

Global Recycling Summit  
&  
6<sup>th</sup> International Conference on  
Material Science and Nanotechnology  
July 22-23, 2019 | Rome, Italy

Posters



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**MATERIAL SCIENCE AND NANOTECHNOLOGY**

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**Magnetron co-sputtered TiO<sub>2</sub>/SiO<sub>2</sub>/Ag thin coatings inhibiting bacterial adhesion and biofilm formation**

**Todorcka Vladkova**

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Protection of medical devices against infections is a significant current challenge raised by increasing number of medical devices associated infections and microbial resistance to conventional antibiotic and multi drugs treatments. Deposition of antimicrobial coatings is one of the current approaches to solution the problem.

The aim of this study was to develop protective coatings for medical devices with improved antibacterial activity, combining the known positive effects of TiO<sub>2</sub>, SiO<sub>2</sub> and Ag nanoparticles, and employing magnetron co-sputtering as an ecology friendly and relatively easy technology. Magnetron co-sputtered TiO<sub>2</sub>/SiO<sub>2</sub>/Ag coatings with different Ag content were fabricated by varying the area of the Ag sheds at constant area of the TiO<sub>2</sub> target and SiO<sub>2</sub> sheds.

Surface characteristics, influencing the bioadhesion: chemical composition, topography, wettability and surface energy were estimated by SEM/EDX, XPS and contact angle measurement, respectively. The inhibitory effect toward bacterial growth on the new developed TiO<sub>2</sub>/SiO<sub>2</sub>/Ag coatings was tested using both, *E. coli* and *P. aeruginosa*. Bacterial biofilm formation in urine flow was evaluated for better characterization of the antimicrobial activity of these coatings.

SEM observation depicted a grain structure of the TiO<sub>2</sub>/SiO<sub>2</sub>/Ag composite coatings with homogeneous dispersion of the Ag nanoparticles. Significant antibacterial activity as well as reduced biofilm formation in urine flow were found: approaching to zero number of leaving *E. coli* and *P. aeruginosa* bacterial cells in the eluate detected after 1-3 h in contact with the studied coatings and significantly decreased, as compared to a silicon surface, biofilm formation after 24-48 h in urine flow.

Observed by SEM, direct contact killing and indicated by FAAS, released silver-mediated killing were proposed as a mechanism of antibacterial action of the studied coatings. Inhibiting bacterial adhesion and biofilm formation, as fabricated magnetron co-sputtered TiO<sub>2</sub>/SiO<sub>2</sub>/Ag coatings, are promising protection for medical devices as indicated by in vitro testing, including in flow.

**Biography**

Vladkova has her expertise in surface engineering starting as a member of a pioneering group in the development of brush type PEG coatings (Coll&Surf,1986) to create bioinert biomaterial surfaces, that do not cause non-desirable response reactions. Later she moves to bioactive biomaterials and material surfaces: bio-integrating biomimetic nanocomposites for bone tissue engineering; antimicrobial collagen based nanocomposites; marine biofouling preventing composition coatings; magnetron sputtered antibacterial coatings for medical devices, etc. Inhibition of bioadhesion and biofilm formation as well as surface characteristics, influencing biofouling (medical and marine) are in the focus of her investigations with a special emphasis on the non-toxic biofouling control including super hydrophobic surfaces utilization.

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Accepted Abstracts



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**Polarized Raman scattering of crystalline semiconductors cut off-axis**

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A unique approach to polarized laser Raman spectroscopy is introduced to investigate the structure and crystallinity of Si wafers based on measured intensity profile and Raman intensity theoretical model. The orientation of the crystal in our model is defined by two angles, the angle between (001) crystal axis and the lab z-axis, and the angle of rotation of the crystallographic xy plane about the crystal's z-axes. Raman selection rules for a given crystal symmetry govern the interaction between the incident polarized laser and analyzed output. The scattered light intensity depends on the laser wavelength, the cross-sectional area from which light is collected, the penetration depth of the laser, and the crystal orientation for specific experimental geometry. An intensity map is generated when wafers of different geometry are rotated about the lab z-axis that varies the angle between the fixed incident light polarization and the crystallographic axes. Calculated Raman intensity for LO- and TO-modes for various crystallographic orientations when the polarizer and analyzer are both horizontal (HH) and when they are perpendicular (HV) are presented. By increasing the crystal's tilt  $\Theta$  from crystal's +z-axis to -z-axis and rotating the crystal about the crystal z-axes for  $\Theta$  from 0-45° a set of predicted profiles for various Si sample cuts are generated. Calculated profiles for the combination of the LO and TO modes for (100), (110) and (111) silicon are in excellent agreement with normalized experimental data published for these geometries. The changes in our Raman intensity profile provides an effective approach in determining the degree of off-axis cut for single crystal Si. Similar studies using our unique polarized Raman scattering applied to GaAs is underway. Our unique approach could be used as an alternate viable method to establish crystallographic orientation for cut off-axis single crystalline semiconductors.

