

## Proceedings of 4<sup>th</sup> NanoWorld Conference held in Paris on March 3-5, 2019

### Plenary Presentations

#### **Nanoscience and Technology for a Sustainable Human Development**

**Claudio Nicolini**

*NanoWorld Conference Chairman and NanoWorld Journal Editor in Chief*

##### **Abstract**

At the end of the NanoWorld Conference in San Francisco April 25, 2018 it was decided to formalize the move of the NanoWorld Journal Headquarter from Texas (USA) at United Scientific Group to Bergamo (Europe) at Fondazione ELBA Nicolini, moving also to Paris the NanoWorld Conferences from March 4-6, 2019. Invited by the President Segeev of the Russian Academy Sciences, in official partnership with the UNESCO in Moscow for the 10th International Forum on "Science for a Sustainable Human Development" held on November 26 and 27, 2018 at the Ritz-Carlton Hotel. The role of nanoscience and nanotechnology for human growth and development in the present worldwide situation in all sector covered by the NanoWorld Journal and Conference. Challenges and open problems still emerging and confronting in both sides of the Atlantic and Pacific Oceans from north to south in cancer, environment, energy, space, climate, industry and society.

#### **Langmuir-Blodgett Protein Multilayer Technology as a Potential Tool for Structural Discovery**

**Eugenia Pechkova**

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##### **Abstract**

The multilayer technology has made possible dramatic advancement in several high-tech areas as layer-by-layer engineering, biocatalysis [1], molecular electronics [2] and protein crystallography [3-5].

Advanced sources of Synchrotron Radiation and X-ray free electron lasers (XFELs) has created many new opportunities for protein crystallography, and therefore, new methods of macromolecule organization into diffracting arrays are required, since current methods of protein crystals production still remains the major problem. We suggest Langmuir-Blodgett multilayer technology and a potential tool for protein structural studies. The multilayers are easy to produce, stable to the temperature and storage [6]. Moreover, heating and cooling procedure increase long-range order of the films, making possible to use it as a target for structural data collection [7].

Then combination of this advanced technology with the novel Cryo Electron Microscopy (Cryo-EM) instrumentation has the potential to become an important tool for the structure determination of proteins that are difficult to crystallize, such as membrane proteins of life science interest and pharmaceutical industry impact.

Future research is needed to combine above cutting-edge technologies at the nano scale, with advanced Langmuir-Blodgett (LB) nanotechnology recently described in details in 2017 Nature Protocol [8].

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## Nanotech-Based Propulsion and Power for Nanosatellites

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### Abstract

New paradigm

Propulsion and power:

\_Government-led (NASA, ESA, etc.) microthrusters development need driven by PERFORMANCE large complex astronomy missions, as the Laser Interferometry Space. Antenna mission for the detection of massive black holes.

\_Commercially driven micro/nanothrusters development driven by reduced VOLUME, MASS and COST.

\_There are several ways to efficiently generate small thrust from small devices.

## The Production, Manipulation and Analysis of Ultrasmall Liquid Volumes

**Christian Riekel**

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### Abstract

The development of high brilliance X-ray sources such as 3<sup>rd</sup> and 4<sup>th</sup> generation synchrotron radiation (SR) as well as X-ray free electron laser (XFEL) sources has allowed developing beamlines with intense micron- and sub-micron focal spots for scattering and imaging applications and suggests exploring advanced sample environments for the production and manipulation of ultrasmall sample volumes. I will discuss in my talk the use and potential of single droplets as sample environments for X-ray scattering experiments. In contrast to microfluidic systems, droplet evaporation in air allows readily studying solution concentration up to residue formation. In the simplest approach microliter solution droplets are deposited on wetting or nonwetting surfaces. Highly oriented crystalline aggregates are often formed at the interfaces as can be shown for amyloids or virus particles. The upcoming of digital microfluidics based on droplet-on-demand (DOD) inkjets provides particular challenges and opportunities. The precise timing of the arrival of picoliter droplets in the beam is particularly interesting for kinetic experiments at pulsed X-ray sources. I will discuss the status of DOD inkjets experiments performed at a 3<sup>rd</sup> generation SR source with a quasi-static beam and indicate challenging possibilities for experiments at 4<sup>th</sup> generation SR as well as XFEL sources.

## Prospects for Transformation of the International Relationship System and the Role of Leading World Actors: USA, China, EU, Russian Federation

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### Abstract

In recent years, the system of international relations is undergoing a process of serious transformation, which finds its expression in the change in the existing relations between the leading world actors: the United States, the European Union, China, Russia and others. The world is increasingly drawn into "sanctions and trade wars", the number of regional military conflicts is increasing, migration waves are growing, the gap between rich and poor countries and regions is widening, the existing systems of international and regional security are collapsing, etc.

The world today is in a situation where short-term changes in individual countries and regions coincide with global shifts. It can be compared with a certain “parade of planets”, when the trajectories of movement of large and small bodies intersect at one point.

Its implementation will be possible as a result of a chain of events, each of which individually can be random or local. However, under the conditions of growing contradictions, their combination threatens to lead to disproportionately high negative consequences. As a result, this scenario can lead to a major conflict between two or several great powers, using a wide range of forces and means, which will inevitably affect most other countries and have a stressful effect on the global economy.

However, historical experience shows that most of the disasters were considered by contemporaries as unlikely and were explained after the fact. Obviously, with the implementation of this option, all parties will incur enormous costs.

Of course, the described scenarios for the development of events can only be viewed as conditional models for the transformation of the current world order. The most favorable so far is the model of a new multipolarity, despite all the possible costs.

## **Featured Presentations**

### **Session: Nanotechnology and Nanosciences-1**

#### **Nanomaterials Based on Chitosan for Biomedical Applications**

**Marguerite Rinaudo<sup>1</sup>, Solomon M. Lemma<sup>2</sup>, Christian E. Garcia G.<sup>3</sup> and Monica Bravo-Anaya<sup>4</sup>**

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<sup>4</sup>*University of Bordeaux, France*

#### **Abstract**

Nanomaterials have been practiced in a wide range of applications, especially in biomedical and pharmaceutical domains and used as in gene transfer, drug delivery, tissue engineering and wound healing. Chitosan is a good candidate to produce nanoparticles and nanofibers due to its own characteristics: it is a linear polysaccharide derived from natural chitin recognized for its biocompatibility, non-toxicity, biodegradability and bacteriostatic properties. Another advantage is that chemical reactions can be performed on the amino group in C-2 position of glucosamine unit, allowing targeting or grafting specific active molecules. In a first part of our work, pure and stable chitosan nanofibers were produced by electrospinning. To get good spinnability, a blend of chitosan/poly(ethylene oxide) was used prior to stabilization and tests. The produced nanofibers were found to be hydrophilic and stable at physiological conditions. The average nanofibers diameter was around 85 nm but fibers size strongly depends on the selected experimental conditions. The stress at break was found around 1.2 MPa (the reduced force related to the material density equals 47 N/(Kg/m<sup>2</sup>)) and 32% elongation at break for pure chitosan nanofibers mat in the wet state. These nanofibers were tested for tissue engineering used as a scaffold for cells development. The second part of our work extended on chitosan/DNA nanoparticles formed by electrostatic interactions between positively charged amine groups on chitosan and negatively charged phosphate groups on DNA, used for nucleic acids delivery. Complex formation mechanism, its composition and its stability were investigated as a function of chitosan characteristics (molecular weight and degree of acetylation).

