methods, their properties and examples of application.
A piezoelectric paper based on SbSI nanowires is reported. The composite of tough SbSI nanowires with very flexible cellulose leads to applicable, elastic material suitable to use in fabrication of, for example, piezoelectric nanogenerators.
Fabrication technology of epoxy resin/SbSI nanowires composite is also presented. In this case nanowires have been added to epoxy resin in mass ratio 1:4, and then ultrasound irradiation have been used for homogenization of the mixture. This nanocomposite has also been used to fabricate a deformation sensor integrated into a FRP (fiber reinforced polymer) laminate structure. These sensors are also presented in this work. The sensors were made from a nanocomposite based on epoxy resin and SbSI nanowires. Performed electrical measurements show that it is possible to determine the laminate deformation as a function of registered voltage.
The investigations of a cellulose/SbSI nanogenerator for shock pressure (p=3 MPa) and sound excitation (f=175 Hz, L=90 dB) allowed to determine its open circuit voltage 2.5 V and 24 mV, respectively. For a load resistance equal to source impedance, maximum output power density P=41.5 nW/cm$_3$ for 0.05-mm-thick sheet of this composite of the cellulose/SbSI nanogenerator was observed.
In case of epoxy resin/SbSI nanowires composite for various kind of excitation: sound (f=175 Hz,L=90 dB), vibrations (f=24 Hz; A=1 mm; F=0.73 N), shock wave (p=6 bar), the following values of open circuit voltage 0.0153 V_{RMS}, 0.166 V_{RMS}, and 4.51 V_{p-p}, were determined respectively. Maximum output power densities of 0.45 nW/cm^3 and 860 nW/cm^3 have been achieved for excitation by sound and vibration respectively for 0.6 mm thick layer of composite.

Keywords: Antimony Sulfoiodide (SbSI), SbSI nanowires, nanocomposites, nanogenerators, nanosensors, energy harvesting, epoxy resin, cellolose, FRP laminates.

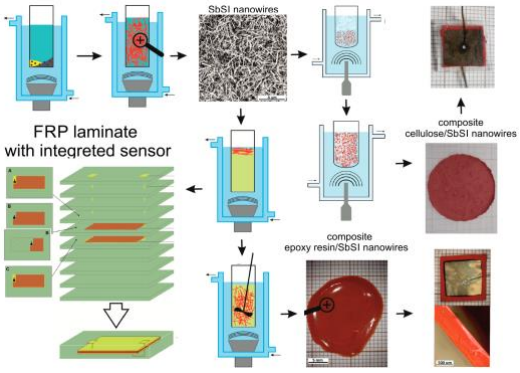


Figure 1. Scheme of sonochemical preparation of: SbSI nanowires, the epoxy resin/ SbSI nanowire and cellulose/SbSI nanowires composites, generator/sensor assembly and scheme of FRP laminate with integrated sensor.

References:

1. Szperlich, P., Toroń, B. (2019) An ultrasonic fabrication method for epoxy resin/SbSI nanowire composites, and their application in nanosensors and nanogenerators, *Polymers, 11*, 479 1-13.
2. Kozioł, M., Toroń, B., Szperlich, P., Jesionek, M. (2019) Fabrication of a piezoelectric strain sensor based on SbSI nanowires as a structural element of a FRP laminate, *Composites Part B, 157*, 58-65.
3. Toroń, B., Szperlich, P., Nowak, M., Stróż, D., Rzychoń, T. (2018) Novel piezoelectric paper based on SbSI nanowires, *Cellulose, 25*, 7-15.

Desity Functional Study of Two Dimensional Monolayer PtX_2[X= S, Se and Te]

Hadeel Alaqi,[1,*] W.A.Diery,[1,]

[1] King Abdulaziz University, Physics Depertment, Faculty of Science, Jeddah, Saudi Arabia

Abstract:
In recent years, Two-dimensional Transition Metal Dichalcogenides (TMDs) having a formula MX_2, where M is a transition metals and X [S, Se, Te] is a chalcogen, have received a lot of research activities due to a set of properties that make them relevant for variety of technological applications including: field-effect transistors, energy storage, and catalysis[1]. Many TMDs have been extensively investigated, both experimentally and theoretically, e.g., MoS_2, $MoSe_2$, and WS_2[2]. However, platinum dichalcogenides have not been explored yet, which are expected to be exfoliated into a mono-layer and find some important applications in the field of electronics.
In this work, we study two major topics in condensed matter physics namely: electrons and phonons in two dimensional monolayer martials namely PtX_2 [X= S, Se and Te], which play an important role in many physical properties of these materials. We use Density Functional Theory (DFT) as implemented in the Quantum Expresso code [3] to study the electronic properties of these matrails. Our calculations predict that all three matrails are semiconductor with band gap that decreases with increasing atomic number of chalcogen element with values of : 1.76ev for PtS_2, 1.29ev for $PtSe_2$ and 0.38ev for $PtTe_2$, in good agreement with the previously calculated values.
The dynamical stability of these materials are investigated by calculating the phonon dispersion using the finite displacement method as implemented by PHONOPY code[4]. Thermal properties including free energy, entropy and heat capacity at constant volume are calculated as a function of time using PHONOPY code.
The existing body of work on these materials indicates the importance of developing a fundamental understanding of the structural, electronic and phonon properties in these materials. Understanding the properties will help to identify which applications are going to benefit from them.

Keywords: Two dimensional, Monolayer, DFT, Semiconductor, Band gab, Phonon.

References:

1. Ganesh R. Bhimanapati, Zhong Lin, Vincent Meunier, Yeonwoong Jung, Judy Cha, Saptarshi Das, Di Xiao, Youngwoo Son, Michael S. Strano, Valentino R. Cooper, Liangbo Liang, Steven G. Louie, Emilie Ringe, Wu Zhou, O Steve S. Kim, Rajesh R. Naik, Bobby G. Sumpter, O Humberto Terrones, Fengnian Xia, Yeliang Wang, Jun Zhu, Deji Akinwande, Nasim Alem, Jon A. Schuller, Raymond E. Schaak, Mauricio Terrones, and Joshua A. Robinson."Recent Advances in Two-Dimensional Materials beyond Graphene", *ACS Nano,* 9 (12), pp 11509–11539 (2015).
2. Lebegue, S. & Eriksson, O. "Electronic structure of two-dimensional crystals from ab initio theory", Phys. Rev. B 79, 115409 (2009).
3. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris,G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L.Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L.
   Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, and R.M. Wentzcovitch, J. Phys.: Condens. Matter 21 395502 (2009).
4. Atsushi Togo and Isao Tanaka." First principles phonon calculations in materials science", Scr. Mater., 108, 1-5 (2015).

EIS Characterization of Passive Films Formed on $Al_xCoCrFeNi$ Alloys

M.López Ríos,[1] N.Florido Suárez[1], I.Voiculescu[2], V.Geanta[2], J.C.Mirza Rosca[1*]

[1] Las Palmas de Gran Canaria University, Mech. Eng.Dept.,Spain
[2] Politehnica University of Bucharest, LAMET, Bucharest, Romania

Abstract:
Electrochemical Impedance Spectroscopy (EIS) measurements have been performed on High Entropy Alloys (HEAs) type $Al_xCoCrFeNi$ with different aluminium content (x = 0.6; 0.8 and 1.0) in order to characterize their passive film and corrosion resistance at 37ºC under simulated physiological conditions (Ringer´s solution) acidulated with HCl at pH=3. The impedance spectra were obtained at different potential values between E_{corr} and + 0.7 V vs. SCE.
Analysis of the impedance spectra was done by fitting the experimental data to different equivalent circuits. Two equivalent circuits, with one time constant and two time constants respectively, can be satisfactory used for fitting the spectra: one time constant represents the characteristics of the passive film and the second one is for the charge transfer reactions.
The polarization resistance and the double layer capacity were compared at different polarization potentials for the detection of the passive film structure and the roughness of the electrode surface.
It can be seen for both materials that the resistence of the passive film is very high and decreases slightly with the potential: the very high resistance of the passive film implies a high corrosion resistance which can be attributed to the formation of the protective oxide layer.
There is a decrease in the values of the parameter n of the CPE (constant phase element used in the mathematically modelling in order to consider also the electrochemical behavior of systems which do not correspond exactly to a pure capacitance) related to the rugosity of the electrode surface.

Keywords: high entropy alloys, aluminium, EIS, equivalent circuit, corrosion resistance, passivation, Ringer solution.

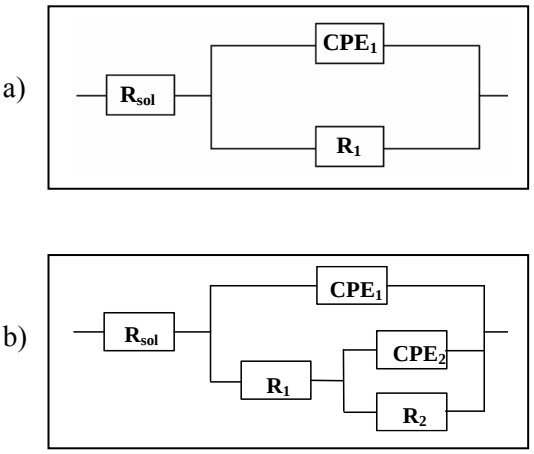


Figure 1: Figure illustrating the equivalent ciruits used for the fitting of the experimental data where R_{sol} is the ohmic resistance of the electrolyte. a) The first circuit has one time constant.
b) The second equivalent circuit fitted for HEAs in Ringer's solution of pH = 3 presents the second time constant which illustrates the slight porosity of the passive layer on the alloy surface (R_1 and CPE_1). So, the equivalent circuit contains in addition a parallel circuit for charge transfer reactions through the passive layer consisting of the double layer capacitance CPE_2 and charge transfer resistance R_2.

References:

1. B. Gwalani, S. Gorsse, D. Choudhuri, Y. Zheng, R.S.Mishra, R. Banerjee (2019) Tensile yield strength of a single bulk Al0.3CoCrFeNi high entropy alloy can be tuned from 160 MPa to 1800 MPa, *Scripta Materialia,* 162, 18-23
2. Z.Li, S.Zhao, R.O.Ritchie, M.A.Meyers (2019) Mechanical properties of high-entropy alloys with emphasis on face-centered cubic alloys, *Progress in Materials Science,* 102, 296-345.
3. D.B.Miracle, O.N.Senkov, A critical review of high entropy alloys and related concepts (2017), *Acta Materialia*, 122, 448-511.

Effects of Nickel Content on the Microstructure, Microhardness and Corrosion Behavior of High-entropy AlCoCrFeNi$_x$ Alloys

M.López Ríos,[1] P.P.Socorro Perdomo[1],
V.Lucero Baldevenites[1], I.Voiculescu[2], V.Geanta[2], J.C.Mirza Rosca[1*]

[1] Las Palmas de Gran Canaria University, Mech. Eng.Dept.,Spain
[2] Politehnica University of Bucharest, LAMET, Bucharest, Romania

Abstract:
The pioneering efforts in obtaining the high entropy alloys (HEAs) created the groundwork for a new concept in alloy design by finding new equiatomic combinations of elements for advanced materials with unique properties.
In this study we investigate the effect of different nickel concentration on the microstructure, hardness and corrosion properties of high entropy alloys from AlCrFeCoNi system.
The analyzed HEAs were AlCrFeCoNi$_x$ with x=1; 1.4 and 1.8. These alloys were obtained by vacuum arc remelting from raw materials with high purity.
The microscopy examination has revealed the dendritic morphology for the reference alloy (AlCrFeCoNi) and the increase of the width of the interdendritic zones by increasing the nickel concentration while Cr is segregated in the interdendritic regions more than in dendrites.
Hardness values decrease with increasing the percentage of nickel because of the dissolution of precipitates in a nickel rich matrix and in consequence forming continuous solid solutions.
The corrosion properties of the HEAs were evaluated using a potentiodynamic polarization method. The alloys were immersed in SBS (Simulated Body Fluid) during one week and the corrosion parameters were registered. The low corrosion rates, low corrosion currents and high polarization resistance attest the good stability of HEAs in simulated biological environment.

Keywords: high entropy alloys, nickel, corrosion resistance, corrosion currents, polarization resitance, passivation, Ringer solution.

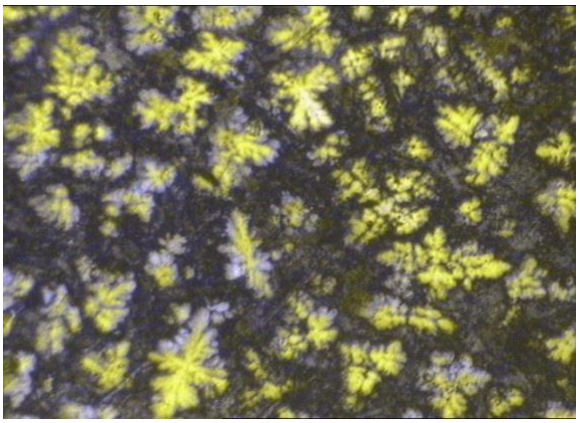


Figure 1: Figure illustrating the dendritic mor - phology of high-entropy AlCrFeCoNi$_{1.4}$ alloy after electrochemical etching in oxalic acid 10% for one minute.

