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Effect of halide-mixing on the electronic transmission in organometallic perovskites

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Abstract: Organic-inorganic hybrid perovskite materials, such as methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), have received a revival of interest in recent years as novel light harvesters with a solar conversion efficiency rapidly approaching 20% [1]. This high efficiency is mainly related to: i) proper band structure, which enable light absorption across most of the solar spectrum; ii) relatively long diffusion lengths; iii) relatively high mobility of charge carriers; and most importantly iv) less sensitivity to topological defects. Because of its tolerance for defects, lead halide perovskite solar cells can be fabricated using low-temperature solution methods that result in low manufacturing cost. In addition, structural, electronic and optical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ can further be refined by chemical engineering, e.g., through mixing halogen atoms. In this respect, Cl and Br are expected to be the most efficient candidates capable of tuning the properties of the material. Despite the large number of experimental and computational studies, the role of halide-mixing remains poorly understood [2,3].

In this work we use density-functional theory in combination with the nonequilibrium Green's function formalism to study the effect of iodide/chloride and iodide/bromide mixing on the electronic transmission in lead based organometallic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, in its room temperature tetragonal phase. We found that the conductance of $\text{CH}_3\text{NH}_3\text{PbI}_3$ can be increased by almost an order of magnitude by partial halide-mixing (see Fig. 1). Largest conductance is observed for small concentration of bromide substitutions located at the equatorial sites. All the systems show similar response to applied voltage: the band gap increases and the transmission decreases with increasing voltage. Our findings are in good agreement with the recent experiment, where on the effect of chlorine substitutions on the structural, electrical and optical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was studied [2]. Full halide substitution has similar effect on the electronic transport properties of the lead-halide perovskites

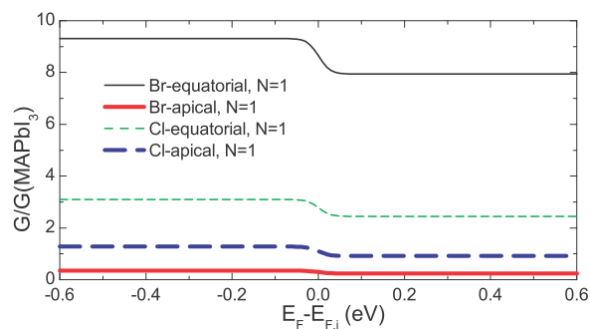


Figure 1: Conductance of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ (solid curves) and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ (dashed curves) samples with a single halide substitution at the equatorial (thin curves) and apical (thicker curves) sites. The results are normalized to the conductance of $\text{CH}_3\text{NH}_3\text{PbI}_3$.

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- [3] E. Edri et al., *Nano Lett.* **14**, 1000 (2014).

Nanoparticles-based Plasmonic Organic Photovoltaic Devices for Enhanced Performance and Stability

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Abstract: Recent advances in polymer synthesis and device engineering of organic photovoltaic devices (OPVs) have led to power conversion efficiencies (PCEs) reaching 10% for single bulk heterojunction devices (Liu *et al.*, 2014). The utilization of randomly distributed nanoparticles (NPs) in almost every layer of the OPV device can significantly enhance both the device performance and stability. In particular, PCE can be enhanced by a) plasmonic near field enhancement absorption from small diameter NPs b) increased optical path length through scattering effects from large diameter NPs and c) enhanced morphology in the photoactive layer (Stratakis, Kymakis 2013). NPs of various sizes, shapes and configurations have been integrated into OPV device architecture in order to tune and enhance, in a wavelength-dependent manner, the optical absorption of the respective devices. As a result impressive improvements in the respective device efficiencies were achieved. In particular, enhancement of both the efficiency and stability of bulk heterojunction polymer-fullerene (P3HT:PCBM, P3HT:ICBA, PCDTBT:PC₇₀BM, PTB7:PC₇₀BM) devices is demonstrated by the addition of Au and Al, formed by ablation of metallic targets in liquids with pico- and femtosecond laser pulses, in either the active layer or in the interface between the buffer and the active layers (Kakavelakis *et al.* 2013,2014). A performance enhancement of 15% to 30% was observed in all polymer-fullerene systems. The highest enhancement of 30% was observed with Al NPs in P3HT:PCBM, while the highest efficiency of 9.1% was observed in the PTB7:PC₇₀BM. The PCE is postulated to be enhanced by exploiting increased absorption around the small diameter NPs integrated into the active layer as well as strong light scattering from the large diameter NPs and clusters, both effects stemming from the excitation of the LSP waves at the NP/photoactive layer interface. Moreover, the devices with Au and Al in the active layer die after ~65 hrs and ~150 hrs under continuous illumination respectively, compared with the pristine devices which die after ~30 hrs (Paci *et al.* 2013). Moreover, particular attention will be paid on the effect of NPs passivation and functionalization on the PCE. In this context, it was found that the highest PCE can be achieved with the incorporation of NPs in the photoactive layer, which the NPs metallic core is in direct contact with the active layer polymer component. On the other

hand, the presence of a terminating coating in the NPs, leads to a reduction in the PCE due to enhanced recombination

Keywords: plasmonic organic photovoltaic, scattering, nanoparticles, laser ablation.

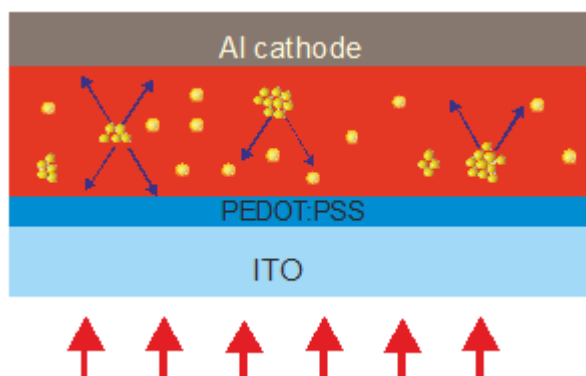


Figure 1: A schematic diagram of the OPV devices, showing distribution of NPs as individual and as clusters

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One-pot Fabrication of Nb-doped TiO₂ Photoanode for Dye-sensitized Solar Cells

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Abstract: Dye sensitized solar cells (DSSCs) have received great attention to use as a potential alternative for low-cost clean energy.(Zhang *et al.*, 2013) A typical DSSC comprises a dye-sensitized nanocrystalline TiO₂ film coating on a transparent conductive oxide (TCO) glass as photoanode, a liquid redox electrolyte containing an I⁻/I³⁻ redox couple, and a platinum (Pt) catalyst as counter electrode (CE). (Oregan *et al.*, 1991) A facile one-pot synthesis of Nb⁵⁺-doped TiO₂ nanoparticles (NPs) with low cost and high yield efficiency for photoelectrode of DSSCs is reported based sol-gel solution. The Nb⁵⁺-doped TiO₂ NPs with Nb dopants of 0~5 mol% are prepared by directly mixing commercial TiO₂ slurry with a functionalized Nb₂O₅ gel following by heat treatment without using hydrothermal method. The functional Nb₂O₅ gel is obtained by UV treatment of a mixture of NbCl₅ powder precursor, ethanol and water as solvent with a certain ratio. The as-prepared NPs, which characterized by field emission scanning electron microscopy (FESEM), field emission transmission electron microscopy (FETEM), exhibit well-crystallized pure anatase TiO₂ phase with uniform particle distribution and average size of about 15~18 nm. The Raman and XPS results demonstrate that the Nb is well doped into the TiO₂ lattice and the substitution of Nb⁵⁺ on Ti⁴⁺ is formed using this cost-effective method. The incorporation of Nb⁵⁺ leads to a stronger and broader light absorption in visible light range (red shift) and a decrease of band gap with increasing Nb dopant content, which importantly enhances the efficiencies of light-harvesting and electron injection, and effectively suppresses the charge recombination. The best energy conversion efficiency of 8.45% is achieved based on 2.0 mol% Nb-doped TiO₂, which presents a significant improvement of 18.9% compared with the undoped TiO₂ cell. (Figure 1(a)) This method provides a simple and cost-effective mass-production route to synthesis n-type metallic ion doped TiO₂ nanoparticles as excellent photoanode materials.

Keywords: TiO₂ nanoparticles; One pot; Doping; Photovoltaic; Dye-sensitized solar cell.

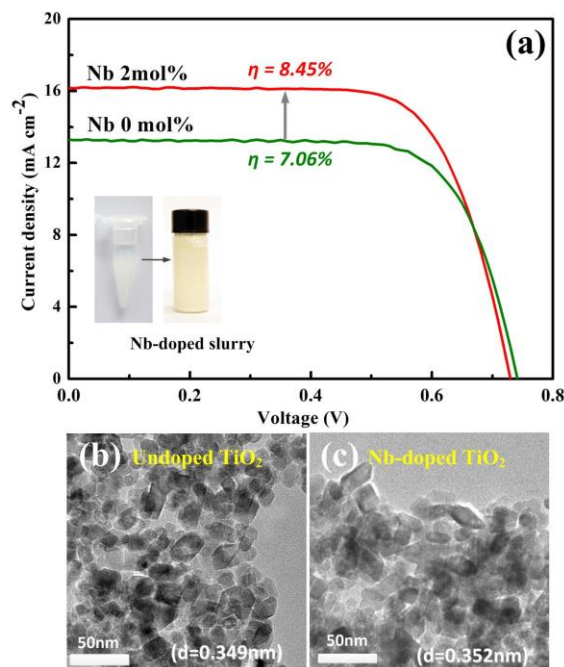


Figure 1. (a) Illustrating the photocurrent density-photovoltage (J-V) curves for DSSCs based on the undoped and 2.0 mol% Nb-doped TiO₂ NPs electrodes. (b)The TEM images of the undoped TiO₂ nanoparticles. (c) The TEM images of the 2mol% Nb-doped TiO₂ nanoparticles.

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Highly stable carbon nanofluids for solar thermal collectors

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Abstract: Carbon nanofluids are engineered materials with controllable thermal and optical properties. For solar thermal collectors they are uniquely well-suited, due to their high spectral absorptivity over the entire solar range (Figure 1). Their application as solar thermal absorbers, however, has been impeded by difficulties in achieving stable nanofluid suspensions at elevated temperatures (Taylor *et al.*; 2013). Dispersing carbon nanotubes (CNTs) in the base fluid is challenging due to the strong inter-particle interaction arising from the high surface energy of CNTs as well as their hydrophobic nature. (Premkumar *et al.*; 2012) A number of chemical functionalization methods including oxidation using strong acids, polymer grafting and mild oxidation using potassium persulfate are available to achieve stable dispersions of CNTs in polar solvents, but polar solvents are limited to relatively low temperature (Zhang *et al.*; 2009, Singh *et al.*; 2009). Thus, high temperature stabilisation techniques for carbon nanofluids have not yet been identified. In this study, a comprehensive series of experiments were conducted to identify appropriate base fluids and functionalization methods to produce CNT nanofluid dispersions with high stability at elevated temperatures of up to 250 °C. Different forms of CNTs including, single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs) were chemically functionalized to obtain stable dispersions in water, Glycerol and Therminol (a synthetic (non-polar) oil). The stability of chemically functionalized carbon nanotube dispersions at different temperatures including 80, 150, 200 and 250 °C was investigated. The results of broadband UV-VIS-NIR spectroscopy showed no agglomeration in the mildly oxidised multi-walled nanotubes (MWCNTs) dispersed in Therminol when heated to 250 °C, highlighting this low-cost material as a potential candidate for use in the new generation of nanofluid-based solar thermal collectors. The nanofluids with high stability at temperatures as high as 250 °C developed in this study are expected to open a new class of highly stable nanofluids for use as solar thermal absorbers.

Keywords: solar thermal collectors, carbon nanotubes, nanofluids, thermal stability.

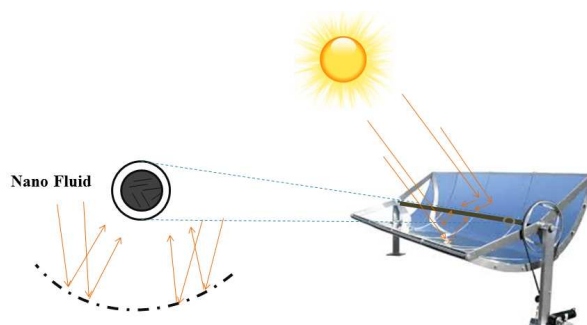


Figure 1: Structure of nanofluid based solar thermal collectors.

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Perovskite Solar Cell Modules built on Vertical TiO₂ Nanorods with High Efficiency and Stability

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Abstract:

Organometallic halide perovskite solar cells (PSCs) has achieved a certified efficiency (PCE) of 20.1%, which is nearly seven times higher than the first report in 2009 (~3%). Typically, perovskite precursor (CH₃NH₃PbX₃, where X=I, Br, Cl) are deposited on a mesoporous or compact thin layer of metal oxide semiconductor (MOS) on a conducting glass substrate (FTO) to fabricate PSCs. Although TiO₂ nanoparticle films are the frequently employed electron transport layers (ETL) in these devices, alternative nanostructures such as nanowires and nanorods are also employed owing to their higher electron mobility. We have employed rutile nanorods (NRs) as ETL in PSCs and found that NRs scaffold is beneficial for long term durable performance. We compared the performance and the durability of two types of scaffolds, i.e., pristine and TiCl₄ treated NRs (Figure 1a), and observed that although the TiCl₄ treatment resulted in ~100% improved performance (PCE ~12.2%) compared to pristine NRs (PCE ~6.4%) the latter showed 10% improvement in performance after ~1300 h whereas the PCE of the former dropped by ~60% of initial value (Figure 1b). We attribute the origin of durable photovoltaic performance in pristine NR based devices to their morphology and crystallinity. Although NRs based devices provide improved electronic transport and durable perovskite solar cells, as demonstrated in our study, the primary issue towards their up-scaling is the difficulty in their patterning. We have patterned NR based large area substrates via laser ablation without significantly damaging the conducting oxide layer. The solid state perovskite solar cells made of these patterned substrates resulted in PCE ~7.8% higher than a reference module of TiO₂ nanoparticles (~6.7%) owing to their improved charge collection. The results demonstrate the first report of high efficiency large area perovskite solar modules based on rutile nanorods.

Keywords: Solar cells, electron collection in perovskite solar cells, stability of perovskite solar cells, 1-dimensional nanomaterials for perovskite solar cells.

