



SYMPOSIUM F

Established and emerging nanocolloids: from synthesis & characterization to applications

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Symposium Organizers:

Pascal André, University of St Andrews, UK

Mathieu Maillard, LMI / Département de Chimie, Villeurbanne, France

Gordana Dukovic, University of Colorado Boulder, USA

Laurence Motte, Université Paris 13, Bobigny, France

Richard Tilley, School of Chemical and Physical Sciences, Wellington, New Zealand

PROGRAM VIEW : 2014 Spring

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Established and emerging nanocolloids: from synthesis & characterization to applications

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Synthesis, Characterisation and "Self/triggered" Assembly of nanoColloids : Laurence Motte, Mathieu Maillard, Liberato Manna

09:00

Colloidal Inorganic Nanocrystals: their Assembly and the Study of their Chemical and Structural Transformations**Authors :** Liberato Manna**Affiliations :** Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova (Italy)

Resume : Colloidal inorganic nanocrystals (NCs) are among the most exploited nanomaterials to date due to their extreme versatility. Research on NCs went through much advancement in the last fifteen years, for example in the synthesis, which opened up the possibility to control their size, shape and topology in chemical composition. An additional step forward was the creation of a wide range of superstructures from the assembly of such NCs, which can be thought of as new types of artificial solids. This, coupled with the possibility to replace the native ligands on the surface of the NCs with shorter molecules, down to single atom ligands, has conferred unique electrical features to films of NCs that make them attractive for low cost alternatives to many technologies. Progress also came from the study of chemical transformations in nanostructures, most notably via cation exchange, which involves replacement of the sublattice of cations in a crystal with a new sublattice of different cations, while the sublattice of anions remains in place. Also, a new field of study has emerged recently, aiming at investigating the transformations in colloidal synthesized nanomaterials under conditions like thermal annealing and/or irradiation. In part this research is boosted by the recent availability of microscopy tools by which one can follow the transformations on individual NCs in-situ, i.e. when such perturbations are actually applied to the sample. The present talk will highlight the recent progress by our group in assembly and in the study of chemical and structural transformations in NCs.

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09:30

In Situ Characterization of Silver Nanoparticle Synthesis in Maltodextrin Supramolecular Structures**Authors :** Nelson S. Bell, Darren R. Dunphy, Timothy N. Lambert, Ping Lu† and Timothy J. Boyle**Affiliations :** Nelson S. Bell; Timothy N. Lambert; Ping Lu; and Timothy J. Boyle Sandia National Laboratories P.O. Box 5800 Albuquerque, NM 87185 Darren R. Dunphy; University of New Mexico Center for Microengineered Materials Department of Chemical and Nuclear Engineering Albuquerque, NM 87131-0001

Resume : A simple, room temperature synthesis of silver nanoparticles (Ag NP) was developed from the reaction of silver nitrate and maltodextrin under alkaline conditions. In this reaction, the maltodextrin acts as both the reducing agent and stabilizing colloidal surfactant. UV-vis spectroscopy, small angle X-ray scattering and Raman spectroscopy provide in situ characterization of the growth nuclei and the subsequent particle evolution. Two stages of Ag NP formation were identified, beginning with size distribution focusing conditions that yielded uniform, sub-5 nm Ag nanoparticles within 6 h. This was followed by aggregation of the particles that ultimately combined into a narrow distribution of 30-35 nm diameter Ag NP by 24 h. Maltodextrin supramolecular structures acting as micelle-like environments for nucleation and aggregation are proposed as the route for developing the final particle size and distribution. Optimized conditions produce nanoparticles with a mean diameter of 30 nm at

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high concentration. Particles were found to be stable in aqueous solutions over an extended period of time. Furthermore, the NPs could be easily precipitated using methanol and stored as dry products. Effective re-dispersion of the Ag NP was achieved by the addition of deionized water. This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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09:45

Ultrathin gold nanowires: growth mechanism and assembly by nanoxerography

Authors : L.-M. Lacroix, P. Moutet, A. Loubat, M. Imperor-Clerc, L. Ressler, G. Viau

Affiliations : LPCNO, Universite de Toulouse, INSA-UPS-CNRS UMR 5215, F-31077 Toulouse, France LPS, Universite Paris-Sud CNRS UMR 8502, Bat. 510, F-91405 Orsay, France