References:

1. B. Gwalani, S. Gorsse, D. Choudhuri, Y. Zheng, R.S.Mishra, R. Banerjee (2019) Tensile yield strength of a single bulk Al0.3CoCrFeNi high entropy alloy can be tuned from 160 MPa to 1800 MPa, *Scripta Materialia,* 162, 18-23
2. Z.Li, S.Zhao, R.O.Ritchie, M.A.Meyers (2019) Mechanical properties of high-entropy alloys with emphasis on face-centered cubic alloys, *Progress in Materials Science,* 102, 296-345.
3. D.B.Miracle, O.N.Senkov (2017) A critical review of high entropy alloys and related concepts, *Acta Materialia*, 122, 448-511.
4. I.Voiculescu, V.Geanta, R.Stefanoiu, D.Patroi, H.Binchiciu (2013)Influence of the chemical composition on the microstructure and microhardness of AlCrFeCoNi high entropy alloy, *Revista de Chimie*, 12, 1441-1444.

Thin ice under pressure on graphene: a theoretical NMR study

A. Jaadouni,[1] E. Rauls,[2] W.G. Schmidt,[1] and U. Gerstmann[1]

[1] University of Paderborn, Department of Physics, 33098 Paderborn, Germany
[2] University of Stavanger, Institutt for Matematikk og Fysikk, 4036 Stavanger, Norway

Abstract:
Bulk water can exist in many forms, liquid, vapor and at least 16 crystalline phases, including the famous hexagonal ice [1]. Theory suggests, that many further phases can occur, if water is adsorbed on surfaces or at nanoscopic pores. Since the discovery of graphene, the adsorption of water has been discussed as a possibility for doping [2], but the electronic properties strongly depend on details of the microscopic structure [3].
Determining the microscopic structure of the adsorbed water, however, provides a major challenge for experiment [4]. Recently, locked between two graphene sheets, a new high-density phase of water has been proposed using transmission electron microscopy (TEM) [5]. The so-called 'square' ice provides a symmetry qualitatively different from both hexagonal ice as well as graphene. Modeling mono-, bi- and trilayer ice lattices within density functional theory (DFT) using the Quantum ESPRESSO code [6], we show that the pressure-induced phase transition from hexagonal to square ice is accompanied (*i*) by a shift of the Fermi-level thereby suppressing doping effects in graphene and (*ii*) by a characteristic change of the NMR chemical shifts. Hence, the detection via NMR spectroscopy appears as a promising alternative to electron imaging, in particular in case of nanostructures with a high amount of disorder, e.g. hydrophobic nanocapillaries.

Keywords: graphene, water adsorption, pressure, NMR chemical shifts, DFT.

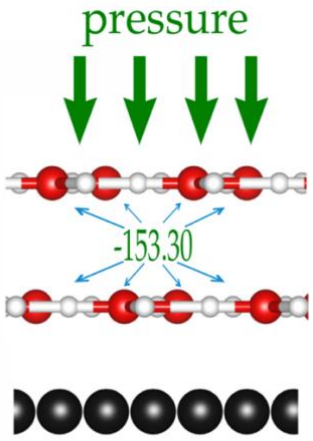


Figure 1: Figure illustrating the pressure induced phase transition towards 'square' ice which is accompagnied by a characteristic change of the ^{1}H and ^{17}O NMR chemical shifts.

References:

1. G. Malenkov, J. Phys. Condens. Matter **21**, 283101 (2009).
2. K.S. Novoselov *et al.*, Science **306**, 666 (2004).
3. T. Wehling *et al.*, Appl. Phys. Lett. **93**, 202110 (2008).
4. Y. Zheng *et al.*, Angew. Chem. Int. Ed. **52**, 8708 (2013).
5. G. Algara-Siller *et al.*, Nature **519**, 443 (2015); Nature **528**, E1 (2015).
6. P. Giannozzi *et al.*, J. Phys. Condens. Matter **21**, 395502 (2009); http://www.quantum-espresso.org

Joint Posters Session II
Properties and applications

Morphology and growth of carbon nanotubes synthesis by impinging flame

L. Marques,[1,*] A. Duarte,[1] E. Fernandes,[1]

[1] Universidade de Lisboa, Instituto Superior Técnico, IN+, Centro de Estudos em Inovação, Tecnologia e Políticas de Desenvolvimento, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal.

Abstract:
Carbon nanotubes (CNTs) have interesting properties which provides them various applications. CNTs exhibit semi-conducting or metallic behavior making them terrific conductors, besides that CNTs have great flexibility, high aspect ratio, tremendous Young's modulus, large surface areas; unique combination of stiffness, strength and tenacity, very high thermal and electrical conductivity [1]. In result, CNTs has been considered the material of the 21st century. Common methods for fabricating CNTs include plasma arc discharge, pulsed laser vaporization/laser ablation and chemical vapor deposition [2]. One particularly elegant approach is flame synthesis. This method is raising considerable interest for the production of CNTs because because it is very simple, economic and possesses the potential for high volume production of CNTs, which is crucial for application in nano-mechanical and electrical instruments, and also it opens the possibility to explore the use of biofuels in the context of CO_2 neutral path [3].
In this work, CNTs (Figure 1) was prepared under controlled premixed impinging flame of propane. It was evaluated the CNTs formation over two different values of Reynolds number at a fixed equivalence ratio. It was given special attention to the mass growth rate and how it evaluates over time. The CNTs were deposited on three different types of stainless-steel substrates and it was verified that the deposition shape and quantity varied accordingly to the Reynolds number used. The results show that by changing the Reynolds number, the flame shape has an important impact on growth process of CNTs.

Keywords: Carbon nanotubes, premixed impinging flame, stainless steel, propane.

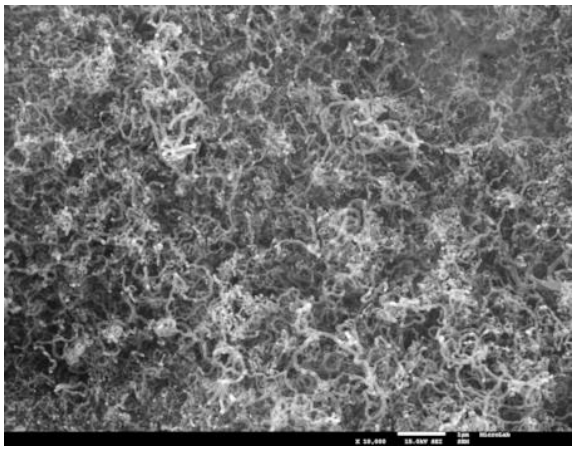


Figure 1: Scanning electron microscopy (SEM) micrographs for carbon nanotube morphology obtained by impinging flame.

References:

1. Poudel, Y. R.; Li, W., Synthesis, properties, and applications of carbon nanotubes filled with foreign materials: a review. *Materials Today Physics* 2018**,** *7*, 7-34.
2. Mubarak, N. M.; Abdullah, E. C.; Jayakumar, N. S.; Sahu, J. N., An overview on methods for the production of carbon nanotubes. *Journal of Industrial and Engineering Chemistry* 2014, *20* (4), 1186-1197.
3. Merchan-Merchan, W.; Saveliev, A. V.; Kennedy, L.; Jimenez, W. C., Combustion synthesis of carbon nanotubes and related nanostructures. *Progress in Energy and Combustion Science* 2010, *36* (6), 696-727.

Investigation of Polyoxometalate-Silica Thin Films for Chemical Gas Sensors

S. Krutovertsev,* L. Krutovertseva, O. Ivanova

JSC "Ecological sensors and systems", Moscow, Zelenograd, Russia

Abstract:
Chemical sensors of sorption type are widely used for gas analysis. Their behavior is determined by sensor characteristics of sensitive sorption layer. Activated inorganic oxide films are regarded as the perspective sensitive layers for sensors which can work at room temperature. The sensor behavior of nanostructured activated silica films produced by sol-gel route was examined. Polyoxometalates have reversible redox behavior, good electronic conductivity and chemical stability. Polyoxometalates of the eighteen series as catalyst of different redox processes were used as additives in the film for gas sensitivity. The sensor's interdigital structure was made by microelectronic planar technology. The active area of the sensor was 4 x 4 mm. The thickness of the electrodes was 0,2 mm. The width of finger pairs of electrodes and distance between them were 20 μm.
The method of hydrolythic polycondensation from tetraethyl orthosilicate solutions was used for forming such films in this work. Films were deposited by a centrifugation method from solutions based on tetraethyl orthosilicate and polyoxometalates. Environment influence on sol preparation and films forming was investigated. Morphology of the layers' surface, infrared spectra, adsorption activity and sensitivity to different gases were studied.
Films had thickness of 0,2-0,3 μm and nanoscale pores. The developed technology of multistep temperature treatment up to 423 K allowed film properties stabilizing. The environment affected markedly the sensor characteristics. Introduction of heteropolyanion into film resulted in film's mass stabilization. The reversible intramolecular redox reaction in polyoxometalate takes place at interaction of gas molecules with film's surface and it changes significantly electrophysical properties of film. The presence of molybdenum in the molecule of polyoxometalate increases reactivity. The polyoxometalates didn't display their catalytic activity at weight content less than 10 % in the film. Gas sensitivity maximum was observed at weight content of doping additive in range of 30–50% in matrix. Addition of polyoxometalate into silica film changed markedly of electrophysical characteristics. It is necessary to take into account the effect of humidity on the sorption characteristics of the films.

Keywords: nanostructured sol-gel film, doped silica film, polyoxometalate, gas sensitivity.

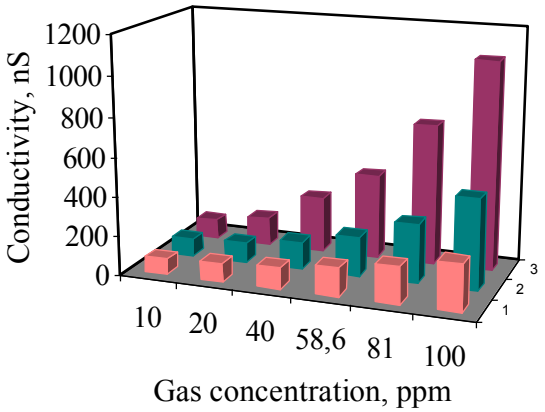


Figure 1: Typical conductivity dependence of $Mn_3P_2Mo_{18}O_{62}$-silica film on gas concentration in air: 1 - water vapours, 2 – ammonia, 3 – ethanolamine.

References:

1. Haralampos N. Miras, Jun Yan, De-Liang Long, Leroy Cronin (2012) Engineering polyoxometalates with emergent properties, *Chem. Soc. Rev.*, 41, 7403.
2. Thabet M.S. (2019), Anderson heteropolymolybdates cluster loaded on zeolite materials: preparation and characterization, *J. Encapsul. Adsorp. Sci.*, 9, 1-12.

Piezotronics effects in Schottky diodes fabricated in AlGaN/GaN heterstructures

B.K. Paszkiewicz, B. Paszkiewicz, M. Wosko, R. Paszkiewicz*

Faculty of Electronics Microsystems and Photonics, Wroclaw University of Science and Technology, ul. Janiszewskiego 11/17, 50-372, Wroclaw, Poland
*corresponding author: Regina.Paszkiewicz@pwr.edu.pl

Abstract:
Piezotronics is a dynamically developed science field dealing with the study of the influence of piezoelectric effects on semiconductor devices [1, 2]. The paper presents the results of measurements and simulations of the influence of external stresses on the load distribution in Schottky diodes fabricated in AlGaN/GaN heterostructure grown on sapphire substrate by MOVPE technique [3]. Samples, with fabricated Schottky diodes, were cut in the form of squares with a side of 2cm. They were cyclically deformed on the O-ring by application of negative pressure in the void area under the sample. The current flowing through the Schottky contacts was measured as a function of pressure and position on the sample (Fig. 1). Charge changes on the Schottky contact under cycylic preasure application was measured (Fig. 2). The measurements were performed under 0V forced polarization conditions using a high-precision semiconductor device tester equipped with an ultra-low currents measurement module. Additionally, optical profilometric measurements of the deflection profile were conducted and on their basis a simulation of stress distribution and piezoelectric polarization in the heterostructure was performed in Comsol Multihpisic using finite element methods. The results of the simulation were compared with experimental results. This allowed to determine the source of the observed phenomena as well as to evaluate the influence of external stresses on the operation of the devices fabricated in AlGaN/GaN heterostructure.

Keywords: piezotronic effect, AlGaN/GaN heterostructures, Schottky diodes, stresses

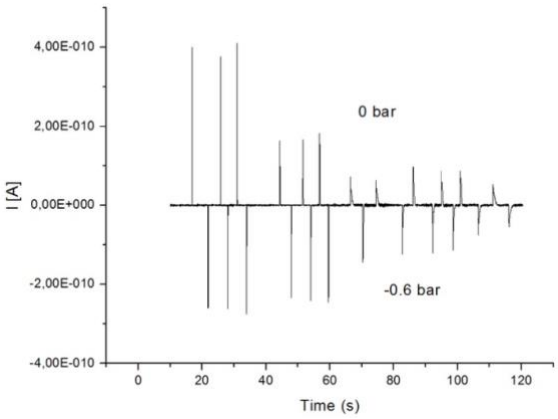


Figure 1: Current flowing through Schottky diode contact under cyclic pressure application (p=0,6 Bar)

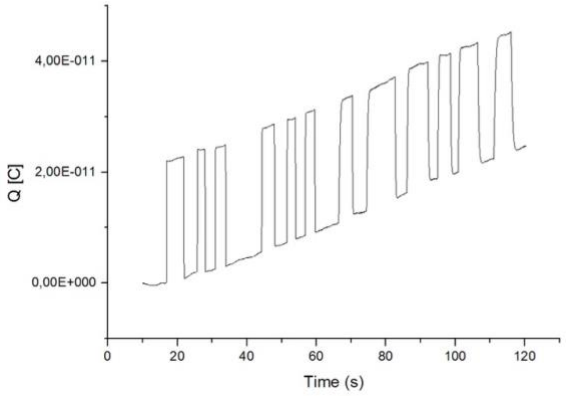


Figure 2: Charge changes on the Schottky contact under cyclic pressure application (V =0 V)

Acknowledgment:
This work was co-financed by the National Centre for Research and Development grants TECHMATSTRATEG No.1/346922/4/NCBR/2017, the National Science Centre grant No. DEC-2015/19/B/ST7/02494, Wroclaw University of Technology statutory grants and by the Slovak-Polish International Cooperation Program. This work was accomplished thanks to the product indicators and result indicators achieved within the projects co-financed by the European Union within the European Regional Development

Fund, through a grant from the Innovative Economy (POIG.01.01.02-00-008/08-05) and by the National Centre for Research and Development through the Applied Research Program Grant No. 178782 and Grant LIDER No. 027/533/L-5/13/NCBR/2014.