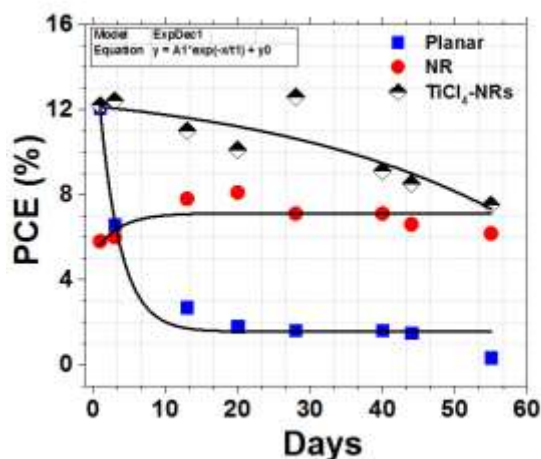
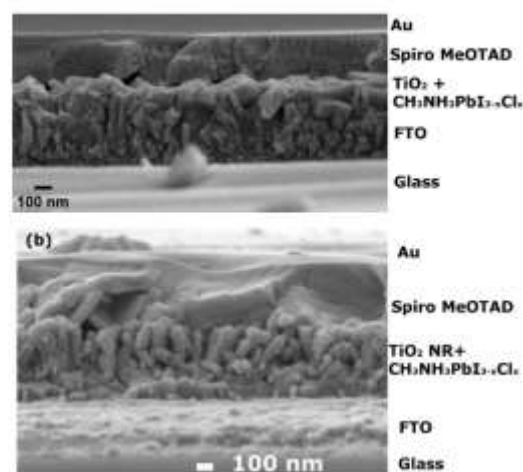


Figure 1: (a) External quantum efficiency (EQE) of nanorods (half-filled black circles) and TiO₂ based (black solid triangles) perovskite modules and (b) J-V curves of the same modules.

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The Development of Alumina Nanofluids-based ferro/ferricyanide Electrolyte and their Applications on Thermogalvanic Cells

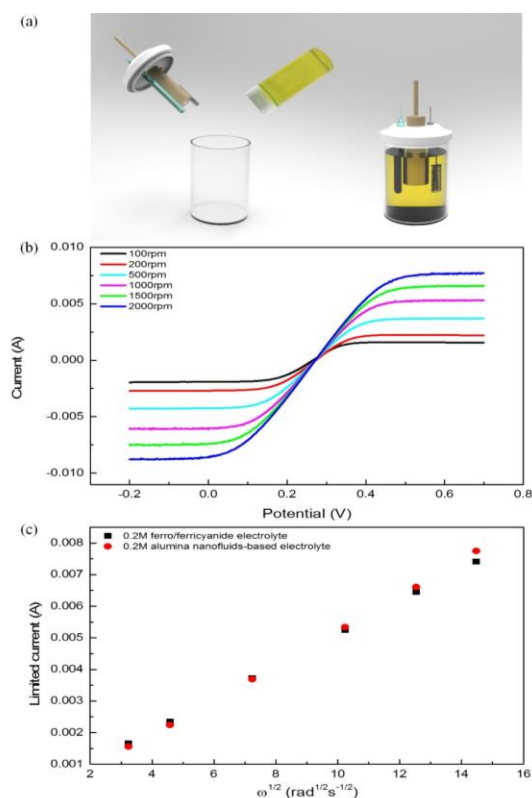
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Abstract: Considerable attentions have been devoted to using nanofluids for augmenting mass transport in colloidal systems. Due to the combined effect of local convection and percolation, nanofluids show a pre-dominant enhancement on conductivity and diffusivity (Prasher *et al.*, 2012). Thus nanofluids are expected to develop critical conductivity of electrolyte for thermogalvanic cells because of aspiring response to convection. However, nanofluids in electrolyte are seldom studied due to intrinsic instability of nanofluids, especially, in electrolyte with high ionic strength. We report practicable processes to fabricate 10nm γ -alumina nanofluids-based ferro/ferricyanide electrolyte with enhancing electrical conductivity and feasible stability by introducing nanogrinding in conjunction with ultrasonic processing. Experimental study is performed to investigate limiting currents of ferro/ferricyanide redox couple in nanofluids based on rotating disk electrode (Figure 1). Diffusion coefficients are deduced from the function of limiting current with respect to angular velocity (Sara *et al.*, 2011). The diffusivity of alumina nanofluids-based electrolyte possesses an obvious enhancement with the increasing of angular velocity, showing a critical derivation from homogeneous pure ferro/ferricyanide electrolyte at high angular velocities. We postulate a new model to describe the diffusivity change of alumina nanofluids-based electrolyte under sheared flow on the basis of both aggregation kinetics and local convection. In addition, thermogalvanic device test is conducted to determine Seebeck coefficient of alumina nanofluids-based electrolyte at temperature differences (Hu *et al.*, 2010). Alumina nanofluids-based electrolyte is confined by relatively high viscosity, which counteracts the thermal conductivity and therefore to capture favorable figure of merit, contributing to high energy conversion efficiency for thermogalvanic cells.

Keywords: alumina nanofluids, electrolyte, stability, electrical conductivity, thermal conductivity, diffusivity, rotating disk electrode, thermogalvanic cells, energy conversion efficiency.

Figure 1: (a) Schematic diagram of the experimental setup for measuring diffusivity of alumina nanofluids-based electrolyte. (b) Voltammograms of ferro/ferricyanide redox couple in alumina nanofluids under various rotating velocities. (c) Limiting current



of 0.2M ferro/ferricyanide electrolyte and 0.2M alumina nanofluids-based ferro/ferricyanide electrolyte as a function of rotating velocity. The slope gives the diffusion behaviors of electrolytes.

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Soft, Compressible and Interdigitated 3D Energy Storage Devices Built by Layer-by-Layer Assembly Inside Aerogels

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Abstract: A controlled formation of fully three dimensional (3D) energy storage devices has been a challenge over the past decade. So far, the few examples of 3D devices rely on advanced processing techniques, limited by material compatibility as well as scalability.

In this study, we propose a new method for a detailed tailoring of interdigitated 3D supercapacitor and batteries inside open-cell and high surface area porous materials such as nanocellulose aerogels (Nyström *et al.*, submitted). The method, consisting of a sequential deposition of active materials via Layer-by-Layer self assembly (Decher, 1997), is rapid (each layer is assembled within seconds), precise (control over the layer thickness at the nanometer level) and versatile (can be used for a very wide range of substrates and materials) (Hamedi *et al.*, 2013).

3D supercapacitors based on carbon nanotubes electrodes were prepared using this method (Figure 1). In order to show the versatility of the method, hybrid batteries were also prepared, incorporating copper hexacyanoferrate nanoparticles (Wessels *et al.*, 2011) as the cathode redox active material.

Our results demonstrate that the self-assembly of interdigitated thin films inside aerogels is a rapid, precise, and scalable route for building high surface area 3D devices. Furthermore, the devices are soft, flexible and stable under extreme compressions (up to 75%).

The presented method and results pave the way for a new class of energy storage devices combining high performance, flexibility and compressibility.

Keywords: high surface area, interdigitated, 3D, electronics, battery, supercapacitor, flexible, compressible, Layer-by-Layer assembly

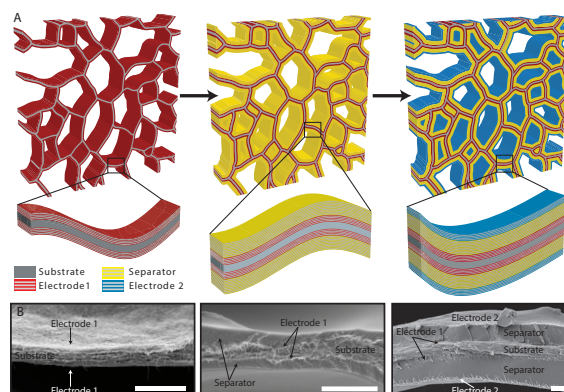


Figure 1: (A) schematic description of the step-by-step build-up of 3D interdigitated devices in the bulk of the aerogel using LbL self assembly, and (B) SEM images of cross sections of LbL-coated aerogels, taken at the corresponding steps of the build-up procedure (the scale bars are 2 μm).

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Numerical study of MAXI₃ (X=Pb, Sn) perovskite based hetero-junction solar cells

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Abstract: The main driver for the development of new solar cells is to address the high cost problem of Si-based technologies. Recently, perovskite based solar cells have been developed, which quickly passed the efficiency threshold of most emerging thin-film devices and thus has triggered a new round of explosive activities in photovoltaic research in using perovskite for solar energy harvest. The current focus for this class of solar cells is largely on further enhancement of efficiency and replacement of Pb. In this work, numerical simulation of MAXI₃ (X=Pb, Sn) perovskite based hetero-junction solar cells were conducted using AMPS-1D, aiming to offer physical insight to guide materials selection and device engineering. MASnI₃ is investigated as an alternative layer for Pb based optical absorber. Both two-layered (SnO₂/Perovskite) and three-layered (SnO₂/Perovskite/p-type) architectures are studied, with perovskite being the major light-absorption material in both cases. The results show that the three-layered device is far more efficient than the two-layered, when the former is designed into a window/absorber/voltage-enhancer (WAV) construction, this being in excellent agreement with the outcome of our recent modelling work [1,2]. Cu₂O is shown to be the best candidate among three p-type materials (P3HT, Spiro-OMeTAD and Cu₂O). Comparing to MAPbI₃, the same efficiency can be achieved using a thinner layer of MASnI₃ as the absorber. With suitable distribution of charged carrier densities through out the three layers, optimal efficiency above 35% can be achieved with a total thickness less than 1 μ m.

Keywords: perovskite solar cell, WAV structure, MAXI₃ (X = Pb,Sn), numerical simulation.

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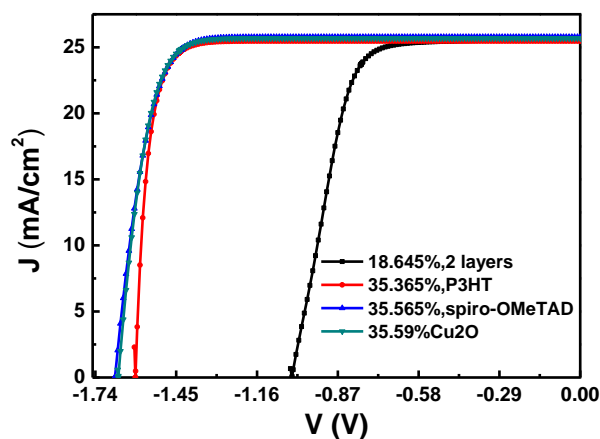


Figure 1: J-V curve using MAPbI₃ as absorber layer. Higher efficiency can be achieved by the three-layered design.

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Stability of organic solar cells using composites materials of inorganic nanostructures and polymers for efficient organic photovoltaics: time-resolved structural/morphological studies

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Abstract: Increasing research interest is devoted to bulk heterojunction (BHJ) organic photovoltaic (OPV) cells, showing low cost large-scale production, flexibility, light weight and low environmental impact. Recently, it has become clear how the optical and transport properties of the organic active film in OPVs, are strongly connected to their structural, morphological and interfacial properties. Here, we discuss our recent results on devices incorporating metallic nanoparticles (NPs) in the photoactive layer, in order to take advantage of the ability of the metallic NPs to rise the BHJ optical absorption by the excitation of Localized Surface Plasmon Resonance. The photovoltaic, structural, morphological and interface properties and aging effects are evaluated by in-situ by time-resolved Energy Dispersive X-ray Reflectivity/Diffraction (EDXR/EDXD) techniques applied jointly with in-situ atomic force microscopy (AFM). The results of our unconventional approach, based on time-resolved EDXR/AFM cross-monitoring, showed the incorporation of metallic NPs allowed to control both the bulk and the interface morphological degradation pathways. In particular, time-resolved EDXR showed that doping the active film of the devices with Au NPs protects the metallic electrode buried interface against degradation (figure 1). This can be ascribed to a NP-mediated mitigation of the photo-oxidation effect at the cathode-active layer interface. As a result, aging experiments demonstrate that Nps doped devices show enhanced PV properties and durability. These findings indicate novel strategies, employing plasmonic metal NPs, as a fundamental step for the development of more stable OPV architectures. Besides the impact of indicating novel approaches for the developing of more efficient and stable organic devices, this work demonstrate the great potential of the joint EDXR/AFM technique in the study of nanolayered structures.

Keywords: Bulk heterojunction organic photovoltaic devices, plasmonic effect, polymer inorganic nanoparticles nanocomposites, time-resolved joint EDXR/AFM characterization, stability enhancement.

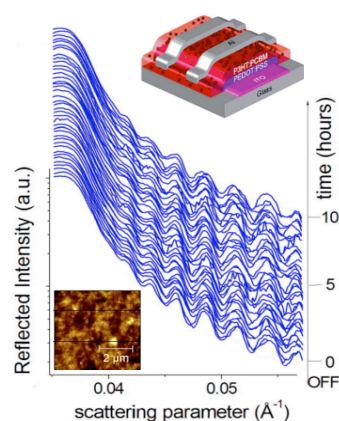


Figure 1: Time-resolved EDXR analysis of OPV device incorporating metal NPs, demonstrating a NPs mediated mitigation of the aging effects.

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Understanding Lithium solvation in ionic liquids from first principles molecular dynamics simulations

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Abstract: Ionic liquids are being considered as an alternative electrolyte for Li-ion batteries. The main reason behind this application is the non-flammability of many ionic liquids that will eliminate one of the major safety issues affecting this technology. In this particular case, we investigate the solvation of lithium (Li) in Ethylammonium Nitrate (EAN). The study relies on a combination of classical, and first principles molecular dynamics simulations using the Gromacs and CP2K software packages, respectively [1,2]. Starting with an existing force field we initially performed a classical simulation in order to obtain a molecular arrangement that was then used as the starting configuration for the first principles simulations. We found that the first principles results give a lower Li-Oxygen average coordination number when compared to recently reported classical simulations [3]. The issue of the discrepancy between classical and first principles predictions for the coordination has been already discussed in the literature for cations solvated in water [4,7]. In particular, our ab-initio simulations conclusively show that only three nitrate molecules solvate the lithium ion in a planar arrangement, namely, the Li ion is located on or very close to the plane defined by the three nitrogen atoms corresponding to nitrate molecules (Figure 1).

Keywords: Li-ion batteries, Ionic liquids, Lithium solvation, First Principles Molecular Dynamics simulations.

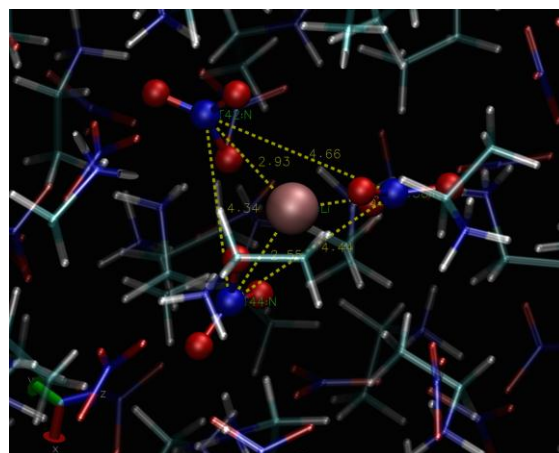


Figure 1: A snapshot illustrating the solvated Li^+ in EAN (Ethylammonium Nitrate)

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Nanomaterials Impacts Across the Life Cycle: Case Study LCA on Organic Photovoltaic Solar Cells

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Abstract: This paper presents the work of an life-cycle assessment (LCA) case study involving organic photovoltaic (OPV) technology, particularly technology using the nanomaterial Phenyl-C61-Butyric-Acid-Methyl-Ester (PCBM), and the implications across the life-cycle of using engineered nanomaterials in product systems.

Although solar technology converts freely available solar into useful forms of energy such as electricity, potential environmental impacts result may from processing, production and disposal of these products and materials. The objective of this paper is to highlight the influence of nanomaterials in the life-cycle impacts of organic photovoltaic cells, particularly their potential impact on human health and ecotoxicity.

