

Posters Session I - A
Advanced NanoMaterials

One-step preparation of amylose and β -carotene nanoparticle inclusion microbeads using amylosucrase from *Deinococcus geothermalis*

Carlos Andres Letona,* Min-Cheol Lim, and Young-Rok Kim

Institute of Life Sciences and Resources & Department of Food Science and Biotechnology, College of Life Sciences, Kyung Hee University, Yongin, Republic of Korea

Abstract: The purpose of this study was to create an one-step inclusion complex of β -carotene nanoparticle (β -cNP) using amylose as a host molecule based on enzymatic polymerization using amylosucrase from *Deinococcus geothermalis* (DgAS). β -cNPs were prepared by rotary evaporation methods using tetrahydrofuran (THF, miscible in water) to dissolve the β -carotene and lecithin as emulsifier. After complete evaporation of THF, well dispersed nanoparticles of β -carotene (β -cNP) with size of 50 nm in water were obtained. Our previous study demonstrated the possible capability of DgAS to produce amylose nanocomposite microbeads which containing hydrophobic guest molecule such as carbon nanotube (Min-Cheol et al.; 2011). In this study we used the β -carotene as a candidate guest molecule, a hydrophobic chemical which is susceptible to photodegradation, chemical oxidation and thermal degradation, those properties make it difficult to use as an ingredient in functional products and thus reduce its bioavailability (C. Boon et al.; 2010). However, to overcome this issue, we added β -cNPs into the DgAS enzyme reaction solution to entrap this guest molecule into the amylose microbeads during the synthesis of amylose chains. Because the β -carotene was present as nanoparticle we could increase the dissolution rate in aqueous phase and provide a more stable interaction with synthesized amylose chains. The morphology of produced amylose microbeads and amylose- β -cNP inclusion microbeads were analyzed by FE-SEM, DSC, XRD and Raman spectroscopy were performed to confirm the inclusion complex of β -cNP into the amylose microbeads. The encapsulation yield test shows a 94% β -carotene were encapsulated in the amylose microbeads. We expect this study helps to enhance the properties of β -carotene and further uses in functional foods or as a food delivery system.

Keywords: Amylose, β -carotene, nano particles, inclusion complex, food delivery.

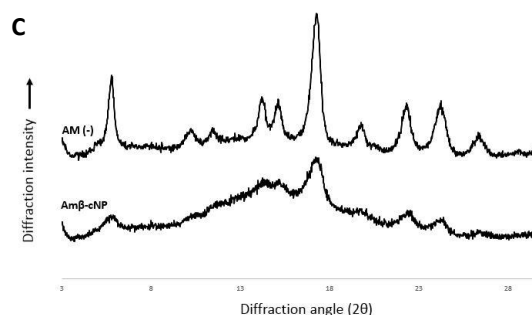
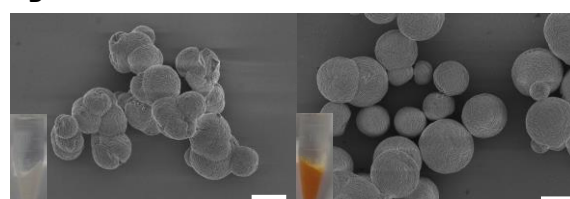
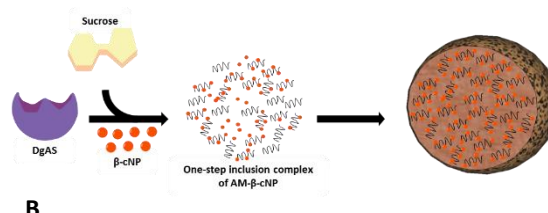
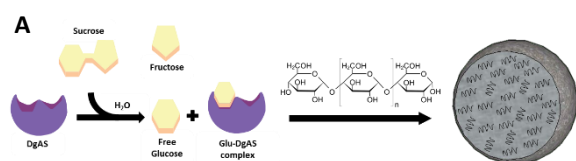


Figure 1: (A) Schematic drawings show the enzymatic synthesis of amylose microbead and amylose and β -cNP inclusion microbead. (B) FE-SEM images of amylose beads without β -cNP and amylose beads with β -cNP (Scale bar is 3 μ m). (C) XRD analysis showing the loss of amylose crystallinity by the complexation with β -cNP.

References:

Min-Cheol L., Dong-Ho S., Ji-Hoon J., Cheon-Seok P., Young-Rok K. (2014) Enzymatic synthesis of amylose nanocomposite microbeads using amylosucrase from *Deinococcus geothermalis*, *RSC Adv.*, 4, 26421.

C. Boon, D. McClements, J. Weiss (2010) Factors Influencing the Chemical Stability of Carotenoids in Foods, *Critical Reviews in Food Science and Nutrition*, 50:515-532.

Acknowledgments:

This work was supported by the Korea Research Foundation Grant (NRF-2013R1A1A2061841).

Encapsulation of water molecules in cyclic peptide nanotube

P. Tiangtrong,¹ N. Thamwattana,² D. Baowan¹

¹Department of Mathematics, Faculty of Science, Mahidol University, Rama VI Rd., Bangkok 10400 Thailand

²School of Mathematics and Applied Statistics, University of Wollongong, Wollongong, NSW 2522, Australia

Abstract: Cyclic peptide nanotubes, form by the self-assembly process of the cyclic peptides, have attracted interest from many areas of science. The manipulation of the functional side chains and the number of amino acids on the cyclic peptides will change the ease of synthesis and ability to control the properties of inner and outer surfaces (Scanlon *et al.*; 2008). Cyclic peptide nanotubes can be used as artificial transmembrane channels for transporting ion, bio molecules and waters into cells. In this research, we study the interaction of a water molecule in a cyclo[(-D-Ala-L-Ala)₄-] peptide nanotube by using the Lennard-Jones potential and a continuum approach. Mathematical modelling and elementary mechanic are utilized to determine an exact formula of the interaction energy between the water molecule and the peptide nanotube. We assume that there are a sphere of two hydrogen atoms uniformly distributed over the surface of water molecule and a single oxygen atom located at its centre, and each cyclic peptide subunit has an inner and an outer cylindrical surfaces. The result shows that the water molecule can be encapsulated into the cyclic peptide nanotube, and the acceptance behaviour does not depend on the number of cyclic peptide subunits. Moreover, we study the offset behaviour of the water molecule when it is inside the nanotube as shown in Fig.1. The water molecule prefers to be off-axis and closer to the inner surface of the cyclic peptide nanotube. We also consider the interaction between two water molecules inside the nanotube. Our study supports the arrangement of water molecule in 1-2-1-2 file (Song *et al.*; 2013, Liu *et al.*; 2010, Engels *et al.*; 1995) inside the cyclic peptide nanotube. This research is a theoretical study to understand the water molecules behaviour inside the cyclic peptide nanotube.

Keywords: cyclic peptide nanotube, water molecules, artificial transmembrane channels, interaction energy, offset positions, Lennard-Jones potential.

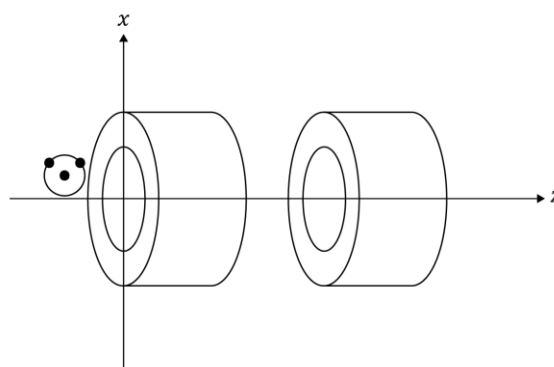


Figure 1: Schematic model for the interaction between an offset water molecule and a cyclic peptide nanotube comprising two cyclic peptide subunits.

References:

- Scanlon, S., Aggeli, A. (2008), Self-assembling peptide nanotubes, *Nano Today*, 3(3-4), 22-30.
- Song, X., Fan, J., Liu, D., Li, H., Li, R. (2013), Molecular dynamics study of Na⁺ transportation in a cyclic peptide nanotube and its influences on water behaviors in the tube, *J. Mol. Model*, 19(10), 4271-4282.
- Liu, J., Fan, J., Tang, M., Zhou, W. (2010), Molecular dynamics simulation for the structure of the water chain in a transmembrane peptide nanotube, *J. Phys. Chem. A*, 114, 2376-2383.
- Engels, M., Bashford, D., Ghadiri, M.R. (1995), Structure and dynamics of self-assembling peptide nanotubes and the channel-mediated water organization and self-diffusion. A molecular dynamics study, *J. Am. Chem. Soc.*, 117(36), 9151-9158.

PDMS Surface Property Study and Sol-gel Modification Methods for the Immobilization of Unstable Enzyme

Hongyan Bi^{1,*}, Ana Carolina Fernandes², Filipe Cardoso², Marina Brito¹,
Susana Isabel Pinheiro Cardoso², Paulo Freitas¹

¹International Iberian Nanotechnology Laboratory (INL), Braga, Portugal
²INESC Microsistemas e Nanotecnologias (INESC MN), Lisbon, Portugal

* Correspondence should be addressed to Dr. Hongyan Bi
Tel: + 351 253 140 112; Fax: +351 253 140 119
E-mail: hongyan.bi@inl.int

Abstract: Microfluidic devices have shown great promises in biomedical and diagnostic applications, tissue engineering, environmental monitoring, food safety, and so on.¹ PDMS based microfluidic devices have been widely used in bioanalytical studies. One of the major applications of the microfluidic chips is to work as an enzymatic reactor for *in-vitro* metabolism studies. We report here the activity maintenance of unstable enzymes immobilized in PDMS microfluidic channels with different strategies, including the sol-gel encapsulation of enzymes, physisorptive adsorption of enzymes to the inner surface of PDMS channels with and without xerogel deposition. From fluorescence characterization, the adsorption of proteins to the unmodified PDMS microchannel showed the largest amount of immobilized proteins in 1 hour, but few proteins could still be maintained on the surface after overnight incubation of the protein solution in such a channel. The sol-gel encapsulation and adsorption on xerogel filled microchannel methods could also form protein modified PDMS microchannel. Ascorbate oxidase, an unstable enzyme, was immobilized by the three protocols in PDMS microchips to form enzymatic reactors. Their activities were evaluated based on their catalysis ability to the oxidation of ascorbic acid. It was found that the enzymatic reactor formed by adsorption of enzyme on the xerogel coated PDMS microchannel showed the strongest enzymatic activity, although the protein adsorption amount should be lower in the case comparing with those of the other two protocols. This protocol holds advantages of i) highly maintaining the enzyme activity because of the short time for enzyme immobilization, and ii) taking advantage of xerogel filled microchannel in reducing diffusional effects of enzymatic reaction in microchannel. This study can provide an easy method to build a PDMS microfluidic channel based bio-device for unstable enzyme catalyzed drug reaction.