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**A proposal for the sustainable treatment and valorisation of olive mill wastes**

**Hafsa Annab<sup>1</sup>, Azzouz Essamri<sup>1</sup>, Nuria Fiol<sup>2</sup> and Isabel Villaescusa<sup>2</sup>**

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Olive mill technology generates a considerable amount of both solid (olive pomace OP) and liquid by-products (olive mill wastewater OMWW) during olives milling season, usually between November and March. These wastes represent a great challenge for olive oil producers since they must find technical, environmental and economic solutions to manage these by-products. The aim of this work was to explore and propose a complete cycle of olive mill wastes treatment. Two sorbents based on olive pomace chemical activation, granular (GAC) and powdered (PAC) activated carbons were successfully synthesized and encapsulated in calcium alginate. The obtained gel beads (GAC-B and PAC-B) were tested as sorbents for gallic acid adsorption. Both sorbents showed great potential for gallic acid sorption; although PAC-B beads resulted to be the most efficient. The major efficiency presented by PAC-B beads for gallic acid removal was attributed to the basic character and high porosity of PAC. In view of an industrial application, PAC-B beads were used to treat OMWW with the aim to adsorb polyphenols from the effluent, and, at time, to reduce the contamination of so strongly polyphenols loaded effluents. The outcomes of this study attest proofs of great potential of PAC-AC beads for polyphenols removal. Briefly, this paper suggests a proposal for sustainable treatment and valorization of both olive mill wastewater and olive pomace, as they can be recycled and reused for own benefit of the industry.

&  
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**Hot electron-mediated plasmonic photocatalysis using heterojunctions of noble metal nanoparticles and semiconductors**

**Karthik Shankar**

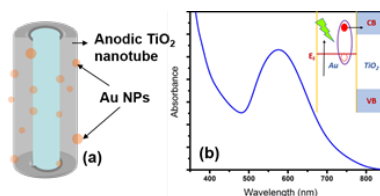
University of Alberta, Canada

**Statement of the Problem:** Several industrially relevant catalytic chemical reactions require either high temperature or high pressure or both. A particularly energy intensive reaction is the transformation of CO<sub>2</sub> into value-added products. The catalyst - typically a finely divided noble or transition metal/alloy, reduces the activation energy barrier for the chemical reaction, by coupling to the vibrational modes of the reactants. Achieving sustainability involves making these reactions more energy efficient by reducing the thermal budget required. A stretch goal is to be able to run the majority of industrial chemical reactions close to room temperature using renewable energy.

**Methodology & Theoretical Orientation:** Plasmonic photocatalysis offers the promise of using light as the energy source to drive a variety of chemical reactions close to room temperature. Surface plasmons are quantized collective oscillations of the electrons in noble metal nanostructures that strongly interact with visible and near-infrared photons. Ultrafast decay of the plasmons either by Landau damping or chemical interface damping results in the creation of highly energetic carriers called hot electrons that can be used to drive a chemical reaction and thus perform work. However, the hot electrons lose their excess energy thermal equilibrium over the picosecond timescale through a sequence of relaxation processes. We studied noble metal-semiconductor heterojunctions as platforms to utilize hot electrons before their relaxation.

**Findings:** TiO<sub>2</sub>-Au nanoparticle (NP) heterojunctions were found to be particularly effective in driving CO<sub>2</sub> reduction and photoelectrochemical water-splitting due to extremely long-lived photoelectrons, which were formed by the ultrafast injection of hot electrons from Au NPs into the conduction band of TiO<sub>2</sub> across a Schottky barrier. Likewise, heterojunctions of graphenic semiconductors (e.g. g-C<sub>3</sub>N<sub>4</sub>, C<sub>3</sub>N<sub>5</sub>) with Ag nanoparticles were excellent for driving surface reactions and effluent degradation under visible illumination.

**Conclusion & Significance:** Hot electron injection into TiO<sub>2</sub> nanomaterials appears to be faster than conventional theory would suggest, and the resulting charge separation is unusually long-lived. Au NP-TiO<sub>2</sub> and Ag NP-graphenic semiconductor are highly promising plasmonic heterojunctions that can potentially photocatalyze a range of important chemical reactions using visible light.



**Fig. 1(a)** Schematic illustration of gold nanoparticles partially embedded in the walls of TiO<sub>2</sub> nanotubes and **(b)** their strong LSPR resonance w/inset showing the band diagram for hot electron injection from Au to TiO<sub>2</sub>.