This work will present a cradle-to-grave LCA comparing OPV solar cells, including the use and end-of-life phases. Previous work of ours included the cradle-to-gate LCA, comparing the functional unit of 1Wp of electricity produced for OPV and conventional cells.

The results of that cradle-to-gate study demonstrate that from a life cycle perspective, organic solar cells perform better than conventional solar cells. The models and results assessed also show that further improvements can still be gained for OPV cells with material choices and fabrication methods of the solar cell.

The results of this previous assessment failed to incorporate the impacts (i.e. toxicity) from the nanomaterials themselves which are used in the active layer of the photovoltaic system. Potential emissions and exposure to nanomaterials could present themselves during manufacturing of the nanomaterials or production of the solar cell itself.

Our recent work is furthering the assessment of OPV cells, by evaluating impacts throughout the entire life-cycle of the product. The use phase and end-of-life considerations are being included by changing the functional unit to agree with various types of use phase scenarios such as solar panels used in throw away devices, medium-term devices, and standard long-term solar arrays and panels. Additionally, various end-of-life considerations will be taken into account including landfilling, incineration and possibly recycling.

In this regard particular attention will be given to the environmental flows associated with the fullerenes across all life-cycle stages. The nanomaterial

impacts including the percent contribution of total life-cycle impacts as well as the emissions, fate/transport, exposure and toxicity resulting from the fullerenes will be assessed. The latter will consist largely of a qualitative assessment, and also an overview of how these points of interest can be better integrated into life-cycle assessment impact methods.

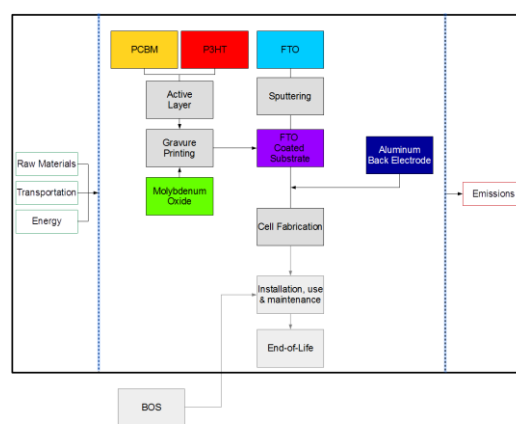


Fig. 1 System boundaries for the life-cycle assessment.

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Sol-gel complex synthesis of biphasic anatase-brookite photocatalysts for hydrogen production

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Abstract: Research of efficient photocatalytic materials for hydrogen production still gain a lot of attraction. The current efforts to synthesize the biphasic titania photocatalytic nanoparticles are based on mixing of titanium precursor (usually titanium alkoxide) with a donor (e.g. lactic acid) in a ratio of 1:3 resulting predominantly in the formation of brookite phase instead of real biphasic structures (Cihlar *et al.*; 2015). Here we present a sophisticated and reproducible method to obtain the anatase-brookite crystals with a high reaction yield. This method requires only mild hydrothermal conditions such as normal pressure and temperature below 100 °C, and does not suffer from the formation of unfavourable single phase product. The aim of work was to study the optimal reactant concentration, titanium isopropoxide and lactic acid, to achieve the highest photocatalytic activity in the production of hydrogen.

The synthesized titania biphasic nanoparticles were characterized by transmission electron microscopy, BET adsorption isotherm, X-ray diffraction spectroscopy and photoelectrochemical spectroscopy. The obtained TEM results (Figure 1) showed the crystallite size corresponds to 3–6 nm which is in a good correlation with results from XRD analysis. BET analysis revealed the active surface as high as 250 m²/g. The photocatalytic activity in the hydrogen production was evaluated with respect to donor and titanium precursor ratio and different forms – either colloidal or deposited. As expected, we have found the photocatalytic activity of prepared biphasic photocatalysts in colloidal form is approximately 9 times higher in hydrogen production than spray-coated dense photocatalytic layers.

Keywords: titania nanoparticles, biphasic photocatalyst, anatase, brookite, sol-gel, chelate synthesis, hydrothermal synthesis, hydrogen production, photoelectrochemical spectroscopy.

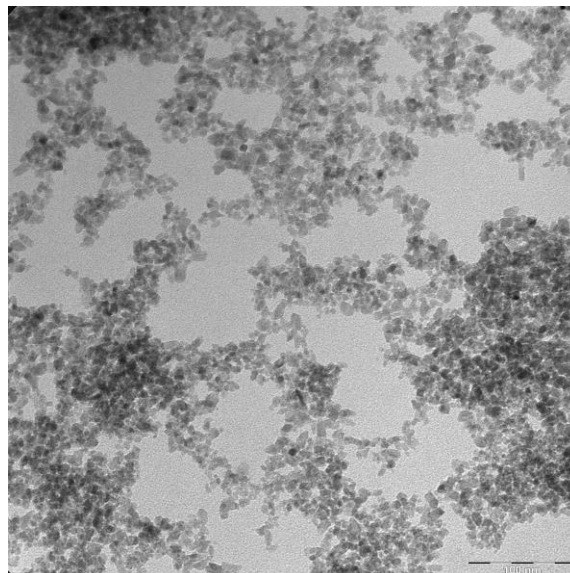


Figure 1: TEM image of biphasic anatase-brookite nanoparticles with the size of 3–6 nm (the bar corresponds to 100 nm).

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Oxygen Electroreduction on Platinum Nanoparticles Deposited on D-glucose Derived Carbon

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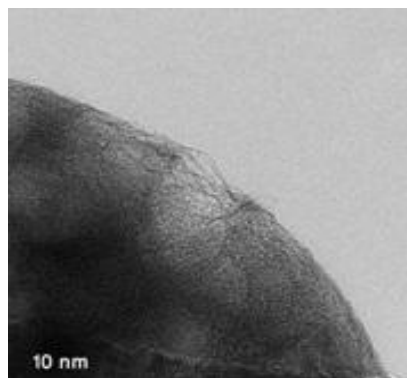
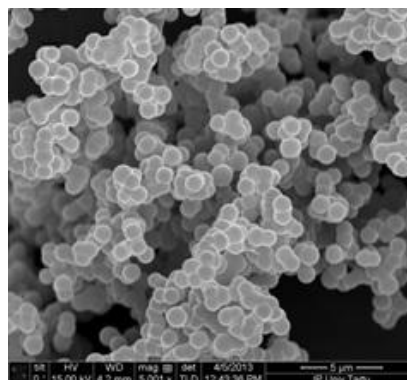
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Abstract: Proton Exchange Membrane Fuel cells (PEMFC) are counted as clean and very promising energy conversion devices. They are still expensive and their performance and durability are not very persuasive. One of the developing aspects is the structure of the carbon support, which can affect the overall performance and price. In this study, a new type of microporous-mesoporous carbon material synthesized from D-glucose and posttreated with CO₂ was used as the carbon support for Pt catalyst. This material, was prepared in the laboratory of the Institute of Chemistry, Tartu University and Pt nanoparticles were precipitated on this support via borohydride reduction method. Both unmodified and modified materials were characterized by physical techniques (XRD, Raman spectroscopy, N₂ adsorption/desorption method, HRSEM, SEM-EDS and HRTEM) and electrochemical techniques (cyclic voltammetry, rotating disk electrode method and electrochemical impedance spectroscopy). Raman spectroscopy technique confirmed the disordered amorphous structure of the synthesized carbon material. The presence of the Pt was attested by SEM-EDS and XRD. N₂ adsorption/desorption data showed the distribution of the pore sizes in materials and revealed the microporous-mesoporous structure of both materials. HRSEM and HRTEM presented a visual image of the C and Pt-HTC materials and confirmed the spherical shape and good dispersion of Pt nanoparticles. Cyclic voltammetry and impedance spectroscopy data, revealed considerably high capacitance for both unmodified and modified materials in 0.5 M H₂SO₄ solution. The ORR activity in 0.5 M H₂SO₄ solution investigated by cyclic voltammetry and rotating disc electrode method showed much higher activity for Pt-HTC compared to pure carbon material.

Keywords: PEM fuel cell cathode, oxygen electroreduction, Pt catalyst, D-glucose derived



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Fabrication of heterostructure between Tin oxides and TiO₂ nanobelts for application in photocatalysis and gas sensing

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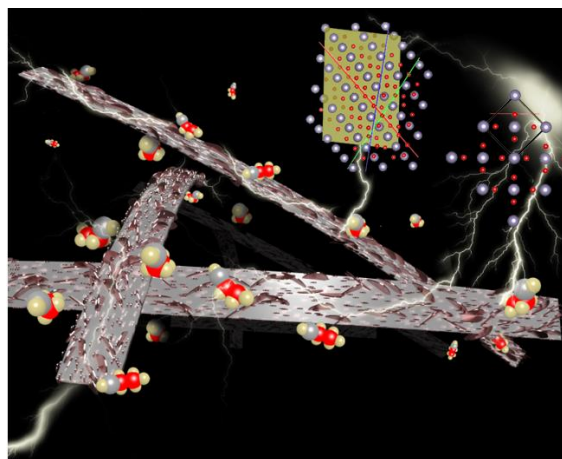
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Abstract: Heterostructure properly designed between semiconductors has been proved efficient for the realization of new or improved properties (Hong Liu *et al.*; 2014). Due to its ultrahigh surface-to-volume ratios and diversified functional properties, one dimensional TiO₂ nanobelts are ideal backbones for the growth of other nanostructures. We report the synthesis of novel hierarchical scaly Sn₃O₄/TiO₂ nanobelts via a facile hydrothermal method, the Sn₃O₄ nanoflakes with a size range of 100-400 nm and thickness of 20-40 nm are perpendicularly grown along the c-axis direction on TiO₂ nanobelts, which are 50-200 nm in width, 20-40 nm in thickness and up to several micrometers in length, to form a heterostructure system. The matching band positions cause greater separation of photoexcited charge carriers, which should be responsible for the enhanced photocatalytic pollutant degradation and hydrogen evolution under either UV or visible light irradiation (Guohui Chen *et al.*; 2015). Further thermal oxidation of Sn₃O₄/TiO₂ at elevated temperature attains SnO₂/TiO₂ heterostructure. Experiments indicated its desirable gas sensitivity toward ethanol at operating temperature as low as 43°C (Figure 1). To elucidate the possible mechanism, the oxidation process of Sn₃O₄ are examed and analyzed. The Sn₃O₄ experiences two processes of decomposition and oxidation, with metal Sn as intermediate phase, resulting in SnO₂ nanosheets and nanoparticles. We anticipate that the exposed high-energy facets of (4.75 -4.75 - 9.594) SnO₂ that converted from triclinic phase Sn₃O₄ should play critical role in the low temperature gas sensing performance. This study provide a photocatalyst with broad spectrum absorption and a gas sensor with intrinsic low operating temperature.

Keywords: TiO₂ nanobelts, Sn₃O₄, SnO₂, heterostructure, photocatalytic activity, hydrogen evolution, thermal oxidation, gas sensing.

Figure 1: Figure illustrating the gas sensitivity towards ethanol and atomic structure for SnO₂ exposed facets in two types: (4.75 -4.75 -9.594) and (001).



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Efficient and Stable Photo electrochemical Water-oxidation Performance of ZnO NRs with Ultrathin Cobalt Layer

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Abstract: Efficient and stable electrochemical water oxidation (ECWO) performance was observed from ultrathin cobalt layer coated aligned zinc oxide (ZnO) nanorod structures. ZnO NRs have been developed on ZnO layer coated FTO substrates using low-temperature chemical bath deposition (Devika *et al.*; 2015). Structural, morphology and optical properties were studied. Prior to ECWO measurements, a thin cobalt layer was coated on ZnO NRs by electrochemical deposition, which plays a role as protective as well as catalyst layer (Figure 1a). The ECWO performance of the structures was studied in specially designed three electrode electrochemical cell using a platinum wire as counter electrode and Ag/AgCl KCl saturated electrode as reference electrode. The measurements were carried out in pH=10 electrolyte solution (borax with sodium hydroxide) (Bora *et al.*; 2014) under dark as well as front illumination (Xenon lamp with and without UV filter) conditions. The photocurrent density (J) versus potential curves of the cobalt coated ZnO NRs anodes are shown in Figure 1b. The dark response of as-grown ZnO NRs is very less, which is in the order of $\mu\text{A}/\text{cm}^2$. However, under UV light illumination, the structures exhibited very good photoresponse and also showed the current density in the order of mA/cm^2 . The ratio between illumination and dark current density at a potential of 0.5 V is found to be 455. Further, very good photoelectrochemical stability in the duration of 30 minutes is noticed at the potential of 0.5 V.

Keywords: ZnO nanorods, ZnO/Co core/shell structures, photoelectrochemical studies, Energy harvesting applications.

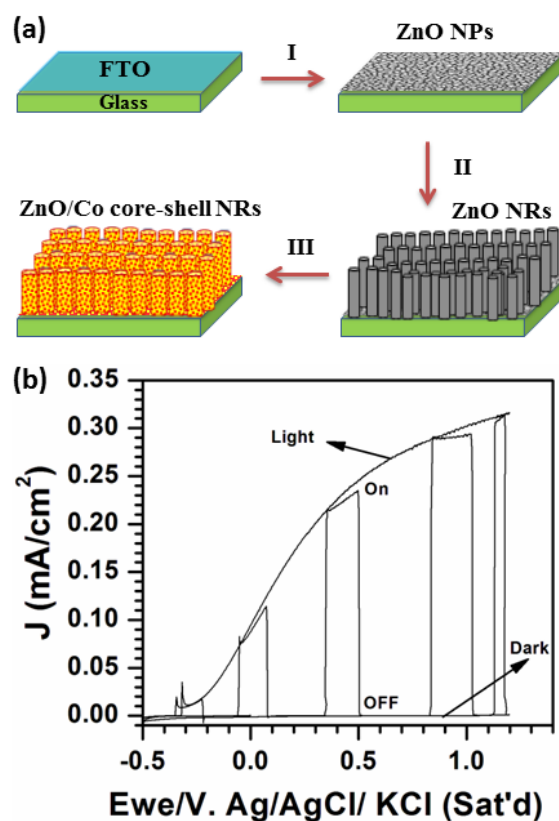


Figure : (a) Schematic diagram of growth of aligned ZnO NRs and (b) photochemical water oxidation response under dark and light (with and without chopping)

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New sensor for direct detection of pesticides in water by Raman spectroscopy coupled with enzymatic functionalized nanoparticles.