References:

1. W. Wu, C. Pan, Y. Zhang, X. Wen, and Z. L. Wang, “Piezotronics and piezo-phototronics - From single nanodevices to array of devices and then to integrated functional system,” Nano Today, vol. 8, no. 6. pp. 619–642, 2013.
2. K. Liu, H. Zhu, S. Feng, L. Shi, Y. Zhang, and C. Guo, “The effect of external stress on the electrical characteristics of AlGaN/GaN HEMTs,” Microelectron. Reliab., vol. 55, no. 6, pp. 886–889, 2015.
3. M. Ras-Zadeh, V. J. Gokhale, A. Ansari, M. Faucher, D. Théron, Y. Cordier, and L. Buchaillot, “Gallium nitride as an electromechanical material,” J. Microelectromechanical Syst., vol. 23, no. 6, pp. 1252–1271, 2014.

REDOX PEPTIDE FILM AS PLATFORM FOR C-REACTIVE PROTEIN IMMUNOSENSORS

Piccoli, J.P.[1]; Soares, A.C.[1]; Oliveira Jr, O.N.[1]; Bueno, P.R[2].; Cilli, E.M.[2]

[1]São Carlos Institute of Physics, University of São Paulo (USP); Brazi; [2]Institute of Chemistry, São Paulo State University (UNESP), Brazil

Abstract:
Detection of diseases requires new devices that can be inexpensive, easy to handle, with rapid, sensitive and selective responses, and that can be used outside specialized laboratories (point-of-care). This is possible with electrochemical immunosensors made of nanostructured films, in which effective immobilization of biomolecules is obtained to recognize the biomarker of clinical relevance. Nanostructured peptide films containing an active redox molecule are useful for immunosensors because they are stable and have controllable physicochemical properties[1]. In this work, synthesis of peptide Fc-Glu-Ala-Ala-Cys-NH_2 containing redox molecules of ferrocene as self-assembled monolayers (SAMs) was studied. A layer of antibodies and/or aptamers of CRP, an inflammatory processes and cardiac disease biomarker, was deposited on these peptide films, developing an electrochemical immunosensor for the detection and quantification of CRP. Techniques such electrochemical impedance spectroscopy and its capacitance derived were performed, achieving immunosensors with limit of detection better than those already studied, 240 pM using the antibody as bioreceptor, and 7,2 pM^2, for the aptamer. The enhanced performance using the aptamer demonstrated better efficiency, once its smallest size allows a better change in the electronic system when occurs the CRP bonding, resulting in a sensitivity of the system almost 8 times superior (87.7%) than the immunosensor constituted by the antibody (11.4%). The PM-IRRAS assays in agreement with the data obtained demonstrated that organization of the system is crucial for an improved detection. The results obtained enable to confirm that peptides monolayers can be used for the development of biosensors with different antigen/antibody systems, which would permit the advance of new point-of-care systems

Keywords: peptide, ferrocene, self-assembled monolayers, capacitance, C-reactive protein.

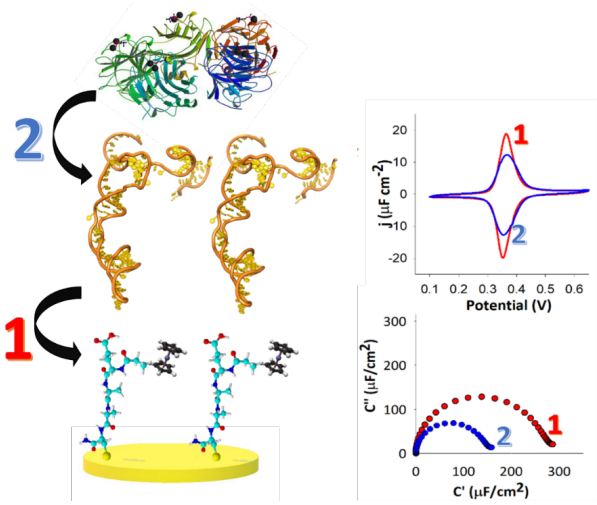


Figure 1: Representative schematic of the redox charging peptide-aptamer SAM and associated voltammetric and capacitive response. *Figure adapted from reference 2.

References:

1. PICCOLI, J. P. et al. The self-assembly of redox active peptides: Synthesis and electrochemical capacitive behavior. Biopolymers, 2016.
2. PICCOLI, J. et al. Redox Capacitive Assaying of C-Reactive Protein at a Peptide Supported Aptamer Interface. Analytical Chemistry, v. 90, n. 5, 2018.

Graphene and Graphene Derivates-based Gas Sensors: State of the Art and Realistic Outlook

S. Luby,[1,*] J. Ivanco,[1]

[1] Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia

Abstract:
The paper comments the state of the art of graphene and graphene derivates employed as active layers in chemiresistive gas sensors. Excellent properties of graphene such as high specific surface area, low noise, planar structure and related flexibility, and integrability are commonly highlighted as strengths in the sensors technologies. On the other hand, graphene has no dangling bonds functioning as prime reaction agents. It must be noted that the listed virtues are mostly related to the highest quality graphene samples [1] prepared either by mechanical exfoliation or chemical vapour deposition, yet most of investigated devices use chemically synthesized graphene derivates instead of genuine graphene. The unrelated reasoning has become a frequent cliché presumably due to the fascination by graphene ending in the press hyperactivity and races for research grants. This led us to propose more adequate view onto a capacity of graphene in gas sensors. We focused on four basic aspects: (i) the substantiation of the low noise for sensing devices, (ii) the assumed versus actual low surface area of the real graphene layers, (iii) the role of graphene sensors among the flexible devices and (iv) integration of graphene sensors into Si circuits. We summarize also the approaches used to increase the adsorption energy and, consequently, the reactivity of detected gases toward the graphene surface being free of dangling bonds. For example, the decoration of graphene by catalytic metals, e.g. Pd, is used by us [2] (Figure 1). It is assumed that at present graphene climbs out from the trough of disillusionment on the Gartner Hype Cycle. Even though no breakthrough of graphene in the gas sensors area is anticipated, specific applications, such as the room-temperature operated sensors, may have good prospects.

Keywords: graphene, graphene derivates, specific surface area, noise, planarity, adsorption energy, integration into Si circuits, hype and reality.

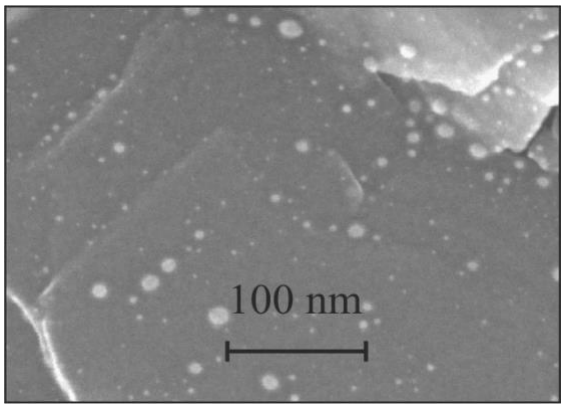


Figure 1: SEM image of few-layer graphene flakes with the thickness of 5 nm prepared by liquid-phase exfoliation from expanded milled graphite and deposited onto the silicon by Langmuir-Schaefer technique. Graphene was decorated by Pd nanoparticles by means of the spin-coating. The density of nanoparticles was $3\times10_{15}$ m^{-2}. They are uniformly distributed over a macroscopic scale with preferential locations at the edges of flakes functioning as the chemically active "hot" sites.

References:

1. Novoselov, K.S., Fal'ko, V.I., Colombo, L., Gellert, P.R., Schwab, M.G., Kim, K. (2012), A roadmap for graphene, *Nature*, 490, 192-200.
2. Kostiuk, D., Luby, S., Siffalovic, P., Benkovicova, M., Ivanco, J., Jergel, M., Majkova, E. (2019), Graphene Langmuir-Schaefer films decorated by Pd nanoparticles for NO_2 and H_2 gas sensors, *Measurement Science Review*, 19, 64 – 69.

Novel Type of SnO_2 Rheotaxially Grown and Vacuum Oxidated Films for NO_2 Sensing at Room Temperature

B. Lyson - Sypien,[1*] M. Kwoka,[1]

[1] Silesian University of Technology, Faculty of Automatic Control, Electronics and Computer Science, Institute of Electronics, Gliwice, Poland

Abstract:
Within this research special attention has been paid to NO_2 sensing characteristics of tin dioxide thin films obtained via rheotaxial growth and vacuum oxidation technique, RGVO [1,2]. This method, which enables to obtain pure SnO_2 films of desired stoichiometry and controlled, well developed morphology, is our unique modification of rheotaxial growth and thermal oxidation, RGTO [3].
In order to study surface chemical properties of SnO_2 samples including presence of contaminations, atomic relative concentrations and bodnings XPS was applied. For the purpose of morphology examination AFM and SEM were used. Gas sensing measurements in the range 1 – 50 ppm NO_2 at room temperature were realized with surface photovoltage gas sensor device described in [4].
SnO_2 RGVO thin films exhibit nanoscale less agglomerated morphology, no undesired carbon contamination is recognized. On the basis of the observed understoichiometry the presence of oxygen vacancies can be concluded. The samples presenting relatively high sensor response in the range 1 – 50 ppm are highly well promissing in terms of NO_2 detection at room temperature and can be examined towards ppb level of NO_2 in the near future.
This research was funded by the research grant of National Science Centre, Poland grant decision DEC-2016/20/S/ST5/00165 and partially realized within the Statutory Funding of Institute of Electronics, Silesian University of Technology, Gliwice, BK as well as BKM.

Keywords: SnO_2 thin films, rheotaxial growth and vacuum oxidation, NO_2 sensor, room temperature.

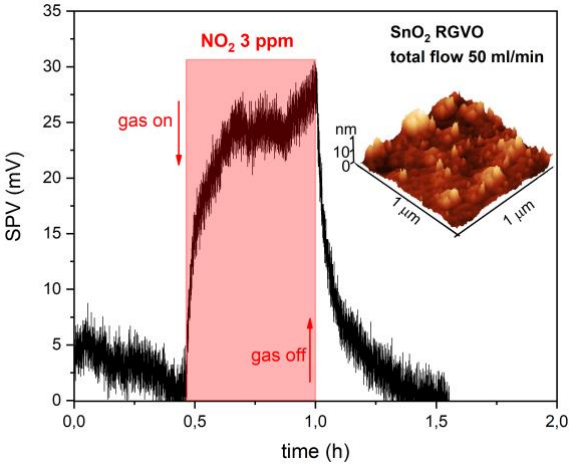


Figure 1: Gas sensor response of SnO_2 RGVO thin film towards 3 ppm NO_2; SPV denotes surface photovoltage; the inset: AFM image presenting morphology of the sample.

References:

1. Kwoka, M.; Krzywiecki, M. (2015), Rheotaxial growth and vacuum oxidation – Novel technique of tin oxide deposition – In situ monitoring of oxidation process, *Mat. Lett.,* 154, 1–4.
2. Kwoka, M.; Krzywiecki, M. (2017), Impact of air exposure and annealing on the chemical and electronic properties of the surface of SnO_2 nanolayers deposited by rheotaxial growth and vacuum oxidation, *Beilstein J. Nanotechnol.,* 8, 514-521.
3. Sberveglieri, G.; Faglia, G.; Groppeli, S.; Nelli, P.; Camanzi, A. (1990), A new technique for growing large surface area SnO_2 thin film (RGTO technique), *Semicond. Sci. Technol.,*5, 1231–1233.
4. Kwoka, M.; Borysiewicz, M.A,; Tomkiewicz, P,; Piotrowska, A.; Szuber, J. (2018), A novel type room temperature surface photovoltage gas sensor device, *Sensors*, 18, 2919-2929.