Resume : Recently, ultrathin gold nanowires (NWs) prepared by reduction of HAuCl₄ in solution of oleylamine (OY) attracted lots of interest due to their size homogeneity (diameter 1.7 nm, micrometer length) [1] with application as foldable optoelectronics membranes [2,3] or elastic coiled springs [4]. Their unique 1D feature confers them remarkable conductivity properties such as quantum phenomena at room temperature [5,6] but the study of the electronic properties of single NW still remains a technological challenge and requires a good understanding of their physical properties. SAXS, NMR and XPS studies allowed us to describe the self assembly of ultrathin Au NWs into a hexagonal super-lattice with a parameter of 9.7 nm well explained by a OY Cl-/OY bilayer at the surface of each NW and suggests a 1D micellar growth mechanism [7]. We have also showed that these Au NWs dispersed in hexane exhibit a negative electric charge that makes them well-suited for a Coulomb force directed assembly by AFM nanoxerography. Isolated NWs were trapped on positive patterns at the surface of PMMA thin layers using this technique opening the way to the connection of individual NWs by soft lithography. 1 H. Feng et. al, Chem. Comm., 2009, 1984 2 Y. Chen et al., Adv. Mater. 2013, 25, 80 3 A. Sanchez-Iglesias et al., Nano Lett. 2012, 12, 6066 4 J. Xu et al., J. Am. Chem. Soc. 2010, 132, 11920 5 S. Pud et al., Small, 2013, 9, 846 6 A. Loubat et al., Nano Res. 2013, 6, 644 7 A. Loubat, submitted

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10:00

Self-Assembly of Colloidal Hexagonal Bipyramid- and Bifrustum-shaped ZnS Nanocrystals into Two-Dimensional Superstructures

Authors : Ward van der Stam, Anjan P. Gantapara, Quinten A. Akkerman, Giuseppe Soligno, Johannes D. Meeldijk, René van Roij, Marjolein Dijkstra, and Celso de Mello Donegá

Affiliations : Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht University, P.O. Box 80000, 3508 TA Utrecht (The Netherlands); Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht (The Netherlands); Institute for Theoretical Physics, Utrecht University, Leuvenlaan 4, 3584 CE Utrecht (The Netherlands); Electron Microscopy Utrecht, Utrecht University, 3584 CH Utrecht (The Netherlands)

Resume : Self-assembly of colloidal nanocrystals (NCs) into ordered superlattices (SLs) is emerging as a versatile approach to design and fabricate novel metamaterials with tailored optoelectronic properties, which are promising for a variety of devices. Current advances in the synthesis of colloidal NCs have extended the ability to control the size, shape and composition, yielding a wealth of complex anisotropic and hetero NCs. Moreover, novel theoretical and simulation techniques have been developed in recent years, allowing more complex problems to be solved. Here, we present an experimental, theoretical and simulation study of the self-assembly of colloidal hexagonal bipyramid- and hexagonal bifrustum-shaped ZnS NCs into two-dimensional SLs. The minimum free energy configurations of individual NCs at the solvent-air interface were calculated and used in isothermal-isobaric Monte Carlo simulations to determine the phase behavior of the ensemble of NCs. The agreement between experimentally observed and simulated NC superstructures is very good, showing that under our experimental conditions the self-assembly is primarily driven by minimization of the interfacial free energies and maximization of the packing density. Interestingly, our work shows that small tip truncation of hexagonal bipyramidal NCs changes the symmetry of the SL from hexagonal to tetragonal, highlighting the importance of shape control in the fabrication of functional materials by self-assembly of colloidal NCs.

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10:15 Discussion/Coffee Break

10:30 **Green Nanolab in a Leidenfrost Drop****Authors** : R. Abdelaziz¹, M. Elbahri^{1,2}**Affiliations** : ¹ Nanochemistry and Nanoengineering, Institute for Materials Science, Faculty of Engineering, University of Kiel, Kaiserstrasse 2, 24143 Kiel, Germany. ² Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Str. 1, 21502 Geesthacht, Germany**Resume** : One of the hot topics of nanotechnology is to develop sustainable method of creating nanoparticles and their integration into useful systems in a simple, economic and eco-friendly green way. A promising candidate for this job is the overheated and charged, green chemical reactor in a form of Leidenfrost drop^{1,2}. Our recent findings showed that if a liquid drop of a precursor solution touches a hot surface which is at a temperature much higher than the boiling point of the liquid, the lower part of the droplet is evaporated, an overheated zone is generated, charges are separated and hence a new vein of green nanochemistry in a levitated droplet is demonstrated³. The levitated Leidenfrost drop is capable of fabricating nanoparticles, creating nanoscale coatings on complex objects and designing porous metal in suspension and foam form. A superhydrophilic and thermal resistive metal-polymer hybrid foam has been successfully fabricated and tested. Our main target is upscaling this method to produce nanopowder of different materials for industrial applications. We believe that the presented nanofabrication technique will be a promising strategy towards the sustainable production of functional nanomaterials. [1] Elbahri et al.: DE/EP/US 2009269495A1 [2] Elbahri et al."Anti-Lotus Effect for Nanostructuring at the Leidenfrost Temp." Adv. Mater., 19, (2007) 1262 [3] Abdelaziz et al.: "Green chemistry and nanofabrication in a levitated Leidenfrost drop" Nat Commun., 4, (2013)