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Abstract: Pesticides are worldwide used in agriculture and industries[Ahlborg *et al.*, 1961]. Some of them are highly toxic and may perturb some vital functions in organisms. In this framework it is very important to dispose of tools able to detect very fast and with very high sensitivity these kinds of compounds. In this work an acetylcholinesterase (ACHE) biosensor was developed in the goal of a direct detection of pesticides in water. Our method is based on Surface Enhanced Raman Scattering (SERS) phenomenon which corresponds to the increasing of a Raman signal when an analyte is at the vicinity of a metallic rough surface. Organophosphored and carbamate pesticides are known to block the activity of ACHE, an important enzyme implied in nervous system functioning[George *et al.*, 1961]. The activity of ACHE is a sensitive indicator of the presence of pesticides and its inhibition was already used for detection purpose. Here, once immobilized via an electrochemical process[Kengne-Momo *et al.*, 2010], the enzyme was placed at the contact of its substrate (acetylcholine(ATC)) and the enzymatic reaction (transformation of the substrate in choline and acetic acid) was monitored by Raman spectroscopy. By using dedicated gold nanoparticles(Au Nps), the Raman signal of the generated products was detected and enhanced giving a specific SERS spectrum, reference spectra of a "healthy" enzyme (figure 1). In presence of pesticides, the enzyme is inhibited leading to the absence of enzymatic reaction and to a different Raman spectra (figure 2). In this study, paraoxon and carbaryl were used as model pesticides and the first results showed that this biosensor gave highly sensitive and very fast responses. This biosensor can be used for a non-specific and on-line detection of enzyme inhibitors.

Keywords: Acétylcholinestérase, Raman SERS, Pesticides, Au nanoparticles.

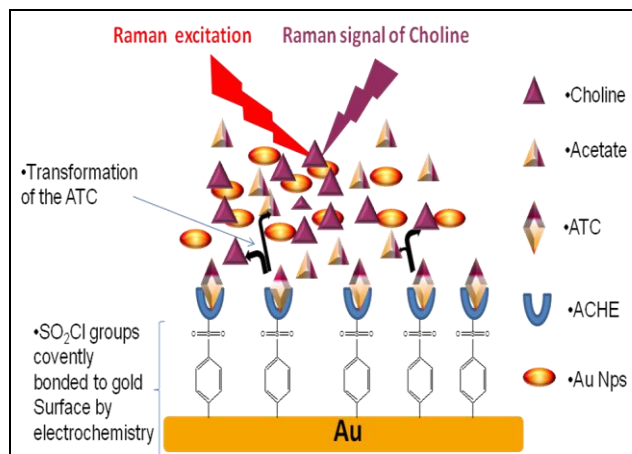


Figure 1: Activity of Acetylcholinesterase in the absence of pesticides.

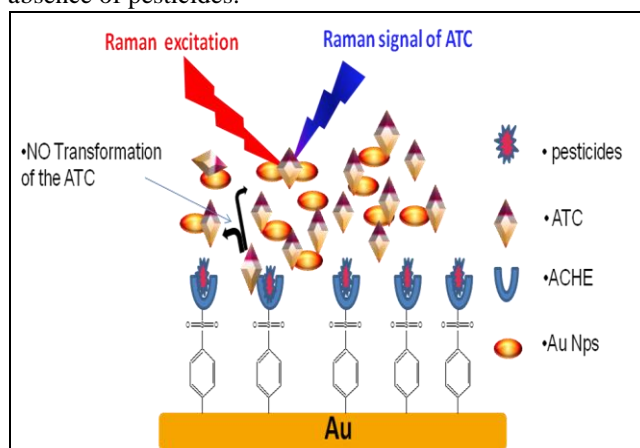


Figure2: Inhibition of the Activity of Acetylcholinesterase by the pesticides.

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Graphene Coating and Nanocrystalline Alloy Structure: Novel Approaches for Remarkable Corrosion Resistance

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Abstract

This talk will present two novel approaches for mitigation of corrosion. The associated research has also involved considerable degree of surface analysis.

Ultra-thin Graphene Layer for Corrosion Resistance

Graphene research was awarded Nobel Prize in 2010 [1]. A monolayer or a few atomic layer thick graphene coatings on metals have been shown to improve their corrosion resistance by nearly orders of magnitude (Figure 1). Though there are very few studies reported on the topic of corrosion resistance due to graphene coating, there is still considerable variability in the degree of improvement. For example, improvement in aqueous corrosion resistance of copper due to graphene coating is reported to vary from insignificant to nearly 2 orders of magnitude [2-5], whereas the improvement for nickel can be in excess of an order of magnitude. This presentation will review the most recent research on graphene that has been claimed as 'the thinnest known corrosion-protecting coating', and potential application of such disruptive approach to corrosion resistance of steels.

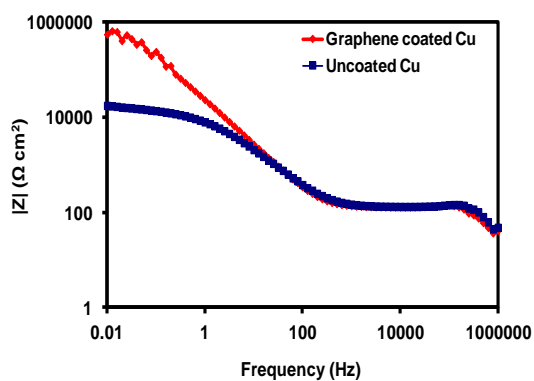


Fig. 1 Bode plots confirming the graphene coated Cu to have ~2 orders of magnitude superior corrosion resistance in sea water than the uncoated Cu [2] (Note, the magnitude of $|Z|$ (on the y-axis) at the lowest frequencies represents corrosion resistance).

Nanocrystalline Structure for Oxidation Resistance

The second part will demonstrate remarkable resistance to oxidation as result of the nanocrystalline alloy structure. This will include an elaborate description of the author's own hypothesis that nanocrystalline structure can impart extraordinary oxidation resistance, and the validation of this hypothesis (as shown in the Figure 2). A thorough surface/subsurface characterization of oxidized alloys, using secondary ion mass spectrometry has provided a sound mechanistic understanding of the remarkable

improvement in oxidation as result of nanocrystalline structure. The data to be presented will include the results establishing that a Fe-Cr nanocrystalline alloy with only 10wt% Cr can provide as much oxidation resistance as a Fe-20Cr alloy, suggesting possibility of Fe-Cr alloys with the necessary corrosion resistance at much lower Cr contents. As another exciting potential application of this work, the nanocrystalline powders of Fe-Cr alloys synthesized in this study could be used for developing corrosion resistance coating having considerably low Cr contents. Keywords: protein folding, nanoporous sol-gel glasses, silica-based biomaterials, circular dichroism spectroscopy, surface hydration, crowding effects, micropatterning, biomedical applications.

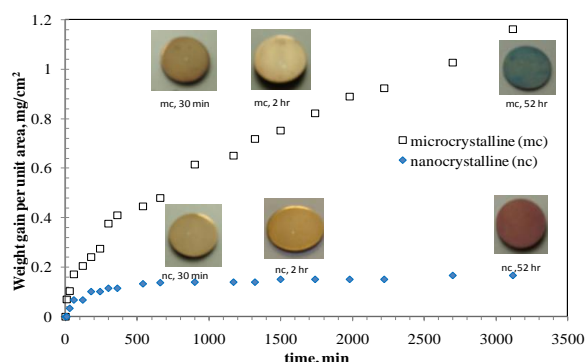


Fig 2: Oxidation kinetics of nanocrystalline (nc) and microcrystalline (mc) Fe-10Cr alloys oxidised at 300 °C for 3120 min [6].

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Characterization and application of multicomponent nanoparticles in the immobilization of heavy metals from water and liquid and solid mining tailings

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Abstract: Iron based nanoparticles have been used in remediation of solvent chlorides, PBCs, pesticides and heavy metals at laboratory level (Liu & Zhao, 2007; Xiong et al., 2009; Zhao et al., 2009; Kim et al., 2011). However there are no studies of applications of nanoparticles to simultaneously remove several heavy metals. In this study multicomponent nanoparticles (Fe/FeSNPs) were synthesized using sodium sulfate, ferric chloride and sodium borohydride. Nanoparticles as prepared were characterized and used to remove a group of heavy metals from water and liquid and solid mining tailings. Dynamic light scattering, transmission electron microscopy, infrared spectrophotometry, X-ray diffraction, and X-ray photoelectron spectrometry were used to characterize nanoparticles. Average size of the spheres is 30 nm. FTIR spectrum of a sample of nanoparticles after removal of Cu^{2+} shows changes on peaks that imply the existence of residual hydroxyl groups on the surface of Fe/FeS nanoparticles. The latter mechanism may promote the formation of complex of Sur-OH-Cu^{2+} and Sur-O-Cu^{2+} during the adsorption of Cu^{2+} . A XRD spectrum provides Fe peaks and amorphous content of FeS. In addition, XPS spectra give peaks of $\text{Fe}2p_{2/3}$ and $\text{Fe}2p_{1/2}$, they show a decrease of binding energy after contacting the Fe/FeSNPs with Cu^{2+} (Cumbal et al., 2014) and peaks of $\text{Cu}2p_{1/2}$ and $\text{Cu}2p_{3/2}$ show CuO formation.

Removal tests were performed contacting the multicomponent nanoparticles with acidic contaminated water and soils. For artificial water samples, heavy metals were removed in more than 95%. Kinetic tests conducted under aerobic environment, pH 3 and 18% (v/v) of nanoparticles demonstrate the best removal is accomplished after 4 hours of treatment and a pseudo-second order of reaction fits experimental data. Tests of isothermal adsorption showed a capacity (q) of approximately 140mg/g for 200mg/L Cu^{2+} as initial concentration. The nanoparticles were also used to remove heavy metals from mining liquid tailings. More than 90% was achieved after 8 hours of treatment. Whereas, in soil samples the immobilization of heavy metals was around 85%. Currently, we are performing leachate tests to find out if the final product is chemically stable.

Keywords: Multicomponent nanoparticles, heavy metals, tailings, mining.

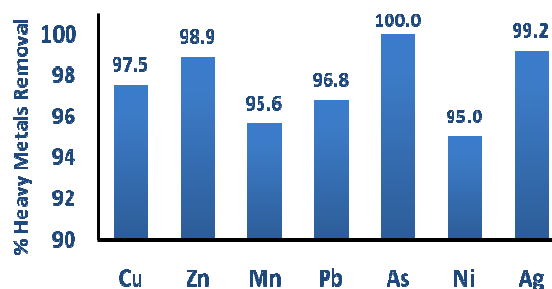


Figure 1: Removal of heavy metals using Fe/FeS nanoparticles from liquid tailings

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Characterization of Nanosized Metallic Sulfide Catalysts Obtained by Thermal Decomposition of Nanoemulsions

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Abstract: Many studies have shown that it is possible to prepare more active hydrotreating (HDT) catalysts using nanotechnology (Song, 2003; Escobar et al., 2005). Nanocatalysts have been developed to improve the catalytic processes in the conversion of heavy fractions (Khadziev et al., 2007; Lott and Lee, 2005). An ultra-dispersed catalyst of cobalt-molybdenum and nickel-molybdenum sulfide (Co-MoS, NiMoS), and the method of preparation (Pereira et al., 2011) were evaluated for the hydrodesulfurization (HDS) of heavy fractions. The effects of the properties of the catalyst's precursors on the final catalysts particle size formation were studied, showing the effect of the aggregation process of the nanoparticles produced.

Despite many researchers and commercial companies having worked on the development of nanotechnologies for the conversion of heavy fractions, it has not yet been possible to establish a process based on nanotechnology in the refinery. Since light crude production is declining, the refinery will treat more heavy oil fractions in the coming years. Consequently, many opportunities are still open to develop process technologies based on nanotechnology that can be technically operational and economically feasible to treat heavy oil fractions.

This paper presents the characterization of the solids obtained by thermal decomposition of nanoemulsion under typical hydrotreating conditions. The products were characterized using ultra-violet spectroscopy (UV-VIS), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM).

Nanosized metallic sulfide catalysts were obtained with a particle size below 100 nm. The figure 1 shows the TEM image of the solid obtained from the thermal decomposition of the emulsion containing molybdenum and sulfur precursor. The image shows the presence MoS₂ slab with a particle size distribution below 100 nm (40 to 50 nm; 30 to 40 slabs/particle).

Keywords: Hydrotreating, hydroconversion, nanosized metallic sulfide catalyst.

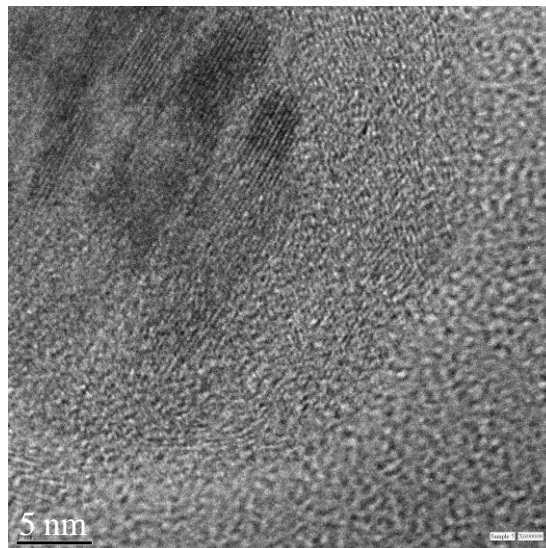


Figure 1: Transmission electron microscopy of molybdenum sulfide

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Surface Functionalization of TiO₂ Nanoparticle and its Application for Biodiesel Production from Locally Sourced Used Cooking Oil

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Abstract: The biodiesel industry is an emerging alternative for managing the demands of transportation, industrial processes and residential consumption by being eco-friendly, biodegradable and readily available [1]. Around 90% of current biodiesel in industry is made by transesterification process of triglycerides with low molecular weight alcohols over homogenous acid or base catalysts. However, the biodiesel industry faces a few problems due to the high costs of biodiesel raw materials and biodiesel processing including separation, purification and neutralisation of by-products have been the main challenges for its commercial availability [2-4]. These problems can be addressed by using cheap feedstocks such as used cooking oil and replacing the conventional catalysts with catalysts highly tolerant to moisture and free fatty acids because free fatty acids and moisture contents in cheap raw materials have adverse on the activity of the catalysts.

The present work is focused on the preparation of a novel functionalised titanium dioxide nano-catalyst from titanium dioxide and suspended 1,3-propanesultone in toluene under reflux for 72 hours at agitation rate of 250 RPM and its tested for the simultaneously esterification and transesterification of locally sourced used cooking oil which contains high concentration of free fatty acids. The synthesised nano-catalyst has been characterised by several analytical techniques, such as FT-IR, XRD, SEM, TEM, XPS, TGA-FTIR, and N₂ adsorption-desorption isotherms.

The effect of catalyst loading, reaction temperature, time of transesterification, and methanol to oil ratio on the biodiesel yield was investigated. It was found that under certain process parameters a yield of 98.3% can be achieved using functionalised TiO₂ as a

catalyst. Furthermore, it was found that the catalyst activity slightly dropped by 3.7% after three runs of transesterification of used cooking oil.