Keywords: sol-gel encapsulation, PDMS microfluidic chip, ascorbic acid; kinetics; utilization factor, biosensor

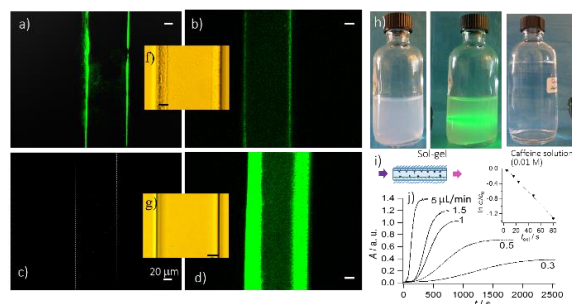


Figure 1: Confocal fluorescence microscopic images of proteins under different deposition methods on PDMS microfluidic channels by (a) sol-gel encapsulation; (b) absorption on xerogel deposited channel; 1 hour (c) and overnight (d) loading on untreated channel. (e) and (f) are the microscopic picture of channel with and without deposition of xerogel. (g) Pictures of synthesized sol-gel suspension compared with aqueous solution. (h) Scheme of microfluidic channel for activity investigation of enzymes by UV/vis absorbance change of substrate. (i) Representative UV/vis absorbance change when controlling the drug substrate through microfluidic channel at different rate. Inlet of (j) is the semi-logarithm plot of the corresponding concentration change of ascorbic acid as a function of the reaction time between them.

References:

- 1 D. Eicher and C. A. Merten, "Microfluidic devices for diagnostic applications," *Expert Rev. Mol. Diagn.* **11** (5), 505-519 (2011).

New Methods for Creating Nanocomposites Based on Carbon Nanotubes and Graphene Nanoplatelets

E.A. Burakova, A.V. Gerasimova, A.V. Melezhyk, A.G. Tkachev

Department "Technology and Methods of Nanoproducts Manufacturing", Tambov State Technical University, Tambov, Russian Federation

Abstract: Carbon nanoparticles (nanotubes, graphene) are widely used as units for building various nanocomposite materials. Commonly, these nanocomposites contain nanotubes and/or graphene and some functional components - for example, nanosized particles (metals, metal oxides, metal sulfides, sulfur), layers (polyaniline, polypyrrole), biological molecules, etc. The common problems in the synthesis of such materials are as follows:

- 1) obtaining solutions of well-dispersed nanoparticles or their precursors with sufficient concentration;
- 2) bringing the components into contact to assemble the desired structure;
- 3) separating the product from solution with saving the designed structure.

Different experimental procedures have been developed to perform those tasks. One of the most flexible approaches used for the synthesis of graphene-based nanocomposites implies the using of water-soluble graphene oxide as graphene precursor and its combination with different functional components; the graphene oxide is then reduced to graphene layers, which trap the particles of a functional component. If desired, the latter can be chemically attached to the graphene layers. Depending on synthesis conditions, the final product can be obtained in the form of a gel or coagulated precipitate. Such an approach is very flexible, but it is confined to using graphene oxide because of specific properties of this compound (high solubility in water, easy reducibility to graphene). It is interesting to develop a similar method of obtaining nanocomposites applicable for different carbon nanoparticles. It should be noted that the solubility of carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) in aqueous solutions of common surfactants is very low (order of 0.001-0.05 g/L) which impedes the mass synthesis of nanocomposites. To overcome this problem, we have developed a new method based on the modification of CNTs and GNPs with phenol-formaldehyde resin (PFR). It was revealed that the water-soluble PFR reacts with the CNTs or GNPs containing surface oxygen groups. Presumably, the PFR is attached to the surface of the oxidized CNTs and GNPs via reactive methylol groups. The solubility of the so modified carbon nanomaterials in water is very high and reaches 10 g/L and more (Figure 1). The solutions are stable and do not precipitate during centrifuging. The presence of oxygen groups on the surface of the CNTs or GNP is essential. The non-oxidized CNTs or GNPs are only slightly solubilized by the PFR. The second issue, valuable for creating

nanocomposites, is that these solutions are stable only at alkaline pH (9-11). Presumably, the ionization of phenol groups in alkaline media prevents aggregation of carbon nanoparticles due to electrostatic repulsion. When the pH is lowered to neutral or acidic, coagulation occurs. Depending on synthesis conditions, the coagulation results in the formation of a precipitate or gel. Some analogy with a classical sol-gel transition in inorganic systems can be drawn. When some nanosized functional component were introduced into the original alkaline solution of PFR-modified carbon nanoparticles, this component appeared to be trapped in the coagulated product. Besides simple trapping of the nanoparticles, different chemical reactions can take place due to high reactivity of methylol groups. These may be the reactions with excess phenolformaldehyde resin, or with precursors of different inorganic nanosized particles. Moreover, complex nanocomposites like CNT/GNP/(functional component) can be easily obtained. Using the approach herein described, we have prepared the following nanocomposites:

a) CNT/PFR, b) GNP/PFR, c) CNT/TiO₂, d) GNP/TiO₂, e) CNT/GNP, f) CNT/epoxy, g) GNP/epoxy, and h) GNP/porous carbon.

The work was performed within the framework of the Federal Target Program "Research and Development in Priority Areas of the Scientific and Technological Complex of Russia for 2014-2020" (State Contract of July 22, 2014 No. 14.577.21.0091; Unique Identifier for Applied Scientific Researches: RFMEFI57714X0091).

Keywords: carbon nanotubes, graphene nanoplatelets, phenolformaldehyde resin, nanocomposites, sol-gel.

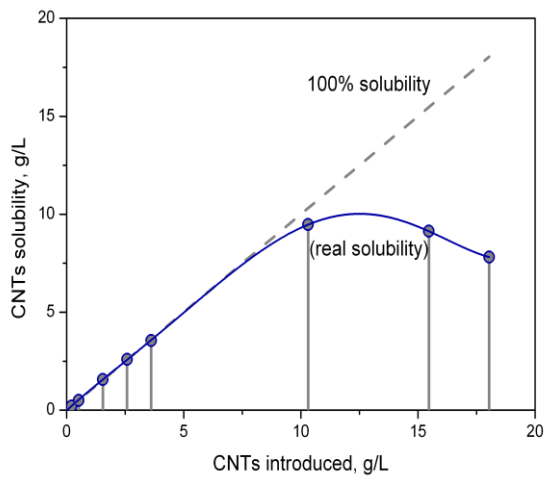


Figure 1: Solubility of the CNTs Taunit-M (external diameter 8-15 nm), modified with phenolformaldehyde resin, in water. The dash line corresponds (theoretically) to the complete dissolution of the original CNTs.

Preparation of Polybutadiene-Silica Nanoparticles via Differential Microemulsion Polymerization and their Hydrogenated Nanoparticles by Diimide Reduction

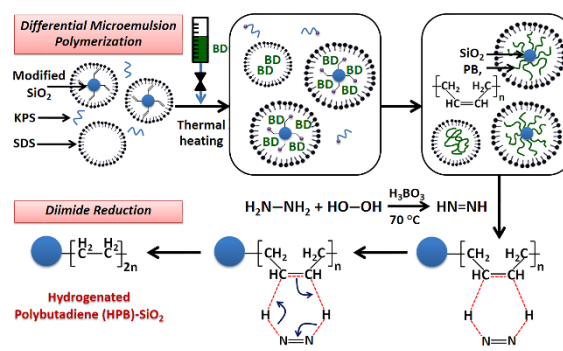
T. Tanchareernrat,^{1*}G. L. Rempel,²P. Prasassarakich¹

¹Chulalongkorn University, Faculty of Science, Department of Chemical Technology, Bangkok, 10330, Thailand

²University of Waterloo, Department of Chemical Engineering, Ontario, N2L3G1, Canada

Abstract: Nanocomposite materials (polymer/silica) have increasing potential for future applications due to the advantageous properties of the polymer species such as elasticity, processibility with silica particles providing high thermal stability and reinforcement (Kongsinlark *et al.*; 2012, Tanchareernrat *et al.*; 2014). Polybutadiene (PB)-silica nanoparticles with core-shell morphology were successfully synthesized via differential microemulsion polymerization using potassium persulfate (KPS) as an initiator and sodium dodecyl sulfate (SDS) as a surfactant. The effects of silica loading and surfactant concentration on monomer conversion, particle size, grafting efficiency and silica encapsulation efficiency were investigated. A high monomer conversion (81.5%), grafting efficiency (78.5%) and small particle size (27 nm) with narrow size distribution was obtained at optimum reaction conditions with low surfactant concentration, 5 wt.% based on monomer. However, the C=C of PB are sensitive to oxygen, ozone and heat resulting in rubber degradation and the reduction of mechanical and thermal properties (Kongsinlark *et al.*; 2013, Piya-areetham *et al.*; 2013). Thus, the PB-silica latex could be hydrogenated by diimide reduction in the presence of hydrazine and hydrogen peroxide providing the hydrogenated polybutadiene (HPB)-silica. The HPB-silica was characterized by ¹H nuclear magnetic resonance spectroscopy. The highest hydrogenation degree of 98.6% was achieved at a ratio of hydrazine to hydrogen peroxide of 0.75:1. A proposed formation mechanism for the formation of PB-silica and HPB-silica core-shell nanoparticles is illustrated in Scheme 1. A new nanocomposite of PB-silica and HPB-silica could be used as a nanofiller in natural rubber (NR). Especially, NR/HPB-silica composites had improved mechanical and thermal properties, and exhibited good resistance toward ozone exposure.

Keywords: emulsion polymerization, diimide hydrogenation, nano-structures, particle-reinforcement, mechanical properties, thermal properties.



Scheme 1: Schematic of a proposed formation mechanism for the formation of PB-silica and HPB-silica core-shell nanoparticles.

References:

- Kongsinlark, A., Rempel, G.L., Prasassarakich, P. (2012), Synthesis of monodispersed polyisoprene-silica nanoparticles via differential microemulsion polymerization and mechanical properties of polyisoprene nanocomposite, *Chem. Eng. J.* 193-194, 215–226.
- Kongsinlark, A., Rempel, G.L., Prasassarakich, P. (2013), Hydrogenated polyisoprene-silica nanoparticles and their applications for nanocomposites with enhanced mechanical properties and thermal stability, *J. Nanopart. Res.* 15, 1612-1617.
- Piya-areetham, P., Prasassarakich, P., Rempel, G.L. (2013), Aqueous-phase hydrogenation of nanosized polyisoprene emulsion using rhodium catalysts, *Eur. Polym. J.* 49, 2584–2595.
- Tanchareernrat, T., Rempel, G.L., Prasassarakich, P. (2014), Preparation of styrene butadiene copolymer-silica nanocomposites via differential microemulsion polymerization and NR/SBR-SiO₂ membranes for pervaporation of water-ethanol mixtures, *Chem. Eng. J.* 258, 290–300.

Construction Copper-Based (I) Superstructures via Recrystallization

Y. Shang^{1,2}, L. Guo¹, G. Y. Shang²

¹ School of Chemistry and Environment, Beihang University, Beijing 100191, P. R. China

² School of Physics, Beihang University, Beijing 100191, P. R. China

Abstract:

Assembling inorganic NPs into 3D superstructures with defined morphologies is of particular interest (Wang *et al.*, 2012). It may form the basis of a new engineering strategy instead of mechanical assembly of individual parts by using simple and elegant manufacturing methods (Kowalczyk *et al.*, 2012; Auyeung, E. *et al.*, 2014). We explore a novel strategy for the construction of 3D Cu₂O superstructures with defined morphologies employing Cu₂O mesoporous spheres (Shang *et al.*, 2012) with the diameter of ~ 300 nm as the building blocks. The concept of “recrystallization-induced self-assembly” (RISA) is successfully achieved in this work (Shang *et al.*, 2014). The key of this unique strategy is governed by a balance between the hydrolysis and recrystallization rate of inorganic CuCl intermediates through precisely adjusting the experimental parameters. The geometry of the products can be tuned as cubes or tetrahedrons, which is proved to be dependent on the growth behavior of CuCl (Figure 1a). The overall strategy in this work could extend the application of recrystallization in guiding the construction of assemblies (Figure 1b, c), such as (CuBr, CuI), and offers a unique clue for assembling larger particles into complicated 3D superstructures.