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10:45 **Ultrasmall silicon nanoparticles: preparation strategies and bioapplications****Authors** : N. Licciardello* , C.-W. Hsu , E. A. Prasetyanto , S. Hunoldt , K. Viehweger , H. Stephan , L. De Cola **Affiliations** :  Institut de Science et d'Ingénierie Supramoléculaires (I.S.I.S.) Université de Strasbourg, France;  Karlsruher Institut für Technologie (KIT) Karlsruhe, Germany;  Helmholtz-Zentrum Dresden-Rossendorf Institute of Radiopharmaceutical Cancer Research (HZDR) Dresden, Germany**Resume** : The use of nanoparticles in multimodal bio-imaging is attracting increasing interest, but toxicity and accumulation in organs still limit their in vivo applications. Silicon nanoparticles (Si NPs) are very promising in this respect as their size, 1.5 - 4 nm, can allow body excretion. In addition Si NPs are photo- and chemical stable, possess bright tunable luminescence and can be covalently functionalized with desired molecules. Indeed several techniques have been described to obtain Si NPs [1-3] with different sizes and bearing various functional groups. Here we report on some optimized wet chemistry techniques to prepare ultrasmall (< 5 nm) Si NPs and, in particular, the focus is on microemulsion methods and hydrothermal synthesis. The obtained Si NPs can bear different functional groups, allowing a wide spectrum of subsequent conjugations. Once functionalized and purified, Si NPs were characterized by HR-TEM and IR spectroscopy, and their photophysical properties were investigated. Reactivity and properties of the NPs obtained by various methods will be compared and the results of in vitro and in vivo experiments will be shown to demonstrate the great potentialities of such ultrasmall Si NPs. This work was financially supported by Helmholtz Virtual Institute "Nano-Tracking", Agreement No. VH-VI-421 1. J. H. Warner et al., Angew. Chem. Int. Ed. 2005, 44, 4550 - 4554 2. M. Rosso-Vasic et al., Small, 2008, 4, 1835-1841 3. Y. Zhong et al., J. Am. Chem. Soc., 2013, 135, 8350-8356

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11:00 **Shape- and size- controlled synthesis of self-assembly Supercrystals from Various Polyhedral nanocrystals****Authors** : Chun-Ya Chiu, Michael H. Huang**Affiliations** : Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan**Resume** : Fabrication of submicron- to micron-sized devices from inorganic nanocrystals normally requires external force to direct their self-organization into ordered structures. In this work, self-assembly supercrystals with finely defined sizes and shapes were synthesized using gold, palladium, and lead

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sulfide nanocrystals with nanocubes and octahedra as building blocks by Solvent Evaporation Technique and diffusional methods. These nanocrystals can contact each other and form submicron- to micron-sized supercrystals with cubic, octahedral, rhombic dodecahedral, and triangular shapes. The self-assembly of nanocrystals have been demonstrated to be strongly shape-guided and size-guided. The accumulation process of nanoblocks was controlled by the dispersion and the superlattices with different crystalized sizes were fabricated. The supercrystals prepared were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and powder X-ray diffraction (XRD), and the microstructures were studied by small-angle X-ray scattering (SXAS) technique. The growth process also investigated. These supercrystals are considered novel superstructures and may show interesting mesoporosity and electrocatalysis properties.

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11:15 **Turkevich in new robes: 3 key questions answered for an old gold nanoparticle synthesis**

Authors : Maria Wuithschick, Alexander Birnbaum, Klaus Rademann, Jörg Polte

Affiliations : Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin

Resume : More than 60 year ago, J. Turkevich described the reduction of HAuCl₄ with sodium citrate which is today one of the most commonly used syntheses of colloidal gold nanoparticles. Many scientific publications provided modified reaction conditions which lead to different particle sizes allowing a modification of the materials' physical properties. However, these recipes were derived from variation of synthesis parameters in a trial and error approach rather than by a comprehensive understanding of the particle growth mechanism. Recently, we showed that particles are formed through a sequence of growth steps comprising fast initial formation of small nuclei, coalescence into bigger seed particles, slow growth of seed particles sustained by ongoing reduction of Au³⁺, and subsequent fast reduction ending with the complete consumption of the precursor species. By an extensive SAXS and UV-vis study we are now able to connect knowledge on all relevant physical and chemical processes with the growth mechanism and answer 3 key questions: How do the different physicochemical processes in the colloidal solution affect the growth mechanism? What determines the final particle size? How can the final size be adjusted precisely? Hence, this contribution addresses two relevant issues: (i) the comprehensive understanding of the most common gold nanoparticle synthesis and (ii) instructions for the deliberate synthesis with sizes on demand.