Keywords: Functionalised TiO₂ nanoparticle, Biodiesel, Used cooking oil, Solid acid catalyst

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Photopolymerization of Water-Soluble Acrylic Monomers Induced by PbS and CdS Nanoparticles

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Abstract: Photo-induced radical polymerization is the most widely used technique because of its applicability to a wide range of monomers, solvents and simple experimental conditions. This process has gained interest and well known in industrial applications. These include coatings, inks, adhesives, varnishes, dyes and photolithography which can be performed without the need of solvents, at room temperature and the reactions are simply initiated by light (typically in the ultraviolet or visible region of the light spectrum). Previous studies have shown that semiconductors or suspensions of semiconductor particles can act as photo-initiators to start the polymerization.^{1,2} Higher photo-efficiencies were observed when smaller colloidal particles were chosen as photo-initiators.² Recently, it was shown that nanocomposite hydrogels can be synthesized through the initiation of polymerization with the use of semiconductor nanoparticles (ZnO, TiO₂, Fe₂O₃, SnO₂, ZrO₂, CdSe, or CdTe) even under sunlight irradiation.³ Much effort has devoted to free radical polymerization techniques mainly because of the presence of a wide range of photo-initiators. However, semiconductors have rarely been used as initiators to prepare polymers. These preliminary works can trigger striking advantages for both the classical photoinitiated polymerization systems and modern curing applications.

In our talk, we will discuss the use of PbS and CdS quantum dots as new photoinitiators. The coating on the surface of these semiconductor materials are important to induce a photopolymerization. In our study, we will try to elucidate the possible mechanism for the radical initiation. The effect of the solvent, wavelength of the light selected for the photopolymerization reactions will be discussed.

Keywords: semiconductor materials, lead sulfide, cadmiumsulfide, quantum dot, photopolymerization



Figure 1: Gelation of the poly(ethyleneglycol) diacrylate induced by PbS quantum dots.

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Design and synthesis of copper chalcogenide nanostructures for energy conversion and storage

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Abstract: Copper chalcogenide nanostructures (i.e., one-dimensional nanowires and nanotubes) have been the focus of interest because of their unique properties and great potential in various applications. Here, we demonstrate our recent results in preparation and application of copper chalcogenide nanostructures. First, we prepared copper telluride nanocubes, nanoparticles and nanosheets through the high-temperature solvothermal approach, and then applied them as anodes of lithium-ion batteries (Han *et al.*; *J. Mater. Chem. A*, 2014). Second, we prepared copper selenide nanowires by the hydrothermal method, and showed their potential application in thermoelectrics (Chen *et al.*; *J. Colloid Interface Sci.*, 2015). These two fabrications are relied on high temperature. In our third report, we prepared Cu_{2-x}E (E = S, Se) micro-/nano-tubes (NTs) with a hierarchical architecture by using copper nanowires (Cu NWs) and stable selenium and sulphur powder as precursors at room temperature, with the assistance of theoretical prediction (Chen *et al.*; *Chem. Eur. J.*, 2015). Interestingly, two-dimensional (2D) nanosheets could be prepared from Cu NWs by simply increasing amount of ligands (or using different ligands) during preparation. The resultant Cu_{2-x}E (E = S, Se) NTs were used as counter electrodes (CEs) of quantum-dot-sensitized solar cells (QDSSCs) to achieve a conversion efficiency (η) of 5.02% and 6.25%, respectively, much higher than that of QDSSCs made with Au CE ($\eta = 2.94\%$). Fourth, copper silver chalcogenide ternary nanoparticles were prepared at room temperature in a large-scale, which showed a temperature-dependent transition of metallic-n-p conductivity. These ternary nanoparticles can simultaneously serve as building blocks of thermoelectric legs for conversion of heat into electricity (Han *et al.*; *J. Am. Chem. Soc.*, 2014). Our research provides several ways to prepare copper chalcogenide nanostructures for diverse applications.

Keywords: copper chalcogenide, nanostructures, semiconductors, room-temperature synthesis, counter electrodes.

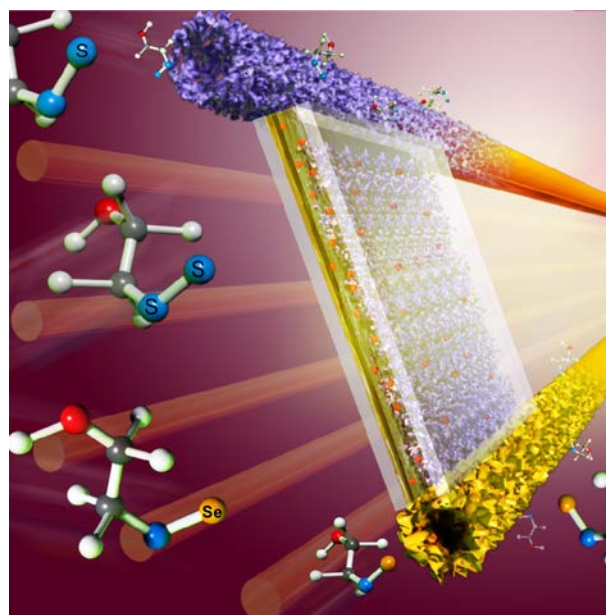


Figure 1: Abstract illustrating the mechanism of reaction from Cu NWs to Cu_{2-x}E (E = S, Se) NTs in the presence of thiol ligands and Cu_{2-x}E (E = S, Se) NTs serving as building blocks for high-performance CEs of QDSSCs.

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Reduced Carrier Recombination in PbS - CuInS₂ Quantum Dot Solar Cells

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Abstract: Colloidal nanocrystal quantum dots (QDs) offer exciting opportunities for solution-processed optoelectronic applications such as photovoltaics due to their size-tunable bandgap and the multiple excitation generation phenomenon, a mechanism by which the Shockley-Queisser limit can be potentially bypassed.^{1,2} So far, metal oxide/QD bi-layer depleted heterojunction is among the most efficient QD solar cell architecture allowing a power conversion efficiency (PCE) as high as 8.92% on PbS QD solar cells.^{3,4} One important issue hindering the progress of many third-generation solar cells is carrier recombination.⁵ In metal oxide/QD heterojunction solar cells, carrier recombination happens not only at the donor-acceptor (TiO₂/QD) interface but also inside the QD layer which has a typical thickness of a few hundred nanometers. Photogenerated charges need to travel across the entire QD active layer to be collected. During this process carrier recombination leads to photocurrent loss and thus, to inefficient solar cells.⁶

Under this context, the possibility to separate electrons and holes in different areas of the active layer, for example by using a mixture of different QDs, can lead to a substantial suppression of the recombination rates. Towards this goal, in this work we propose an "bottom-up" approach based on the partial spatial segregation of charge carriers to boost photocurrent in QD solar cells. Here, Zn-doped CuInS₂ (Zn-CIS) QDs, *p*-type QDs of reduced toxicity compared to PbS, are incorporated into the PbS matrix of TiO₂/PbS QD heterojunction solar cells. In this binary QD blend Zn-CIS QDs provide recombination "shelters" where only holes but not electrons from PbS are allowed to enter. Different volume fractions of Zn-CIS QDs in the PbS QD matrix were examined: a 10% (v/v) addition of Zn-CIS QDs can lead to a ~30% increase in short circuit current density (*J*_{sc}), a ~20% increase in power conversion efficiency (PCE), and prolonged recombination time constants compared to solar cells built from PbS QDs only. In agreement with the charge transfer process identified through ultrafast pump/probe spectroscopy between these two QD components, transient photovoltage characteristics of single-component and binary QDs solar cells reveal longer carrier recombination time constants associated with the incorporation of Zn-CIS QDs. This work presents a straightforward, solution-processed method based on the incorporation of another QDs in the PbS QD matrix to control the carrier dynamics in colloidal QD materials and enhance solar cell performance.

Keywords: nanocrystal solar cells, quantum dot solar cells, charge separation, carrier recombination, PbS nanocrystals

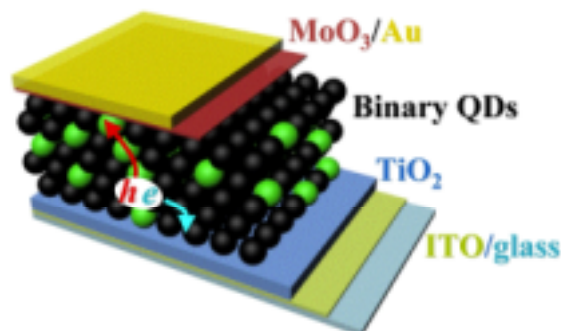


Figure 1: Figure illustrating the fundamental process reducing carrier recombinations in the binary QD solar cells investigated in this study.

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Session V: Other Nano Applications

Nanotechnology in Food Packaging Industry: Opportunities and Challenges

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Abstract: Nanosciences and nanotechnologies are highly promising areas for research and industrial innovation, with a potential both to boost the competitiveness of many industries which will lead to new emerging and fast growing markets. It is predicted that nanotechnology production approaches will change about 25% of the food packaging business in the next decade, which means a yearly over \$ 30 billion market. The major market trends include enhancing the performance of packaging materials, prolonging shelf life, antimicrobial packaging and interactive/sensorial packaging.

One of the main priorities in food packaging technology is to keep the original properties of the food. This goal is achieved by keeping all the nutrients in the original conditions, by ensure minimum interaction between environment and the packaged food and reducing microbial growth

In the field of nanoparticles and nanotechnology-based thin films, new approaches using nanoscale effects can be used to design, create or model nanocomposite systems with significantly optimized or enhanced properties of high interest to the food, health and biomedical industry. With the development of nanotechnology in various areas of materials science the potential use of novel surfaces and more reliable materials by employing nanomaterials and nanostructured thin films in food packaging, security pharmaceutical labels, novel polymeric containers for food contact, medical surface instruments, bio-implants, and even coated nanoparticles for bionanotechnology can be considered.

The use of plastic containers in the food and beverage market has dramatically increased because they are lightweight, unbreakable, convenient, resealable and they may be clear. PET bottles have gradually replaced glass bottles and metal cans as the most common packaging for liquid foods, such as carbonated soft drinks, tea, water, soy sauce and edible oil. In this field of new packaging technologies, nanostructured architectures coatings such as nanocomposite films are given the unique role of enhancing food impact over the consumer's health. For example, the unique properties of diamond like carbon (DLC) film, including its chemical inertness and impermeability, make it possible for new applications in food, beverage and medical market segments. The ability of using thin films and nanoparticles with transparent properties a more flexible and transparent packaging materials will provide the consumers with fresher and customized packs where the products can be observed as they are.

In this presentation it will be presented an overview of the nanotechnology approaches to produce nanostructured materials for food and health industry. Topics to be discussed include introduction to nanocoatings concepts (from functional nanocomposite and graded coatings to smart nanomaterial surfaces used in packaging and biomedical industry) produced by clean PVD technologies (Physical Vapour Deposition) and other deposition techniques. An overview of the current research, existing technological applications and future industrial materials and components will be highlighted. As example for future trends in nanotech-based food packaging will also include research and development on sensorial packaging which can monitor the food and transmit information on its quality. For instance, the ultimate pH of meat greatly affects its quality. Monitoring this parameter can give to consumers information regarding manner of transportation of animals from the farm to the abattoir; diet restrictions; mixing animals of different lots and pathological conditions. With embedded nanosensors in the packaging surface materials, consumers will be able to check the food quality inside or even to track the history of the pack. Electronics built on thin film substrates could be used in future sensory packaging applications (examples include nanoRFIDs).

Nanotechnology: Promises and challenges for future

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Abstract: Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometers. All things, both living and non-living, are constructed of atoms. The nano-scale sparks so much interest because when a substance is artificially created, structured atom by atom, it can have different or enhanced properties compared with the same substance as it occurs naturally, which includes increased chemical reactivity, optical, magnetic, or electrical properties. Nanotechnologies aim to exploit these properties to create devices, systems, and structures with new characteristics and functions. For example, researchers hope to construct from the very 'bottom' (that is to say, atom by atom) a substance as strong as diamond, but more flexible and far less expensive. It would also be possible to manufacture a substance in the shape and size needed such as a thin string as strong as steel.

So far Nanotechnology is applied in various areas (1) applied design a water filtration system on the nano-scale that is so efficient, it only lets water molecules through it. (2) Is used to create filters and sensors to screen out toxins or adjust flavors, and packaging to sense when the food inside is spoiling and alert the customer. (3) The ability to assemble Nano-scale particles that could be targeted at certain parts of the body or certain viruses in the blood. (4) Economical solar cells to make solar power economical and diminish our dependency on coal, oil, nuclear fuel and fuel wood. (5) To clean up the environment. To clean up oil spills, imagine a scrubber built from tiny nanotubes that could manipulate the atoms in an oil spill to render it harmless.

Just like any new technology, there are varieties of health, environmental and safety risks to this technology from free rather fixed manufactured nanoparticles. In initial studies, manufactured

nanoparticles have shown toxic properties. They can enter the human body in various ways, reach vital organs via the blood stream, and possibly damage tissue. Due to their small size, the properties of nanoparticles not only differ from bulk material of the same composition but also show different interaction patterns with the human body. These promises and challenges of Nanotechnology will be presented here.

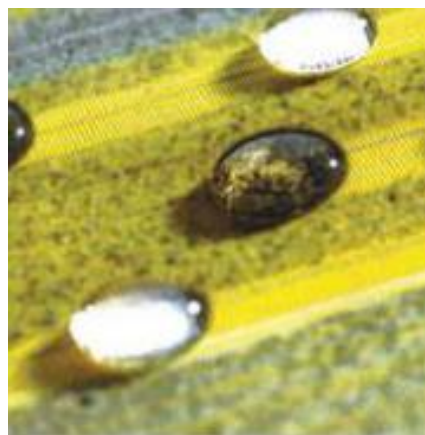


Figure 1: An illustration of water shield self-cleaning paint using Nano-particles

Keywords: Nanoparticles, Safety, risks, chemical reactivity, filtration system, applied design, nano-particle drug delivery.

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Antimicrobial properties of graphene oxide and reduced graphene oxide

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Purification of water from contaminants toxic to humans is attracting an increasing interest due to the rise of environmental pollution and scarcity of the available water resources in large areas of the earth.

Carbon-based materials are suitable for both the filtration of microorganisms and the ability to adsorb heavy metals, provided that their surfaces are adequately functionalized [1]. In particular, graphene oxide (GO) was recently proposed for the removal of pollutants from water [2]. GO is composed of graphene flakes with carboxyl, hydroxyl and epoxy groups at the edges or the surfaces. Moreover, GO shows semiconducting properties and the energy gap can be tuned by a reduction of the oxygen functional groups. Recently, graphene and GO were tested as antimicrobial agent affecting the integrity of *E. coli* bacterial membrane [3]. Our work aims to elucidate the antimicrobial properties of the GO or rGO.

GO in water solution was prepared by the Hummer's method while rGO was obtained by laser irradiation of the initial GO solution. The solutions were characterized by IR and UV-visible spectroscopy as well as by scanning electron microscopy (SEM) (an example is shown in figure 1) and transmission electron microscopy (TEM).

Antimicrobial properties have been investigated using *Escherichia coli* ATCC25922 as a model organism. Survival rates of *E.coli* were evaluated by CFU count after 1h or 2h exposure to GO and rGO. In our experimental system, rGO seemed to be more effective than GO in reducing bacterial survival, with only 20% of the initial *E. coli* population

being able to survive. These results were then confirmed by the WST-1 Assay, an assay able to investigate bacterial metabolism. Moreover, our analysis on the mechanism of action of GO and rGO indicated that their antimicrobial effect was mainly due to mechanical damage exerted towards the bacterial membrane. Furthermore, Fish Embryo Toxicity (FET) test showed that neither mortality nor sublethal effects were caused by the different solutions tested.