#### **Biogenic Nanostructures of Microbial Origin: Spectroscopic Characterisation**

**Alexander A. Kamnev**

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#### **Abstract**

In this talk, several types of nano-sized structures are considered that can be produced by microbial cells and either (i) utilised in regular bacterial metabolism or (ii) deposited (intra- or extracellularly) as a result of metabolic activity. Group (i) includes inorganic nano-crystalline cores of bacterial iron-storage macromolecules (various ferritin-like proteins) and granules of biopolyesters (polyhydroxyalkanoates synthesised and accumulated under stress conditions as intracellular carbon-and-energy storage materials). Group (ii) includes nanoparticles of elementary substances occasionally produced as a result of bacterial

dissimilatory reducing activity (either enzymatic or purely chemical, i.e. involving cellular biomolecules as reducing agents). The results will be presented using examples of ubiquitous soil bacteria of the genus *Azospirillum* studied worldwide owing to their agricultural importance. Structural data on bacterial ferritin iron cores (studied *in situ* using Mössbauer spectroscopy in cell biomass) [1], intracellular poly-3-hydroxybutyrate granules (studied *in situ* using FTIR spectroscopy) [2], as well as the formation of gold (Au<sup>0</sup>) [3] and selenium (Se<sup>0</sup>) nanoparticles [4, 5] will be discussed. The nanoscale structures under study show specific nano-size features which make their properties different from those of the same bulk-like materials. (Supported in part by The Russian Foundation for Basic Research, Grant # 17-08-01696-a).

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## Plasmonic Polymersomes: Towards Tunable Drug Carriers

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<sup>3</sup>Department of Chemistry, Rutgers University-Camden, NJ, USA

<sup>4</sup>Department of Engineering, Rutgers University-New Brunswick, NJ, USA

### Abstract

Polymersomes are robust vesicles that self-assemble from amphiphilic diblock copolymers. They are of tremendous interest in the field of drug delivery due to their ability to stably encapsulate molecules within both the hydrophobic region of the bilayer membrane and hydrophilic lumen of the vesicle. In this study, light-stimulated release of hydrophilic encapsulants has been achieved through the incorporation of plasmonic nanoparticles, facilitating disruption of the membrane upon ultrafast, single-pulse irradiation. Cargo release can be controlled ranging from complete vesicle rupture and instantaneous release, to membrane pore formation and diffusion. To gain full control over the system, it is important to understand the light-nanoparticle-membrane interactions from a mechanistic standpoint, and thus, initial studies have been performed on micron-scale vesicles that can be studied with fluorescent microscopy. However, of equal importance is the ability to scale the system down to the nano-regime for future applications in drug delivery.

## Mechanical Control of Electrons at the Nanolevel and a Possible Field Effect Transistor with Extremely Low Dissipation

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### Abstract

A generalization of the (Landau-Pekar) polaron concept permits to establish soliton-assisted transport in the form of electron surfing on a supersonically moving lattice soliton. Building upon such generalization, the concept of solectron was introduced. The solectron is a dynamic bound state electron-anharmonic lattice deformation. For illustration, the case of a lattice with quantum Morse interactions is used. Then an added, excess electron is considered in the "tight-binding" approximation. Eventually, there is electron trapping by the supersonically moving lattice soliton. Depending on values of the electron-phonon/soliton interaction, the electron transport is provided sub- or super-sonically. In an initial situation where there is an external electric field applied, the possibility exists of transport with no field over several orders of magnitude. On the other hand, the possibility also exists of charge transport with no need of electric field at all, from say a source to a drain along "natural channels" (crystallographic axes). Hence the electron surfing process is a clear case of mechanical control of electrons at the nano-level. As an application of the above given concepts, a solectron field effect transistor (SFET) has been designed, based on the electron surfing offering a ballistic-like flight

of the solectron. This opens up the possibility of extremely low energy consumption in computation.

## High Efficiency, Quantum Dot Enhanced Photonic Crystal LEDs for Monolithic Micro-display Applications

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<sup>1</sup>Electronics and Computer Science, University of Southampton, UK

<sup>2</sup>Department of Physics, University of Southampton, UK

### Abstract

Nanostructured optical materials known as photonic crystals have been proposed as a great method to enhance LED and solar cell device efficiency. Despite a drive to improve efficiency for general lighting and display applications LED colour conversion technology has not changed dramatically over recent years. However the advent of quantum dot material provides an exciting new way to improve efficiency and colour quality. In this talk I present groundbreaking work on quantum dot enhanced photonic crystal LEDs and solar cells. By modifying the device configuration of an LED, we change the energy conversion process which generates light, and engineer conventional loss mechanisms out of the device. We increase colour conversion efficiency from the benchmark of around 35% provided by a regular LED to an equivalent of 110%. This is achieved not by breaking the rules of physics but by harnessing two additional energy conversion processes (photonic quasi-crystal light extraction, and Resonant Energy transfer) as opposed to just luminescent colour conversion to give phenomenal performance improvement. I present demonstrator LED devices, and describe work towards creating a super-high efficiency micro-LED display for 3D virtual reality applications and projection systems such as head up displays. By applying RET technology to Silicon Solar cells we are able to boost efficiency by 18%.

## Gas Sensors Based on Functionalized Nanostructured Nanomaterials

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### Abstract

The monitoring of the environment requires devices that must be fast, sensitive, stable and selective to detect the pollutants and toxic gases/vapors in a simple and efficient way. The chemical modification of multiwalled carbon nanotubes (MWCNTs) with a long chain mercapto-acid is reported to improve the sensitivity and the response time of gas sensors. We developed sensors employing MWCNTs decorated with gold nanoparticles and modified with different thiol monolayer. Morphological and compositional analysis by Transmission Electron Microscopy (TEM), Fourier Transform Infra-red Spectroscopy (FTIR) and X-ray photoelectron spectroscopy were performed to characterize the gold nanoparticles and to check the bonding of the thiol monolayer. The detection of gas by MWCNT/Au and MWCNT/Au/Thiol shows that the presence of the self-assembled layer increases sensitivity, selectivity and ameliorates response dynamics of the sensors.