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11:30 **Synthesis of metal oxide nanoparticles. Shape control.**

Authors : Susagna Ricart,¹ Alba Garzón-Manjón^{1,2}, Eduardo Solano^{1,2}, Leonardo Perez-Mirabet², María de la Mata¹, Roger Guzmán¹, Jordi Arbiol¹, Teresa Puig¹, Xavier Obradors¹, Ramón Yáñez², Josep Ros²

Affiliations : 1) Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Cerdanyola del Vallès, Barcelona, Spain. 2) Dept. Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, Barcelona, Spain

Resume : Polyol (thermal, microwave) and solvothermal methodologies are used to synthesize different metal oxides nanoparticles such as magnetite (Fe₃O₄), cerium dioxide (CeO₂) and zirconium dioxide ZrO₂. By modifying the precursors, and following the same synthetic route, it is possible to control the size and shape of the nanocrystals obtained. The general route is carried out in triethylene glycol (TREG) media, due to its high boiling point and, which acts also as a capping ligand of the nanoparticles, stabilizing them in polar solvents. Nanoparticles have been characterized by several common physical laboratory techniques: HRTEM, IR, X-Ray Powder Diffraction (XRPD), magnetometry via Superconducting Quantum Interference Device (SQUID). With these techniques, the final size, shape, composition, crystal structure and magnetic behaviour have been studied, showing the high quality crystals generated. In addition, we demonstrate the high efficiency of all three one-pot methodologies that have been optimized to synthesize different families of nanoparticles. In the case of magnetic nanoparticles appropriate tuning of the size and shape of nanoparticles gives an added value as they can exhibit shape dependent phenomena and subsequent utilization of them as building blocks for the fabrication of nanodevices is a matter of significant interest. An easy shape-controlled synthesis of magnetite nanoparticles by modifying the 1,5-substituents of propanedionate chain of the iron (III) precursor without changes on the additive or synthetic route is presented. It is shown the effect brought about by the presence of fluorine either in the substituent or in the media; in this case

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formation of FeF₂ nanocrystals is observed. The research leading to these results has received funding from EU-FP7 NMP-LA-2012-280432 EUROTAPES project

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11:45

MAGNETIC NANOPARTICLES, 2D AND 3D STRUCTURES BY MICROWAVE ASSISTED THERMAL DECOMPOSITION

Authors : Oana Pascu, Muling Zeng, Anna Laromaine, Gervasi Herranz, Anna Roig

Affiliations : Institut de Ciència de Materials de Barcelona (CSIC) Campus de la UAB, 08193 Bellaterra, CATALONIA, SPAIN

Resume : Microwave chemistry is being accepted as a non-conventional, fast, clean, economic and eco-friendly method representing a new trend not only for modern organic synthesis but also for inorganic and hybrid nanomaterials. We will present our recent works on the materials obtained with this versatile approach that has enable us the fabrication of nanoparticles [1] and other complex nanocomposite materials [2], including magnetic cellulose and 3D magneto photonic materials[3] Magneto-photonic crystals are receiving attention due to prospects for new photonic devices with enhanced magneto-optical response and non-reciprocal optical effects. To look for this enhanced functionality we have fabricated three dimensional magneto-photonic crystals by infiltrating the voids of direct and inverse opals with magnetic nanoparticles using a microwave assisted route. High magnetic load and long-range order have been fundamental to obtain large magneto-optical responses at wavelengths near the photonic band-edges. Results demonstrate the potential of exploiting microwave assisted synthesis to obtain novel functional magnetic nanocomposites intended for photonic applications by using light polarization in photonic structures as a powerful strategy to customize the magneto-optical spectral response of magnetic nanoparticles. 1.J. Phys. Chem. C 116 (2012), 15108 2.European Journal of Inorganic Chemistry (2012), 2656 3.Nanoscale 3 (2011), 4811

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12:00

Lunch Break

Optical & Magnetic Probing of nanoParticles : Pascal André, Richard Tilley, Jean-Yves Bigot

13:45

Ultrafast magnetism in nanoparticles studied with femtosecond laser pulses

Authors : J.-Y. Bigot*, H. Kesslerwan, V. Halté, M. Vomir

Affiliations : Institut de Physique et Chimie des Matériaux de Strasbourg, Université de Strasbourg and CNRS 23 rue du Loess, 67034 Strasbourg, France