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**Formulation of non-ionic surfactant vesicles (NISV) prepared by microfluidics for therapeutic delivery of siRNA into cancer cells**

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**Introduction:** RNA interference involves the degradation of a target messenger RNA through the incorporation of short interfering RNAs (siRNA) [1]. The application of siRNA based therapeutics is limited by the development of an effective delivery system. A novel type of nanoparticles known as non-ionic surfactant vesicles (NISV) are commonly used for drug delivery of various therapeutics, are relatively safe and non-expensive, have not been extensively studied for siRNA delivery [2]. Therefore, the aim of this study was to investigate the potential of NISV prepared by microfluidics for siRNA delivery.

**Methods:** NISV were prepared by microfluidic mixing which is a recently developed method used to prepare lipid based nanoparticles and results in the production of small vesicles with efficient encapsulation of a therapeutic agent. To prepare NISV, specific volumes from each stock solution of the NISV components were mixed together to prepare the lipid phase. The lipid phase was injected into the first inlet and the aqueous phase into the second inlet of the microfluidic micromixer, with the mixing temperature set at 50°C. The flow rate ratios (FRR) between the aqueous and organic phase was set at 3:1 and the total flow rates (TFR) of both phases was set at 12 ml/min. This allows for fast mixing between the two phases at high flow rates and at a temperature above the phase transition of the lipids. Dispersions were then collected from the outlet stream and immediately diluted in order to reduce the final ethanol content in the preparation to 6.25% (v/v). Cytotoxicity evaluation of NISV were carried out on non-small lung cancer cells (A549) and mouse melanoma cells (B16-F10-LUC). siRNA targeting green fluorescent protein (GFP) in copGFP-A549 cells, or luciferase in B16-F10-LUC cells were encapsulated in NISV. Inhibition of GFP expression by anti-GFP siRNA (siGFP) delivered using NISV was evaluated by flow cytometry, polymerase chain reaction, and Western blotting. Nude BALB/c mice inoculated with B16-F10-LUC cells that induce melanoma expressing luciferase was used to assess the NISV ability to deliver siRNA in vivo.

**Results:** Cytotoxicity studies indicated that NISV were not toxic at or below 40 µg/ml. NISV formulations had high siRNA encapsulation efficiency. Fluorescent microscope and flow cytometry studies indicated high cellular uptake by the cells compared to naked siRNA, which was not taken up by the cells. NISV were able to deliver siGFP to the cells and significantly suppress GFP expression. These results were confirmed by transfecting the luciferase producing B16-F10-LUC cells with anti-luciferase siRNA (siLUC). Measuring the level of luciferase expression after siLUC transfections using a luciferase protein assay system successfully demonstrated the suppression of luciferase expression. NISV were then used in in vivo experiments using nude BALB/c mice. After intra-tumoural injection, siLUC was delivered to the cells and suppressed luciferase expression at a significantly higher level than mice treated with naked siLUC. These in vivo results confirm the ability of NISV to successfully deliver siRNA into the cytoplasm of the target cells and suppress the target protein.

**Conclusion:** NISV have been demonstrated extensively and for the first time to have the potential to be used as a delivery system for siRNA. These results have shown that NISV can be used to overcome the barriers, such as low stability and poor cellular uptake, in siRNA-based therapeutics.

### Reduced graphene oxide for energy harvesting and storage

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The need for clean and sustainable energy sources to meet the exponentially rising energy demands of the world has compelled scientists to look for new power generation strategies. Photovoltaic and thermoelectric (TE) energy conversion is proved as an alternative route to obtain electric power economically and to harvest widely distributed waste heat, respectively [1,2]. At the same time the renewal of interest to fundamental mechanisms of energy storage in electrochemical supercapacitors (SCs) was boosted by the progress in development of novel materials (mainly carbon based) for nanostructured electrodes [3]. SCs can be charged faster than batteries, leading to a very high power density, and do not lose their storage capabilities over the time. The main shortcoming of SCs is their low energy density, meaning that the amount of energy, which SCs can store, per unit weight is very small, particularly when compared to batteries. There is a wide range of the materials for electrodes and electrolytes but all of them have limitations. Preliminary design criteria and cell specifications are following: flexible, low weight and cheap. Thus, obtaining the freestanding electrodes by simple vacuum filtration will decrease the total weight of full cell device and total cost.

At the same time, reduced graphene oxide (rGO) has attracted significant attention in recent years due to its extraordinary physical and chemical properties [3]. Thanks to the combination of the excellent mechanical properties and compositional tunability, rGO-based materials are exciting systems for their potential applications [4,5]. Within this context, use of rGO in solar cells, TE generators and electrodes for SCs is very perspective and needs to be further investigated. In the current work structural and microstructure properties, as well as electrical, TE and electrochemical characteristics of rGO-based films and papers are presented and their relation is studied.