Surface Modification of Biodegradable Magnesium Mesh for Guided Bone Regenration by Hydrothermal Treatment

Y. Jang, [1,*] I. Park, [2,*] S. Wu, [1] M. Lee, [1] J. Ji, [1] M. Oh, [2] J. Yoon, [2]

[1] Chonbuk National University, School of Dentistry, Department of Dental Biomaterials, Institute of Oral Bioscience and Institute of Biodegradable Material, BK21 plus Program, Jeonju, South Korea
[2] Chonbuk National University, Division of Advanced Materials Engineering, Research Center for Advanced Materials Development and Institute of Biodegradable Materials, Jeonju, South Korea

Abstract:
Guided bone regeneration using a membrane is widely used to treat a severe bone defect in the orthopedic and dental fields. The biodegradable polymer membranes have excellent biocompatibility, but their low strength and structural defect by degradation can cause unexpected collapse of space by external force, which results in insufficient bone formation and clinical failure. Meanwhile, non-biodegradable metallic membranes have excellent strength and ductility, which are useful to apply to large bony defect and make a counter of membrane to suit a bony defect. However, non-biodegradable metallic membrane can cause the inflammatory reactions by irritation and corrosion due to long-term implantation, and the membrane can be broken or deformed by external repetitive load. Thus, lots of studies for the biodegradable metallic membranes are recently conducting because of their excellent mechanical properties and needlessness for secondary surgery to remove the membrane after the completed bone healing. Magnesium has good biocompatibility, biodegradability and the most similar elastic modulus to bone. However, magnesium alloys developed for biomaterial have faster biodegradation rate than the ideal rate, which causes unfavorable results for bone regeneration by the increased ion release and the decreased mechanical strength. Thus, many surface modification methods of magnesium have been developed to retard the biodegradation and enhance the biocompatibility. Especially, calcium phosphate coating on magnesium has been actively studied to facilitate osteogenesis. In this study, calcium phosphate coatings were formed on the magnesium meshes by hydrothermal treatment in aqueous solution including 0.25 mM Ca-EDTA and 0.25 mM KH_2PO_4 at 90 °C for various times. The hemispherical calcium phosphate single layer with 2 μm thickness was densely formed on the surface of magnesium by hydrothermal treatment for 2 hours, but double layer, composed of hemispherical calcium phosphate layer with 2 μm thickness at the bottom and acicular calcium phosphate layer with 8 μm thickness at the top, was formed by hydrothermal treatment for 10 hours. Corrosion current density (I_{corr}) and polarization resistance (R_p) measured by electrochemical corrosion tests significantly increased by hydrothermal treatments for over 2 hours. The cytocompatibility was evaluated by WST-8 and ALP analyses. The better proliferation and differentiation of mouse osteoblast-like cells (MC3T3-E1) were identified in the specimens coated by hydrothermal treatments for 2 and 5 hours in comparison with those of untreated magnesium.

Keywords: magnesium mesh, hydrothermal treatment, calcium phosphate coating, biodegradation, electrochemical corrosion behavior, cytocompatibility.

Acknowledgments: This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MSIT) (No. 2018R1D1A1B07049491 and 2019R1A2C1010250).

References:

1. Retzepi, M.; Donos, N. (2010), Guided bone regeneration: biological principle and therapeutic applications. Clin. Oral Implant. Res., 21, 567–576.
2. Staiger, M.P.; Pietak, A.M.; Huadmai, J.; Dias, G. (2006), Magnesium and its alloys as orthopedic biomaterials: A review. Biomaterials, 27, 1728–1734.
3. Cui, W.; Beniash, E.; Gawalt, E.; Xu, Z.; Sfeir, C. (2013), Biomimetic coating of magnesium alloy for enhanced corrosion resistance and calcium phosphate deposition. Acta Biomater., 9, 8650–8659.

Material and Biological Characteristics for Scaffold composed of Tooth and Tricalcium Phosphate Powders

M. Lee, [1,*] J. Gong, [1] Y. Jang, [1] I. Park, [2], J. Ji, [1] T. Bae, [1]

[1] Chonbuk National University, School of Dentistry, Department of Dental Biomaterials, Institute of Oral Bioscience and Institute of Biodegradable Material, BK21 plus Program, Jeonju, South Korea
[2] Chonbuk National University, Division of Advanced Materials Engineering, Research Center for Advanced Materials Development and Institute of Biodegradable Materials, Jeonju, South Korea

Abstract:
Scaffolds are usually used for the dental and orthopedic treatments such as the bone augmentation of bone defect and periodontal treatment. To form the enough new bone in bone defect rapidly, a scaffold should have the macro/micro porous interconnected structure for ion exchange, sufficient mechanical property, good biocompatibility and bioactivity, suitable biodegradability bone conductivity. Various calcium phosphates have been widely applied as a scaffold material for bone regeneration since it is a major component of bone and teeth. Among them, β-tricalcium phosphate (β-TCP) has the moderate bioabsorption rate, good biocompatibility and bone conductivity, but it has less bone formation and osteoinduction abilities and lower mechanical property in comparison with hydroxyapatite (HAp). HAp is a major inorganic component of bone and teeth, and has crystallographic and compositional similarities to bone, high strength and excellent biocompatibility. However, it has poor biodegradability. Therefore, scaffolds using biphasic calcium phosphates (BCP) mixed with various concentrations of TCP and HAp have been recently developed to obtain desired mechanical properties and absorption rate for bone graft, which are now successfully used for bone regeneration in many clinical fields. Although many material and clinical studies have been conducted to determine the optimal mixing ratio of TCP and HAp for optimal bone regeneration, there is currently no clear conclusion regarding the ideal ratio of BCP for clinical application. In this study, the material and biological properties were evaluated after manufacturing various scaffolds with mixed powders of tooth and β-TCP in various ratios. To prepare the scaffolds, the polyurethane foams were immersed for 1 min in various solutions in which tooth and β-TCP powder were mixed using ethanol, poly vinyl butyl and triethyl phosphate. And then, polyurethane foams was blasted using air compressor, and dried at 80°C for 5 min. This process was repeated three times. Finally, heat treatment was conducted 1300°C to remove polyurethane foam.
As the mixing ratio of the tooth powder increased in scaffold, crystal sizes on the surface were smaller and the surface hardness increased. Better hydrophilicity and cytocompatibility were identified on the scaffolds in which β-TCP and tooth powder were mixed with ratios of 7: 3 and 5: 5 in comparison to those of the scaffolds made of teeth or TCP only. It was also confirmed that more new bones were formed along the walls of the scaffolds in which β-TCP and tooth powder were mixed with ratios of 7: 3 and 5: 5 through micro-CT and histological analyses after implantation of scaffolds in defected femur of rabbits for 12 weeks.

Keywords: scaffold, bone regeneration, biphasic calcium phosphate, tricalcium phosphate, tooth powder, biocompatibility, rabbit tibia defect model.

References:

1. Habraken W, Habibovic P, Epple M, Bohner M. (2016), Calcium phosphates in biomedical applications: materials for the future? Mater. Today. 19(2):69-87.
2. Ebrahimi M, Botelho MG, Dorozhkin SV. (2017), Biphasic calcium phosphates bioceramics (HA/TCP): concept, physicochemical properties and the impact of standardization of study protocols in biomaterials research. Mater. Sci. Eng. C. 71:1293-312.
3. Gauthier O, Goyenvalle E, Bouler J-M, Guicheux J, Pilet P, Weiss P, et al. (2001), Macroporous biphasic calcium phosphate ceramics versus injectable bone substitute: a comparative study 3 and 8 weeks after implantation in rabbit bone. J. Mater. Sci.: Mater. Med. 12(5):385-90.

Chitosan/ Hydroxyapatite/Magnetite Biocompatible Scaffolds for Bone Tissue Engineering

A. Pistone,[1*] D. Iannazzo,[1] C. Celesti,[1] E. Piperopoulos,[1] D. Ashok,[2] A. Cembran,[2] A. Tricoli,[3] D. Nisbet[2]

[1] University of Messina, Department of Engineering, Messina, Italy
[2] Laboratory of Advanced Biomaterials, Australian National University, Canberra, Australia.
[3] Nanotechnology Research Laboratory, Australian National University, Canberra, Australia

Email: pistone@unime.it

Abstract:
Bioadsorbable scaffolds have received increasing attention as innovative systems for the development of osteoconductive biomaterials for bone tissue engineering.[1] Among the different biopolymers used for the development of these scaffolds, chitosan (CS), a natural polysaccharide, has shown significant promise due to its inherent biocompatibility and biodegradability. Hydroxyapatite (HA) powder is often added to chitosan matrix in order to synthesize composites with improved mechanical properties and osteoconductive properties compared to the chitosan hydrogel alone.[2] Magnetic nanoparticles have been also investigated for biological and medical purposes, such as hyperthermia, contrast agents for magnetic resonance imaging and magnetic drug delivery and their biocompatibility has been validated by several studies.[3]

We report a study about chitosan based composites synthesized adding nanosized HA and/or MGN in a chitosan matrix by *in situ* precipitation technique. The nanocomposites were characterized by optical and electron microscopy, TGA, XRD and by *in vitro* cell culture studies. In situ precipitation has proved to ensure superior homogeneous dispersion of HA inside the chitosan matrix with respect to what observed starting by HA powder. Morphological and chemical characterizations confirmed the distribution of crystalline HA and MGN in the biopolimeric matrix obtained by in situ precipitation; HA showed low or medium values of crystallinity and/or nanosized crystallites (20 nm), ensuring a high metabolic activity. The synthesized composites showed good biocompatibility and the ability to support cell attachment and proliferation; remarkably, the inclusion of magnetite increases the number of osteoblast cells that infiltrated the hierarchical scaffold and, more importantly for implant therapy, increases the number of viable osteoblast cells at the scaffold interface (Fig. 1). The composite CS/HA/MGN demonstrated superior bioactivity with respect to pure CS and to the CS/HA scaffolds, making it a suitable and promising materials for guided bone growth.

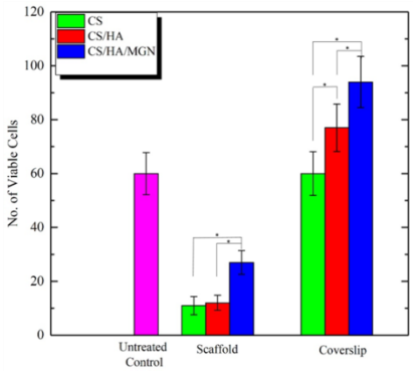


Figure 1: Biological characterization of chitosan based nanocomposites.

Keywords: nanocomposites, chitosan-based polymers, hydroxyapatite, magnetic nanoparticles, tissue engineering.

References:

1. J. Wang, L. Wang, Z. Zhou, H. Lai, P. Xu, L. Liao and J. Wei, (2016) Biodegradable Polymer Membranes Applied in Guided Bone/Tissue Regeneration: A Review. *Polymers* 8, 115;(20 pp).
2. S. Saravanan, R.S. L., N. Selvamurugan, (2016) Chitosan based biocomposite scaffolds for bone tissue engineering, *Int. J. Biol. Macromol.*, 93, 1354–1365.
3. A. Pistone, D. Iannazzo, S. Panseri, et al. (2014),Hydroxyapatite-magnetite-MWCNT nanocomposite as a biocompatible multifunctional drug delivery system for bone tissue engineering. Nanotechnology, 2014, 25, 425701.

Effects of Magnetic Nanoparticles and External Magnetic Fields on Glioblastoma Wnt Signaling Pathway

Seung Hyun Yang[1,2], Yuna Choi[1], Mirae Park[1], Hyun Wook Rho[1], Hye-Young Son[1,3], Yong-Min Huh[1,3*]

[1] Department of Radiology, College of Medicine, Yonsei University, Seoul, Korea
[2] Interdisciplinary Program in Nanomedical Science and Technology, Yonsei University, Seoul, Korea
[3] YUHS-KRIBB Medical Convergence Research Institute, Seoul, Korea

Abstract:
In recent decades, lots of magnetic nanoparticles are invented and developed for many purposes. One of the biggest advantages of magnetic nanoparticles was their very large surface area to mass, it can effectively used for the drug or gene delivery, and also used for magnetic resonance imaging contrast agent[1].
Some researchers were tried to very interesting studies, such as make an 'artificial receptor trimerigation' for cell signaling[2], tumor migrations and tumor cell capture[3] using magnetic nanoparticles and an external magnetic field. It was very tremendous and precious experiment and shown another possibility with magnetic nanoparticles.

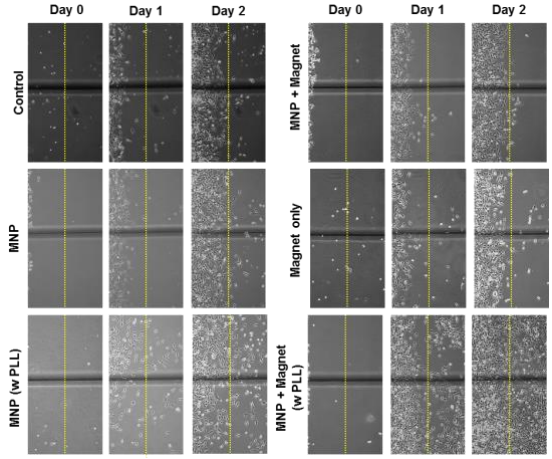


Figure 1: Cell migration assay of various conditions using U-87 MG glioblastoma cells. The magnets were located on the right side.

Many studies have confirmed excellent value for the application of magnetic nanoparticles and external magnetic fields. We have also tried many experiments using magnetic nanoparticles such as iron oxide or manganese ferrite nanoparticles for drug and gene delivery or imaging contrast agent. Unfortunately, sometimes we have found that some tumor models using both magnetic nanoparticles and an external magnetic field show faster tumor growth than other conditions. Therefore, we have biologically verified the relationship between magnetic nanoparticles and external magnetic fields.