Resume : When studying nano-materials with ultrashort optical pulses, with femtosecond duration, the objects are suddenly brought out of equilibrium and one can observe the relaxation of energy and momentum in a broad time scale ranging from tens of femtoseconds to a few nanoseconds. For magnetic systems, the momentum is the important dynamical quantity to determine as it carries the information on the magnetic state. In particular it allows understanding how the magnetic moment of the nanoparticles (the macro-spin) varies due to the new equilibrium state set after the pulse excitation. In that context the dynamics strongly depends on the anisotropy of the magnetic nano-systems which are considered. In this contribution we will illustrate the effects related to this dynamical change of anisotropy. We first examine the case of CoPt and core-shell Co-Pt nanoparticles. For CoPt nanoparticles, the large anisotropy defines the equilibrium state of the magnetization. The macro-spin can therefore start precessing after the optical perturbation sets a new equilibrium state. This precession can be observed during hundreds of picoseconds and it is an ideal situation to characterize the FMR (ferromagnetic resonance) parameters of the magnetic nano-objects. In the case of the core-shells, the absence of anisotropy axis prevents from observing a clear dynamical torque and the magnetization dynamics simply results from a heating of the spins which transfer their momentum to the lattice on the picosecond time scale. Second, we address the important question of the inter-particles interactions. We will show how it can affect either the energy relaxation (charge dynamics) or the magnetic momentum (spins dynamics) in assemblies of cobalt super-paramagnetic nanoparticles. For well-organized assemblies, like for example in self-assembled supracrystals of Co nanoparticles, a spectacular collective vibration of the nanoparticles takes place. In contrast, the magnetic

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order due to inter-particles dipolar interaction is not strong enough to induce major dynamical change of the macro-spin, else than the single particle case. The spatial limits defining the conditions of collective effects will be examined in a theoretical model. Finally we will give some perspectives that may lead to further interesting material developments regarding the design of anisotropic nano-systems like for example in cobalt ferrites. JYB acknowledges financial support from the European Research Council via the ERC Advanced Grant ATOMAG (ERC-2009-AdG-20090325 247452) and the Agence Nationale de la Recherche in France, Labex NIE.

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14:15

Optical properties of HgTe nanocrystals

Authors : G. Allan a, C. Delerue a, A. Al-Otaify b, D.J. Binks b, S.V. Kershaw c, S. Gupta c, A.L. Rogach c

Affiliations : aIEMN-Department ISEN, UMR CNRS 8520, Lille 59046, France. bSchool of Physics and Astronomy & Photon Science Institute, University of Manchester, Oxford Road, Manchester M13 9PL, UK. cDepartment of Physics and Materials Science & Centre for Functional Photonics (CFP), City University of Hong Kong, Hong Kong S.A.R.

Resume : HgTe nanocrystals presently receive growing interest because the negative band gap in bulk HgTe enables tunability of the gap from the infrared to the near infrared in quantum dots thanks to the quantum confinement. Therefore we propose a tight-binding model of HgTe which gives an accurate band structure in a wide energy range of energy compared to recent ab initio calculations. The inverted band structure near the Fermi level and its temperature dependence are also very well described. Using this model, we study the effects of the quantum confinement on the electronic structure of HgTe quantum dots. We calculate the optical absorption spectra of quantum dots with various shapes and diameters up to 10 nm, including excitonic effects using a configuration interaction approach [1]. The optical spectra are consistent with recent experimental data. We also simulate the multiple exciton generation and we discuss the results of ultrafast transient absorption spectroscopy experiments performed on HgTe nanocrystals. [1] G. Allan and C. Delerue, Phys. Rev. B 86, 165437 (2012). [2] A. Al-Otaify, S.V. Kershaw, S. Gupta, A.L. Rogach, G. Allan, C. Delerue and D.J. Binks, Phys. Chem. Chem. Phys. 15, 16864 (2013).