## Circulating Motions in a Droplet upon a Superhydrophobic Chip for Conformational Changes of Biological Materials

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### Abstract

Superhydrophobic surfaces (SHSs) based on pillared substrates support aqueous droplets in a quasi contact-free (Cassie-Baxter) state. Such droplets provide wall-free microfluidic environments for dissolved and colloidal biological materials allowing studying self-assembly and conformational changes during evaporation by X-ray scattering and complementary techniques [1]. As an example, the confinement of the solute in the “so-called” coffee ring is due to the convective flow and the diffusion process to the droplet interface. While the evaporation of aqueous droplets can be well described analytically [2] or by simulations, our understanding of the microfluidic environment and the induced flow in evaporating droplets containing solutes is still quite limited. Our current work addresses this topic by combining optical microscopy and simulations. We quantified the flow of monodisperse spherical polystyrene (PS) particles in drying droplet on a smart superhydrophobic surface by Particle Tracking

Velocimetry (PIV) (Figure 1A). We observed that particles do not segment but describe vortex-like motions (Figure 1B). These internal motions during evaporation lasts as long as the droplet keeps a spherical shape and they have an averaged magnitude value of 0.1 mm/s which can induce shear stresses and explain the conformational changes of biological matter like amyloid fibrils [1]. First results on PIV and simulations will be presented.

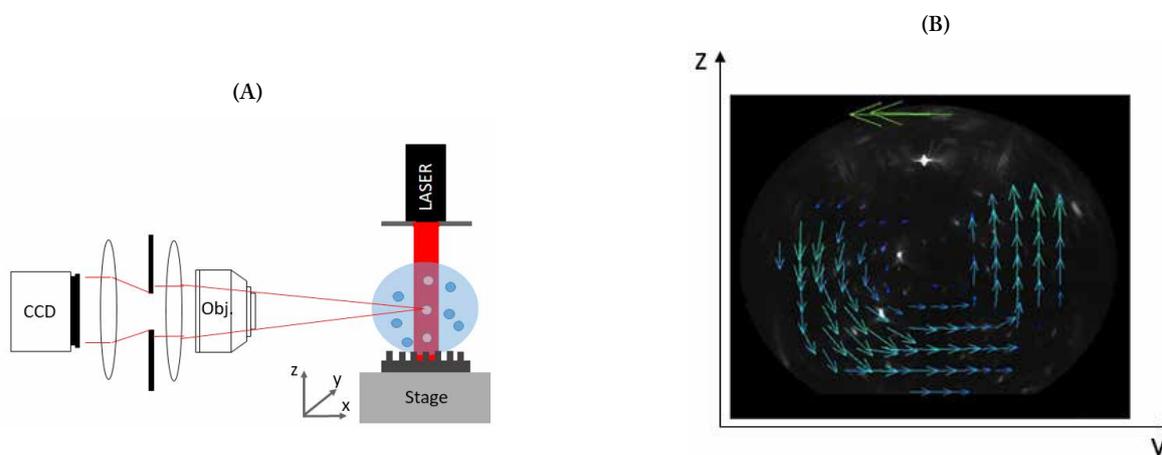


Figure 1: (A) Schematic Particle Tracking Velocimetry setup. (B) Recirculating flow of polystyrene particles.

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## Session: Nanotechnology and Nanosciences-2

### **Ternary Organic Solar Cell with Near-IR Absorbing Selenophene-DPP Based Non-Fullerene Acceptor and Efficiency Above 10%**

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## Abstract

Non-fullerene acceptors (NFA) are currently a main target of interest in OSCs as the lower cost, the energy levels and optical properties can be finely tuned to minimize the energy loss, being the performance is the range of 13-14%. However most of these molecules require multi-step synthetic procedures and new molecules with simple synthetic approach and affording high efficiencies are required.

Recently we have designed new NFA small molecules consisting of a diketopyrrolopyrrole (DPP) central core linked to different acceptors via thiophene donor linker and employed as acceptor along with small molecule or polymer as donor for the bulk heterojunction OSCs and achieved PCEs in the range of 7-9% 1-4 Herein, I'll present a new NFA, denoted as MPU4, consisting in a DPP central core connected by selenophene moieties to two terminal rhodanine (Rh) units. Ternary solar cells fabricated with SMD as donor and MPU4 and PC71BM as acceptors afforded PCE as high as 10.05%.

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## Integration of Molecular Machines into Supramolecular Materials

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### Abstract:

Switchable functional molecules capable of producing mechanical work constitute an active focus in nanotechnologies as they can be a source of components for molecular-based devices and materials. In particular, the dynamic nature of mechanically interlocked molecules allows their components to undergo relative internal movements, which can be exploited in translation and circumrotation. When it comes to using molecular machines to facilitate the creation of materials on the macro-scale, the primary concern is whether the nano-sized machines will be able to amplify their mechanical behavior to create a response in the bulk material. Hence, one of the most fundamental and challenging objectives associated to nano-machines rests on their coupling (in space and time) in order to transfer controlled motions from the molecular arena to the supramolecular and macroscopic scale.

In the present work, we have developed two kinds of responsive contractile polymeric materials, which can behave as artificial muscles: i) The first one concerns nano-machines linked into a supramolecular polymer in which we produced micrometric motions (contraction/extension) by the integration of thousands of single contractile nano-switches by altering the pH of the solution; just like myofibrils do when packed in bundles in muscles. ii) The second one is based on the connection of light-driven rotary motors acting as reticulation units in an entangled polymer network. Small-angle neutron scattering (coupled with light and X-ray scattering) has been used to investigate the structure of the supramolecular self-assemblies of nano-machines before and after the induced structural changes as well as the dynamics of the contraction process at different length and time scales. We discuss here the relation between the local and overall structure of the self-assemblies and the properties of the materials. We show that these findings open up new possibilities of using molecular machines in smart responsive materials.

## Nano Fire and Nanoscale Thermal Energy Harvesting

Zhiyu Hu

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### Abstract

Fire has been an integral feature of our planet for over 400 million years. It has also defined human culture from the very beginning. Fire history is the story of how fire and humans have coevolved. The prevalence of human civilization is largely attributable to their control over fire and humanity's ecological signature on the world is fire. History has demonstrated that every innovation in utilization of fire had brought significant and prolonged impacts on each step of social developments. Until now, all the fire or combustion is in macro-scale and in three dimensions.