Now we report the influence of different result using magnetic nanoparticles and an external magnetic field. We used poly-L-lysine (PLL) to make 12 nm size manganese ferrite magnetic nanoparticles highly uptaked U-87 MG glioblastoma cell, then exposed external magnetic field using neodymium magnet in vitro (Figure 1). Then we could observe tumor cell migration under the influence of the external magnetic field, which means that the magnetic nanoparticle uptaked cells were sufficiently exposed to the external magnetic field.

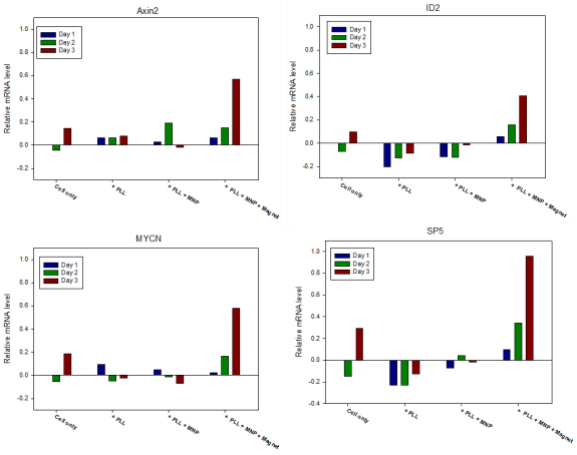


Figure 2: Effects of magnetic nanoparticles and external magnetic field on mRNA levels of U-87 MG cells. The relative mRNA levels were measured by qPCR.

Subsequently, magnetic nanoparticle uptaked cells were implanted in Balb/c nude mice on the right thigh and exposed to an external magnetic field using neodymium magnets for 2 weeks. Four weeks after the cells were injected, we observed that tumors from mice exposed to

magnetic fields grew faster than tumors from unexposed mice. We also implanted same cells in right frontal lobes of Balb/c nude mice. Which is external magnetic field exposed mice were shown worse survival than without an external magnetic field.

To find this reason of result, we confirmed several mRNA levels in vitro. Some mRNA levels were elevated under magnetic nanoparticles and external magnetic field and these mRNAs were mostly related with the Wnt signaling pathway[4] which is one of the key cascades regulating cancer (Figure 2).

This study will helpful for cancer study using drug and gene delivery, cell capturing and magnetic resonance imaging study which are using magnetic nanoparticles and affected by external magnetic field. We also believe that this study will be useful in establishing new tumor models for studying the Wnt signaling pathway.

Keywords: magnetic nanoparticles, manganese ferrite nanoparticles, external magnetic field, Wnt signaling pathway

References:

1. Lee, J.-H.; Huh, Y.-M.; Jun, Y.-w.; Seo, J.-w.; Jang, J.-t.; Song, H.-T.; Kim, S.; Cho, E.-J.; Yoon, H.-G.; Suh, J.-S.; Cheon, J., Artificially engineered magnetic nanoparticles for ultra-sensitive molecular imaging. Nature Medicine 2006, 13, 95.
2. Lee, J.-H.; Kim, E. S.; Cho, M. H.; Son, M.; Yeon, S.-I.; Shin, J.-S.; Cheon, J., Artificial Control of Cell Signaling and Growth by Magnetic Nanoparticles. Angewandte Chemie International Edition 2010, 49 (33), 5698-5702.
3. Shi, W.; Wang, S.; Maarouf, A.; Uhl, C. G.; He, R.; Yunus, D.; Liu, Y., Magnetic particles assisted capture and release of rare circulating tumor cells using wavy-herringbone structured microfluidic devices. Lab on a Chip 2017, 17 (19), 3291-3299.
4. Lee, E.; Yang, J.; Ku, M.; Kim, N. H.; Park, Y.; Park, C. B.; Suh, J. S.; Park, E. S.; Yook, J. I.; Mills, G. B.; Huh, Y. M.; Cheong, J. H., Metabolic stress induces a Wnt-dependent cancer stem cell-like state transition. Cell Death &Amp; Disease 2015, 6, e1805.

Cell-penetrating Peptides and their Influence on Polyomavirus-based Nanosystems

M. Hubalek Kalbacova[1*], J. Vanova[2], A.Hejtmankova[1,2], J. Zackova Suchanova[2], P. Sauerova[1], J. Forstova[2], H. Spanielova[2,3]

[1] 1st Faculty of Medicine, Chareles University, Prague, Czech Republic

[2] Faculty of Science, Charles University, Prague, Czech Republic

Abstract:

Cell penetrating peptides (CPP) and histidine rich peptides have been used to enhance intracellular delivery of various associated cargos[1] including viral particles. We selected four peptides: cationic octaarginine (R8), histidine-rich peptides (LAH4 and KH27K) and fusogenic peptide (FUSO), and examined their effect on infection of mouse polyomavirus (MPyV) or on transduction of reporter gene by viral vectors derived from MPyV, simian virus 40 (SV40) or mouse papillomavirus (MusPV). We investigated these viral vectors as model cargos as well as the potential gene and drug delivery vehicles. Peptides R8, LAH4 and KH27K but not FUSO were found to enhance both MPyV infection, and transduction rates when non-covalently associated with wild-type virus or polyomavirus-based vectors prior to adding to cells. LAH4 and KH27K peptides were shown to induce aggregation of fluorescently labeled viral particles on cellular surface. Moreover, LAH4 caused massive and rapid association of viral particles with cells. We also demonstrated that LAH4 and R8 destabilize viral particles during their co-incubation. Taken together, peptides that are effective as transduction enhancing agents for polyomavirus-based viral vectors alter two very important features of viral particles: their metastability and mode of entry. Elucidating the precise mechanism of the peptides' action is important for understanding peptide function as well as for further optimizing scalable viral and non-viral based gene delivery protocols.

Keywords: cell penetrating peptide, polyomavirus, viral vectors, intracellular delivery

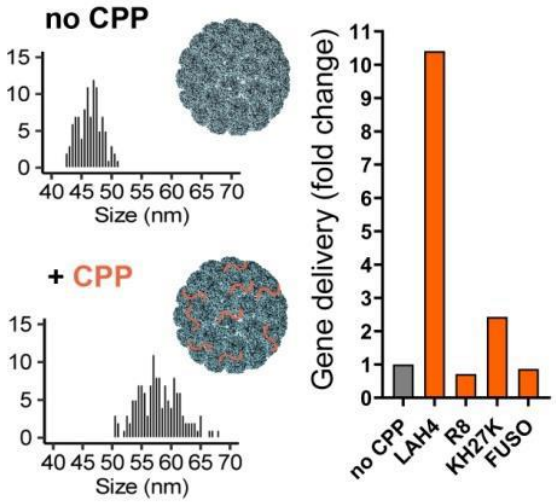


Figure 1: Effect of CPP on viral particle size and infectivity.

References:

1. Deshpande,P., Jhaveri, A., Pattni, B., Biswas, S. Torchilin, V., (2018), *Drug Deliv*.,25,517
2. Fernand, D., Genries, S., Scherman, D., Galy, A., Martin, S., Kichler, A.(2013),*J. Virol. Methods,* 189, 375
3. Vaysse, L. Burgelin, I. Merlio, J.P. Arveiler, B., (2000) *Biochim. Biohphys. Acta BBA – Gen. Subj.1475, 369*

Drug-carrying gold-iron nanowires for local treatment of glioblastoma multiforme

J. M. Taylor[1], M. Williams[1], M. P. Ryan[1], A. E. Porter[1]

[1]Imperial College London, London Centre for Nanotechnology, United Kingdom

Abstract:

Locally administered nanotechnology and chemotherapy are of growing clinical importance in multiple types of cancer, particularly in glioblastoma multiforme (GBM). The blood-brain barrier prevents many useful technologies from reaching the tumour and targeting approaches have thus far failed to overcome this obstacle. To effectively treat GBM, emerging technologies will require multi-modality due to the heterogeneity of the disease. This poster-presentation will describe a novel, multimodal gold-iron nanowire with potential as a drug carrier. Gold nanoparticles are useful for radiotherapy, photothermal therapy and near infra-red triggered-release whereas iron nanoparticles are useful for magneto-thermal therapy, triggered-release and MRI. Combining gold and iron into a nanowire would create a nanoparticle with the useful properties of both materials. Further, the particles can be functionalised with chemotherapy drugs and by exploiting the different surface chemistries of gold and iron different drugs could be attached to the gold and iron segments of the nanowire. The intention is to create a nanoparticle which can be administered to a brain tumour through a process similar to a brain-needle biopsy and used for combination therapy (Figure 1). Nanowires are electrochemically deposited, and the resulting structures will be discussed. Initial studies of the therapeutic effect of the nanowires in glioblastoma cells will be presented.

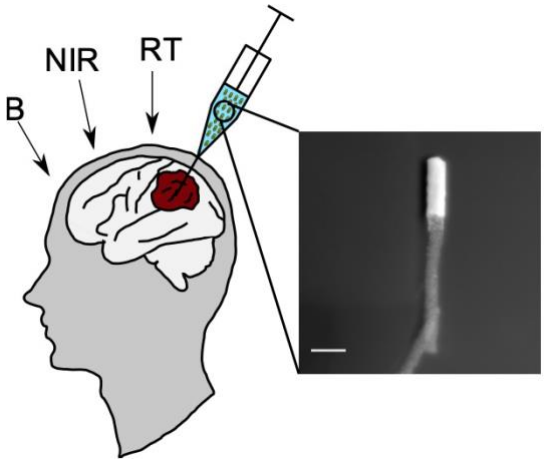


Figure 1: Schematic representation of the proposed route of gold-iron nanowire therapy. B, NIR and RT denote application of an external magnetic field, administration of near infra-red radiation and radiotherapy respectively. The inset image is a Z-contrast scanning-TEM of a gold-iron nanowire, scale bar 100nm.

Keywords:

Nanomedicine, Cancer, Glioblastoma, Tumour, Nanowire, Radiotherapy, Photo-Thermal, Magneto-Thermal, Hyperthermia, Muliti-Modal, Drug-Delivery, Nanotechnology, Gold, Iron, Electrochemistry, Electrodeposition, Triggered Drug-Release

Methylene blue-loaded PLGA nanoparticles as adjunct in periodontal antimicrobial photodynamic therapy

Carla Raquel Fontana[1]*, Juçaíra Stella M Giusti[2], Nikolaos S. Soukos[3], Mansoor M. Amiji[4] Vanderlei Salvador Bagnato[2]

[1] Universidade Estadual Paulista (UNESP), Faculdade de Ciências Farmacêuticas, Campus Araraquara, Departamento de Análises Clínicas, Rodovia Araraquara-Jau s/n, Araraquara 14800-903 SP, Brazil; phone +55-16-33015727

*Correspondence: fontanacr@fcfar.unesp.br Tel.: +55-16-3301-5727

[2] Instituto de Fisica de Sao Carlos, Universidade de Sao Paulo, Caixa Postal 369, 15980-900, Sao Carlos, SP, Brazil ; jsmgiusti@gmail.com; vander@ifsc.usp.br

[3] Applied Molecular Photomedicine Laboratory,The Forsyth Institute, 245 First Street, Cambridge, MA 02142, USA, n.soukos@neu.edu

[4] Department of PharmaceuticalSciences, School of Pharmacy, Bouvé College of Health Sciences, Northeastern University, 140 The Fenway, Room 156, 360 Huntington Avenue Boston, MA, USA; m.amiji@neu.edu

Abstract:

Antimicrobial photodynamic therapy (aPDT) is increasingly being explored for treatment of periodontitis. Here, we investigated the effect of aPDT on human dental plaque bacteria in suspensions and biofilms *in vitro* using methylene blue (MB)-loaded poly(lactic-co-glycolic) (PLGA) nanoparticles (MB-NP) and red light (660 nm). The effect of MB-NP-based aPDT was also evaluated in a clinical pilot study with 10 adult human subjects with chronic periodontitis. Dental plaque samples from human subjects were exposed to aPDT - in planktonic and biofilm phase - with MB or MB-NP (25 μg/mL) at 20 J/cm² *in vitro*. Patients were treated either with ultrasonic scaling and scaling and root planing (SRP) or ultrasonic scaling + SRP + aPDT with MB-NP (25 μg/mL and 20 J/cm²) in a split-mouth design. In biofilms, MB-NP eliminated approximately 25% more bacteria than free MB. The clinical study demonstrated the safety of aPDT. Both groups showed similar improvements of clinical parameters 1 month following treatments. However, at 3 months ultrasonic SRP + aPDT showed a greater effect (28.82%) on gingival bleeding index (GBI) compared to ultrasonic SRP. The utilization of PLGA nanoparticles encapsulated with MB may be a promising adjunct in antimicrobial periodontal treatment.

Keywords: photodynamic therapy, poly (lactic-co-glycolic, human dental plaque, bacteria, biomedical applications, microbiological and clinical study.

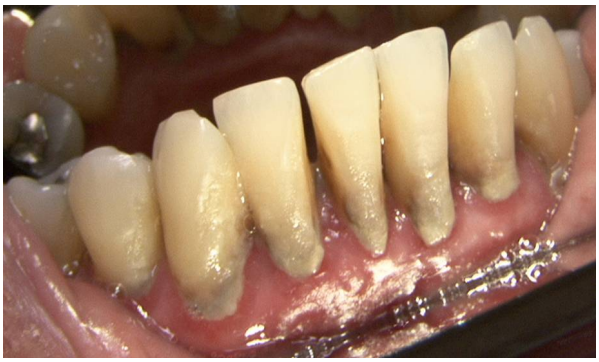


Figure 1: Figure illustrates the fundamental question that we are trying to solve clinically. With *in vivo* and *in vitro* studies, we aimed at the complete elimination of the dental biofilm and the decontamination of the periodontal pockets. To this end, we evaluated the adjuntive action of nanoparticles loaded with methylene blue for the reestablishment of periodontal health through antimicrobial photodynamic therapy

References:

1. Klepac-Ceraj V, et al. Photodynamic Effects of Methylene Blue-Loaded Polymeric Nanoparticles on Dental Plaque Bacteria. *Lasers Surg Med* 2011; 43:600–606. doi: 10.1002/lsm.21069.
2. Calixto GMF, et al. Nanotechnology-Based Drug Delivery Systems for Pho-

todynamic Therapy of Cancer: A Review. *Molecules*, 2016, *21*, 342, doi:10.3390/molecules21030342.