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14:30

AFM-Raman study of assembling of carbon and gold nano-particles

Authors : Angelina D Orlando, Guy Louarn, Jean-Yves Mevellec and Bernard Humbert

Affiliations : Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, B.P. 32229, 44322, Nantes cedex 3, France
Angelina.d.Orlando@cnsr-imn.fr

Resume : With a strong acceleration since the year 2000 and the number of papers dedicated to a ?nano? subject, nowadays, Raman spectrometry is a method of choice to characterize and understand nano-materials and colloids. Moreover Raman offers a ?bottom-up? approach of nanostructured materials, which comes as a good complement to methods like electron microscopy or X-ray diffraction. Surface- and tip-enhanced Raman and LSPR spectroscopies have been developed over the past 15 years as unique tools for uncovering the properties of single particles and single molecules that are unobservable in ensemble measurements. Measurements of individual events provide insight into the distribution of nanoparticle properties that are averaged over in ensemble experiments. Localized optical spectroscopy can provide detailed information on the identity of molecular species and changes in the local environment, respectively. Our group develops a new approach combining an AFM and a confocal-Raman microscope, where AFM microscope is used to image and to manipulate nano-particles under the confocal optical microscope coupled at the Raman spectrometer. In this presentation, we will show the results obtained with some symmetric structures of assembling of gold nano-particles, in the vicinity of a single carbon nanotube. We will investigate the consequence on the Raman spectra as a function of the different geometries of AuNPs aggregates. We will discuss the different interactions between AuNPs aggregates and the carbon nanotube. In particular, we will focus on the enhancement of the local electrical field by metallic nano-structures to probe single object.

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Synthesis of flexible magnetoelectric hybrid films: CoFe₂O₄ nanoparticles inside ferroelectric polyvinylidene fluoride (PVDF) matrix

Authors : Laurence Ourry 1, Sofia Marchesini 1, Ngo Thi Lan 2, Silvana Mercone 2, Damien Faurie 2, Fathi Zighem 2, Sophie Nowak 1, Michel Delamar 1, Souad Ammar 1, Fayna Mammeri 1

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Affiliations : 1 ITODYS, Université Paris Diderot, Sorbonne Paris Cité, 75013 Paris, France 2 LSPM, Université Paris Nord, Sorbonne Paris Cité, 93430 Villeteuse, France

Resume : The multifunctionality of multiferroic materials strongly depends on the efficiency of couplings between different ferroic orders. Improving the magnetoelectric (ME) coupling at room temperature between ferroelectric (FE) and ferromagnetic (FM) orders can allow the manipulation of the magnetization by an electric field and vice versa, opening the way for writing and reading at low energy cost in magnetic memories. Moreover, the opportunity to control this ME coupling through a low mechanical and reversible stress using flexible hybrid films makes it more appealing for new smart applications. In this context, we first prepared CoFe₂O₄ nanoparticles (NPs) using the polyol process. Half of the NPs were functionalized in order to promote interactions between NPs and PVDF. Then, flexible CoFe₂O₄-PVDF based hybrid films were prepared by dispersing NPs in a solution of PVDF and melt processing. The polymer polar phase content and the hybrid interface between both components are key parameters for improving coupling between FM and FE phases in nanocomposite. As PVDF exhibits two main polymorphs, α (apolar phase) and β (FE phase), we first studied the influence of temperature to obtain the highest content of β phase. Finally, in situ tensile tests were combined either to X-ray diffraction in order to monitor the α to β phase transition or to near-field microscopy (in magnetic and piezoelectric force configuration) for local ME effect imaging.

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15:00

Evaluation of the elastic properties of assemblies of nanoparticles by ultrafast opto-acoustics

Authors : A. Ayouch(1), X. Dieudonné(2), G. Vaudel(1), H. Piombini(2), K. Valle(2), P. Belleville(2), V. Gusev(1) , P. Ruello(1)

Affiliations : (1) Institut des Molécules et Matériaux du Mans, UMR-CNRS 6283, Université du Maine, Avenue O. Messiaen, 72085 Le Mans, France (2) CEA, DAM, Le Ripault, BP 16, 37260 Monts, France