Taking advantage of micro/nanofabrication technologies, we were able to fabricate nanoscale catalytic thin film in various patterns. Our previous studies achieved spontaneous self-ignition and self-supporting combustion with gas-phase methanol in air over nanoscale platinum particles at ambient temperature. Subsequently, additional investigations have found that combustion at nanoscale correlates closely with the microstructural properties of platinum nanocatalyst. The size, morphology, as well as distribution of nanocatalysts have a significant impact on the catalytic combustion of methanol. Traditionally, nanocatalytic particles are mainly synthesized via chemical methods and used to create sustainable nanoscale fire. However, nanocatalytic particles such as platinum nanoparticle has a strong tendency to agglomerate, coalesce, and sinter during combustion, which reduces the electrochemically active surface area and significantly decreases catalytic activity. The aggregation of nanocatalyst and the contamination introduced from solvents or precursors could hinder their application in micro-manufacturing.

In this study, we reported a novel method of creating a sustainable fire at nanoscale and in two dimensional patterns for the first time, which featured with rapid temperature response, uniform temperature distribution, and ultrahigh temperature gradient (up to 1300 K/mm). This nanoscale fire may find promising applications in power supply micro/nano systems such

as portable power systems and nanoscale heat source, and would open new routes for energy conversion at nanoscale such as the development of nanoscale heat engine in the near future. Given that nanoscale fire exhibits high energy density and rapid thermal response at ambient temperature, this research also offers an interesting avenue toward developing nanoscale heat sources, which could be used in many potential areas such as MEMS power devices or sensor systems.

As a test case, we have built sub-micro-thick thermoelectric (TE) array with 0.1 mK ultrahigh temperature sensitivity. The small sizes of those TE arrays would allow packing more than 40,000 units in single 3" wafer. The initial experiment demonstrated that the TE array was very sensitive to any thermal condition changes and could produce continuous electrical power from one's palm. With further improvements, the TE array should be able to harvest thermal radiation from ambient air directly. As thermal energy exists everywhere in the world, it is fair and inexhaustible. Our TE array may offer the most promising way to obtain unlimited energy supply in future.

## ZnO Nanostructure Based Photocatalysis for Water Purification

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### Abstract

Water is not only vital to all forms of life as it is also an unavoidable precious resource in a wide range of industrial processes. With the ever-increasing human and industrial needs, it becomes more and more necessary to find new cheap, environmental friendly and efficient ways to refine industrial and urban wastewaters, ensuring the availability of clean drinkable water in the future.

Compare to the classical water treatment methods such as coagulation, sedimentation, filtration, etc.; the semiconductor-based photocatalysis is a well-known and efficient process for achieving water depollution, with very limited rejects in the environment. Metallic oxides, such as zinc oxide (ZnO), are excellent photocatalysts, able to mineralize a large scale of organic pollutants in water, under UV irradiation that can be enlarged to visible range by doping nontoxic transition metal elements such as Ag and Fe.

In this work, we report the enhanced photocatalytic efficiency with high surface/volume ratio nanostructured ZnO. The doping with metal elements (Ag and Fe), as well as carbon doping showed a notable enhancement on the photodegradation of different dyes (MB, OM, AR14). ZnO nanostructure is also a promising candidate in microfluidic application for their easy-controllable synthesis and integration in a microfluidic system. ZnO nanostructures can also be synthesized on civil engineering materials for self-cleaning road application to avoid the soil pollution.

## Thermal Stability of Nanostructured Semiconductor Sulfides

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### Abstract

Metal sulfide semiconductor nanostructures represent the most promising group of nanostructured materials with excellent optical and electrical properties for such applications as photoelectrochemical cells, photoconductors, infrared detectors, nonvolatile memory devices and resistive switches. As a rule, microelectronic devices and infrared detectors, containing a nanostructured sulfide, operate in air at elevated temperatures up to 400-450 K, at which uncontrolled nanoparticle growth and variation in the phase composition of sulfide nanoparticles may take place, leading to the degradation of their electrical and optical properties, and the operation instability of electronic devices with nanostructured sulfides. In present study, the data on the recrystallization and thermal stability of phase composition and particle size of semiconductor nanostructured PbS, Ag<sub>2</sub>S, SnS, and CdS sulfides and sulfide solid solutions are considered.

The analysis performed showed that the nanostructured semiconductor sulfides possess the thermal stability of nanoparticle size in the region from room temperature to  $0.4 T_{melt}$  or  $0.5 T_{melt}$  where  $T_{melt}$  is a melting temperature. The temperature interval of thermal stability of phase composition of sulfide nanoparticle coincides almost with an interval of thermal stability of nanoparticle size. The temperature range above 450-700 K, in which the nanoparticle size increases from 2 to 3-6 times and larger, corresponds to the region of collective recrystallization of sulfides nanopowders. The activation energies of collective recrystallization for nanostructured lead and silver sulfides are found. In the process of collective recrystallization, the larger is the activation energy, the smaller is the nanoparticle size, other factors being equal.

## Graphene-Metal Nanoparticle Hybrid Materials: Structure and Properties

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### Abstract

Graphene-covered metal nanoparticles (NPs) constitute a hybrid material which provides a unique platform to study plasmonic effects, surface-enhanced Raman scattering (SERS), and metal-graphene interactions at the nanoscale. Additionally, the corrugation of graphene can be tuned by the size and shape of the NPs, in order to enhance its chemical activity. This can open a route in tailoring the properties of graphene/nanoparticle hybrid structures towards sensing applications. We prepared such hybrid materials by transferring graphene onto closely spaced metallic nanoparticles (Au, Sn) produced on silica and highly oriented pyrolytic graphite (HOPG) substrates. The morphology and physical properties of NP-supported graphene was investigated by atomic force microscopy (AFM), optical reflectance spectroscopy, scanning tunnelling microscopy and spectroscopy (STM/STS), and confocal Raman spectroscopy.

The study of graphene/Au NPs shows that the graphene Raman peaks are enhanced by a factor which depends on the excitation wavelength, in accordance with the surface plasmon resonance of the Au NPs, and also on the graphene-nanoparticle distance which is tuned by annealing at moderate temperatures. STM and STS measurements show that charge transfer occurs from the underlying NPs to the graphene. Furthermore, we show that tunnelling spectroscopy can be used to measure the electronic band gap of graphene-covered semiconducting NPs.