3. Fontana CR, et al. The antibacterial effect of photodynamic therapy in dental plaque-derived biofilms. *J Periodontal Res*, 2009, *44(6)*, 751-9, doi: 10.1111/j.1600-0765.2008.01187.x.
4. Lucky SS, Soo KC, Zhang Y. Nanoparticles in Photodynamic Therapy. *Chem Rev*, 2015, *115 (4)*, 1990–2042, doi: 10.1021/cr5004198

Properties of Ion Pair Amphiphile Complexes as Possible Drug Delivery Systems

J. Krouská,[1,*] M. Havlíková[1], J. Szabová[1], L. Mravcová[1], C.-H. Chang[2], F. Mravec[1]

[1] Materials Research Centre, Faculty of Chemistry, Brno University of Technology, Czech Republic
[2] Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan

Abstract:
Ion pair amphiphiles (IPA), a class of pseudo-double-chain surfactants, are formed by the interaction of oppositely charged surfactants/lipids with subsequent removal of their counterions. These systems, when they are dispersed in an aqueous medium, form vesicles which are suitable as carriers of low [1] or high molecular weight (e.g. DNA [2]) substances. The vesicular form of the carrier makes it possible to incorporate water-insoluble substances as well as water-soluble substances into these systems (Figure 1). A major advantage of these systems is their enormous versatility. By combining various surfactants/lipids with suitable properties, a very wide range of vesicular systems with different properties (e. g. phase transition temperature) can be prepared. Pure IPA systems have a very little physical stability. The improvement can be achieved by incorporating another, typically double-chained, surfactant/lipid into the IPA vesicle structure. This, in addition to increasing stability, also has the positive effect of creating interaction sites for oppositely charged polymeric substances. These substances can then be vesicle carried (DNA) or serve as a protective colloid (e.g. hyaluronan).
This contribution is focused on comparing the well known IPA system, a compound of dodecyl sulphate anion and hexadecyltrimethylammonium cation, with new systems where standard surfactants are replaced by analogs with different structures. Carbethopendecinium bromide was selected as a cationic surfactant. This surfactant has a different hydrophilic head structure and affects the stability and size of the formed vesicles. Similarly branched form of sodium tetradecyl sulphate has a significant influence on the character and way of formation of vesicular systems. The addition of a stabilizing agent, in the form of a double-chain positive surfactant, has also a different effect. In conclusion, the combination of different forms of surfactants/lipids will lead to a high diversity of emerging vesicular systems.

Keywords: ion pair amphiphile, vesicular systems, physical stability, dynamic light scattering, zeta potential

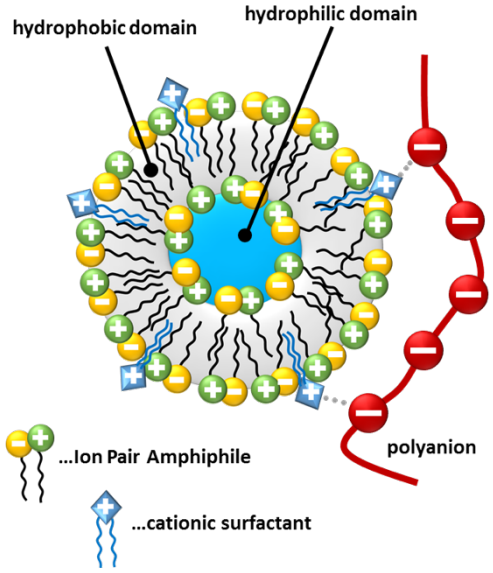


Figure 1: Schematic design of positively charged vesicular system suitable for solubilization of biologically active substances as well as for interaction with negatively charged poly - mers.

References:

1. Bramer, T., Dew, N., Edsman, K. (2007) Pharmaceutical applications for catanionic mixtures, *J. Pharm. Pharmacol.,* 59, 1319-1334.
2. Lee, C.-H., Yang, Y.-M., Leu, K.-L., Lin, H.-Y., Liang, C.-H., Chang C.-H. (2015), Exploring physical stability characteristics of positively charged catanionic vesicle/dna complexes, *Colloid. Polym. Sci*., 293, 2239-2247.

Acknowledgement: This work was supported by the Czech Science Foundation, project No. 19-14024J (GACR), and Ministry of Science and Technology, Taiwan, project No. MOST108-2923-E-006-006-MY3.

Solid Lipid Nanoparticles for Topical Antiseptic Delivery and Release in Wound Healing

M. Rysová,[1,*] H. Tománková,[1] M. Schaabová[1], M. Buzgo[2], T. Zajíc[1,3]

[1] Technical University of Liberec, iNTEC Department, Liberec, CZ
[2] Grade Medical s.r.o., Prague, CZ, [*]*miroslava.rysova@tul.cz*
[3] Regional Hospital, Centre for Laboratory Medicine, Liberec, CZ

Abstract:
Wound healing is a complex process which, in some cases, might be disrupted and slowed down by ongoing infection and inflammation. Over the course of time, these processes, if not treated, may lead to life-threatening states demanding a surgical intervention and/or amputation. Risk of such as complications is even increased by the patient´s health condition such as diabetes mellitus (DM) or other chronic disease, inflammation, immunosuppression, nutritional status, vascular insufficiencies, and more.[1] Approximately 7.3% of the DM patients experience wound infection often followed by amputation. For example, the population of patients diagnosed with DM in 2011 reached 2.5 million in the UK alone.[2] This upsurge emphasize the importance of development of new highly effective drug delivery systems for wound management. According to the actual wound treatment trends, attention of researchers is dedicated to in situ drug application and number of novel nanoparticulate dosage forms has been developed. Solid lipid nanoparticles (SLN), belonging to semisolid dosage forms group, represent an interesting dosage form – as they are easy to produce and offering very good encapsulation efficiency for variety of compounds including proteins, hydrophilic drugs and lipophilic compounds in an organic solvents free system[3]. In this study, we present applicability relevant data of gentamicin doped SLN for contaminated wound treatment. These nanoparticles, characteristic by low melting temperature enabling sustained drug release at the body conditions over 72 hours, were formed by emulsification technique and were subsequently evaluated for particle size distribution, antibacterial activity against model strains *E. Coli* and *S. Gallinarum* and cytocompatibility to Hacat keratinocytes and dermal fibroblasts *in vitro*.

Keywords: Solid lipid nanoparticles, drug delivery, antibiotic delivery, wound healing, infection treatment, biomedical applications.

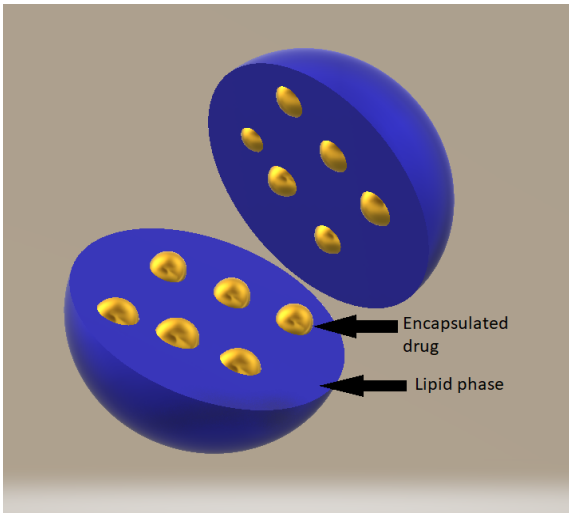


Figure 1: Figure illustrating the SLN nanoparticle structure with drug embedded in the lipid matrix.

Acknowledgements: This work was supported by the ministry MPO of the Czech Republic project MPO Trio FV10605 and the ministry MŠMT of the Czech Republic and the European Union - European Structural and Investment Funds programme - project Hybrid Materials for Hierarchical Structures (HyHi, Reg. No. CZ.02.1.01/0.0/0.0/ 16_019/0000843).

References:

1. Hess, C. T. (2011), Checklist for factors affecting wound healing, *Adv. Skin Wound Care,24(4), 192.*
2. Ashraff, S. et al. (2018), Complications of stump heling among diabetic population, *Turk. J. Endocrinol. Metab*., 22, 91-97.
3. Perez, L. B. et al. (2016), Solid lipid nanoparticles for encapsulation of hydrophilic drugs by an organic solvent free double emulsion technique, *Col Surf B Biointerfaces*, 140, 317-323.

AT101-loaded cubosomes: translational diffusion investigated with NMR technique and *in vitro* therapeutic efficiency

Dorota K. Flak[1*], Vivian Adamski[2], Grzegorz Nowaczyk[1], Kosma Szutkowski[1], Michael Synowitz[2], Janka Held-Feindt[2], Stefan Jurga[1]

[1]NanoBioMedical Centre, Adam Mickiewicz University Poznań, Poland
[2]University Hospital Schleswig-Holstein, Campus Kiel, Department of Neurosurgery, Kiel, Germany

Abstract:

Cubosomes are colloidal nanoparticles (NPs), formed by the steric or electrostatic stabilization process modulated by the self-assembly of surfactant-like lipids forming the non-lamellar phases in excess water and in the presence of a stabilizer. The internal structure of these NPs consists of single membrane bilayer forming a lattice structure type network with two continuous intertwining, but non-intersecting aqueous channels. Their exotic structure with an extensive system of water channels enables the trapping of number of active cargo, incl. pharmaceutics with different polarity, and further their diffusion to the ambients. This feature ensures increased drug solubility and its *in vitro* and *in vivo* uptake. An important advantage of these systems is also their outstanding colloidal stability. The pharmaceutical use of cubosomes is still in its infancy in comparison to liposomes, however due to their unique properties and number of promising research results on raw unmodified lipid NPs it is expected to grow.

In this study the synthetic approach for cubsomes preparation, but also AT101 drug loading and release studies will be presented. AT101 polyphenol gossypol drug has been used as it is considered as a promising drug for *Glioblastoma multiforme* (GBM) therapy. However, due to its poor solubility in water-based it possess low bioavailability, which further affects its limited response rate during the treatment. Therefore, it will be presented that AT101 can be efficiently loaded into cubososmes, forming highly stable colloids with continuous sustained drug release profile. This finding will be supported with the results from the high-resolution diffusion NMR, allowing for the resolving the translantional motion of each of compounds in the cubosome-water dispersion and to investigate, whether the AT101 drug is loaded into the cubosome particle. In addition the effect of the drug loading on the nanoparticles formation and structure will be presented.

Keywords: AT101, cubosomes, glyceryl monooleate, lipid, NMR diffusometry, Pulsed Gradient Spin Echo NMR, dynamic light scattering, cryo-TEM, drug delivery, GBM therapy.

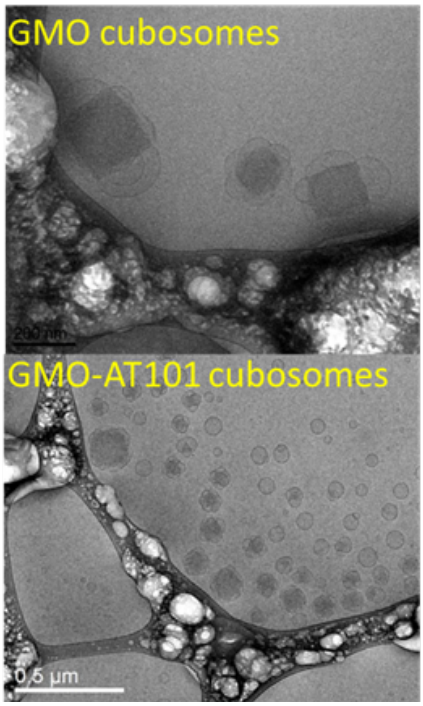


Figure 1: Cryo-TEM images of unloaded GMO cubosomes and drug loaded GMO-AT101 cubosomes.

References:

1. Azmi, I.D.M., Moghimi, S.M., Yaghmur, A., Cubosomes and hexosomes as versatile platforms for drug delivery, *Therapeutic Delivery*, 6 (2015) 1347-1364.
2. Barriga, H.M.G., Holme, M.N., Stevens, M.M., Cubosomes: The Next Generation of Smart Lipid Nanoparticles?, *Ang. Chem. Int. Ed.,* 0 (2018).