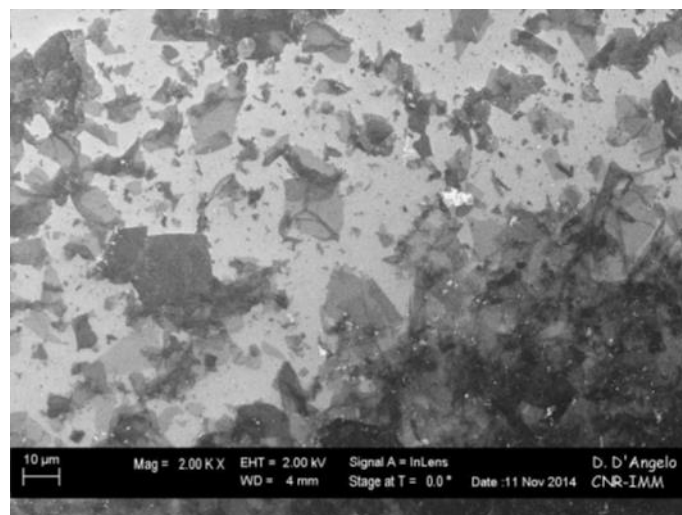


Fig.1. SEM image of GO reduced by 4h laser treatment.

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Phosphonium Quat-Modified Nanoclays for In-Situ Polyester Nanocomposite Development: Optimisation of Modification for Particle Performance.

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Abstract: Bentonite clays are often used as a functional nano-additive to polymers for enhanced mechanical and physicochemical properties for a range of applications. To realise the nano effect of well dispersed discrete particles it is necessary to organically modify the particles to overcome the thermodynamic incompatibility of the inorganic clay with the polymer matrix. This paper describes the synthesis and characterisation of an organically-modified nanoclay for the development of a polymer composite that provides enhanced gas barrier properties to packaging film when print applied to the plastic film substrate. In-situ polymerisation of the polyester-nanoclay composite was selected for optimum clay nanoparticle dispersion due to the exfoliating effect of the growing polymer chains. In addition, this presents the opportunity to involve a reactive clay modifier that can participate in the chain propagation process, providing the clay particle with very strong linkage to the polymer matrix, potentially resulting in good stability and enhanced mechanical and barrier properties.

Quaternary ammonium surfactants are commonly used for surface modification, providing both compatibility with the matrix and separation of the particles by intercalation. Phosphonium salts offer a more thermally stable alternative to ammonium modifiers; a property that is particularly attractive considering the relatively high temperatures to which the particles are exposed to during polyester synthesis. Organoclays were synthesised by cation exchange modification of sodium montmorillonite (Na^+MMA) with (1-Tetradecyl)triphenylphosphonium bromide (TDTPPBr), (3-Carboxypropyl)triphenyl phosphonium bromide (CPTPPBr), and (1-Hexyl)triphenyl phosphonium bromide (HTPPBr). Particle intercalation was evaluated using standard techniques, including XRD and TEM for inter-gallery spacing of the modified nanoclays, and TGA for thermal stability. Also, a technique was developed to measure dispersibility of the modified particles in an appropriate solvent, using the Mie scattering model to relate light scattering and absorption energy to particle size, enabling the prediction of potential exfoliation in the polymer composite and/or coating formulation. The shorter alkyl chain modifiers (CPTPPBr and HTPPBr) displayed limited affinity for the clay surface in the cation exchange process, resulting in low

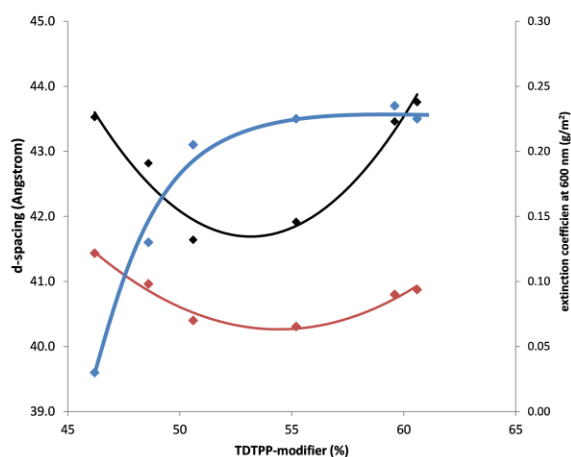


Figure 1: Correlation of organoclay d-spacing (blue diamonds) and particle dispersion spectral performance versus modified clay organic content. Clay particle extinction coefficients calculated from mass of inorganic component (black diamonds) and mass of total organoclay (red diamonds).

modifier to inorganic ratio and poor platelet separation and dispersion quality. By contrast, TDTPPBr showed high surface adsorption behaviour, resulting in good intercalation and dispersion quality. A relationship between organic modifier content and clay tactoid d-spacing was observed, with maximum d-spacing achieved well before maximum surfactant adsorption was reached. Particle dispersion evaluation revealed that there was also a relationship between modifier addition and dispersion quality, suggesting there is an optimum modifier to clay mass ratio that coincides with the onset of the d-spacing plateau, beyond which dispersion quality deteriorated. TDTPPBr-modified organoclay properties compared well with commercial grade ammonium-modified organoclays, with greater d-spacing observed and comparable dispersion quality. Phosphonium-modified clays exhibited enhanced stability up to typical polyester esterification reaction temperature ($\sim 250^\circ\text{C}$) compared to the commercial grades.

Keywords: organically-modified nanoclay, phosphonium salts, gas barrier, in-situ polymerization, thermal stability, tactoid d-spacing, platelet separation, extinction coefficient, Mie scattering, nanoparticle dispersion.

Efficient Design of Flexible and Low-cost Dual Band RFID inkjet printed antenna using silver nanoparticles ink

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Abstract: This work aims to fabricate light and flexible antennas, printing techniques are used such as screen and inkjet procedures. In this paper, a dual band RFID is fabricated using new, efficient and low cost printing technique based on commercial inkjet printer. A simple CPW Z-shaped antenna is fabricated on a low cost paper substrate with conductive silver nanoparticles (~100 nm size) ink which has been selected to implement the antenna shape and to improve the characteristics of the antenna depending on their higher surface to volume ratio, with thickness of the printed layer around 230 microns. The fabricated antenna has dual bands frequency for this shape; one at 780 MHz and the other at 1.4 GHz. The resistance of the antenna has been improved through annealing up to less than 1 ohm/cm².

Keywords: printed antenna, inkjet-printing, silver nanoparticles ink.

I- Introduction

Radio Frequency Identification (RFID) is an important wireless technology that has wide variety of applications, such as mobile radio communication devices [1-3]. However the currently used fabrication techniques and materials are relatively costive and badly affect on the environment. In this paper, we use feasible and commercial method for printing on extremely low cost substrates for fabricating electronic circuits and RF structures using a normal inkjet printer with avoiding custom and expensive equipment. The used ink is silver Nano-particles inks ensure higher performance of inkjet-printing process. So, we would discuss the printing technique and the analysis of a simple printed antenna via silver nanoparticles ink.

II- Experimental Work

A simple Z-shaped printed antennas is selected to be the printed antenna design due to its conformability and its higher gain [4]. The geometry of the antenna is shown in Fig.1. The ink is filled via silver nanoparticles ink into a special cartridge to be fitted with the printer. The morphology of the surface is imaged using JEOL SEM. The printed antenna has been analyzed using a network analyzer. The antenna is connected with a SMA connector using conductive tape with resistance equals to 2 Ω / cm.

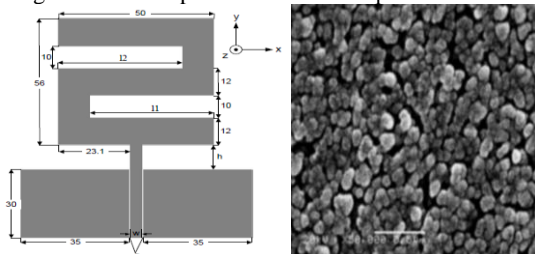


Figure 1: Figure illustrating Z-shaped CPW-fed printed antenna configuration (dimensions in mm) and SEM image of the morphology of the antenna's surface

I- Results & Discussions

Both printed antennas on a board and on a glossy paper are shown in Fig. 2. Fig.1 shows the SEM image of the morphology of the antenna's surface which is printed on a glossy paper at room temperature. The SEM image shows

smooth and uniform morphology. The mean diameter of the nanoparticles is found to be around 100 nm, and the mean thickness of the printed layer around 230 microns. Fig. 4 shows the network analyzer characterization of the printed antenna with a notch band close to 900 MHz.

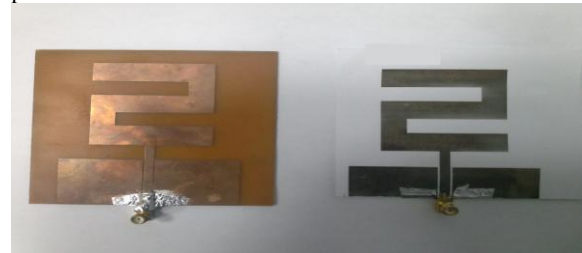


Figure 2: Figure illustrating Z-shaped antenna on glossy paper and PCB.

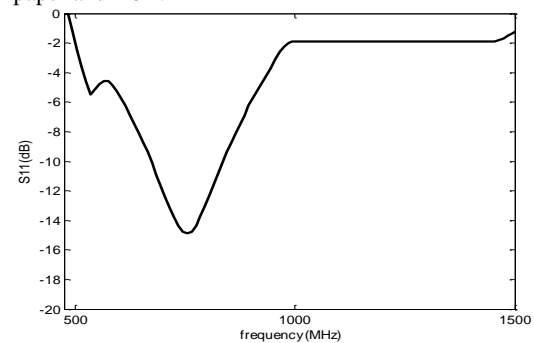


Figure 3: Network analyzer analysis of the printed antenna.

II- Conclusion

This paper present an efficient design for RFID inkjet printed antenna on a flexible, low-cost and environmental friendly material a using silver nanoparticles ink producing a dual band frequencies that can be used in different RFID applications. Our future work is try to testing the effect of expose samples to temperature, printing multilayer and both at different temperature value and how could this affect the return loss, radiation pattern, antenna gain ... etc.

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0D based resistive switching mechanism

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Abstract: The ever increasing demand for massive information storage and high speed management of the information has boosted the search for new non-volatile memory devices in the last decade. Local transport properties (I-V characteristics) exploring NP/perovskite oxide interfaces is of crucial importance for both, the study of the resistive switching mechanism and the development of new resistive memories. In particular, the observation of resistive switching in 2D and 1D systems is promising for using low dimensional nanostructures in non-volatile data storage devices. Thus, for instance, hysteretic I-V curves in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) thin films (Moreno *et al.*, 2010, Peña *et al.*, 2014) or Zn oxide nanowires (Cheng *et al.*, 2013) can be used to identify the bipolar or unipolar nature of the observed switching process.

We present a further generation of nanoscale memristors based on unipolar resistive switching behaviour, observed in self-assembly of magnetic nanoparticles (NPs). Local transport properties on iron-oxide/manganite nanostructures (Fe-NP/LSMO) are studied using conductive scanning force microscopy (CSFM). Iron-oxide nanoparticles were assembled on top of fully spin-polarized manganite thin films by RF sputtering (Konstantinovic *et al.*, 2013). Assembly of nanoparticles exhibits at room temperature a voltage-current hysteresis with four different states: initial, electroformed, IN and OFF (Figure 1). Such behaviour could be interpreted in terms of two simultaneous bipolar responses, associated to two existing interfaces (tip/NP and NP/manganite) and their corresponding Schottky's barrier.

Keywords: MEM resistors, resistive switching mechanism, CSFM, iron-oxide nanoparticles, functional oxides

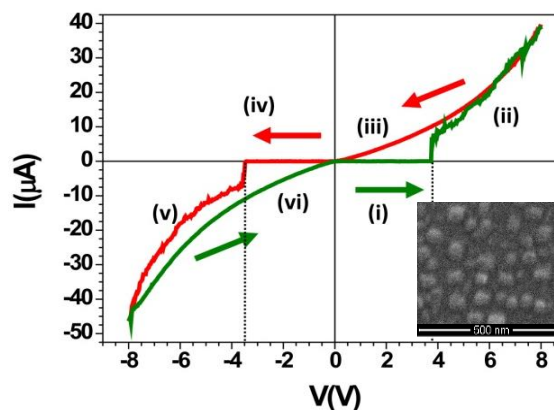


Figure 1: Figure illustrating typical I-V characteristics of Pt/Fe-NP/LSMO system presented in linear scales. The voltage sweep direction and current response is indicated by arrows and roman numbering.

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Photocatalytic Silver/Silver Chloride Polymer Nanocomposites

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Abstract: The photochemical activity of silver chlorides is well known in black and white photography, in which a portion of the Ag^+ in the silver chloride crystals is photo-reduced to Ag^0 to provide the image. It has been shown that if the silver chloride crystals are of a nanosize then upon exposure to UV light, smaller nanosize domains of Ag^0 are produced on the surface of the silver chloride through the partial photoreduction of Ag^+ to Ag^0 (Wang *et al.*, 2008, Choi *et al.*, 2010). These Ag^0 nanodomains exhibit surface plasmon resonance effects. The resulting hybrid silver/silver chloride nanoparticles exhibit interesting photocatalytic properties and are considered to be members of a group of photocatalysts known as plasmonic photocatalysts (Choi *et al.*, 2010, An *et al.*, 2010). Here the photocatalytic mechanism and photostability of the nanoparticles is enhanced by the surface plasmon resonance of noble metal nanodomains on the surface of the silver chloride nanoparticles (Choi *et al.*, 2010, An *et al.*, 2010, Zhang *et al.*, 2013).

In our recent work, novel silver/silver chloride composite materials were produced using the support materials of polyurethane paint dispersions and nylon 6,6 (Tate and Johnston, 2014). This was achieved through the development of a simple aqueous synthesis method, utilising the substrate to control the size and shape of the silver chloride nanoparticles and their stabilisation within the support material. These were then exposed to UV light to generate the silver nanodomains and hence form plasmonic silver/silver chloride photocatalysts. This successfully incorporated the plasmonic photocatalyst nanoparticles within the support material.

UV-Visible spectroscopy, XRD, SEM and EDS were used to characterise the silver/silver chloride nanoparticles and their distribution within the composites. The photocatalytic activity of silver/silver chloride composites was evaluated by the photodegradation of methylene blue, and were shown to be effective photocatalysts. Due to the inherent antimicrobial properties of the silver/silver chloride nanoparticles, the composite materials were also seen to display significant antimicrobial action against *E. Coli*. These novel composite materials have promising applications in water treatment, where the photocatalytic mechanism is effective in the reduction of organic

contaminants, whilst the Ag^+ simultaneously imparts antimicrobial action. This has led to the design and incorporation of these novel nanocomposites into a lab-scale reactor system for water treatment.