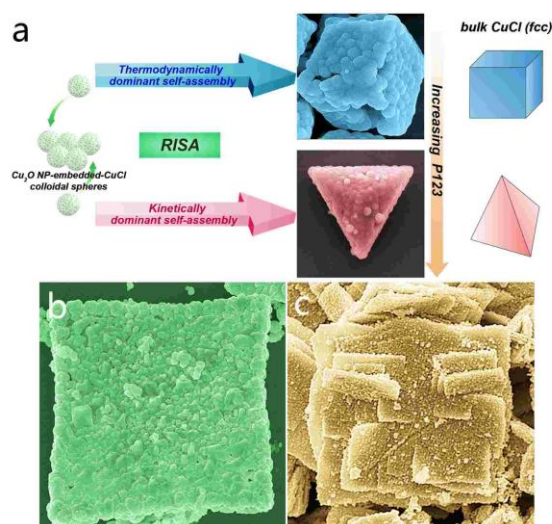


Figure 1: (a) Correlation between the geometry of the Cu₂O superstructures and their self-assembly kinetics; (b) SEM image of CuBr superstructure; (c) SEM image of CuI superstructure.

References:

Wang, T.; Zhuang, J. Q.; Lynch, J.; Chen, O.; Wang, Z. L.; Wang, X. R.; LaMontagne, D.; Wu, H. M.; Wang, Z. W.; Cao, Y. C. (2012), Self-Assembled Colloidal Superparticles from Nanorods, *Science*, 338, 358-363.

Kowalczyk, B.; Bishop, K. J. M.; Lagzi, I.; Wang, D. W.; Wei Y. H., Han, S. B.; Grzybowski, B. A. (2012), Charged Nanoparticles as Supramolecular Surfactants for Controlling the Growth and Stability of Microcrystals, *Nat. Mater.*, 11, 227-232.

Auyeung, E.; Li, T. I.; Senesi, A. J.; Schmucker, A. L.; Pals, B. C.; de la Cruz, M. O.; Mirkin, C. A. (2014), DNA-Mediated Nanoparticle Crystallization into Wulff Polyhedra, *Nature*, 505, 73-77.

Shang, Y.; Zhang, D. F.; Guo, L. (2012), CuCl-Intermediated Construction of Short-Range-Ordered Cu₂O Mesoporous Spheres with Excellent Adsorption Performance, *J. Mater. Chem.*, 22, 856-861.

Shang, Y.; Shao, Y. M.; Zhang, D. F.; Guo, L. (2014), Recrystallization-Induced Self-Assembly for the Growth of Cu₂O Superstructures, *Angew. Chem. Int. Ed.*, 53, 11514-11518.

Bio-reduction of Graphene Oxide by Natural Products

E. ÖZTÜRK^{1,2}, S. ŞİMŞEK¹, B. ÖZBEK¹

¹Yildiz Technical University, Chemical Engineering Department, Istanbul, Turkey

¹Yildiz Technical University, Central Science and Technology Application and Research Center, Istanbul, Turkey

Abstract: In recent years, graphene which is one of the carbon nanomaterials has generated a great deal of interest especially in material science owing to its unique properties such as high surface area, excellent thermal conductivity, high optical transparency and exceptional mechanical strength (Edwards *et al.*, 2013). Graphene has a hexagonal arranged structure of bonded sp² carbon atoms, promises a wide range of areas from electronics to biomedical applications (Agharkar *et al.*, 2014).

Graphene has been produced by different methods like micromechanical cleavage, electrochemical exfoliation, epitaxial growth on silicon carbide, chemical vapor decomposition and chemical reduction of graphene oxide (Edwards *et al.*, 2013; Whitener *et al.*, 2014). Chemical reduction of graphene oxide is the most common method which includes exfoliation of graphite to graphene oxide and reduction of graphene oxide to graphene by reducing agents like hydrazine and its derivatives. Although this method provides cost effective and bulk production, the toxic nature of reducing agents restricting its applications in bio-related sciences. To overcome this disadvantage, scientists have turned their faces to green chemistry. Based on the studies in which the biomolecules, microorganisms and plant extracts were used as reducing agents for the synthesis of metal particles, the possibility of usage natural-based molecules for the reduction of graphene oxide has been investigated (Agharkar *et al.*, 2014; Thakur *et al.*, 2014; Irvani, 2011). Besides the non-toxic structure of these natural compounds, utilization of them as reducing agents, provide cheaper synthesis reactions due to cheap raw material and low-cost isolation processes.

In the present study, to exploit the superior features of the reactions which are performed by green chemicals and to increase the usage chance of graphene derivatives in bio-related applications, the graphene oxide was synthesized by Hummer's method. Then, the aqueous extracts of plants (rose hip, melissa, salvia, lavandula, laurel and yarrow) were used for reduction process. The reduction performance of plant extracts were examined and characterized by using Ultraviolet-Visible Spectroscopy, Fourier Transform-Infrared Spectroscopy, Scanning Electron Microscope and Thermogravimetric Analysis. After characterization process, the optimum samples were determined. Thus, the potential uses of the optimum samples to generate biologically safe and biocompatible composites are aimed for the further studies.

Keywords: graphene oxide, bio-reduction, green reduction, natural product, characterization

References:

- Edwards, R.S. and Coleman, K.S. (2013), Graphene synthesis: relationship to applications, *Nanoscale*, 5, 38-51.
- Agharkar M., Kohrekar S., Hidouri S. and Azeez M. M. (2014), Trends in green reduction of graphene oxides, issues and challenges: A review, *Materials Research Bulletin*, 59, 323-328.
- Whitener Jr. K. E. and Sheehan P. E. (2014), Graphene synthesis, *Diamond & Related Materials*, 46, 25-34.
- Thakur S. and Karak N. (2012), Green reduction of graphene oxide by aqueous phytoextracts, *Carbon*, 50, 5331-5339.
- Irvani, S. (2011), Green synthesis of metal nanoparticles using plants, *Green Chemistry*, 13, 2638-2650.

Simple Synthesis of Magnetic Nanoparticles for same shape and size without Size separation

H. Y. NOH¹, Y. J. EOM¹, Mohamed Abbas^{1,2} and C.G. KIM^{1,*}

¹Daegu Gyungbuk Institute of Science and Technology, Department of Emerging Material Science, Daegu, South Korea

²National Research Centre, Ceramics Department, 12311 Cairo, Egypt

Abstract : Much progress for synthesis of nanoparticle process for shape and size control has been made over the twenty years. Among many material for nanoparticle, magnetic nanoparticles based on iron have been studied by many researcher because it is particularly applicable to bio and medical fields for tracking target cells (Pankhurst. Q. A., J. Phys. D: Appl. Phys. 2003, 36, R167-R181). Studies for magnetic property in accordance with shape and size of nanoparticle is necessary for using bio-medical application (Colombo. M et al, Chem. Soc. Rev 2012, 41, 4306-4334). Therefore, we study easy synthesis of magnetic nanoparticle for shape control and analysis the magnetic properties depend on same shape of particles and different component materials on similar size. We study to compare two magnetic nanoparticles (Fe_3O_4 , CoFe_2O_4) using thermal decomposition method (Park. J et al., Angew. Chem. Int. Ed. 2007, 46, 4630-4660). For this study, we control experimental conditions which are just one surfactant concentrations and experimental time for making easy synthesis. And we obtain same shape (cube, hexagon) and same size (50~60 nm) of Fe_3O_4 and CoFe_2O_4 nanoparticles respectively. Like this way to make nanoparticle, We measured X-ray diffraction (XRD) and Electron Diffraction Pattern (EDP) for identifying crystalline planes of making nanoparticles. By measuring Electron Diffraction Spectroscopy (EDS) we ascertain existence of each materials. And we get high resolution images of each nanoparticles using Field Emission Transmission Electron Microscope (FE-TEM) (Figure 1). Finally, for measuring magnetic property, We use Superconducting Quantum Interface Device (SQUID). In the result, We observe making same shape of nanoparticle about different materials by same condition and changing each nanoparticle shape by temperature and surfactant concentrations. And we obtained saturation magnetization value at 4 K exhibited that Fe_3O_4 is 120 emu/g and CoFe_2O_4 is 53 emu/g. This study will discuss more simple synthesis process for controlling shape and size using thermal decomposition and suggest more effective shape and size of magnetic nanoparticle on bio-medical applications.

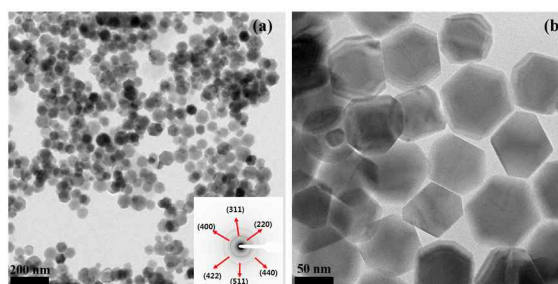


Figure 1 : High resolution FE-TEM and EDP images (a) Hexagon shape of Fe_3O_4 magnetic nanoparticle and its crystalline plane (b) High resolution image of hexagon shape of Fe_3O_4 magnetic nanoparticle.

Keywords: Magnetic nanoparticle, Thermal decomposition, Superconducting Quantum Interface Device (SQUID), Shape control, Fe_3O_4 , CoFe_2O_4 , Simple synthesis, shape control

References:

Colombo. M et al., Biological Applications of Magnetic Nanoparticles. Chem. Soc. Rev 2012, 41, 4306-4334.

Park. J. et al., Synthesis of Monodisperse Spherical Nanocrystals. Angew. Chem. Int. Ed. 2007, 46, 4630-4660.

Pankhurst. Q. A., Applications of magnetic nanoparticles in biomedicine. J. Phys. D: Appl. Phys. 2003, 36, R167-R181.

Acid hydrolysis to improve the production of Bacterial Cellulose Nanocrystals

P. Paximada¹, E.A. Dimitrakopoulou¹, C. Fasseas², I. Mandala¹

¹Agricultural University of Athens, Department of Food Science and Human Nutrition, 75 Iera Odos, 11855, Votanikos, Athens, Greece

²Laboratory of Electron Microscopy, Dept. Crop Science, Agricultural University of Athens, Greece

Abstract: A research area that has been receiving much attention recently is the modification of cellulose for the development of nanocrystals. Cellulose is the most abundant natural polysaccharide, being the major structural component of plants. Recently, bacterial cellulose (BC) has received attention and has been used in many areas, thanks to its distinctive advantages. BC provides material with limited contaminants present and specifically without any hemicelluloses or various by-products which generally surround cellulose molecules. With this advantage, it is possible to hydrolyze BC with milder conditions and, thus, avoid the use of strong acids.

This work aims at examining the various factors that affect cellulose nanocrystals (BCNCs) extraction from bacterial cellulose (BC). Specifically, the effect of hydrolysis time, temperature and the kind of acid on the properties of the obtained nanocrystals were studied. In order to evaluate the effects of hydrolysis on BC, morphology, rheology, phase separation and particles size were investigated.

The morphology of BCNCs, examined by TEM, showed a decrease in the nanocrystals' length when increasing hydrolysis time, as expected. What is more, characteristic features of BCNCs were their large aspect ratios and flat, ribbon like cross sections. As far as the G' and G'' are concerned, they were dependent on the hydrolysis time and the kind of the acid used. The rheology profiles of all the samples were shear thinning. The present nanoscale cellulose fibrils open several challenging options for applications in many industries.