Electrochemical immunosensors for detection of drug resistant bacterial infection

R. Grinyte[1], B. Pérez-López[1], J.L. Muñoz-Gomez[1], M. McConnell[2], J. Dominguez[2], J.J. Infate[2], J. M. Cabot[1], M. Masa[1]

[1] Technological Center LEITAT C/ de la Innovació, 2, 08225 Terrassa (Barcelona), Spain
[2] Campo Hospital Universitario Virgen del Rocio, Av. Manual Siurot, s/n, Centro de Documantacion Clinica, 41013 Sevilla, Spain

Abstract:
Antibiotic resistance is one of the biggest threats to global health according to the world health organization. By 2050, non-curable infections are estimated to kill 10 million people per year worldwide - more than currently die from cancer - unless action is taken. The nosocomial infections are contracted in hospitals or health care facilities, and occur after 48 hours following hospitalization of medical care. In the world, the average is 5 to 10% of hospitalized patients are affected by nosocomial infections [1]. In 87% cases, bacteria are the most common cause. Besides that, infected patients are usually asymptomatic in the early stages of infection. Because of this, many health complications appear mainly due to a diagnostic delay [2]. Following the protocol, blood samples are taken and brought to the microbiology laboratory for its analysis, and this period takes a minimum of 2 days. An rapid diagnostic contributes to increase the successful clinical results. The development of electrochemical immunosensors can be envisaged as a promising alternative for detection and rapid identification of these bacteria associated to this kind of infections. These immunodevices can show excellent analytical capabilities such as sensitivity, reproducibility and feasible miniaturization. For this reason, a sensitive immunosensor is being developed for an early and fast detection of antibiotic resistant *Acinetobacter baumannii* bacteria.
We report comparison of electrochemical biosensors with different detection methods: label-free, with gold nanoparticles (NPs) and with enzyme. Self-assembled monolayers of thiols were spontaneously formed on a gold electrode and functionalized with antibodies specifics to *Acinetobacter baumannii*. Bacteria were detected label free method with differential pulse voltammetry (DPV) technique. For another detection method, gold NPs were functionalized with detection antibodies specific to bacteria with DPV technique. In the last detection method detection antibodies were labeled with enzyme and bacteria were detected by enzymatic reaction with amperometric technique. The results demonstrate that immunoassay based on enzymatic detection shows the best sensitivity and specificity while label free method suffer from nonspecific adsorption of biomolecules and gold NPs based method suffer of the loss of conductivity of NPs covered by antibodies.

Keywords: immunosensor, antibiotic resistance *Acinetobacter baumannii*, electrochemistry, screen printed electrodes, surface modification with biomaterials, diagnostic device.

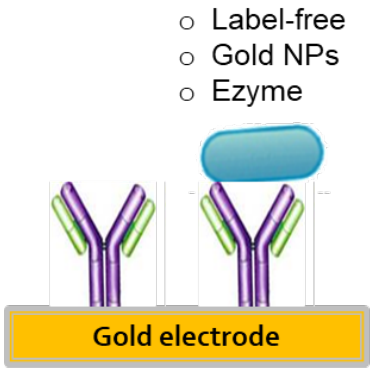


Figure 1: Detection methods of *Acinetobacter baumannii* (Gram negative)

References:

1. WHO. The burden of health care-associated infection worldwide. 2016. [Online] Available from: http://www.who.int/gpsc/country_work/burden_hcai/en/
2. Raberalam T., Balde M., Hantova S., Vena A., Marchandin H., Sorli B., (2017) *Procedia Technology*. 27, 295 – 298.

Fabrication and characterization of micro/nanofibrous scaffolds made using drawing method and its application for tissue engineering

A. Shynkarenko[1], D. Azulay[2], S. Hauzerova[3], A. Klapstova[3], M. Moucka[1], D. Lukas[4]

[1]Technical University of Liberec, Faculty of Mechanical Engineering, Liberec, Czech Republic
[2]AFEKA collage, Mechanical Engineering, Tel Aviv, Israel
[3]Technical University of Liberec, Faculty of Textile Engineering, Liberec, Czech Republic
[4]Technical University of Liberec, Faculty of Science, Humanities and Education, Liberec, Czech Republic

Andrii.shynkarenko@gmail.com

Abstract:
Nanofibrous materials currently find a wide range of medical applications including tissue engineering scaffolds. Recently, production via Electrospinning has played a dominant role in this area. Here we introduce an alternative method we have called the drawing method, which allows us to produce individual nanofibers which can be precisely placed in two dimensional (2D) layers (Bajakova 2011). This is achieved thanks to a special arm manipulator we have designed, which includes control system software. The aim of this work is to produce scaffolds with precise geometry from the biodegradable polymers PolyCaproLacton (PCL) and PolyCaproLacton copolymer (PCL-PLA) (Figure 1). Moreover, we have demonstrated the ability of our device to create regular 2D nanofibrous grades from a tempered polymer solution, and the use of different polymer solutions for the creation of one grade. All scaffolds were analyzed with a scanning electronic microscope (SEM) and tested in vitro (Strnadova 2019, Stanislav 2015). The crystallinity of the resulting manufactured polymeric structures was evaluated using differential scanning calorimetry (DSC). Our results indicate that this drawing method could lead to the widespread production of tissue engineered scaffolds.

Keywords: drawing method, nanofibrous, tissue engineering, scaffolds.

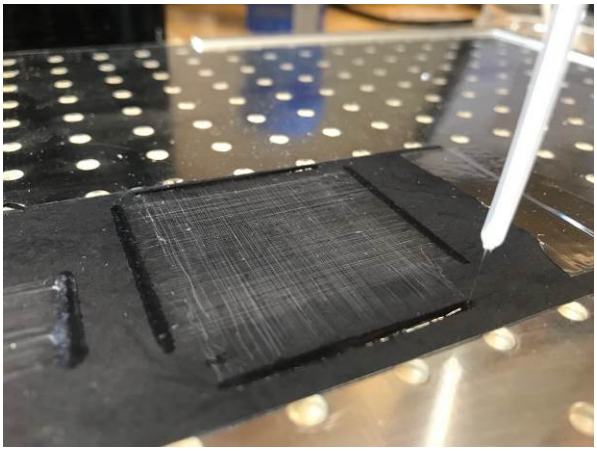


Figure 1: Scaffold made using drawing method.

References:

1. Bajakova J, Chaloupek J, Lukas D, Lacarin M. 2011. "Drawing"–The Production of Individual Nanofibers by Experimental Method. 21–23 September 2011, Brno, Czech Republic, EU
2. Strnadova K, Stanislav L, Krabicova I, Sabol F, Lukasek J, Rezanka M, Lukas D, Jencova V (2019). Drawn aligned polymer microfibres for tissue engineering. Journal of Industrial Textiles. 152808371882531. http://dx.doi.org/10.1177/1528083718825318
3. Stanislav L (2015) Nanofibers production using drawing technique. Dissertation, Technical University of Liberec.

Combined silk fibroin/nanohydroxyapatite scaffold with antibiotic addition for bone regeneration

D.Polakova[1,2*], I.Vichova[2], M. Schaabova[2], P. Kejzlar[2], L. Martinova[2], M.Rysova[2]

[1] Technical University of Liberec, Faculty of Mechantronics, Informatics and Interdisciplinary Studies, CZ

[2] Institute for Nanomaterials, Advanced Technologies and Innovation, Liberec, CZ

Abstract:
Osteomyelitis has still been a challenging surgical issue in current orthopaedy. Approximately 80% of all chronic osteomyelitis cases are caused by posttraumatic or postoperative inflammation. About one third of these cases develops into chronic state because of a formation of bacterial biofilm on the implanted materials. A biocompatible material with antibacterial activity, acceptable morphology and degradation rate would be an optimal choice for bone replacement.
Following the biomimetic approach we created a scaffold combining organic and inorganic components, and we enhanced it with broad-spectrum antibiotic in order to prevent postoperative bacterial contamination. The organic part of the scaffold is made of silk fibroin, which is a natural fibrous protein derived from *Bombyx mori* cocoons. Silk fibroin has been currently intensely studied for an application in tissue engineering and regenerative medicine due to its very good compatibility on human cell lines. The inorganic part of the scaffolds represents hydroxyapatite, which is the main mineral component of human bones. Its content naturally varies from 50 to 70%. We prepared a set of scaffolds with increasing nanohydroxyapatite content up to 50% (w/w). The influence of nanohydroxyapatite content along with addition of antibiotic on bone cell line viability and metabolic activity was tested. We also studied morphology of pristine scaffolds and antimicrobial activity towards different bacterial strains. Both hydroxyapatite and antibiotic content did not cause cytotoxic effect on selected human cell lines when tested under *in vitro* conditions. Addition of the antibiotic markedly affected bacterial growth both inside the scaffold and in its close surrounding with no effect on the scaffold's mechanical stability or morphology of all samples with hydroxyapatite content. The silk fibroin/nanohydroxyapatite scaffold has a strong potencial to be a suitable scaffold for bone tissue.

References:

1. Beck-Broichsitter BE, Smeets R, Heiland M. Current concepts in pathogenesis of acute and chronic osteomyelitis. *Curr Opin Infect Dis*. 2015;28:240–5.
2. Clarke B. Normal bone anatomy and physiology. *Clin J Am Soc Nephrol.* 2008; 3:131-139.

Keywords: silk fibroin, nanohydroxyapatite, scaffold, antibiotic, tissue engineering, bone, biomaterial, osteomyelitis.

Novel nanofibers from polyamide/polyethylenimine for enzyme immobilization

Milena Maryšková,[1,2,*] Markéta Schaabová,[1] Hana Tománková,[1] Vít Novotný,[1] Miroslava Rysová[1]

[1] Technical University of Liberec, Institute for Nanomaterials, Advanced Technologies and Innovation, Czech Republic
[2] Technical University of Liberec, Faculty of Mechatronics, Informatics and Interdisciplinary Studies, Czech Republic

Abstract:
Endocrine disrupting chemicals are highly resistant organic compounds commonly occurring in water environment. They can interfere with endocrine system of animals and humans causing serious chronical diseases[1]. In last decades, enzymes from the group of oxidoreductases have been studied for their potential to effectively degrade these compounds. In order to repeatedly use such enzyme, it is necessary to ensure its insolubility in water. This method is called enzyme immobilization[2]. We have developed novel polyamide/polyethylenimine (PA/PEI) nanofibers as a promising support material for immobilization of various biomolecules. Our nanofibers excelled in a unique combination of mechanical endurance provided by polyamide 6 and affinity towards biomolecules ensured by numerous amino groups of polyethylenimine. Enzyme laccase was successfully immobilized onto PA/PEI nanofibers using a simple and fast method providing an exceptional activity and stability of the attached enzyme. Furthermore, laccase was tested towards the degradation of a highly concentrated mixture of endocrine disrupting chemicals in real water with adjusted pH. Our PA/PEI-laccase samples are a suitable material for wastewater treatment.

Keywords: nanofibers, polyamide, polyethylenimine, laccase, immobilization, wastewater treatment

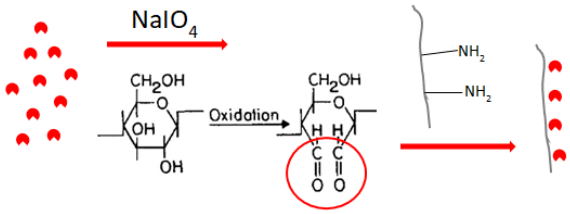


Figure 1: Figure illustrating the immobilization technique based onlaccase oxidation using sodium periodate. This enzyme-modification step creates reactive groups on enzyme that enable a covalent binding to the amino groups of the nanofiber matrix[3].

References:

1. Diamanti-Kandarakis E, Bourguignon J-P, Giudice LC, Hauser R, Prins GS, Soto AM *et al.* Endocrine-disrupting chemicals: an Endocrine Society scientific statement. *Endocr Rev* 2009; **30**: 293–342.
2. Datta S, Christena LR, Rajaram YRS. Enzyme immobilization: an overview on techniques and support materials. *3 Biotech* 2013; **3**: 1–9.
3. O'Shannessy DJ, Hoffman WL. Site-directed immobilization of glycoproteins on hydrazide-containing solid supports. *Biotechnol Appl Biochem* 1987; **9**: 488–496.

DNA Tetraplex-based Biosensors for Cell Analysis

A. Dembska, [1,*] A. Świtalska, [1] A. Fedoruk-Wyszomirska, [2] B. Juskowiak, [1]

[1] Faculty of Chemistry, Adam Mickiewicz University, 61-614 Poznan, Uniwersytetu Poznanskiego 8, Poland; email: aniojka@amu.edu.pl
[2] Institute of Bioorganic Chemistry, PAS, 60-704 Poznan, Noskowskiego 12/14, Poland

Abstract:
Functional nucleic acid-based biosensors are emerging tools that are capable of monitoring ions and metabolites in cell populations or whole animals [1]. In our research we focus on G-quadruplexes and i-motifs for sensor applications as probes generating a fluorescent signal in response to changes in environmental conditions (the presence of biometals or pH changes).
G-quadruplex analogues have been widely used as molecular tools for detection of potassium ion (K^+) [2]. In our group, we developed cholesterol-anchored fluorescent probes based on G-quadruplexes for spontaneous anchoring into the hydrophobic interior of living cell membrane [3]. The Ch(F-TBA-T) probe was labeled with FAM (carboxyfluorescein) and TAMRA (carboxytetramethylrhodamine) dyes and showed a very high binding preference for K^+ over Na^+ ions. Fluorescent bioimages indicated the successful anchoring of the Ch(F-TBA-T) to the outer cell membrane of HeLa cells (Figure 1). These structurally simple cholesterol-based fluorescent probes have good potential for *in vivo* monitoring the transport of K^+ ions through the sodium-potassium pump.
I-motif based nanoswitches and biosensors are suitable for monitoring pH fluctuations in the physiological range [4]. In our studies upon the dual-pyrene labeled molecular beacons (MBs) with i-motif in the loop, we found that such MBs can be successfully transfected into living cells, where they accumulate in lysosomes and are able to react effectively to pH changes induced by chloroquine [5]. Recently, we have developed MBs integrated with the i-motif, labeled with cytosine fluorescent analogue (tC) and energy acceptor from tC. The possibility of using MBs for measuring pH changes *in cellulo* has been demonstrated.