Keywords: Silver/Silver Chloride, Photocatalyst, Nanocomposite

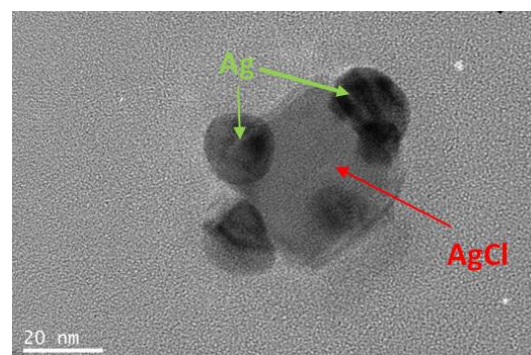


Figure 1: TEM image of Ag/AgCl plasmonic photocatalyst nanoparticle.

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Ammonia gas sensing properties of ZnO nanowires synthesized by thermal oxidation of Zn film

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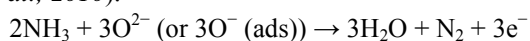
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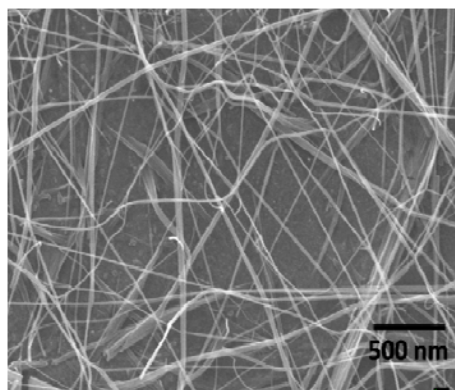
Abstract: ZnO is a semiconducting metal oxide material having potential applications in sensors, optical and solar cell devices (Wang.; 2004). Gas sensing properties of various ZnO nanostructures such as nanowires, nanorods, nanobelts and nanotubes have been widely investigated for a variety of gases (Mirabbaszadeh *et al.* ; 2012). However, sensitivity, reduction in operating temperature, low cost and integration in MEMS processing are some of the issues which are still being addressed.

In this work, long, dense and uniformly distributed ZnO nanowires have been synthesized and studied as the sensing element for detection of ammonia gas. 130 nm thick Zn film was deposited on oxidized Si substrate by RF magnetron sputtering in Ar ambient at the rate of 4.5 nm/min. After that, film was thermally oxidized at 600 °C in moist environment for 1 hour. The structural phase of post-oxidized sample indicated that Zn film was completely oxidized to form ZnO. The SEM image showed that dense nanowires were formed. A sensor was fabricated incorporating ZnO nanowires and deposited Cr-Au IDE structure of 30 μm width/gap. The resistance between IDE pads was measured in air ambient and in presence of test gas (ammonia). Exposure to ammonia gas results in release of electrons and thus the resistance decreases as per following reaction (Chang *et al.*; 2010).

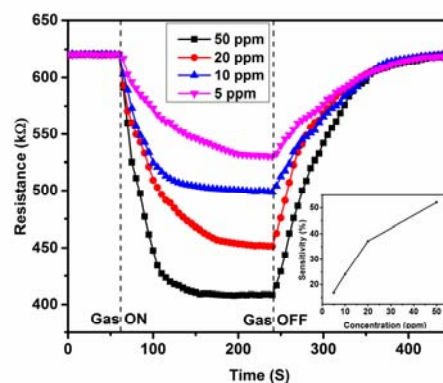


The sensor showed excellent sensitivity of about 17% for 5 ppm of ammonia gas at 200 °C operating temperature.

Keywords: Thermal oxidation, ZnO nanowires, Gas sensing, Ammonia.



(a)



(b)

Figure: (a) SEM image of ZnO nanowires synthesized from 130 nm thick Zn film oxidized at 600 °C in moist environment (b) Change in resistance of ZnO nanowire upon exposure to 5-50 ppm of ammonia gas

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Long-term corrosion protection by a nano-composite thin PEA-TiO₂-HMDSO coating

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Abstract: Lately there has been a tremendous interest in corrosion protection by different organic coating systems due to new regulations coming into place (Montemor, 2014). Here we present a thin nano-composite coating system showing very good corrosion protective properties for carbon steel during an extended period of 100 days. As basecoat a 10 μm thick, UV-cured, polyester acrylate (PEA) coating (Sababi, 2013) was used. Then a middle layer of TiO₂ nanoparticles, ca. 1 μm thick, was deposited on the PEA basecoat by liquid flame spray (LFS) to enhance the surface roughness, following the procedure described by Teisala et al (2010). To lower the surface energy of the coating, a thin top coat layer of hexamethyldisiloxane (HMDSO), ca. 0.05 μm thick, was applied on the surface by plasma treatment. The nano-composite coatings were applied onto carbon steel substrates and then immersed in 3 wt% NaCl solution to evaluate the corrosion protection. The corrosion protective properties of the individual layers were also evaluated for comparison. Open circuit potential (OCP) and electrochemical impedance (EIS) measurements were performed regularly during the long exposure. The PEA basecoat alone show an impedance level of $10^5 \Omega\text{cm}^2$ for more than 80 days. The addition of the TiO₂ particle layer on top of the PEA did not significantly change the corrosion protective properties of the coating. However, the whole coating system consisting of all three layers (PEA-TiO₂-HMDSO), ca. 11 μm thick, exhibits a superhydrophobic surface and a remarkable improvement of the corrosion protective properties. The impedance of the nanocomposite coating remains over $10^8 \Omega\text{cm}^2$ for the long time of 100 days (figure 1). Interestingly, the photos of this surface (immersed in 3 wt% NaCl) show that corrosion started after 20 days, probably at a pin hole in the coating, but did not proceed during the prolonged exposure (inset in figure 1). The combined properties of each layer in this coating system result in an excellent corrosion protection of the underlying carbon steel substrate.

Keywords: corrosion protection, nanocomposite, organic coating, electrochemical impedance, contact angle, liquid flame spray.

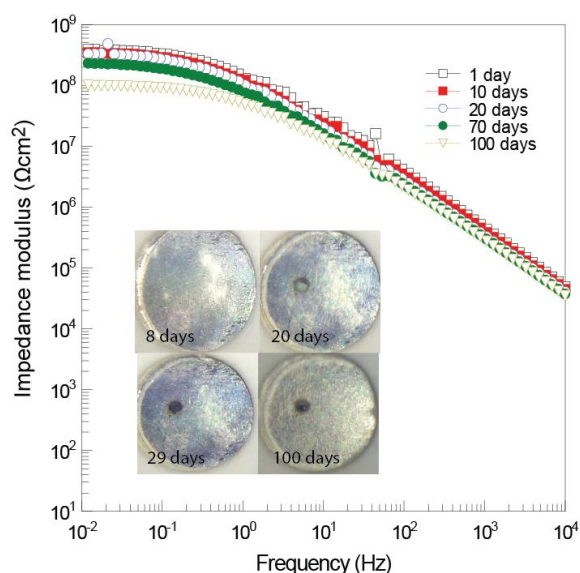


Figure 1: Bode plots of the electrochemical impedance spectra for the nano-composite coating immersed in 3 wt% NaCl solution, showing the good corrosion protective properties of the coating lasting for the very long period of 100 days. Also included are photos of the surface taken at different times of immersion, showing that corrosion started at a local defect, proceeded very slowly over time and did not cause the whole coating to fail.

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Branched Polymer Nanoreactors for Catalysis by Design

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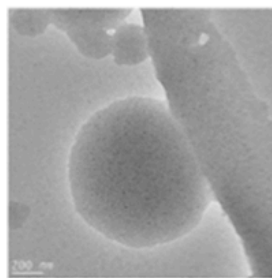
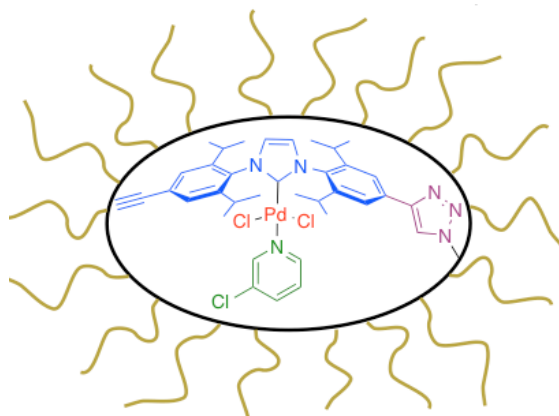
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Abstract: Nature's enzymes are extremely efficient catalysts. Their remarkable properties result from precise preorganization of the local environment and functional groups around the catalytic sites and close participation of metal ions, prosthetic groups and cofactors (Fersht, 1999).

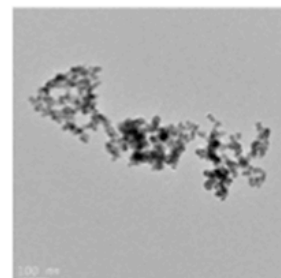
Chemist-designed, enzyme-inspired nanoscale catalysts have been the focus of intensive investigation, and a number of highly successful designs have been reported (Gao, 2012; Dwars *et al.*, 2005). Among the nanoscale catalyst supports, branched constructs such as dendrimers and star polymers are unique in that they can be designed to approximate some of the key features of natural biopolymers (Hecht and Fréchet, 2001). To date, the complexity of synthetic approaches to these well-defined branched macromolecules, especially those bearing reactive or catalytic moieties, has limited their use in catalysis. Striking examples of organocatalysis with globular macromolecules are more prevalent than examples of metal-complex catalysis, in part due to the difficulties involved in tethering of elusive transition metal ions to carbon-and-heteroatom based supports.

Here we shall present several examples of enzyme-inspired organotransition metal catalysts supported on branched macromolecules with nanoscale dimensions. The catalytic activities and properties of such systems are unattainable with small-molecule versions of the same catalytic moieties. The presentation will have a specific focus on Grubbs-type alkene metathesis catalysts for ring-opening polymerizations of monomers with low degrees of strain, and palladium-NHC cross-coupling catalysts not susceptible to aggregation.

Keywords: star polymers, catalysis, nanoreactors, alkene metathesis, cross-coupling reactions, N-heterocyclic carbenes, click chemistry, crowding effects, site isolation.



Star polymer catalyst after a Stille reaction



Small-molecule PEPPSI catalyst after a Stille reaction

Figure 1: A star polymer nanoreactor for Pd-catalyzed cross-couplings. Unlike the corresponding small-molecule catalyst (PEPPSI), the polymer nanocatalyst demonstrates remarkable stability to aggregation.

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Novel Nanogold Coloured Wool Textiles, Aulana® for Luxury Markets

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Abstract: Nanogold particles in different colours have been formed and bound to the keratin protein in wool fibres to produce an innovative, boutique colour range of nanogold-wool textiles, branded Aulana®, for high value international luxury markets.

Aulana® captures the exciting and unique opportunity whereby the prestige and high value of gold are linked directly to the high quality of New Zealand wool through the use of nanogold as novel stable colourfast colourants in the wool, for the international high quality fashion apparel, luxury textiles, carpet and rug markets (Johnston and Lucas 2013; www.aulana.co.nz) (Figure 1). This utilises the localised surface plasmon resonance properties of nanogold wherein the colour exhibited by the gold is dependent upon the size and shape of the nanogold particles and the dielectric constant of the surrounding material (Johnston and Lucas 2011, 2013; Liz-Marzán 2004, Kelly et.al. 2003). XPS measurements show the gold in the nanoparticles is chemically bound to the sulfur and nitrogen containing amino acids in the wool fibre proteins (Johnston and Lucas 2011). SEM images and associated X-ray elemental mapping show they reside predominately on the cuticle surfaces and edges. Spherical particles of gold about 10-20 nm are pink-purple in colour. Figure 2 (left) shows the relation between the gold nanoparticle size and the colour of the nanogold wool product. Precise control of the particle size enables the colour to be changed progressively through shades of pink, red, purple, blue-grey to grey (Figure 2 right). Nanogold colourants cannot fade or denature in sunlight and hence the nanogold coloured wool products exhibit excellent lightfastness.

The proprietary Aulana® technology and product suite have been developed from a laboratory scale using 0.1 g wool and progressed to pilot and commercial scale production now using kilogram quantities of wool in loose, combed top or yarn form (Figure 2 right) and fabric, as required. Precise control over the gold nanoparticle formation and chemical binding to the wool fibres to produce a uniform, durable nanogold-wool product is essential. Noble Bond Ltd, the owner of the Aulana® brand, is commercialising Aulana® products for use in luxury wool apparel, upholstery textiles, rugs and carpets. Aspects of the science, technology and the product

development of these innovative nanogold wool products will be presented.

Keywords: nanogold, wool, textiles, Aulana, rug

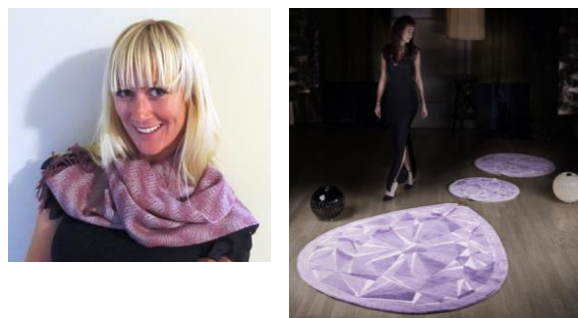


Figure 1: Nanogold Aulana® scarf (left) and Aulana® “Midas” rug (right).

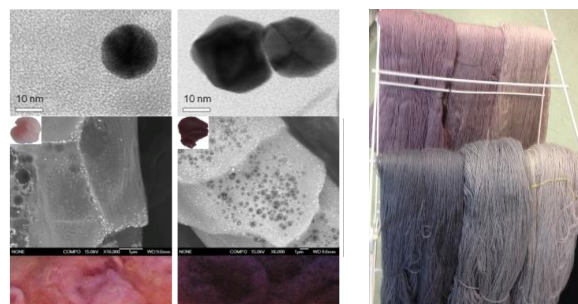


Figure 2: (left) TEM and SEM images of gold nanoparticles on the cuticle surfaces and edges for pink and purple nanogold coloured wool; (right) nanogold wool yarn in pink and grey colours.

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Nanotechnology for more Efficient Sustainable Buildings

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Introduction: Construction is a massive global industry, with a very high environmental footprint. Many key players in the construction industry are pushing towards a more sustainable future, adopting new materials and new techniques. Green building professionals want to apply sustainable development in the design, construction and operation of buildings. They struggle to minimize the use of non-renewable resources like petroleum, natural gas and coal, and reduce waste and pollutants. Energy conservation is highly important to green building as it both saves resources and minimize waste and pollutants.

“It is not as though nanotechnology will be an option; it is going to be essential for coming up with sustainable technologies.” advises Paul Anastas, director of the American Chemical Society-Green Chemistry Institute.

Globally, nanotechnologies are expected to reduce carbon foot print in three key areas: transportation, insulation in residential and commercial buildings, and generation of renewable photovoltaic energy. It is needless to mention that the last two of these three areas are centered in the building industry, pointing that building will in fact lead the green nano revolution.

Case Study: Focusing on energy efficiency, proceeded a study contains three examples (detached single family house) represents conventional architecture, sustainable architecture and nano-enhanced sustainable architecture, the study illustrated how the convergence between sustainable architecture and nanotechnology using today's *on-shelf* certain nanomaterials products would make better, healthier, and energy efficient architecture.