## Lightweight Advanced Nanocomposites for Electromagnetic Interference Shielding Application

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### Abstract

Now-a-days, there is an increase in electromagnetic radiation from the rapid developments of commercial electronic devices and therefore there is creation of an electromagnetic pollution. The electromagnetic radiations emitted from various electronic devices are responsible for malfunctions in these devices and also generated human health issues. It has triggered us to fabricate advanced electromagnetic interference (EMI) shielding nanocomposites. The activity of shielding nanocomposite material is governed by on the electrical conductivity, dielectric permittivity, magnetic permeability, etc. Graphene, a two-dimensional carbon nanomaterial, demonstrated extraordinary mechanical, electrical, and thermal characteristics. Moreover, the ferromagnetic spinel ferrite nanoparticles have ability to absorb incident magnetic field and therefore shields the propagation of incident electromagnetic waves. Therefore, graphene and spinel ferrite nanoparticles have promising application as a nano-filler in polymer for the development of advanced nanocomposite for electromagnetic interference shielding application. This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic – Program NPU I (LO1504) and OP VVV (“HR Award”) project at CPS.

## Silver Nanoparticles in Carbon Fiber-Reinforced Polymer Material for Protection against Damage by Laser and Thermal Irradiation

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### Abstract

Due to their excellent mechanical properties and their low overall density, carbon fiber-reinforced polymers (CFRPs) are used for many lightweight applications. In order to enhance the material's performance against high energy laser radiation and exposure to heat sources, silver nanoparticles were introduced into the matrix material. The goal of the nanoparticle infusion is to increase the scattering and reflection properties of the resin with respect to incident radiation.

With increasing amounts of silver nanoparticles (up to 10 wt.%), the neat resin of a CFRP material shows higher resistance against laser treatment with a low power UV-laser.

For thermal irradiation, the CFRP material, prepared with up to 10 wt% silver nanoparticles (referring to polymer matrix), was treated from one side with different heat fluxes, showing increasing times to ignition by cone calorimetry. Scattering and

specular reflectance of (infrared) light is analyzed before irradiation and shows enhanced scattering of samples with increasing silver particle content, which correlates linearly to the time to ignition and is likely due to particle size. Particle size changes during combustion, as particles melt together and build up reflecting surfaces.

Additionally, investigations of potential risks for health and environment before, during and after combustion of this new material were performed, because the release of nanoparticles was suspected. Initial results suggest no additional hazards, because silver nanoparticles were only released integrated in resin matrix material at sample production and sample preparation. Furthermore, there was no silver detected in the exhaust gas during combustion of the material.

## Nanostructured Mesoporous Electrocatalysts for Renewable Energy Sources

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### Abstract

Nanostructured mesoporous materials are of interest for a variety of applications for developing a renewable and clean energy sources. This work presents the synthesis of entirely new classes of nanostructured mesoporous transition metal oxides, hydroxides and phosphate nanocatalysts with improved electrocatalytic properties for hydrocarbon oxidation, water splitting and fuel-cell reactions. Mesoporous nanocatalysts of nickel, cobalt and titanium oxides, hydroxides and phosphates with high surface areas, high degrees of mesoporous order, and different architectures are prepared via the chemical deposition of metal ions dissolved in the aqueous domain of liquid crystalline phases of nonionic surfactant templates. The compositions, periodicities, surface areas, pore diameters, and architectures of the nanocatalysts can be varied in a controllable way through changes in the template compositions and the type of surfactant. The electrochemical and catalytic activity of the resulting mesoporous nanocatalysts investigated and screened for hydrocarbon (urea, methanol and ethanol) oxidation and water splitting reactions of hydrogen and oxygen evolution.

## High Performance Thermoelectric Materials: From Synthesis to Applications

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### Abstract

Thermoelectric (TE) materials have the capability of converting into electricity by collecting wasted heat, which not only improve fuel efficiency but also provide alternative energy supply in multiple applications. In order to construct high performance TE devices, superior TE materials have to be developed via various strategies, broadening the market of TE application. We focused on major novel strategies to achieve high-performance TE materials and their applications. The carrier concentration and electronic structure of directly spun carbon nanotube (CNT) web were manipulated with various molecular dopants to optimize the electrical transport properties. The dopant coating on the CNT bundle efficiently suppressed the phonon transfer along the CNT web direction, which led to a reduction of the thermal conductivity of the CNT web. In addition, the surface of exfoliated black phosphorus (BP) was successfully functionalized with Au nanoparticles (NPs) for TE applications, leading to significantly enhanced TE performance for a controlled Au NP content. The nanostructure engineering and defect engineering also greatly improved the stability. Given these interesting and unique properties of Au-decorated BP, a vertical TE generator is prepared, showing high power output of 79.3 nW ( $\Delta T = 2^\circ\text{C}$ ) and highly stable voltage response as temperature sensor. As future plan, it is highly required to synergistically optimize and integrate all the effective factors to further improve the TE performance, so that highly efficient TE materials and devices can be more beneficial to daily lives.

## Chemical Surface Functionalization of Multi-walled Carbon Nanotubes (CNTs)

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### Abstract

Carbon nanoparticles (CNPs) have attractive properties such as nanoscale diameter, high aspect ratio, low-weight, and extraordinary mechanical, optical, and thermal properties. From different types of CNPs, carbon nanotubes (CNTs) and graphene have attracted much attention in the last two decades. Many investigations have shown that a small amount of these nanomaterials resulted in a substantial improvement in the electro-mechanical properties of their composite materials.

However, due to their agglomeration or tangled coils as a result of strong van der Waals interactions, their functionalisation is essential in achieving proper dispersion in polymer matrices in order to obtain outstanding electro-mechanical properties. There are different methods of functionalization such as gas phase oxidation, liquid phase oxidation and chemical phase oxidation.

In this study acid nitric was used to chemically functionalize the surface of multi-walled carbon nanotubes (MWCNTs). The functionalisation efficiency of the resulting MWCNTs were characterised and quantified by using a range of analytical techniques, including: thermo-gravimetric analysis (TGA), Raman spectroscopy, and Fourier transform infrared spectroscopy (FTIR). The results of the various analyses showed that the functionalization process successfully attached the functional –COOH group covalently to the surface of the CNTs.