Keywords: Bacterial cellulose, nanocrystals, hydrolysis

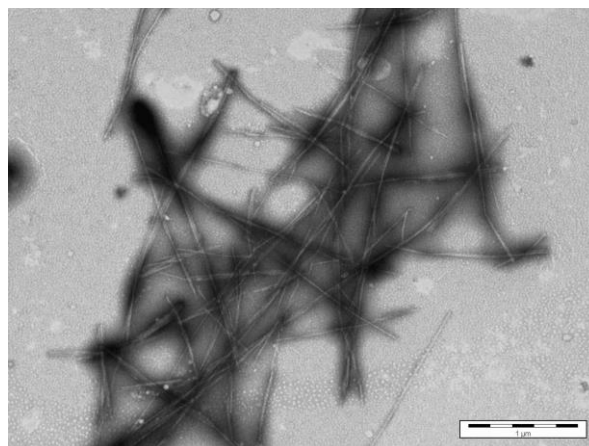


Figure 1: Bacterial cellulose nanocrystals after 72 hour hydrolysis.

Acknowledgements: This work is part of the “Nonas-tru” project (11ΣYN-2-718), implemented within the National Strategic Reference Framework (NSRF) 2007-2013 and co-financed by National (Greek Ministry - General Secretariat of Research and Technology) and Community Funds (E.U.-European Social Fund)

High Pressure Laminates containing Fluorinated Polyhedral Oligomeric Silsesquioxanes

S. Magina,^{1*} D. Evtuguin,¹ I. Portugal,¹ J. Ferra,² P. Cruz,³

¹CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal

²EuroResinas – Indústrias Químicas SA, Sines, Portugal

³SONAE Indústria de Revestimentos (SIR), Maia, Portugal

Abstract: High Pressure Laminates (HPLs) are considered the most versatile and ubiquitous decorative materials used by the furnishing and building industries to produce furniture, countertops, flooring and wall panelling surfaces. They exhibit high durability and special surface properties including chemical, heat, stain and wear resistance. HPLs consist of an assembly of resin-saturated layers of kraft-paper, topped by a single decorative paper layer and in some cases a finishing protective overlay (Figure 1), cured by heat and high-pressure treatments.

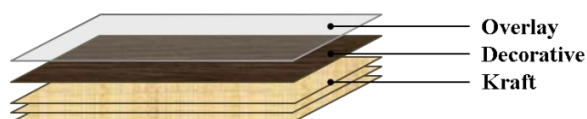


Figure 1. Scheme of a typical assembly of an HPL.

The development of hydrophobic surfaces is achieved by reducing the surface free energy (e.g. by incorporating/grafting a low surface energy material such as a fluorinated compounds) and/or by increasing the surface roughness for instance using compounds such as Polyhedral Oligomeric Silsesquioxanes (POSS). Both strategies can be combined using a fluorinated POSS such as Fluorohexyl-POSS (FH-POSS).

FH-POSS (1H,1H,2H,2H-nonafluorohexyl)₈Si₈O₁₂, was synthesized through the simple, single-step, base-catalyzed condensation of 1H,1H,2H,2H-nonafluorohexyltriethoxysilane in alcoholic media (Tuteja *et al.*, 2007; Mabry *et al.*, 2008). The fine white powder obtained was characterized by Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and Powder X-Ray Diffraction (XRD).

FH-POSS particles were incorporated (0.25%, 0.50%, 0.75% and 1.0% w/w) into melamine-formaldehyde (MF) resin formulations. Decorative and overlay papers were impregnated with the FH-POSS-MF resin formulations in order to provide multiple functionalities to the ensuing HPLs, namely abrasion resistance (due to the robust polyhedral Si-O cages of POSS) and dirt-repellence (particularly, due to the rich fluor-based alkyl chain that lowers the surface free energy of the ensuing HPLs' surfaces).

The HPLs produced using the standard paper (STD) and the FH-POSS-based decorative and overlay

papers were tested by proven industrial procedures (EN 438-2:2005). Contact angle (CA) measurements were carried out using three probe liquids (water, formamide and diiodomethane) to assess wettability of the FH-POSS-HPLs and to determine the optimal amount of FH-POSS to use.

FH-POSS-HPLs presented higher CA comparing to the STD-HPL hence higher hydrophobicity, especially when using at least 0.50% of FH-POSS in the MF resin formulation. Higher loads (0.75% and 1.0% of FH-POSS particles in the MF resin) provided better results however the ensuing HPLs have an undesirable wittish appearance. CA measurements made over a two-month period showed that FH-POSS-HPLs became more hydrophobic, suggesting an improvement in dirt-repellence properties that occurs during resin curing.

Additionally, an increase of the abrasion resistance of FH-POSS-HPLs comparing with the STD-HPL was observed, being proportional to the FH-POSS content.

Keywords: high pressure laminates, fluorinated POSS, contact angle, surface free energy, abrasion resistance.

References:

Tuteja, A., Choi, W., Ma, M., Mabry, J. M., Mazzella, S. A., Rutledge, G. C., McKinley, G. H., Cohen, R. E. (2007), Designing Superoleophobic Surfaces, *Science*, 318, 1618-1622.

Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, B. D. (2008); Fluorinated Polyhedral Oligomeric Silsesquioxanes (F-POSS), *Angew. Chem. Int. Ed.*, 47, 4137–4140.

Acknowledgements: This work was developed in CICECO–Aveiro Institute of Materials and is funded by ERDF Funds through Operational Competitiveness Programme – COMPETE in the frame of the project 2GLAM – FCOMP-01-0124-FEDER-23006. Sandra Magina thanks Margarida Nogueira (from SIR) for experimental support during paper impregnation and HPL production.

Green Synthesis of Gold Nanoparticles by Using *Peltophorum pterocarpum* Flower Extracts

M. Balamurugan,¹ S. Kaushik,² S. Saravanan^{1*}

¹Centre for Photonics and Nanotechnology, Sona College of Technology, Salem – 636 005, Tamilnadu, INDIA

²The Indian Public School, Senapathipalayam, Erode- 638112, Tamilnadu, INDIA

Abstract: Nanotechnology emerges from the physical, chemical, biological and engineering sciences where novel techniques are being developed to probe and manipulate single atoms and molecules. Among the noble metal nanoparticles, gold has enormous potential applications in various fields (Daniel *et al.*, 2004). Currently, we are in the need to develop safe, reliable, clean and eco-friendly methods for the preparation of nanoparticles. The biosynthesis of metal nanoparticles, as an emerging highlight of the intersection of nanotechnology has received increasing attention due to a growing need to develop rapid, clean, non-toxic, simple and environmentally friendly synthetic technologies. The use of plants parts in similar synthesis methodologies is a stimulating prospect that is currently under enormous investigation, having significant potential utilization (Mollick *et al.*, 2014). In this present study, gold nanoparticles (Au NPs) were synthesized by using aqueous chloroauric acid as gold precursor and *Peltophorum pterocarpum* (PP) flower extract both as reducing and capping agent in water solvent.

Keywords: gold nanoparticles, green synthesis.

A 20 mL of PP flower extract was slowly dripped into 1 mM of aqueous chloroauric acid to synthesize the Au NPs at room temperature as well as elevated temperature. After adding the flower extract a visible colour changes were observed as the yellow color solution turn to pale pink, it indicates the formation of Au NPs. The colour changes in the precursor solution is a preliminary identification for formation of metal nanoparticles.

The obtained samples were characterized by using various technique including UV-Visible Spectrophotometer (UV-Vis) and Transmission Electron Microscopy (TEM). Figure 1 shows the UV-Vis spectrum (350-800 nm) of Au NPs before and after mixing the flower extract. The spectra illustrate the reduction of gold ions and formation nanoparticles. After adding the PP flower extract into gold precursor, the intensity of UV-Vis absorbance increased with time duration, it indicated the formation of Au NPs. The spectrum shows sharp absorption maximum (λ_{max}) around ≈ 557 nm and confirmed the presence of Au NPs. This peak appeared due to the excitation of electrons in the conduction band of Au NPs induced by the electromagnetic field (Mollick *et al.*, 2014).

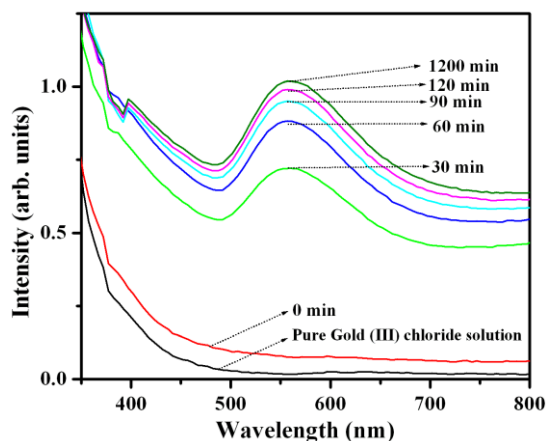


Figure. 1. UV-Vis. spectrum of gold nanoparticles prepared at room temperature.

Figure 2 shows the TEM image of gold nanoparticles prepared at room temperature. The image shows the nanostructure and morphology of Au NPs with good dispersion and the size of the NPs varied from 10-30 nm.

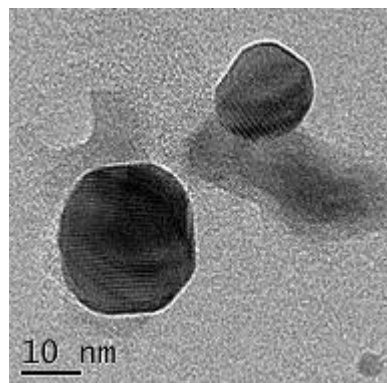


Figure. 2. TEM image of gold nanoparticles prepared at room temperature.

References:

- Daniel, M.C., Astruc, D. (2004) Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology, *Chem. Rev.* 104, 293-346.
- Mollick, M.M.R., Bhowmick, B., Mondal, D., Maity, D., Rana, D., Dash, S.K., Chattopadhyay, S., Roy, S., Sarkar, J., Acharya, K., Chakraborty, M., Chattopadhyay, D. (2014) Anticancer (in vitro) and antimicrobial effect of gold nanoparticles synthesized using *Abelmoschus esculentus* (L.) pulp extract via a green route, *RSC Adv.*, 4, 37838–37848.

STABILIZATION METAL NANOPARTICLES BY CROWN COMPOUNDS WITH AMINE AND HYDROXYL GROUPS IN MACROCYCLIC RING AND STUDING THEIR PROPERTIES.

A.L.Shabanov¹, Z.O.Gakhramanova¹, L.Z.Vezirova¹, A.M.Maharramov², M.A.Ramazanov²,
U.A.Hasanova², F.V.Hajiyeva²

¹Azerbaijan State Oil Academy, Department

²Baku State University, Department Chemical Physics of Nanomaterials, Nanoresearch Laboratory, Zahid Khalilov Str. 23, Baku, Azerbaijan

nanomaterials@bsu.az, mamed_r50@mail.ru

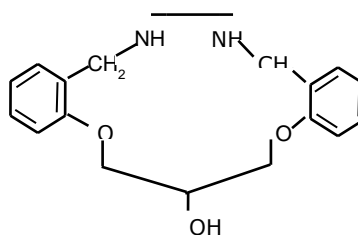
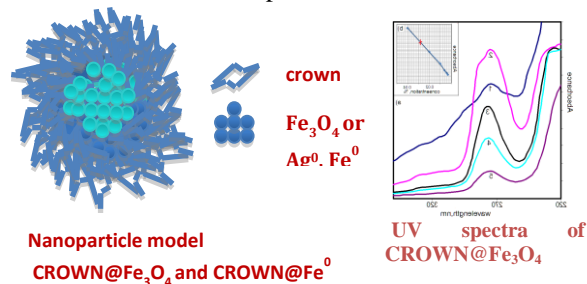
Abstract. In this work presented the results of researches on stabilization of metal nanoparticles by crown compounds with amine and hydroxyl groups in macrocyclic ring and studying their properties.