Resume : New functional materials are currently can be created by assembling the nanoparticles. In order to obtain the desired macroscopic properties of a new material a perfect control of the contacts between nanoparticles is necessary. Therefore, the physics and chemistry of nanocontacts are among the central issues for the design of the nanocomposites. We demonstrate that the ultrafast opto-acoustic technique, based on the generation and detection of resonance vibrations of the colloidal films by femtosecond laser pulses [1-3], i.e., resonance hypersonic spectroscopy, is very sensitive to the elastic properties of the contacts between the nanoparticles composing the films as well as to the properties of the contacts between the nanoparticles and the substrate. In particular, we observe and evaluate how strongly the interaction of the nanoparticles via either van der Waals-bonded or covalent-bonded coatings modifies such macroscopic parameter as the sound velocity in the colloidal solid. Starting from the measured resonance vibration frequencies it is possible to estimate quantitatively, first, the macroscopic elastic modulus of the colloid, second the rigidities of the nanocontacts between the nanoparticles and, finally, the surface energies of the nanoparticles coated by molecular layers. Our experimental measurements and theoretical analysis demonstrate that, by using for coating of the nanoparticles the molecular layers with high surface energy/tension, it is possible to increase the rigidities of the inter-particle contacts of the colloidal films [4]. References: [1] Thomsen, C.; Grahn, H. T.; Maris, H. J.; Tauc, J. Surface Generation and Detection of Phonons by Picosecond Light Pulses. *Phys. Rev. B* 1986, 34, 4129–4132. [2] M. Lomonosov, A. Ayouch, P. Ruello, G. Vaudel, M. R. Baklanov, P. Verdonck, L. Zhao, V. E. Gusev Nano-Scale Non-Contact Depth-Profiling of Mechanical and Optical Properties of Nanoporous Low-k Materials Thin Films , *ACS Nano*, 2012, 6 (2), pp 1410–1415. [3] C. Mechri, P. Ruello, V. Gusev, Confined coherent acoustic modes in tubular nanoporous alumina film probed by picosecond acoustics methods, *New. J. Phys.* 14 (2012) 023048. [4] A. Ayouch , X. Dieudonne , G. Vaudel , H. Piombini , K. Valle , V. Gusev , P. Belleville , and P. Ruello, Elasticity of an Assembly of Disordered Nanoparticles Interacting via either van der Waals – Bonded or Covalent-Bonded Coating Layers. *ACS Nano*, 6, 10614-10621 (2012)

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15:15

Enhanced optical and nonlinear optical properties of silicon carbide nanoparticles through fluorescent-plasmonic coupling for cell labeling applications

Authors : Maxime Bokseveld1, Ning Sui1, Marie-Virginie Salvia1, Virginie Monnier1, Yuriy Zakharko2, Vladimir Lysenko2, Luigi Bonacina3, Jean-Marie Bluet2, Yann

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Chevolot1, Eliane Souteyrand1

Affiliations : 1- Universit? de Lyon, Institut des Nanotechnologies de Lyon?INL, UMR CNRS 5270, Site Ecole Centrale de Lyon, 36 Avenue Guy de Collongue, F-69134 Ecully Cedex, France 2- Universit? de Lyon, Institut des Nanotechnologies de Lyon?INL, UMR CNRS 5270, Site Ecole INSA Lyon, 7 Avenue Jean Capelle, F-69621 Villeurbanne Cedex, France 3- GAP Biophotonics, University of Geneva, 22 Chemin de Pinchat, CH-1211 Geneva 4, Switzerland.

Resume : Metal nanoparticles are now widely used in biodetection due to their surface plasmon resonance. In presence of metal nanoparticles, fluorescence of optical emitters can be greatly enhanced thanks to plasmonic-fluorescent coupling. Metal can also provide an efficient enhancement of nonlinear optical properties such as two-photon excited fluorescence or second harmonic generation. This can offer higher sensitivities in biological imaging and the possibility to achieve multimodal detection. We have engineered tuneable plasmonic-fluorescent nanohybrids in order to enhance the fluorescence signal of silicon carbide (SiC) nanoparticles. These nanohybrids consist in Metal@SiO₂ core-shell nanoparticles onto which SiC nanoparticles are covalently grafted. The synthesis methods of these nanohybrids will be detailed. The influence of several parameters on their fluorescence properties will be investigated: nature of metal core (Au, Ag), diameter of metal core (from 20 to 150 nm) and silica thickness (from 10 to 80 nm). Finally, first results concerning the metal-enhanced nonlinear optical properties of SiC nanoparticles will be shown.

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[\(close full abstract\)](#)

15:30

Evidence of anomalous magnetic behaviour in tuned YCrO₃ nanoparticles

Authors : Inderjeet Singh, Amreesh Chandra

Affiliations : Department of Physics, Indian Institute of Technology, Kharagpur, 721302 West Bengal, India

Resume : Size confinement is a promising technology to tailor the physical properties of multifunctional systems. Recently, Cr-based systems have shown simultaneous presence of ferromagnetic, ferroelectric, photoluminescence and catalytic properties which makes them important functional materials. We report a significant enhancement in the magnetic response of YCrO₃ nanoceramics below 10K. Significant control over the particle size could be obtained by synthesizing the particle under droplet confinement in inverse miniemulsion. YCrO₃ nanoparticles shows antiferromagnetic characteristics below 140K with significant increment in the magnetic moment when the sample is cooled below 10K. The hysteresis loop nature shows a cross over to a weak ferromagnetic characteristics. This magnetic behaviour can be explained using the concept of elongated grains or mesocrystals. Interesting modulation in the ferroelectric properties are also discussed by analyzing the frequency dependent dielectric and XRD data.