## **Numerical Simulation for Thermal Regulation of Photovoltaic Thermal Systems Using MWCNT Nanofluids**

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### **Abstract**

Photovoltaic applications are the mean that converts solar light into electricity. However, the photovoltaic panels' efficiency is highly affected by heat storage and surrounding heat, leading to decrease in their efficiency. Solving this problem led researchers to propose a new hybrid photovoltaic thermal system PV/T that generate electricity parallel to absorbing heat for other applications. Entering the era of Nanotechnologies encouraged more researchers to utilise these technologies in PV/T system using suspension of Nano particles in the base fluid called Nanofluids.

This paper presents a numerical simulation for thermal regulation of PV/T systems using ANSYS FLUENT software for Multi wall carbon nanotubes (MWCNT—water based) Nanofluids.

The results were validated with experimental results using Nano particles volume concentrations range from (0–0.3%) at Nanofluid flow rate of 1.2 l/min. Photovoltaic panel temperature decreased by 11 °C at peak solar radiation using 0.075% MWCNT concentration. The system efficiency based on the numerical simulation achieved an overall value of 60.1% over the test period. A very good agreement between the numerical and experimental results was also achieved.

## **Poster Presentations**

### **Single-Particle States and Optical Transitions in InP/InAs/InP Spherical Core/Shell/Shell Heterostructure**

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### **Abstract**

The modern development of nanoscience and nanotechnology makes it possible to effectively manipulate the properties of nanoparticles. On the one hand, it is possible by controlling of their chemical composition and morphology, and by controlling change of their geometric dimensions in the nanometric region. The combination of several functions in a single nanoscale geometry was achieved, in particular, by creating of the core/shell/shell type composite spherical semiconductor nanostructures.

In the present work, one-electron states and optical absorption in the InP/InAs/InP nanocomposites are theoretically considered. The analysis was carried out for the conditions when, due to the anomalously small dimensions of the composition components, the quantum size effect in the InAs layer begins to manifest brightly. The energy spectrum of electrons, heavy and light holes in the layer is calculated numerically for different thicknesses of the layer. The oscillator strengths for interband optical transitions are calculated and the corresponding absorption curves for diagonal and nondiagonal interband transitions are presented. The values of the intensities of these transitions are also compared. Due to the size quantization of the motion of charge carriers in InAs layer, the absorption has a strictly resonant character, and the intensity of the off-diagonal transitions is strongly suppressed in comparison with the intensity of the diagonal transitions.

## Nanoparticle Mediated Release from Polymersomes under Single Pulsed Femtosecond Irradiation

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### Abstract

The self-assembly of amphiphilic diblock copolymers into polymeric vesicles, commonly known as polymersomes, is an area of high interest in research due to the potential applications in the field of drug delivery. Polymersomes are fully synthetic robust vesicles comprised of a hydrophobic membrane and a hydrophilic core, providing the ability for stable dual-encapsulation of a variety of molecules. Methods have been developed for triggered encapsulant release using ultrafast, single-pulse irradiation with visible and near infrared light to provide a non-invasive method of achieving spatial and temporal control. We have shown that the incorporation of gold nanoparticles (AuNP) within the vesicle membrane provides wavelength specific vesicle rupture at 532 nm. The encapsulation of gold nanorods provides the ability to shift the polymersome response wavelength to the near-infrared.

## Single Step Hydrophobic Functionalization of Gold Nanoparticles

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### Abstract

The ability to locate gold nanoparticles (AuNPs) into a hydrophobic region is of vital importance to their application in biomedical applications. Here, we present a simple single-step method based on the Pulsed Laser Ablation in Liquid (PLAL) technique to produce alkanethiol functionalized gold nanoparticles suspended in decane. Considerations will be discussed to subvert the photodegradation and subsequent coating of the AuNPs with unwanted hydrocarbons. Additionally, particles size distribution and colloid stability will be discussed in terms of alkanethiol concentration and laser parameters (e.g. wavelength, fluence, and pulse duration). Various alkane chain lengths were used to modify the degree of hydrophobicity. The use of a secondary post-irradiation step is shown to greatly reduce particle size and polydispersity, but can come at the cost of purity.

## Niazimicin and its Phytonanoparticle Modulate Caspase-9 Splice Variants, IAP's and NFκB Signalling in Lung Cancer Cells

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<sup>2</sup>Department of Chemistry, Faculty of Applied Sciences, Durban University of Technology, Durban, 4001, South Africa

### Abstract

**Background:** *Moringa oleifera* (MO), a traditional medicinal tree, is found throughout South Africa. Its several medicinal properties include anticancer and anti-inflammatory activities which have been attributed to bioactive compounds such as Niazimicin. Gold nanoparticles have shown good anticancer potential. We investigated the antiproliferative effect of Niazimicin and their synthesised gold nanoparticles (NAuNP) in A549 lung cancer cells.

**Methods:** NAuNP was synthesised via a one-pot green synthesis technique. Cytotoxicity of Niazimicin and NAuNP was evaluated in A549 cells (MTT assay). Apoptosis was assessed by quantifying caspase-3/7, -8, -9 and ATP levels (luminometry). The mRNA expression of SRSF1 and caspase-9 splice variants was determined by qPCR. Protein expression of SRSF1 (SRp30a), ILP2 (BIRC8), cIAP1 (BIRC2), cIAP2 (BIRC3), c-myc, p-p53, p53, Smac/DIABLO, Bax, Bcl2, NFκB and IκBα was assessed by western blotting.

**Results:** Niazimicin and NAuNP induced a dose-dependent decline in A549 cell viability with IC<sub>50</sub> of 456.7 µg/ml and 264.1 µg/ml respectively (24h). Niazimicin and NAuNP induced apoptosis by significantly increasing caspase-9, -3/7 activities and significantly decreasing caspase-8 and ATP levels. A significant decrease in protein expression of ILP2 (BIRC8), cIAP1

(BIRC2), cIAP2 (BIRC3), c-myc, Bcl2, NF $\kappa$ B and I $\kappa$ B $\alpha$  was noted. In addition, there was a significant increase in SRSF1 mRNA and protein expression of SRSF1 (SRp30a), p-p53, p53, Bax and Smac/DIABLO. Alternate splicing was activated with caspase-9a significantly increased and caspase-9b being reduced.

**Conclusion:** Niazimicin and N AuNP possess antiproliferative effects via activating alternate splicing, pro-apoptotic proteins and reducing anti-apoptotic caspase-9b, its interaction with IAPs and NF $\kappa$ B signalling responsibly for non-small cell lung carcinoma.