Synthesis and studies of functional substituted crown ethers is a matter of great scientific and practical interest. These macroheterocyclic compounds can reveal biological activity due to unique structural peculiarities. Nitrogen containing crown ethers are attractive research objects because its possible application in boundary with organic chemistry fields.

Introduction of amine and hydroxyl groups in macrocyclic ring of crown ethers influences on supramolecular properties of synthesized compounds. The results of carried researches show that the presence of two amine and one hydroxyl groups in macrocyclic ring leads to self-assembling of crown compounds in such a way that it becomes able to include the metal and metal oxides nanoparticles in its cavity. The synthesized crown ether was used as stabilizer of Fe₃O₄, Fe⁰, Ag⁰ nanoparticles. It is assumed that the presence of these functional groups in macrocyclic ring allow crown ether molecule to pass from two-dimensional structure (2D) to three-dimensional structure. So, it is supposed to be the existing multi-central non-valence interactions between crown ethers molecules and metal nanoparticles that lead to formation of supramolecular assembly.

Structure of prepared compounds have been analysed by elemental analysis, IR, NMR and mass-spectroscopy methods of analysis. Prepared nanostructures crown@Fe₃O₄, crown@Fe⁰, crown@Ag⁰ have been studied by scanning electron SEM, atomic force microscopy AFM, X-ray diffraction methods of analysis. On the basis of carried out analytical researches were found the size of metal and metal oxides nanoparticles that stabilised by macrocycle is in 6-17 nm interval. The quantity of loading of nanoparticles was determined on the basis of Lambert-Buger-Ber law as well as atom absorption spectroscopy method of analysis. It was found that the results of both analysis methods are correlated very well.

Key words: crown-compounds, supramolecular chemistry, diazacrown ethers, hydroxyl containing crown ether, metal nanoparticles.



References:

1. Jean-Marie Lehn **Supramolecular Chemistry: Concepts and Perspectives** :19 MAY 2006 ISBN: 9783527293124 ISBN: 9783527607433
2. Shabanov A.L. Synthesis and perspectives of functional substituted crown ethers // *Rus. Chem. J. (J. Of Rus.. Chem. Soc. D.I. Mendelejev)*. 1991. T 36. № 4. C. 456 - 467.
3. Etwood J.V., Etwood J.L. *Supramolecular Chemistry*. M.: «Academkniga» 2007. P. 480

Novel Fractal Metamaterial subwavelength structure for sensors application

Y Trabelsi¹, H Alkorre², J Stiens³, M Kanzari⁴ and R Vouncks⁵

¹ *Univesity of Tunis ELManar, National Engineering School of Tunisia (ENIT), Tunisia*
^{2,3,5} *Vrije Universiteit Brussel, Belgium, Pleinlaan 2 ,1050 Brussel.*

Abstract:

The fractal metamaterial configurations , operating at the millimeter-wave scale are studied , in terms of design, fabrication, and characterization.

We report our work conducted on the design, simulation and -fabrication of microwave sensors based on a fractal split-ring resonator (FSRR) structure operating at 140 GHz. Furthermore, we attained a wide and of high transmittance left-handed band, as was established by transmission measurements and corresponding simulations.

We observed both numerically and experimentally at around 140 GHz a tapered frequency band for which the fractal SRR metamaterial was High resonant frequency and had a negative permittivity and permeability. The effect of different geometrical restrictions and the order of the fractal curve on the performances are investigated.

We analyzed the transmission band with respect to fractal order of two configuration connected and disconnected metals form witch composed the considered metamaterials slab at the normal incident propagation direction.

Keywords :

metamaterial; sensing ; Thin-film sensor; Split Ring resonators, Fractal SRR .

References :

H. Tao, N. I. Landy, C. M. Bingham, X. Zhang, R. D. Averitt, and W. J. Padilla, "A metamaterial absorber for the terahertz regime: design, fabrication and characterization," *Opt. Express* 16, 7181 ,2008.

J. F. O'Hara, R. Singh, I. Brener, E. Smirnova, J. Han, A. J. Taylor, and W. Zhang, "Thin-film sensing with planar terahertz metamaterials: sensitivity and limitations," *Opt. Express* 16, 1786,2008.

C. Debus and P. Haring Bolivar, "Frequency selective surfaces for high sensitivity terahertz sensing," *Appl.Phys. Lett.* 91, 184102 ,2007.

A. K. Azad, J. Dai, and W. Zhang, "Transmission properties of terahertz pulses through subwavelength double split-ring resonators", *Optics Letters*, Vol. 31, No. 5, pp. 634-636, 2006.

T. Koschny and M. Kafesaki. , " Effective Medium Theory of Left- Handed Materials". *Physical Review Letters*, Vol. 93, No. 10, pp. 1-4, 2004.

Combined Mechanical Disordering – Reactive Synthesis, Possible Method of Bulk Nanocrystalline Intermetallics Obtaining

R.L. Orban¹, A. Lawley², M. Orban¹

¹Technical University of Cluj-Napoca, Romania

²Drexel University, Philadelphia, USA

Abstract: The vast potential of intermetallics applications in the modern technique, arising from their known very attractive properties, became obvious [1]. Their elaboration is based on reaction synthesis from components, e.g. in ExoMelt process [2]. However, even if, after casting in ingots, at elevated temperatures they exhibit a certain ductility, allowing processing by hot working. e.g. to obtain billets, tubes, sheets and even forgings, their further machining into final products is nearly impossible due to the high brightness and low fracture toughness at ambient temperature, drastically limiting their applications [1]. These are determined, as it is known, by their low symmetry of crystal structure (e.g. with only three slip systems in NiAl [1], which prohibits the operation of at least five independent slip systems required for plastic flow [3]).

A promising way to overcome these drawbacks of intermetallics is their obtaining in a nanocrystalline state. The most facile way for this purpose seems to be Mechanical Alloying applied to the reactive component mixture (MA), continued after the compound synthesis (the crossing point of curves a and b in Fig. 1), with Mechanical Disordering (MD)[4]. But this leads to their obtaining as fine nanocrystalline powder. Several methods have been proposed to obtain bulk nanocrystalline materials from this powder (e.g. spark plasma sintering, double sintering etc.), without of their consecration [5].

In this paper is proposed a new possible method of bulk nanocrystalline intermetallics obtaining, in two stages: i) controlled MA, applied to the stoichiometric elemental powdered component mixture – determining their strong cold working and energetic state increasing - conducted only up to the

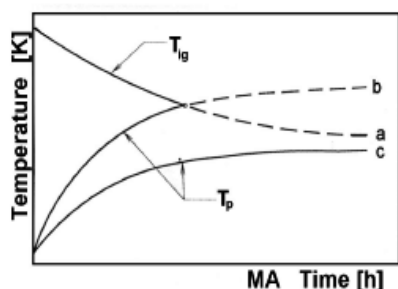


Fig. 1.

particle crystal structure disordering and its transformation into a nanocrystalline one, without to be reached the ignition temperature, T_{ig} , of compound synthesis reaction (before a-b crossing point, Fig. 1); ii) Compound reactive synthesis from the as obtained nanocrystalline powder mixture, combined with its consolidation. It is expected that, due to the high

energetic state of nanocrystalline powder and intimate mixture of components, both synthesis and consolidation (e.g. under an appropriate pressure) are possible in solid state, by diffusion [6], at a low enough temperature to preserve the nanocrystalline structure in the obtained bulk material.

The method has been successfully applied to the obtaining of bulk nanocrystalline NiAl (Fig. 2).

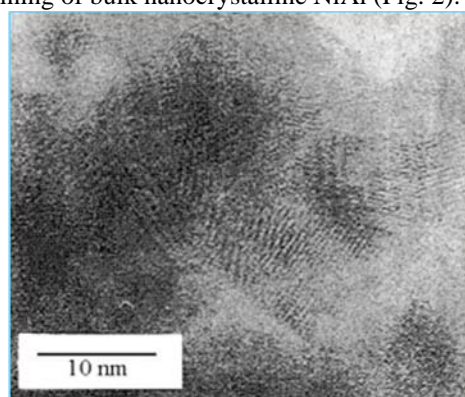


Fig. 2.

Its conducting conditions will be extensively presented in the proposed paper.

Keywords: Intermetllics, Mechanical Alloying, Reactive synthesis, Bulk nanocrystalline NiAl.

Fig. 1. Variation of the Ignition Temperature of Synthesis Reaction and of Particle one, vs. MA time.

Fig. 2. HRTEM image of the obtained bulk NiAl.

References:

- [1] Sauthoff, G. Definition of Intermetallics & General Considerations. In *Intermetallics*, John Wiley & Sons, 2008, p. 1-13.
- [2] Deevi, S.C.; Sikk, V.K., Exo-Melt™ process for melting and casting intermetallics. In *Intermetallics*, Vol. 5, Iss. 1, 1997, p. 17-27.
- [3] Reed-Hill, R.E. Dislocation & Plastic Deform. In *Physical Metallurgy Principles*, 2008, p. 119-157.
- [4] Orban, R.L. New Research Directions in Powder Metallurgy. In *Romanian Reports in Physics*, Vol. 56, No. 3, 2004, p. 557-570.
- [5] German R.M. *Powder Metallurgy and Particulate Materials Processing: The Processes, Materials, Products, Properties and Applications..* MPIF, Princeton, New Jersey, USA, 2005.
- [6] Ferro, R.; Saccone, A. Direct synthesis of intermetallic phases/Solid-state synthjesis. In *Intermetallic Chemistry*, Elsevier, 2008, p. 566-572.

Effect of blending ratio of polymer layer on structural properties of polymer-coated mesoporous silica nanoparticles

Ş. Ünal, B. Özbek

Yildiz Technical University, Department of Chemical Engineering,
Davutpasa Campus, 34210, Esenler/Istanbul, Turkey;
tel. +90 212 383 4761, fax: +90 212 383 4725;
e-mail: suunal@yildiz.edu.tr.

Abstract: Mesoporous silica nanoparticles (MSNs) have great potential as nanocarrier for biomolecules because of its biocompatibility, low toxicity, large surface area, high porosity, modifiable pore diameter, and adjustable surface properties¹. Chitosan (CS) is non-toxic, user-friendly, abundant and widely-used inexpensive polysaccharide. The amino and hydroxyl groups of chitosan provide great potential as adsorbent of protein and heavy metal ion, as catalytic matrix for enzyme immobilization and as carrier for drug loading processes². Chitosan has a highly hydrophilic and a swelling structure in aqueous media which causes to lose its mechanical strength because of its high water content³.

Blending PAA and CS provides increased mechanical strength and pH stability via eliminating the structural disadvantage of chitosan⁴. Linear polymers (such poly(acrylic acid) (PAA) chain were grafted onto the surface of MSNs) show pH-dependent behaviour which can provide increased enzyme reuse and also the usage as biosensor⁵.