Keywords: i-motif, G-quadruplex, molecular beacon, FRET, pyrene, potassium sensing, intracellular pH, fluorescence imaging.

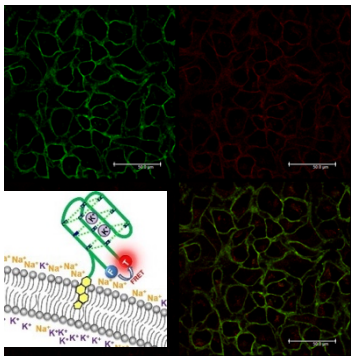


Figure 1: Confocal microscopy images of HeLa cells treated with 50 nM Ch(F-TBA-T) for 3.5 h: (A) FAM channel; (B) FRET channel; (C) overlap of (A) and (B); as well as (D) the cholesterol−anchored G-quadruplex.

Funding: This research was financed by the National Science Centre of Poland, Grant No. 2015/19/N/ST4/00407 and Grant No. 2015/17/B/ST4/03627.

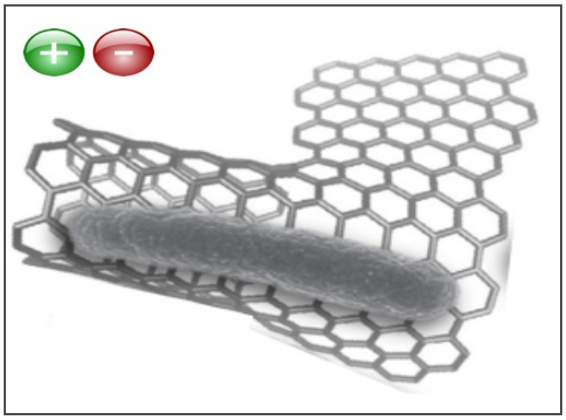
References:

1. Alsaafin, A., McKeague, M. (2017), Functional nucleic acids as in vivo metabolite and ion biosensors, *Biosensors and Bioelectronics*, 94, 94-106.
2. Takenaka, S., Juskowiak, B. (2011), Fluorescence Detection of Potassium Ion Using the G-Quadruplex Structure, *Anal. Sci*., 27, 1167 -1172.
3. Switalska, A., Dembska, A., Fedoruk-Wyszomirska, A., Juskowiak B. (2018), Cholesterol-Bearing Fluorescent G-Quadruplex Potassium Probes for Anchoring at the Langmuir Monolayer and Cell Membrane, *Sensors*, 18, 2021.
4. Dembska, A. (2016), The analytical and biomedical potential of cytosine-rich oligonucleotides: A review, *Anal. Chim. Acta*, 930, 1-12.
5. Dembska, A., Kierzek, E., Juskowiak, B. (2017), Studying the influence of stem composition in pH-sensitive molecular beacons onto their sensing properties *Anal. Chim. Acta*, 990, 157-167.

Wrapping, Inhibition and Adsorption of Bacteria by Polycationic Graphene Sheets via Electrostatic Attraction

O. Wagner*, R. Ahmed, L. C. Camacho, A. Vaishampayan, D. Wight, E. Grohmann, R. Haag*
Department of Chemistry, Freie Universität Berlin, Germany * haag@chemie.fu.berlin.de

Abstract
Bacteria are one of the smallest living organisms on the planet. Even though bacteria play a great role in enabling life, they can be equally life destroying as well. We report a new approach to bind or inhibit bacteria, by exploiting the high amount of negatively charged phosphate groups on (gram-positive and gram-negative) bacteria by creating positively charged, flexible, micrometer-sized polymer sheets that adsorb and wrap around bacteria.
Graphene oxide (GO) as giving starting material is grafted with polycationic polymer chains, which are subsequently modified to introduce quaternary amine side chains as permanent positive charges. The positively charged and flexible sheets of the GO-PTEMA function as strong unspecific adsorber material for bacteria by binding the negatively charged cell surfaces of gram-positive and gram-negative bacteria [1,2]
This effect was further used in a water filter scenario by functionalizing cellulose fibers with GO-PTEMA, which resulted in LOG-3 reduction of E. coli with only 600 mg filter material



references

1. E Kłodzińska et al., *Electrophoresis,* **2010**, *31*, 9, 1590-1596.
2. S. L. Walker, J.E. Hill, J.A. Redman, M. Elimelech, *Appl. Environ. Microbiol*., **2005**, *71*, 6, 3093.

Environmentally-friendly reduced graphene oxide functionalized with hyaluronic acid for targeted cancer photothermal therapy

R. Lima-Sousa[1], D. de Melo-Diogo[1], C. G. Alves[1], E. C. Costa[1], P. Ferreira[2], R. O. Louro[3], A. G. Mendonça[1,4] and I. J. Correia[1,2,*]

[1] Centro de Investigação em Ciências da Saúde, Universidade da Beira Interior, Covilhã, Portugal
[2] Departamento de Engenharia Química, Universidade de Coimbra, Coimbra, Portugal.
[3] Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Oeiras, Portugal
[4] Departamento de Química, Universidade da Beira Interior, Covilhã, Portugal
* E-mail address: icorreia@ubi.pt

Abstract:
Reduced graphene oxide (rGO) is one of the most promising nanomaterials for application in cancer photothermal therapy (PTT).[1] This nanomaterial has a high near infrared (NIR) absorption, producing, upon interaction with NIR light, hyperthermia that can cause the death of cancer cells.[1] However, rGO is commonly produced using hazardous agents (e.g. hydrazine hydrate), hindering its biocompatibility.[2] Furthermore, the broader use of rGO in cancer PTT is also limited by its poor colloidal stability and inability to target cancer cells.[3] To address these limitations, herein rGO was produced using an environmentally-friendly reduction method and was functionalized with a hyaluronic acid based amphiphilic polymer (HA-rGO) for application in targeted breast cancer PTT (Figure 1).[2]
For the production of rGO, the concentration of L-ascorbic acid (1.5 and 3 mM) and the time of reduction (30 to 120 min) were optimized. The results revealed that by treating GO with 3 mM of L-ascorbic acid for 60 minutes, at 80 ºC, yields rGO with suitable NIR absorption (mass extinction coefficient of 12.67 L/(g.cm)), at 808 nm) and adequate size distribution for photothermal applications. Subsequently, the attained rGO was functionalized with an HA-based amphiphilic polymer, leading to an improvement in nanomaterials' colloidal stability and cytocompatibility. The HA-rGO also demonstrated a higher internalization in CD44 overexpressing cells, revealing its targeting capacity. Finally, the combination of HA-rGO and NIR light (808 nm, 1.7 W/cm^2, 5 min) decreased cancer cells' viability to about 6%, further confirming the potential of this nanomaterial for cancer photothermal therapy.

Acknowledgments: The authors would like to acknowledge funding from POCI-01-0145-FEDER-007491, UID/Multi/00709/2013, CENTRO-01-0145-FEDER-028989, POCI-01-0145-FEDER-031462, SFRH/BD/103507/2014. R. Lima-Sousa and C. G. Alves acknowledge funding from the grant UBI Santander/Totta.

Keywords: Breast cancer, Hyaluronic acid, L-Ascorbic acid, Near infrared light, Photothermal therapy, Reduced graphene oxide.

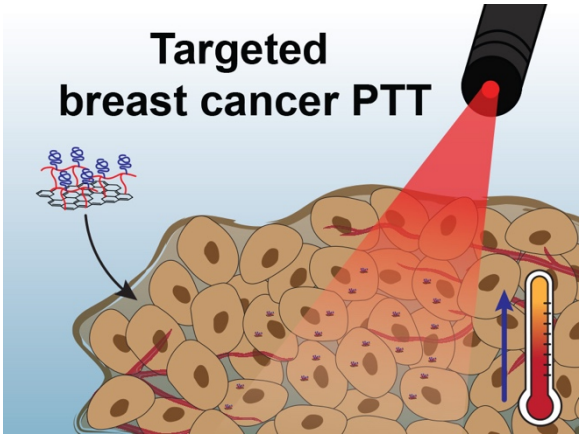


Figure 1: Schematic illustration of the targeted breast cancer PTT mediated by HA-rGO.

References:

1. de Melo-Diogo, D., Pais-Silva, C., Dias, D. R., Moreira, A. F., Correia, I. J. (2017) Strategies to Improve Cancer Photothermal Therapy Mediated by Nanomaterials, *Adv. Healthcare Mater.*, 6, 1700073.
2. Lima-Sousa, R.; de Melo-Diogo, D., Alves, C. G., Costa, E. C., Ferreira, P., Louro, O. R., Correia, I. J. (2018) Hyaluronic acid functionalized green reduced graphene oxide for targeted cancer photothermal therapy, *Carbohydr. Polym.*, 200, 93-99.
3. de Melo-Diogo, D., Lima-Sousa, R., Alves, C. G., Costa, E. C., Louro, R. O., Correia, I. J. (2018) Functionalization of graphene family nanomaterials for application in can-cer therapy, Colloids Surf., B, 171, 260-275.

POxylated Graphene Oxide for cancer phototherapy and combinatorial drug delivery

D. de Melo-Diogo,[1] E. C. Costa,[1] C. G. Alves,[1] R. Lima-Sousa,[1] P. Ferreira,[2] R. O. Louro,[3] I. J. Correia[1,2,*]

[1] Centro de Investigação em Ciências da Saúde, Universidade da Beira Interior, Covilhã, Portugal
[2] Departamento de Engenharia Química, Universidade de Coimbra, Coimbra, Portugal
[3] Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Oeiras, Portugal
[*] E-mail address: icorreia@ubi.pt

Abstract:
Graphene oxide (GO) nanostructures functionalized with poly(ethylene glycol) have been widely explored for cancer photothermal therapy and drug delivery.[1] However, PEGylated GO can suffer from the accelerated blood clearance phenomenon,[2] which has motivated the investigation of alternative coatings to functionalize GO. Herein, GO was functionalized with a poly(2-ethyl-2-oxazoline)-based amphiphilic polymer (POx) and co-loaded with doxorubicin (DOX) and D-α-Tocopherol succinate (TOS) for application in cancer chemo-phototherapy (Figure 1).[3] The POxylated GO displayed an enhanced colloidal stability and generated a temperature increase upon interaction with near infrared light, thereby confirming its photothermal potential. Moreover, cells incubated with POx-GO remained highly viable (> 88%), suggesting the good cytocompatibility of the functionalized material. Subsquently, the analysis of the anticancer capacity of different DOX:TOS combination molar ratios (from 5:1 to 1:5) revealed that the 1:3 DOX:TOS molar ratio has a optimal synergy towards breast cancer cells (lowest combination index for fractions affected of 0.2, 0.5 and 0.8). Further investigation showed that the 1:3 DOX:TOS combination also induces a 2-times weaker effect on healthy cells when compared to cancer cells, being selected for encapsulation in the POx-GO. The delivery of the selected drug combination by POxylated GO to cancer cells led to an improved therapeutic outcome when compared to the action of the free drug combination. Furthermore, the exposure of the dual-drug loaded POx-GO to near infrared light could further improve its therapeutic capacity by 1.56-fold. Overall, POxylated GO is a promising platform for cancer chemo-phototherapy.

Acknowledgments: the authors would like to acknowledge funding from POCI-01-0145-FEDER-007491, UID/Multi/00709/2013, CENTRO-01-0145-FEDER-028989, POCI-01-0145-FEDER-031462 and SFRH/BD/103507/2014. R. Lima-Sousa and C. G. Alves acknowledge funding from the grant UBI-Santander/Totta.

Keywords: Cancer, Combination therapy, Drug delivery, Graphene oxide, Photothermal therapy, POxylation.

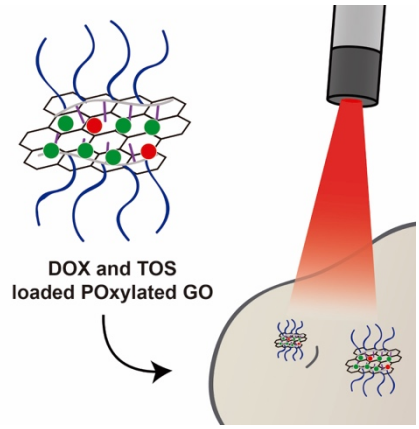


Figure 1: Schematic illustration of the chemo-phototherapy mediated by POxylated GO.

References:

1. de Melo-Diogo, D., Lima-Sousa, R., Alves, C.G., Correia, I.J. (2019), Graphene family nanomaterials for application in cancer combination photothermal therapy, *Biomater. Sci.,* In Press.
2. Im, H.J., England, C.G., Feng, L., Graves, S.A., Hernandez, R., Nickles, R.J., Liu, Z., Lee, D.S., Cho, S.Y., Cai, W. (2016), Accelerated Blood Clearance Phenomenon Reduces the Passive Targeting of PEGylated Nanoparticles in Peripheral Arterial Dis-

ease, *ACS Appl. Mater. Interfaces*, 8, 17955-17963.
3. de Melo-Diogo, D., Costa, E.C., Alves, C.G., Lima-Sousa, R., Ferreira, P., Louro, R.O., Correia, I.J. (2018), POxylated graphene oxide nanomaterials for combination chemo-phototherapy of breast cancer cells, *Eur. J. Pharm. Biopharm.*, 131, 162-169.