## **Preparation and Characterization of Poly( $\gamma$ -Glutamic Acid)/Tyramine Photo-Crosslinkable Hydrogels for 3D Bioprinting**

**Hee Cheol Kim<sup>\*</sup>, Hyeong Chan Nam, Ji Youn Shin, Su Jun Kim and Won Ho Park**

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### **Abstract**

Poly( $\gamma$ -Glutamic acid) ( $\gamma$ -PGA) is natural occurring anionic biopolymer secreted by *Bacillus subtilis* strain.  $\gamma$ -PGA consists of the amide bond between  $\alpha$ -amino group and  $\gamma$ -carboxy group.  $\gamma$ -PGA is water soluble, biocompatible, biodegradable and non-toxic polymer. Due to these advantages,  $\gamma$ -PGA gains interest for biomedical application, such as wound dressing, tissue engineering, and 3D bioprinting.

3D bioprinting is an emerging technology that fabricate three-dimensional complex structure for biomedical application. 3D bioprinting is able to directly produce the various shapes required by the patient, such as tissue-like structure, Y shape blood vessel shape, and ear shape. Among typical 3D bioprinting methods, the extrusion 3D bioprinting that laminates filaments is widely used in biomedical fields due to the high cell activity. The stability of filament is critical factor for 3D bioprinting and depends on bio-ink viscosity and crosslinking method. In the previous studies, the stability of filament was obtained by the UV crosslinking method, but its biomedical application is limited due to the cytotoxicity of photoinitiator.

In this study,  $\gamma$ -PGA based bio-ink was prepared by introducing tyramine to carboxylic acid group, and  $\gamma$ -PGA/tyramine photo-crosslinkable hydrogel was fabricated by visible light crosslinking system. The performances including the mechanical properties, gelation behavior, swelling ratio and gel fraction of hydrogels were examined in detail. Also, 3D bioprintability of photo-crosslinkable hydrogel was evaluated.

## **Biodegradable Poly(Lactic Acid) Microbeads by Melt Electrospaying**

**Hyeong Chan Nam<sup>\*</sup>, Su Jun Kim, Ji Youn Shin, Hee Cheol Kim and Won Ho Park**

*Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, South Korea*

### **Abstract**

The microbeads (MBs) are plastic particles with size from 5  $\mu$ m to 1 mm, which are promising materials for use in various applications such as facial scrub and drug encapsulation carrier. These MBs have been usually made from non-biodegradable polymers. However, the environmental issue is recently raised due to their non-degradation and adsorption property of persistent organic pollutants (POPs) in the marine condition, resulting in the ecocide of marine environment. Above all, almost the MBs have been prepared by wet process such as emulsification, spray dry which use a number of toxic solvents. Due to these severe problems, enormous countries have already started to ban the use of non-degradable MBs. Therefore, it is urgent to develop biodegradable MBs via eco-friendly methods.

Poly(lactic acid) (PLA) is a biodegradable aliphatic polyester which can obtain using raw materials from nature. PLA has many excellent properties, such as biocompatibility, high mechanical strength, cost effectiveness, and melt processability.

Electrospray is a simple and effective method for bead preparation, and is applicable to both polymer solution and melt. Also, this process is affected by various processing parameters, such as voltage and needle diameter.

In this study, the molecular weight of PLA was controlled by electron beam (E-beam) irradiation, which cleavages the PLA molecular chains, and then the MBs were prepared by eco-friendly melt electrospaying process. The various physical/chemical properties, such as morphology, biodegradability and POPs adsorption properties were investigated, and the possibility of PLA MBs for an alternative to non-degradable MBs was confirmed.

## Rheological Properties of Dual Thermal and Photo-crosslinked Methylcellulose Hydrogel

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### Abstract

Hydrogel is hydrophilic polymer structures containing large amounts of water which are physically or chemically cross-linked three-dimensional networks. Also, it has properties similar to biological tissues and has been applied to biomedical fields including tissue regeneration, drug delivery systems, biochemical sensors. Among the various hydrogels, the stimuli-sensitive hydrogels exhibit a reversible sol-gel transition through external stimuli, such as temperature, pH, pressure, and electrical signals. By contrast, the photo-crosslinked hydrogel is chemically cross-linked via covalent bonding and thus irreversible, and also have a strong gel strength.

The aqueous methylcellulose (MC) solution is known to exhibit a sol-gel transition depending on the temperature, and its gelation behavior can be controlled by the molecular weight, concentration and additive types. The gelation of MC solution occurs by an intermolecular hydrophobic interaction between the methoxy groups in MC molecules. So, its strength is too weak to be applied. In order to improve the mechanical strength, dual thermal and photo-crosslinked MC hydrogel was synthesized via two-step processes. Firstly, some carboxyl groups were introduced to the MC backbone. Next, tyramine groups were coupled to the carboxyl groups of the MC-COOH using the conventional carboxyl-amine coupling reaction. The tyramine modified MC (MC-Tyr) was fabricated into hydrogels using crosslinking system by visible light.

In this study, the degree of tyramine substitution was investigated at various reaction conditions. Also, the gelation behavior of the MC-Tyr solution was examined according to the type and concentration of photo-initiators and irradiation time.

## Electrospun PVA Nanofibrous Membranes Containing Chitin/Chitosan Nanowhiskers for Dye Adsorption

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### Abstract

Chitin is the second most abundant natural polymer on the planet, and can be obtained from shells of crustaceans, exoskeletons of insects and microorganisms. Chitosan has a degree of deacetylation of more than 50%. Due to its biocompatibility and biodegradability, it is used in various fields such as agriculture, foods, cosmetics, and wastewater treatment. The removal of the amorphous region by acid hydrolysis of chitin enables the extraction of chitin nanowhiskers (CtNWs) and chitosan nanowhiskers (CsNWs), which are nano-sized needle-shaped crystals. The CtNWs have a high aspect ratio and a large surface area. Thus, they are effective to remove the organic dye pollutants in waste water solution because the functional groups, such as hydroxyl groups and amine groups, are rich on their surface.

Poly(vinyl alcohol) (PVA) has non-toxic, water-soluble, biocompatible, and biodegradable properties which is widely used in the biomedical fields. Also, it has excellent fiber forming ability and highly hydrophilic properties.

The electrospinning is used to make nanofiber from polymer solutions and melts. The electrospun nanofiber can be a future material for wastewater treatment because of its attractive properties, such as porosity, tunable pore size and high surface area to volume ratio.

In this study, PVA nanofibrous membrane containing various contents of CtNWs/CsNWs was fabricated by electrospinning, and its physical/chemical properties were examined. The adsorption capacity of the nanofibrous membrane was evaluated using methylene blue, and its applicability as an adsorbent for wastewater treatment was confirmed.