In the present study, chitosan/poly(acrylic acid) shell was coated on mesoporous silica nanoparticle cores through polymerization. First, MSNs were successfully prepared via sol-gel method¹. Subsequently, acrylic acid (AA) monomers were polymerized on the MSNs. The effect of the ratio between the amounts of CS and AA to the physicochemical properties of particles was investigated through necessary characterization methods.

Keywords: Silica nanoparticle; chitosan; polymer; poly(acrylic acid); coatings

References:

1. Peng et al. (2013), "A pH-responsive nano-carrier with mesoporous silica nanoparticles cores and poly(acrylic acid) shell-layers: Fabrication, characterization and properties for controlled release of salidroside" *International Journal of Pharmaceutics* 446: 153–159.
2. Zhao H., Xu J., Lan W., Wang T., Luo G., (2013), "The Microfluidic production of porous chitosan/silica hybrid microspheres and its Cu(II) adsorption performance", *Chemical Engineering Journal* 229: 82–89.
3. Lei Z., Bi S., (2007), "The silica-coated chitosan particle from a layer-by-layer approach for pectinase immobilization", *Enzyme and Microbial Technology* 40: 1442–1447.
4. Dai J., Yan H., Yang H., Cheng R. J. Dai et al., (2010), "Simple method for preparation of chitosan/poly(acrylic acid) blending hydrogel beads and adsorption of copper(II) from aqueous solutions", *Chemical Engineering Journal* 165: 240–249.
5. Tang H., Guoa J., Sun Y., Chang B., Ren Q., Yang W., (2011), "Facile synthesis of pH sensitive polymer-coated mesoporous silica nanoparticles and their application in drug delivery", *International Journal of Pharmaceutics* 421, 388–396.

Targetting and Applications of Magnetic Nanoparticles

P. Taparia,^{1,*} S. Jindal,²

¹Department of Metallurgy and Material Sciences, Indian Institute of Technology, Roorkee, India

² Department of Biotechnology, Indian Institute of Technology, Roorkee, India

Abstract: Recent advances in targeting and application of "intelligent" Magnetic Nanoparticles (MNPs), which have led to widespread experimentation due to their multi-modal capabilities, have been reviewed. Particularly, application of MNPs is highly promising for the treatment of fatal diseases such as Cancer. Dual usage of MNPs to perform drug delivery and optical imaging has been studied in vivo and in vitro. Further, the role of MNPs in Positron Emission Tomography (PET) and Magnetic Hyperthermia will be discussed in detail. Therapeutic potential of 'intelligent' MNPs having a suitable recognition layer and a therapeutic load, is high; but their development is challenging. Polymer, Protein and Silane based recognition layers are being examined to solve this problem. Moreover, these core/shell structures of MNPs have the advantages of good dispersion, high stability against oxidation, favorable specificity and appreciable amount of drug that can be loaded to the shell after coating. Also, recent literature has shown that reliance solely on the Enhanced Permeability and Retention (EPR) effect is insufficient for nanoparticles to penetrate the tumor intersitium, as a result, the use of active and intelligent targeting agents has become increasingly important. Here we also review some of the drawbacks associated with the use of MNPs for drug delivery.

Keywords: Positron Emission Tomography, Magnetic Hyperthermia, Recognition Layers, shell coating, Enhanced Permeability and Retention, targeting agents, drug delivery, biomedical applications.

References:

Chomoucka, J., Drbohlavova, J., Huska, D., Adam, V., Kizek, R., Hubalek, J. (2010) Magnetic nanoparticles and targeted drug delivering, *Pharmacological Research*, 62, 144-149.

Spencer, D. S., Puranik, A. S., Peppas, N. A. (2015) Intelligent nanoparticles for advanced drug delivery in cancer treatment, *Current Opinion in Chemical Engineering*, 7, 84-92.

In_xGa_{1-x}N/GaN QDs by coaxial growth on non-polar n-GaN NW

Ji Hyeon Park, Jae Kwan Sim, Dae Young Um, Taek Soo Jang, Da som Lee and Cheul Ro Lee*
Semiconductor Materials Process Laboratory, School of Advanced Materials Engineering, Engineering College,
Research Center for Advanced Materials Development (RCAMD), Chonbuk National University, Baekje-daero
567, Jeonju 561-756, Republic of Korea

Abstract: Nanowires based devices are among those techniques and have drawn much attention in the last few years for improving device performances.

In This abstract demonstrates for the merits of an immediate InAlGa_N capping layer over self-assembled In_xGa_{1-x}N/GaN GaN quantum dots (QDs) coaxially grown on the m-plane and r-plane of n-GaN nanowires on Si (111) substrate using metal organic chemical vapor deposition. For comparative analysis, we prepared In_xGa_{1-x}N/GaN QD samples both with and without quaternary capping. Figure 1 shows the UHR-SEM image of the proposed structure with In_xGa_{1-x}N QDs on a single n-GaN NW when quaternary capping was applied over dots in the active region. InAlGa_N capping layer acted as a strain-driven phase separation alloy. Inhomogeneous surface strain over the dots helped this quaternary alloy in forming an indium concentration gradient over In_xGa_{1-x}N QDs and thus, indium out-diffusion from the dots was reduced. Quaternary alloy capped samples exhibited vertically stacked, highly dense, pyramidal In_xGa_{1-x}N/GaN QDs of improved carrier confinement grown as the active region on n-GaN NWs. In contrast, the nonexistence of InAlGa_N capping over InGa_N/Ga_N QDs caused deformation of the dots due to In-Ga inter-diffusion between the dots and the Ga_N barrier layer. Figure 2 shows the temperature dependent PL study was carried out for the sample composed of quaternary alloy capped In_xGa_{1-x}N QDs on n-GaN NWs. This coaxially fabricated In_xGa_{1-x}N/GaN QDs on defect free n-GaN nanowires have various excellent characteristics and can be widely applicable to new optoelectronics semiconductor devices.

Key Words: InGa_N quantum dots, Ga_N nanowire, InAlGa_N capping, inhomogeneous strain, metal organic chemical vapor deposition, blue light emitting diodes

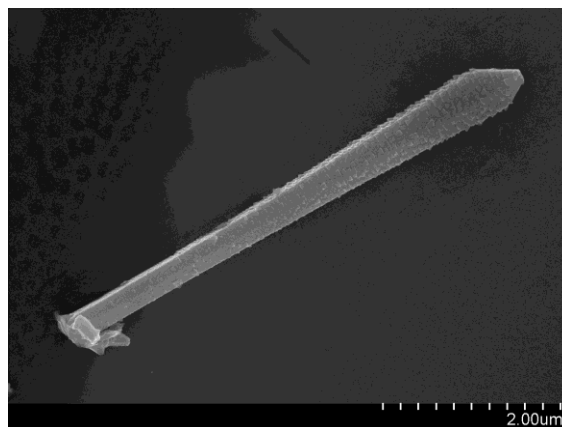


Figure 1: Ultra-high resolution SEM (UHR-SEM) image of a single n-GaN NW composed of InAlGa_N capped two layered active In_xGa_{1-x}N QDs inside.

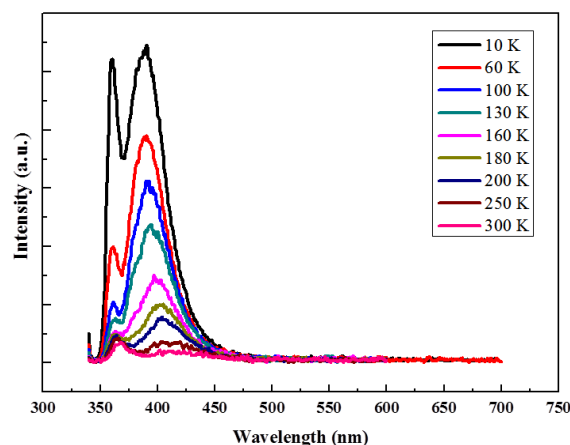


Figure 2: Temperature dependent PL study was carried out for the sample composed of quaternary alloy capped In_xGa_{1-x}N QDs on n-GaN NWs.

References:

- A. M. Morales, C. M. Lieber, (1998) *Science*, **279**, 208-211.
- Z. Zhong, F. Qian, D. Wang, C. M. Lieber (2003) *Nano Lett*, **3**, 343-346.
- O. L. Muskens, S. L. Diedenhofen, M. H. M. van Weert, M. T. Borgström, E. P. A. M. Bakkers, J. G. Rivas,(2008) *Adv. Funct. Mater*, **18**, 1039-1046.

The Effect Of Assembly Conditions and Nanoparticle Conditions on Size, Morphology and Polydispersity Of Magnetic Nanoparticle Clusters

Sarah M. Martyn,¹ Dr. Dermot F. Brougham¹

¹School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland

Abstract: Colloidally stable superparamagnetic iron oxide nanoparticles (SPIONs) are well known to be excellent contrast agents in MRI applications^{1,2}. Larger particles are preferable; however the effectiveness of SPIONs as contrast agents is limited by their size, as above a threshold of ~20 nm, ferromagnetic properties emerge, causing irreversible aggregation which can lead to the formation of blockages in the vasculature of patients.

One potential alternative is the formation of controlled aggregates of the SPIONs into polymer stabilized assemblies (NPCs)³. These assemblies retain the superparamagnetic properties of the individual particles while increasing the effectiveness of the system as a contrast medium. In this study the effect of NP shape and size, polymer type and other assembly conditions, on the formation of NPCs was investigated. NPC properties were analyzed by transmission electron microscopy (TEM), dynamic light scattering (DLS), hyperthermia and field cycling nuclear magnetic relaxation spectroscopy (FFC-NMR). These analyses combined have allowed us to determine the effect of cluster size and morphology on the magnetic properties of the NPCs generated.

On preparation of colloidally stable NPCs signal suppression was observed in sample relaxivity, a shift in the frequency at which maximum relaxivity was also observed, consistent with the presence of larger particles. It should be noted that these observations were more profound in the case of faceted nanoparticles. The ratio of R_2/R_1 at 60 MHz was also found to increase dramatically on the formation of clusters indicating that NPCs are potentially useful as T_2 weighted MRI Contrast agents.

Keywords: Nanoparticles, Iron Oxide Nanoparticle Assemblies, size-control, Nuclear Resonance Dispersion Relaxometry, superparamagnetism, MRI, contrast agents, biomedical applications.

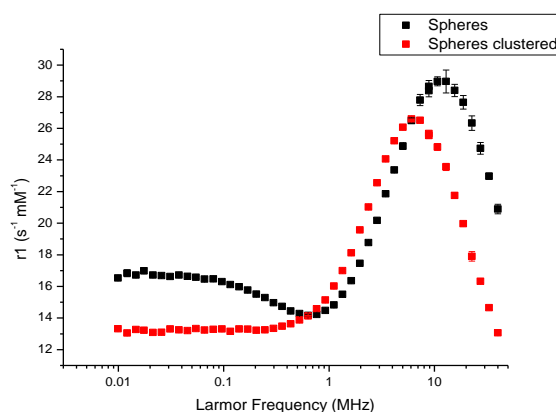
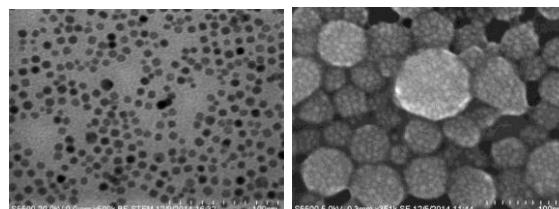


Figure 1: Iron Oxide nanoparticles (top-left) and Nanoparticle Clusters prepared by polymer mediated assembly (top-right), (below) Nuclear Magnetic Relaxation Dispersion Curve demonstrating a shift in magnetic response as a result of the clustering experiment

References:

- 1 Pankhurst, Q.A., Connolly, J., Jones, S.K., Dobson, J.. (2003). Applications of magnetic nanoparticles in biomedicine. *Journal of Physics D: Applied Physics*. 36 (13), R167-R181.
- 2 Babes, L. 'Synthesis Of Iron Oxide Nanoparticles Used As MRI Contrast Agents: A Parametric Study'. *Journal of Colloid and Interface Science* 212.2 (1999): 474-482. Web. 20 Apr. 2015.
- 3 Stolarczyk, J.K., Ghosh, S., Brougham, D.F.. (2009). Controlled growth of nanoparticle clusters through competitive stabilizer desorption. *Angewandte Chemie International Edition*. 48 (1), 175-178.