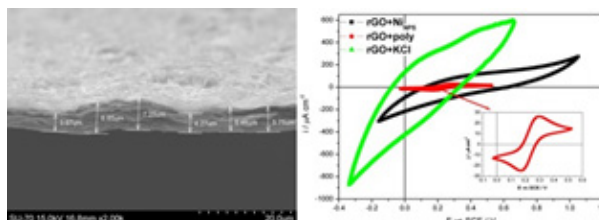


Figure 1: Scanning electron microscopy image (left) and electrochemical characterization (right) of rGO-based paper with Ni nanoparticles (rGO+NINPs), polycarbonate (rGO+poly) and potassium chloride (rGO+KCl) additives



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**Structural, electronic, mechanical and thermodynamical properties of some double Perovskite oxides: A DFT calculation**

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Recently, perovskites have been investigated with great attention both theoretically as well as experimentally in physics, chemistry, and material science because of their variety of applications in science and technology. The double perovskites are very important members of this diverse perovskite family having different structures, composition and physical properties in the fields of spintronics, multiferroics, half metallic, ferromagnetic, magneto-dielectric, and magneto-optics [1,2]. Magnetically, double perovskite family exhibits a wide range of magnetic behaviours[3]. Full-potential linearized augmented plane wave (FP-LAPW) method based upon density functional theory (DFT) as employed in WIEN2K has been used to calculate structure, electronic, magnetic and thermodynamical properties. Structural investigation has been carried within GGA scheme of PBE. For electronic (Fig. 1a), magnetic and mechanical investigations GGA, GGA+U, mBJ approximations have been employed. These perovskites occupy cubic structure with space group Fm-3m (225). Most of the double perovskites show ferromagnetic nature and if spins are plotted, interestingly, they show half-metallicity, which make these materials application in spintronic devices. Further, electronic band profile of these materials depicted another feature used in indirect band gap semiconductors. The mechanical properties like Young's modulus (Y), Poisson's ratio (n), Bulk modulus (B) and Shear modulus (G) have been also calculated from the value of elastic constants. Furthermore, temperature and pressure dependent thermodynamic properties have also been calculated within quasi-harmonic Debye approximation. We have plotted specific heat at constant volume (Cv) in Fig1b, thermal expansion (a), Grüneisen parameter and Debye temperature. The Debye temperature can be used in describing the excitation of phonons and to designate various lattice thermal phenomena while the Grüneisen parameter explains the phonons contribution to specific heat.

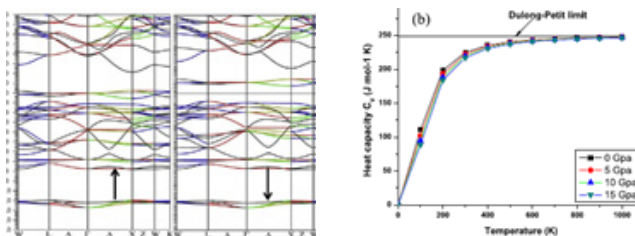


Fig.1 (a) Band structure along high symmetry directions showing half-metallic nature (b) variation of Cv under temperature reaching to Dulong-Petit limit Ba2CdOsO3

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**Recycling and reuse of human excreta for energy generation: A review**

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Almost a billion people in developing world have no access to toilet and practice open defecation. But that waste should not go waste. Rather than tainting the environment and transmitting diseases, it could actually be harnessed to heat or power for millions of homes. The review paper will discuss about utilization of human excreta to produce biogas/energy as an alternative renewable energy. Utilization of human waste is considered beneficial in terms of the process because it does not require additional starter (micro organisms seeds) and a supply of micro organisms occurs continuously during the feeding of raw materials. Product gas resulting from typical dry human feces have LHV and energy values of 17.2 MJ/kg and 24 MJ/kg, respectively, at optimum equivalence ratio of 0.31 values that are comparable to wood biomass. Non- sewerer Sanitary Systems (NSS) are emerging as one of the solutions to poor sanitation because of the limitations of the conventional flush toilets. The new sanitary systems are expected to safely treat fecal waste and operate without any external connections to sewer, water supply or energy source. The Nano Membrane Toilets (NMT) is unique domestic –scale sanitary solution to treat human waste on site. The Reinvent the Toilet Challenge (RTTC) is one of the pioneering schemes initiated in 2011 under the Water, Sanitation and Hygiene (WASH) programme of the Bill and Melinda Gates Foundation to increase access to safe, sustainable and affordable sanitation.

In the present communication merits, demerits, advantages, limitations of various engineered technologies employed will be critically reviewed on the basis of their innovations, user friendliness, cost effectiveness, maintenance etc. Also, health aspects of biogas generated, design and R &D aspects of biogas plant fed by human excreta with or without supplementary feed stocks, treatment of slurry and its use, strategy for promotion and integration with other programmes will be thoroughly discussed.