## Catalytic Activity of Electrochemically Exfoliated Graphite Decorated with Silver Nanoparticles Synthesized by UV-irradiation Method

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### Abstract

The catalytic activity of electrochemically exfoliated graphite decorated with silver nanoparticles (EEG@Ag NPs) was assessed against toxic dyes (methylene blue and methyl orange) and 4-nitrophenol. It was previously shown, that the silver

nanoparticles can accelerate the reduction process, which is related to the electron transfer from NaBH<sub>4</sub> into organic compounds. Moreover, well dispersed ultrafine silver nanoparticles with defected surface have very high catalytic activity. Therefore, to improve electron transfer into dyes and 4-nitrophenol nanocomposite with Ag NPs was synthesized by deposition of metallic nanoparticles on the surface of graphite-based catalyst support.

The electrochemically exfoliated graphite was synthesized using potassium iodate as new electrolyte. The EEG@Ag NPs were synthesized by simple and low-cost UV-irradiation method without using organic modifiers. The structure and morphology of synthesized nanocomposite were examined using X-ray diffraction method, electron microscopy, Raman spectroscopy and Fourier-transform infrared spectroscopy. The nanocomposite was tested as catalyst for reduction of different organic compounds. It was confirmed, that the EEG@Ag NPs can be used to reduce methylene blue, methyl orange and 4-nitrophenol. The high catalytic activity can be associated with ultrafine size of Ag NPs and high adsorption of organic molecules on the surface of EEG.

## Lattice and Optical Properties of Semiconductor Pb<sub>1-x</sub>Ag<sub>x</sub>S Solid Solutions

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### Abstract

Fine powders of single-phase limited cubic solid solutions Pb<sub>1-x</sub>Ag<sub>x</sub>S based on PbS with a metal sublattice alloyed with silver have been synthesized by chemical bath co-deposition from aqueous solutions of lead acetate Pb(CH<sub>3</sub>COO)<sub>2</sub>, silver nitrate AgNO<sub>3</sub>, thiocarbamide N<sub>2</sub>H<sub>4</sub>CS, ammonium hydroxide NH<sub>4</sub>OH, and sodium citrate Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>. The maximum relative content of silver in prepared solid solutions Pb<sub>1-x</sub>Ag<sub>x</sub>S reaches  $x = 0.15$ . The thermal expansion of semiconductor solid solutions Pb<sub>1-x</sub>Ag<sub>x</sub>S was measured by dilatometry method in the temperature range 295-580 K. Substitution of Pb by Ag in Pb<sub>1-x</sub>Ag<sub>x</sub>S leads to a decrease in the coefficient of thermal expansion associated with a change in the anharmonicity of atomic vibrations and a weak increase in the elastic properties. For single-crystal particles PbS and solid solutions Pb<sub>1-x</sub>Ag<sub>x</sub>S, spatial distributions of the elastic modulus  $E$ , Poisson's ratio  $\mu$ , and linear compressibility  $\beta$  as a function of the direction  $[hkl]$  are found.

The optical properties of the synthesized fine powders PbS, Ag<sub>2</sub>S and Pb<sub>1-x</sub>Ag<sub>x</sub>S have been studied from the reflectance spectra, and band gap  $E_g$  of the PbS, Ag<sub>2</sub>S and Pb<sub>1-x</sub>Ag<sub>x</sub>S powders was determined from these reflectance spectra. To calculate the band gap energy of the synthesized sulfide powders, the Kubelka-Munk function was used. Calculation has shown that band gap  $E_g$  for fine powders PbS, Pb<sub>0.92</sub>Ag<sub>0.08</sub>S, Pb<sub>0.88</sub>Ag<sub>0.12</sub>S and Ag<sub>2</sub>S changes from 0.46 to 0.89 eV. Thus, the replacement of lead with silver in PbS is accompanied by an increase in the band gap width.

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## TiO<sub>2</sub> Nanotubes Arrays Modified by Conjugated Polymers for Photocatalytic Application

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### Abstract

Photocatalytic hydrogen generation in the water splitting process is an attractive and promising route, which allow to obtain pure energy. Because of the majority of photocatalysts are active just under UV-Vis light, there are necessity to synthesis of materials active under visible light. The composite contains TiO<sub>2</sub> nanotubes and conjugated polymers with a narrow band gap could be as photocatalyst for photochemical water splitting, CO<sub>2</sub> photoconversion and photodegradation of pollutant in aqueous and gas phase.

The aim of this work was synthesis of the photocatalyst that contains hierarchical ordered TiO<sub>2</sub> nanotubes arrays modified by conjugated polymer for photocatalytic application. The TiO<sub>2</sub> nanotubes with the different morphology (length, diameter, space between nanotubes) were obtained via anodic oxidation of titanium foil. The morphology was controlled by electrolyte composition used during anodization. Then, material was used as the working during electrodeposition of the polymer layers via cyclic voltammetry. Thiophene and its derivatives with benozthiadiazole was used as monomers. The length of a polymer chain was controlled by number of cycles of cyclic voltammetry influent on the band gap of the polymers. Moreover, electrodonating and electrowithdrawing units presented in the chain additionally declined the band gap and allowed to excite photocatalyst by visible irradiation.

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## Silver Nanostructures with Tuned Optical Properties by Photochemical Approach

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### Abstract

Photochemistry is a powerful tool for controlling size and shape of metal nanoparticles. In this context, a fast and green photochemical approach capable of generating nano-layers of silver nanoparticles on glass substrates was developed [1, 2].

The influence of chemical and photonic parameters on the morphology of silver nanostructures was studied with a view to adjusting their size and shape so as to tune their plasmonic characteristics and optical properties. In a further approach, a particular process was developed to control the spatial organization of the nanoparticles in order to generate thin layers exhibiting both a high electric conductivity and a fair reflectivity.

Promising prospects of application of such smart plasmonic surfaces should open up as biocide films, electronic components, surface enhanced Raman scattering (SERS), optical sensors or light filters.

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## Best Poster Award Winners

Chosen by Associate Editors Professors Christian Riekkel and Eugenia Peshkova

The two authors of the best posters chosen for the NWC Poster Award considering the importance of the topics. Namely:

1. **Charlette Tilo**, Durban University of Technology, South Africa (SA), entitled “Niazimicin and its Phytonanoparticle Modulate Caspase-9 Splice Variants, IAP’s and NFκB Signalling in Lung Cancer Cells”, until now the most frequent death cause in cancer decease;
2. **Mariam Mezghani**, an Engineer in Material Science who works in a group of the CNRS at the Institute of Materials Science of Mulhouse in France, with research activity focused on the photochemistry applied to the synthesis of nanoparticles and nanomaterials.

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