Polyurethane/GO Nanocomposites and Vapor Barrier properties

Eunsung Yoo,^{1,2,*} Kwangbo Shim,^{1,2} Hoon Huh¹

¹Korea institute of industrial technology, Cheonan, Korea

²Hanyang University, Seoul, Korea

Abstract:

Polyurethane(PU) has been used in various applications such as fibers, coatings, adhesives and biomimetic materials. Despite of good deformability, low stiffness and tensile strength can limit its use in structural applications, especially for PU with low hard block content. Water vapor and gas permeability can be another drawback. The weak mechanical and gas barrier properties can be reinforced by the elastomeric matrix with rigid, impermeable nanofillers.

The graphene with two dimensional structure(2D) has a unique electron mobility ($> 20,000 \text{ cm}^2/\text{Vs}$), very high thermal conductivity ($480\text{-}530 \text{ W/mk}$) and excellent mechanical properties (Young's modulus : $\sim 1 \text{ TPa}$, Ultimate strength : $\sim 130 \text{ GPa}$). It has been considered as a promising functional filler. Adding highly exfoliated carbon layers can significantly change a mechanical and electrical properties of polymers at extremely small loading. Unlike carbon nanotubes that can provide similar mechanical and electrical benefits, these impermeable two-dimensional sheets can reduce gas permeability of host membranes

In this study, we focused on preparation, morphology, and properties of PU/GO nanocomposites. Solvent blending was also used to prepare GO and isocyanate treated GO composites. We observed mechanical, and water vapor barrier properties of PU by addition GO.

Keywords: polyurethane, water vapor barrier, PU/graphene nanocomposites, isocyanate treated GO .

References:

- Woods, G. The ICI Polyurethanes Book; Wiley: New York, 1990.
- Lamda, N. M. K.; Woodhouse, K. A.; Cooper, S. L. Polyurethanes in Biomedical Applications; CRC Press: Boca Raton, FL, 1998.
- Liff, S. M.; Kumar, N.; McKinley, G. H. *Nat. Mater.* 2007, 6, 76–83.
- Koerner, H.; Price, G.; Pearce, N. A.; Alexander, M.; Vaia, R. A. *Nat. Mater.* 2004, 3, 115–120.
- Osman, M. A.; Mittal, V.; Morbidelli, M.; Suter, U. W. *Macromolecules* 2003, 36, 9851–9858
- Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. *Science* 2008, 321, 385–388.
- Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* 2004, 306, 666–669.

Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature* 2006, 442, 282–286.

Ramanathan, T.; Abdala, A. A.; Stankovich, S.; Dikin, D. A.; Herrera-Alonso, M.; Piner, R. D.; Adamson, D. H.; Schniepp, H. C.; Chen, X.; Ruoff, R. S.; Nguyen, S. T.; Aksay, I. A.; Prud'Homme, R. K.; Brinson, L. C. *Nat. Nanotechnol.* 2008, 3, 327–331.

Kim, H.; Macosko, C. W. *Macromolecules* 2008, 41, 3317–3327.

Kim, H.; Macosko, C. W. *Polymer* 2009, 50, 3797–3809.

Fabrication of Electrospun Polyvinyl Alcohol / Polysaccharide Composite Nanofibers and their Prebiotic and Antibacterial Activities

Walaa Wahbi,^{1,2} Rania Siam,^{1,3} Wael Mamdouh^{1,2*}

¹Yousef Jameel Science and Technology Research Center (YJSTRC), School of Sciences and Engineering (SSE), The American University in Cairo (AUC), AUC Avenue, P.O. Box 74, New Cairo 11835, Egypt.

²Department of Chemistry, School of Sciences and Engineering (SSE), The American University in Cairo (AUC), AUC Avenue, P.O. Box 74, New Cairo 11835, Egypt.

³Department of Biology and Biotechnology Graduate Program, School of Sciences and Engineering (SSE), The American University in Cairo (AUC), AUC Avenue, P.O. Box 74, New Cairo 11835, Egypt

Abstract: In an attempt to develop novel natural nanofibers with enhanced prebiotic and antimicrobial activities, polymer composites and nanomaterials play a vital role and exhibit superior properties. Among the different types of nanomaterials, nanofibers have attracted a lot of attention in various fields due to their large surface area per unit mass and advanced mechanical performance. Nanofibers are potential candidates to be used in many fields such as drug delivery systems, nano-sensors, filtration media, and medical applications, etc (Ramakrishna *et al*; 2006). Electrospinning technique was used and the experimental parameters were optimized to fabricate uniform electrospun polysaccharide composite nanofibers (CNFs) to be tested for their prebiotic and antimicrobial activities. The aqueous solution of polysaccharides could not be directly electrospun into nanofibers. Therefore, electrospinning was aided by mixing polysaccharides with polyvinyl alcohol (PVA)(Wang *et al*; 2011). We report the influence of different parameters (concentration, applied voltage and solution flow rate) on the composite nanofibers fabrication. The most uniform nanofibers were obtained were tested for their prebiotic activity with *Lactobacillus sp.* and antibacterial activity with *E. coli* and *S. aureus* bacteria. The fabricated composite nanofibers showed enhanced prebiotic and antibacterial activity compared to the original solutions. These results open new avenues for fabricating prebiotic and antibacterial products from natural materials with superior biomedical activities.

Keywords: electrospinning, nanofibers, prebiotic, polysaccharides, natural materials.

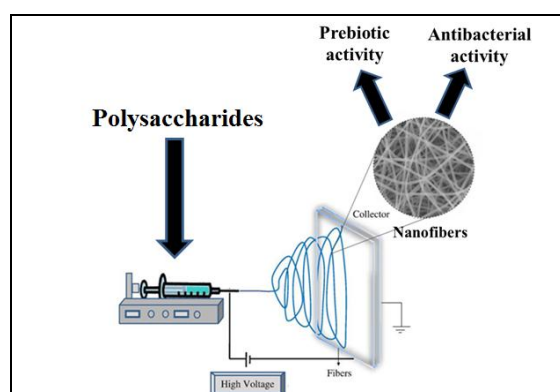


Figure 1: Figure illustrating the study and representing the results: Fabrication of natural composite nanofibers from using polysaccharides and investigating their prebiotic and antibacterial activities.

References:

- Ramakrishna, S.; Fujihara, K.; Teo, W.; Yong, T.; Ma, Z.; and Ramaseshan, R(2006). Electrospun nanofibers: solving global issues, *Mater. today* , 9, 40–50.
- Wang, H.; Wang, W.; Jiang, S.; Zhai, L.; Jiang, Q., (2011), Poly(vinyl alcohol)/Oxidized Starch Fibres via Electrospinning Technique: Fabrication and Characterization, *Iran. Polym. J.*, 20, 551–558.
- Zanin, M. H. A.; Cerize, N. N. P.; A. M. de Oliveira(2011). Production of Nanofibers by Electrospinning Technology: Overview and Application in Cosmetics. *Nanocosmetics and Nanomedicines*; pp. 311–332.

Efficiency improvement in Dye Sensitized Solar Cells by Plasmonic effect of green synthesized Silver Nanoparticles

S.Saravanan,^{1*} R.Kato,² M.Balamurugan,¹ S.Kaushik,³ T.Soga²

¹Centre for Photonics and Nanotechnology, Sona College of Technology, Salem – 636005, Tamilnadu, INDIA

² Department of Frontier Materials, Nagoya Institute of Technology, Nagoya 466-8555, JAPAN

³The Indian Public School, Senapathipalayam, Erode- 638112, Tamilnadu, INDIA

Abstract: Eco-friendly green synthesis with plant extracts plays a very important role in nanotechnology, without any harmful chemicals. In this report, the synthesis of uniform silver nanoparticles (Ag NPs) was developed by treating silver ions with *Peltophorum pterocarpum* (PP) extract at room temperature and elevated temperatures. The X-ray diffraction analysis confirmed that the synthesized Ag NPs are single crystallines. Ag NPs, with an approximate size of 15–30 nm were observed in the transmission electron microscopy (TEM) image. A plasmonic effect of silver nanoparticles (Ag NPs) in dye-sensitized solar cells (DSSCs) is studied.

Introduction: Synthesis of NPs is presently an important area of research, searching for an eco-friendly manner and green materials for current science. The biological method has emerged as a green alternative, for it is environment-friendly, cost-effective, and easily scaled-up. In the last few years a concept of surface plasmon resonance has been introduced to the DSSC employing noble metals of Ag (Ishikawa *et al.*, 2004) or Au.

Keywords: silver nanoparticles, green synthesis, plasmonic effect, dye sensitized solar cell.

Synthesis of Silver Nanoparticles (Ag NPs): Fresh 3 grams of PP flowers were washed and immersed in 300 mL boiling distilled water for 30 minutes. The cooled filtrate obtained was stored at 4°C for further use. The 100 mL of 0.01 M AgNO₃ aqueous solution was reacted with 20 mL drops of the obtained extract solutions in a flask with stirring for 30 minutes and then continued stirring for 1hour.

Characterization of Ag NPs: Phase formation of the synthesized NPs was characterized by X-ray diffraction. Four main characteristic diffraction peaks for Ag were observed at $2\theta=38.1, 44.3, 64.7, 77.7$, which correspond to the (111), (200), (220), and (311). Figure 1 (a) and (b) depicts the TEM and SAED pictures of Ag NPs respectively. As shown in the figure the morphology of the AgNP was spherical with an average size of 15-30 nm.

DSSC preparation: The TiO₂ (P-25) layers with/without Ag NPs (1, 2 and 3 wt%) have been immersed in an ethanol solution of a Ruthenium complex based dye for 18hrs. DSSCs were fabricated by attaching a Pt glass counter electrode to photoanode, by inserting polymer film (50 μm) between two electrodes, and injecting the iodide based electrolyte into the space between two electrodes.

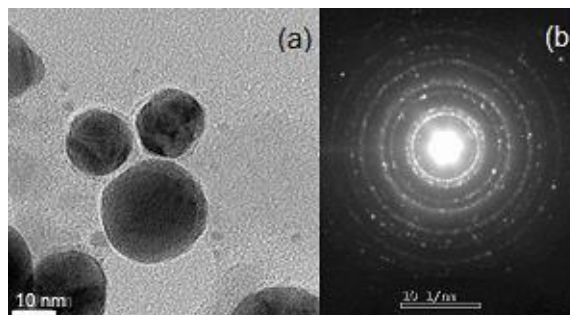


Figure 1. (a) TEM and (b) SAED picture of green synthesized silver Nanoparticles.