The study reviews the convergence between sustainable architecture and nanotechnology via diagnostic approach in the theoretical level of analysis, using comparison of three examples of architecture, following the scientific methods, by a number of tools collected from multiple scientifically trusted resources, to guarantee the best theoretical results.

The results of this case study are rough results, but it is the nearest thing to the right. More in-depth real life research would reveal more precise results.

Tools to form and analyze the results and show indications that helps in understanding the case study:

- Common factors of sustainability measuring systems LEED and BREEAM.
- Solar Irradiance Calculator.
- Energy Load Estimation Calculator.
- Carbon calculator.
- EPC (Energy Performance Certificate).
- Home energy check.

	LEED	BREEAM	Common
Site	•	•	•
Management		•	
Health	•	•	•
Energy	•	•	•
Water	•	•	•
Materials	•	•	•
Transportation	•	•	•
Waste	•	•	•
pollution		•	
Innovation	•		
Awareness	•		

Table1: Illustrates comparison of key areas of rating of two of most important rating tools of sustainability: LEED and BREEAM, where the dot illustrates fulfilment of the key area. It shows clearly the common factors between the two methods, (Site – Health – Energy – Water – Materials – Transportation – Waste) seven key areas are the most important factors which must be fulfilled by a building in order to be GREEN certified.

This study is fulfilled by 2 steps:

1)Applying 7 key areas common in sustainable building measuring tools:
 (Site - Materials - Water - Energy - Waste - Transportation - Health)

✓ Waste – Transportation – Health:

Those keys will not be concluded in the comparison and will be considered fulfilled as it is mostly affected by inhabitants' behavior (Waste – Transportation) or irrelevant to the research (Health).

•Transportation: Using less private transportation in favor of public transportation, bicycling or walking.

•Waste: Following waste reduction guide lines (reduce – reuse – recycle).

•Health: Using Nanomaterials regarding indoor environmental quality (air/water purification).

✓ Site - Materials - Water - Energy

Core of comparison, will be fulfilled based on three levels:

- Heat gain/loss (Site – Materials).
- Energy consumption (Water - Energy).
- Using renewable energy sources to produce energy needed.

2)Analyzing consumption efficiency:

1. Environmental efficiency.

Measuring carbon foot print of energy used in every case.

2. Energy efficiency.

Rating how effectively energy that is needed around the property is used.

3. Economic efficiency.

Economic efficiency is measured by money, the balance between revenues and costs, this will be via 3 steps:

- Cost of energy for every case according to Egyptian electricity selling prices.
- How much economic beneficial is using sustainable technology and nanomaterial.
- How much economic using solar energy instead of governmental electricity grid.

Conclusion:

Home Energy Check		
Conventional House	Sustainable House	Nano Sustainable House
<p>Your estimated EPC rating</p> <p>A = Very energy efficient - lower running costs G = Very inefficient - very high running costs</p>	<p>Your estimated EPC rating</p> <p>A = Very energy efficient - lower running costs G = Very inefficient - very high running costs</p>	<p>Your estimated EPC rating</p> <p>A = Very energy efficient - lower running costs G = Very inefficient - very high running costs</p>

Table 2:Conventional house is way inefficient compared to sustainable and nano-sustainable houses, comes last with F rating is prove for very high running cost in terms of energy, that assures the great beneficiary of sustainable technology used.

Enhancing sustainable technology with nanomaterials, resulted in better efficiency, and thus better rating (A instead of B)

After using sustainable technologies and nanomaterials in residential sector (detached single family house):

- 1-Reduction in energy cost 90%, which covers cost of installed technology.
- 2-Very environmental beneficial, reducing carbon emissions by 95%, saving more than 900 trees.
- 3-Using nanomaterials proved to raise EPC from B to A.
- 4-Clean and healthy indoor environmental quality due to nanomaterials used.
- 5-Energy efficiency house equals higher property value.
- 6-It is sure that enhanced house costs more to build, choosing to go green means higher cost and higher value as well.

While choosing a conventional house that costs less to build, you will have a higher energy bill each month.

7-Well insulated building needs only a smaller, thus cheaper heating and cooling system, the heating and cooling system may only be needed as an occasional supplement. Savings on the initial and running cost of a heating and cooling system surely will offset much of additional cost for converting house into sustainability.

8-If the green house is supported by solar PV system, this would significantly reduce electricity bill, and in some countries applying FiT , the house turns to be source of income.

9-Using Nano-based materials in green house was a significant effect in two areas of three, first in reducing energy loads used by the house, and second in generating energy needed by the house.

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Dynamic and Static Fluid Loss Characteristics and Rheological Properties of Nano-Based Drilling Fluids

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Abstract: Nanotechnology has already contributed significantly to technological advances in energy industry and has the potential to revolutionize drilling industry. Nanomaterials are considered to be the one of the best candidates for smart fluids formation which can improve the performance of conventional drilling fluids. The demand for more efficient drilling technologies necessitates development of innovative drilling fluids. Drilling deeper, longer and more challenging wells in harsh HPHT (High-Pressure and High-Temperature) environments has been made possible by improvements in drilling technologies, including more efficient and effective drilling fluids. The key challenge in developing such drilling fluids is to maintain the stability of key fluid properties such as rheology and fluid loss particularly at higher temperatures and pressures. Formulation of novel water-based fluids under the optimal concentrations, increase the efficiency of drilling operations for the maximum recovery of new and matured HPHT reservoirs. The aim is for oil industry to apply improved drilling fluid recipes, so as to achieve more efficient drilling process with a simultaneous reduction in the environmental footprint. Nanoparticles can play significant role in the development of such smart drilling fluids because due to their small size it is anticipated that they will provide unique filtration properties.

This work focuses on the lab techniques for assessing and analyzing advanced water-based drilling fluids containing iron oxide and silica nanoparticles. These nanofluids are used to reduce fluid loss in water-based drilling fluid containing bentonite. Their performance is assessed utilizing both API HPHT/LPLT (American Petroleum Institute, Low-Pressure and Low-Temperature) filter press as well as a dynamic HPHT filter press with agitation. Comparison between static and dynamic conditions depicts the behavior of the fluids in different environments under elevated pressures and temperatures. Scanning Electron Microscope (SEM) pictures were used to analyze the nanoparticle size range. Analysis by SEM of the filter cake produced reveals their good performance by giving deep insights for their microstructure, the interfacial phenomena and the interaction between bentonite particles and the nanoparticles. Zeta potential measurements using Phase Analysis Light Scattering (PALS) method were used to assess

the stability of the developed suspensions. The changes in the rheological properties of the nanofluids were measured at HTHP conditions using a standard Fann type viscometer, vane cup rheometer and concentric cylinder rheometer and showed good rheological behavior.

The examined nanoparticles have the potential not only to significantly reduce the fluid losses but also to maintain the rheological properties of the fluid. Their relatively low concentration in the drilling system provides a base for more efficient, environmental friendly and safer drilling practices. Their unique characteristics are expected to play a vital role in solving many technical challenges encountered during oil and gas drilling operations.

Keywords: nanoparticles, nano-fluids, drilling fluid, rheology, fluid loss, HPHT drilling

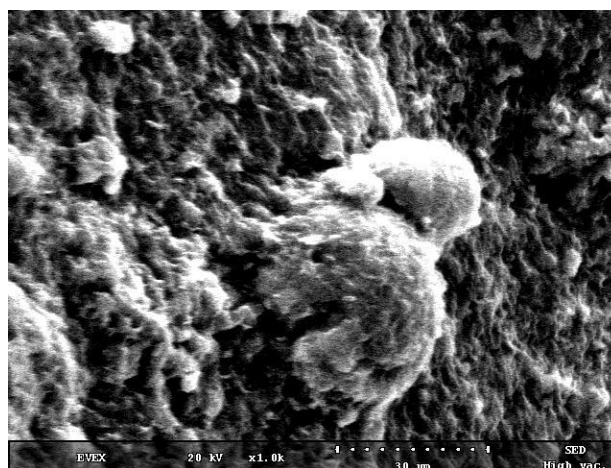


Figure 1: SEM image (30 μm magnification) for the surface of filter cake formed with the addition of 0.5 wt.% iron oxide nanoparticles.

Surface-Bound Ligands Modulate Chemoselectivity and Activity of a Bimetallic Nanoparticle Catalyst

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Abstract: Transition metal nanoparticles (NPs) and nanoclusters are a privileged class of metal colloids (Rocoux *et al.*, 2002). Their high surface areas, and the strong correspondence between particle sizes/shapes and surface chemistries make these species uniquely suited for applications in catalysis (Bell, 2003; Astruc *et al.*, 2005). Small, catalytically active NPs are also some of the more unstable colloids due to their tendency to aggregate. To address this problem, NP catalysts are typically arrayed on solid supports, which may also act as synergistic co-catalysts. NPs and metal clusters can also be stabilized and solubilized with the aid of surface adsorbates, which range from simple surfactants and amphiphilic copolymers to strongly binding/soft ligands, such as thiols. Naturally, the adsorbate-stabilized NPs lose some or all of their catalytic competency (Narayanan *et al.*, 2005; Niu and Li, 2013). The metal surface accessibility is limited compared to “naked” NPs, and the catalytic sites are easily poisoned by thiols and amines.

We describe an approach to dispersible, catalytically-active, adsorbate-stabilized NPs. Our design is based on bimetallic NPs comprised of metals that feature significantly different affinities towards a specific class of adsorbates. Thus, with judicious choice of metal composition and surface ligand chemistry, the particle aggregation could be prevented, while the catalytic activity of the unprotected “islands” of the non-adsorbing metal could be preserved (Figure 1). This approach was applied to a bimetallic (PtFe) NP catalyst stabilized by carboxylate surface ligands that bind preferentially to one of the metals (Fe). NPs stabilized by fluororous ligands were found to be remarkably competent in catalyzing the hydrogenation of cinnamaldehyde, while NPs stabilized by hydrocarbon ligands were significantly less active. The chain length of the fluororous ligands and the composition of the surface monolayer played a key role in determining the chemoselectivity of the FePt NP catalysts.

Keywords: nanoparticles, catalysis, selective hydrogenation, cinnamaldehyde, ligand effects, fluororous chemistry, nanocatalysis.

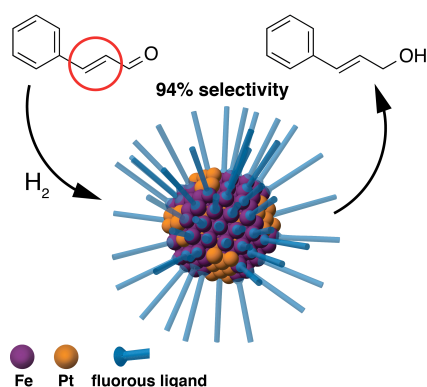


Figure 1: Catalysis with selectively-protected bimetallic FePt NPs. With judiciously chosen fluororous ligand, remarkable activity and selectivity of catalysis were achieved.

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Effects of Nanotechnology Materials on Architectural Design – Applications, Possibilities and Future Trends

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Abstract: Materials have been affecting architectural design since the beginning of human civilization and architectural expression. In the 20th century *Le Corbusier* quoted that a “house is a machine for living in”. Now, the 21st century leads towards a new correlation: “a house can be a living machine, a living organism”. The use of advanced technology has provided a wide range of possibilities in the implementation of architectural design. Nanotechnology in construction materials enables high performance in terms of energy, light, security and intelligence (Leydecker, 2008), and furthermore provides new, innovative and revolutionary materials that can alter the design and performance of buildings. This has led to the launch of the Nanoarchitecture, where nanotechnology integration concerns not only the use of nanomaterials and manipulation techniques but also the reconsideration of forms and design methods – ultra high performance buildings (dynamic, interactive) (Johansen, 2002). In this sense, external surfaces can react and adapt to the environment, featuring the qualities of self-assembly, self-healing and self-repair. Nanomaterials are proven to be effective at aiding structures that suffer climatic strain both in performance and economy over time (Parthenopoulou, Angelides, 2010) and in enhancing existing structures. Throughout a research in existing and potential applications of nanotechnology and smart materials in architecture, this study demonstrates the level of influence of nanomaterials on architectural design and attempts at setting the basis for proposing an innovative system of outer “skin”.

Keywords: nanomaterials, nanoarchitecture, construction applications



Figure 1. Architectural nanotechnology projects: NanoVentSkin (left) is a surface system that consists of nanoturbines that filter the air and produce energy and Carbon Tower (right) is made entirely out of carbon nanofibers.

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Synthesis, Characterization and Catalytic Performance of Supported Nickel Nanoparticles in Methane Steam Reforming

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Abstract: Steam reforming of methane from natural gas provides the main source of hydrogen for most of petrochemical and petroleum refining applications. The efficiency of the reforming process depends upon an effective catalyst and thus this work aimed to produce a highly active nickel based nano-catalysts for methane reforming which is resistant to deactivation. Two nickel based catalysts namely nickel supported on 10wt% silica/alumina (Ni/SA) and nickel nanoparticles dispersed over 10wt% silica/alumina (Ni.NPs/SA) were synthesized and their catalytic activities for the steam reforming of methane were investigated. Ni/SA was prepared using deposition precipitation method while for the synthesis of Ni.NPs/SA nanoparticles were synthesized as a first step and dispersed over the surface of the substrate. Catalysts were characterized using various analytic techniques such as transmission electron microscopy (TEM), nano-scanning electron microscopy (NSEM), X-ray photoelectron spectroscopy (XPS), nitrogen physisorption, temperature programmed reduction (TPR) and temperature programmed oxidation (TPO). Methane steam reforming was carried out in quartz fixed bed reactor (in temperature range between 600-900⁰C and at atmospheric pressure) connected online to a mass spectrum.

Among the catalyst tested, Ni nanoparticles supported on 10wt% SiO₂.Al₂O₃ exhibited better catalytic performances in methane steam reforming than that of Ni/SA. In all temperature studied Ni.NPs/SA catalyst exhibited high methane conversions (100% methane consumption was achieved at operating temperature of 750⁰C), high selectivities to H₂ and excellent thermal stability. Even under the sever conditions of S/C = 1, at an operating reaction temperature of 750⁰C (for a period of 60 hours), it showed stability, higher methane conversions, better selectivities to H₂ and excellent resistance to coke deposition as compared to that of Ni/SA catalyst.

Keywords: steam reforming, Ni nanoparticles, coke deposition.

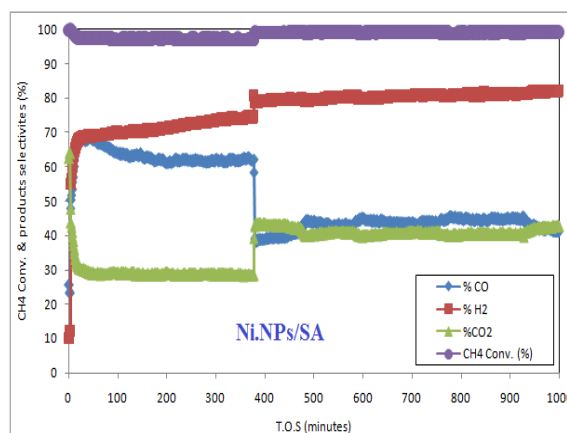


Figure 1: Figure illustrating the performance and products distribution in time on stream over Nickel Nanoparticles in methane steam reforming at 800⁰C.

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