Results and Discussions: Short-circuit current density (Jsc) and conversion efficiency are shown in Figure 2 for non doped and 1, 2 and 3 wt% of Ag NPs doped DSSCs. As shown in the figure the efficiency has decreased for 1 wt% and for 2 wt% of Ag doped the efficiency increased from 2.83% to 3.62% (nearly 28% when compared to the non doped sample). Also the Jsc has increased for 2, 3 wt% of Ag doped sample. The FF is also increased nearly 7% for 2 wt% compared to the non doped sample.

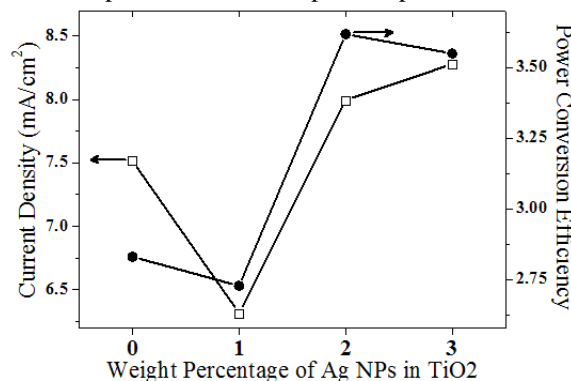


Figure 2. The short circuit current density and power conversion efficiency against the Ag doping.

Conclusions: In this study, we developed a simple, green, and efficient route to synthesize Ag NPs by treating silver ions with PP flower. DSSCs were fabricated with different doping of green synthesized Ag NPs in TiO₂. The 2 wt% of Ag doping in TiO₂ increased the efficiency around 28%.

Reference:

Ishikawa, K. Wen, C.-J. Yamada, K. and Okubo, T. (2004), The photocurrent of dye-sensitized solar cells enhanced by the surface plasmon resonance, *Journal of Chemical Engineering of Japan*, 37, 645–649.

Obtention of Spirulina nanoparticles by mechanical milling

Neri-Torres, E.E.^{1*}, Chanona-Pérez, J.J.¹, Cárdenas-Pérez, S.¹, Marín-Bustamante, M.Q.¹, Cásarez-Santiago, R.G.¹, Calderón-Benavides, H.², Chamorro-Cevallos, G.¹, Suárez-Najera E.¹

¹Escuela Nacional de Ciencias Biológicas-Instituto Politécnico Nacional, Prolongación de Carpio y Plan de Aya-la s/n, Col. Santo Tomas C.P. 11340 México, D.F.

²Escuela Superior de Física y Matemáticas-Instituto Politécnico Nacional. Av. Instituto Politécnico Nacional Edificio 9, Unidad Profesional Adolfo López Mateos, Zacatenco, C.P. 07738, México, D. F.

Abstract: Nanotechnology has taken great importance in the food industry for create different functional and nutraceutical foodstuffs, since the nanoscale material construction cause changes on the bioactive potential of biological due the material becomes thousand times more small that the original. The target is to reach particles with nanometer sizes for improve the functional and nutraceutical potential of the proteins, amino acids, essential fatty acids, minerals, sulfolipids, glycolipids and phycoliproteins contained in Spirulina (Belay, 2008).

The raw material was aspersion-dried powder of *Arthrospira maxima* (Spirulina), which had an initial size of 6 ± 5 μm . A Spex mill was used according to reported by Lu & Lay (1998) in a kinetic experimental design which was applied to obtain the nanoparticles. The work was performed in four times (1, 2, 3 and 4 hours), due to the Spirulina may be considered how a soft material. After the milling, the powder was collected and stored in controlled environment. Atomic force microscopy (AFM, Multimode V, Bruker, USA) was used to measure the particle size by image analysis (Figure 1A) take into account the ISO 13322 ($p=0.1$ and geometric standard deviation "GSC" of 1.15). The results showed that two hours of milling was the optimal condition for obtain a 75% of Spirulina nanoparticles below of 100 nm and an average size of 91 ± 3.5 nm. In the case of milling times of 3h and 4h the increase of particle size could be due to a heating of samples caused by an agglomeration phenomena into the powders. The characteristic mean size was also calculated with images obtained with scanning electron microscopy (SEM, JSM-7800F, Jeol, USA) and the number mean size was calculated how is described in the standard ISO 13322 ($p=0.05$ and GSC of 1.15). To determine the measurement was performed an image analysis with imageJ (1.48v). The results obtained by means of SEM were agreeing with the particle size distribution obtained by AFM (Figure 1B). On the other hand, the transmission electron microscopy (TEM, JEM-2100, Jeol, US) was used to corroborate the size particle in the time of 2 hours of milling reached the nanoscale. In the Figure 1C there are some alignment patterns that could be due to a linear arrangement of polymeric structure of the carbohydrates contained in the Spirulina. An important parameter of the powders material is the repose angle; the results showed that the repose angle was increased in relation to decrease of particle size. The values of repose angle at 1h and 2h of milling were showed significant difference with the reference and the milling samples at 3h and 4h also have significant difference with the reference.

The smallest values of particle size have concordance with the greatest values of repose angle due to that the

samples were very cohesive. In the case of crystallinity index values, these decreased when the milling time was increased.

Then with these findings we proceeded to carry out a proof of X-rays spectroscopy (DRX, Rigaku miniflex 600, US). To obtain the crystallinity index was applied the method of Segal. Those data also observed a tendency to decrease of crystallinity index, however, it is not evident a large change because is possible that the material into the mill present molecular rearrangement by the container's friction force.

In conclusion was possible to obtain nanoparticles with a mean particle size of 91 ± 3.5 with only two hours of milling. Thus the Spex mill is simple technology to obtain nanoparticles due that it requires short times of milling and low consume of energy. It was possible to observe relationships between the particles size, crystallinity index and repose angle.

Keywords: Spirulina, nanoparticles, electron microscopy

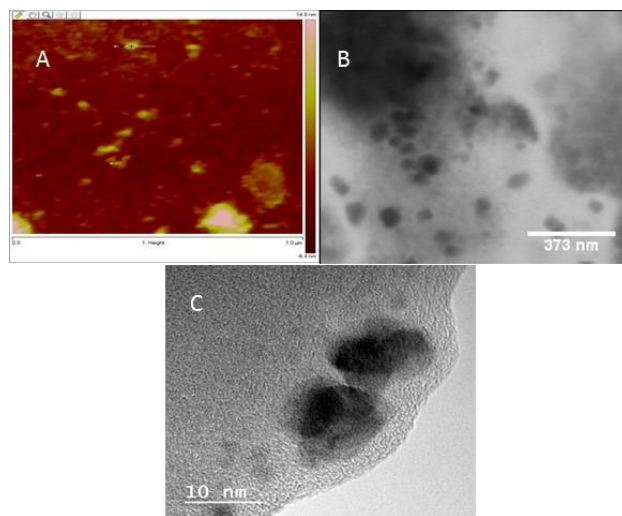


Figure 1. Evidence of each microscopy technique used for the characterization of nanoparticles of *Arthrospira maxima*. A) AFM, B) SEM y C) TEM.

References:

- Belay, A. Spirulina (*Arthrospira*): Production and quality assurance. In: Spirulina in human nutrition and health. 2008. Ed. Gershwin, M.E., Belay, A. Taylor and Francis. USA. Pp 1-26.
- Lü, L., Lai, M. O. 1998. Mechanical alloying. Kluber academic publishers. Massachusetts, USA.

The influence of removal of stabiliser on the selective oxidation of cycloalkenes using supported gold nanoparticles

Hamed Alshammari^a, Peter J. Miedziak^b and Graham J. Hutchings^b

^aChemistry Department, Faculty of Science, Ha'il University, P. Box 2440, 81451 Ha'il, Saudi Arabia

^bCardiff Catalysis Institute, Cardiff University, Park Place, Cardiff, UK CF10 3AT

Abstract: The oxidation of cyclic alkenes such as cyclohexene and cyclooctene has been carried out under green solvent-free conditions using ambient air as the oxidant gas with a carbon-supported gold catalyst. We show that oxidation of cyclic alkenes under solvent free conditions can be oxidised in the absence of radical initiators when the cyclic alkenes are free of stabilisers. We show that radical initiators are only required for this reaction when the cyclic alkene contains a stabilizer molecule, such as 6-bis(*t*-butyl)-4-methylphenol (BHT) or 3-octadecyl-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propanoate (Irganox 1076). We show that either removing the stabilizer chemically or sourcing the cycloalkane without the stabilizer the oxidation, both with and without radical initiator, is identical as showing in figure 1 and 2. This indicates that the only function of the radical initiator is to counteract the stabilizer.

Keywords: oxidation of alkene, nanoparticle, initiator.

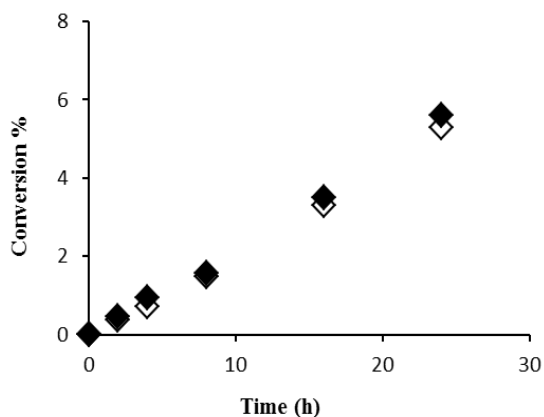


Figure 1: Effect of reaction time for the conversion of *cis*-cyclooctene containing stabilizer with TBHP (solid diamonds) and *cis*-cyclooctene after removal of stabilizer without TBHP (open diamonds). Reaction conditions: 5 ml of *cis*-cyclooctene, 0.06g Au/G, glass reactor, TBHP (0.032×10^{-3} mol), 80 °C and atmospheric pressure.

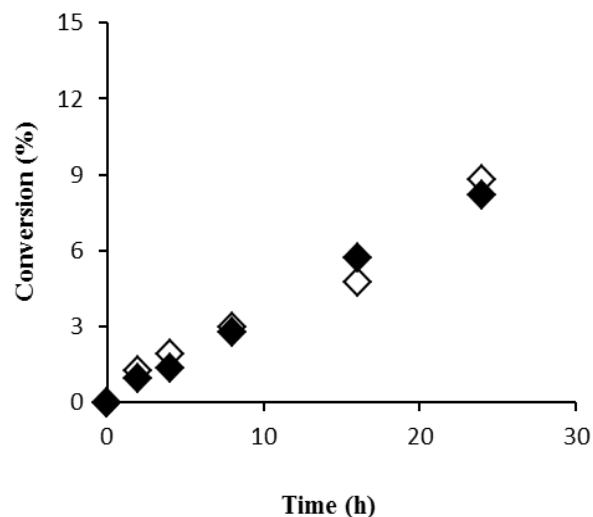


Figure 2: Effect of reaction time for the conversion of cyclohexene containing stabilizer with TBHP (solid diamonds) and cyclohexene inhibitor-free without TBHP (open diamonds). Reaction conditions: 5 ml of cyclohexene, 0.06g Au/G, glass reactor, TBHP (0.032×10^{-3} mol), 60°C and atmospheric pressure.

References:

M.D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D.I. Enache, A.F. Carley, G.A. Attard, G.J. Hutchings, F. King, E.H. Stitt, P. Johnston, K. Griffin, C.J. Kiely, *Nature*, 437 (2005) 1132-1135.

S. Bawaked, N.F. Dummer, N. Dimitratos, D. Bethell, Q. He, C.J. Kiely, G.J. Hutchings, *Green Chemistry*, 11 (2009) 1037-1044.