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15:45

Discussion/Coffee Break

Synthesis and Crystallinity of nanoColloids : Richard Tilley, Laurence Motte, Colin Raston

16:00

Materials synthesis using vortex fluidics

Authors : Colin L. Raston

Affiliations : Centre for Nanoscale Science and Technology, School of Chemical and Physical Sciences, Flinders University, Bedford Park, SA 5042, Australia Email colin.raston@flinders.edu.au

Resume : A vortex fluidic device (VFD) which can operate under continuous flow conditions or confined mode has a wide range of applications. The microfluidic device generates thin films with intense shear, and within these films nanomaterials can be fabricated in a precise way for both bottom up and top down approaches, and can be used to control the pore size and wall thickness of mesoporous materials, and much more. Controlling chemical reactivity and selectivity is at the core of gaining access to new compounds and materials. The traditional approach of carrying reactions out using batch processing can suffer from anisotropic mixing and poor heat transfer, which can result in competing reactions, and there are issues in being able to selectively control a kinetic versus a thermodynamic product. To this end we have developed a low cost and modular vortex fluidic device (VFD),¹ for controlling chemical reactivity and selectivity in general. The VFD allows reactions to be

F.III.
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carried under scalable continuous flow conditions, which is significant also for down stream applications, such that the research reactor is the production reactor, bypassing the classical approach of pilot stage to production stage batch processing. In this continuous flow mode of operating the VFD, jet feeds deliver reagents to the base of a rapidly rotating tube (typically a 10 mm diameter NMR tube), with intense micro-mixing and shear from the viscous drag as the microfluidic thin film whirls along the tube. The thin films ensures uniform heat transfer and mixing, and the waves and ripples break the surface tensions and result in high mass transfer of gases. All molecules are treated in the same way, which can be varied by varying the VFD control parameters, including concentrations, temperature, flow rates, tilt angle θ of the tube, rotational speed, and surface contact angle, as well as using field effects (magnetic and UV). The VFD is also effective in generating thin films with intense shear for finite volumes of liquid for tilt angles $\theta \geq 0^\circ$, as a confined mode of operation.¹ Thus the VFD can be used for scaling up or scaling down under intense shear. The application of the VFD operating under both continuous flow and confined mode will be presented. These include: (i) top down synthesis of nanomaterials, as in exfoliating graphite and h-BN,² (ii) controlling the size of metal nanoparticles grown on graphitic material (graphene, nanotubes and nano-onions),³ (iii) the synthesis of mesoporous silica at room temperature, with the ability to control the pore size arising from the shear on the Pluronic P123 micelles,⁴ (iv) protein folding and probing the structure of self organised systems in general, (iii) preparing metal organic frameworks (MOFs), and more. [1] L. Yasmin, X. Chen, K. Stubbs and C. L. Raston. "Optimising a vortex fluidic device for controlling chemical reactivity and selectivity." Sci. Rep. 2013, 3, 2282. [2] X. Chen, J. F. Dobson and C. L. Raston, Chem. Commun., 2012, 48, 3703. [3] Y. A. Goh, X. Chen, et al., Chem. Commun., 2013, 49, 5171 - 5173. [4] C. L. Tong, R. A. Boulos, C. Yu, K. S. Iyer, and C. L. Raston, RSC Advances, 2013 2013, 3, 18767.

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[\(close full abstract\)](#)

16:30

Nanoparticle hetero-dimers

Authors : Melissa R. Dewi, Thomas Nann*

Affiliations : Ian Wark Research Institute, University of South Australia, Mawson Lakes Blvd, Adelaide, SA 5095, Australia

Resume : If nanoparticles are the basic building blocks of complex nanoarchitectures, nanoparticle hetero-dimers made out of separate and individual particles represent the first level of sophistication. Despite the fact that high quality nanocrystals of almost any inorganic material can be synthesised since the beginning of this millennium, the preparation of simple hetero-dimers, consisting of two dissimilar nanoparticles and linked by at least one covalent bond, has not been achieved yet. Unlike the seeded-growth method, where one type of nanocrystal is grown on top of another, the method presented here is generic and does not require any fundamental compatibility between the two types of nanoparticles. Our method is based on a two-step approach: in the first step, the two types of nanoparticles are mono-functionalised, which means they bear functionality in just one spot of their surface. The hetero-dimerisation is then being undertaken in a second step. Particles have been mono-functionalised by attaching them covalently to a solid support, passivating their surface and subsequent cleavage of the linker between particles and solid support. Then, two types of nanoparticles need to be functionalised with different functional groups and finally dimerised. In this presentation, we will show the new synthesis method and examples for the hetero-dimerisation of dissimilar nanocrystals.

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16:45

Synthesis of CeO₂ nanoassemblies using a flow-type reactor and their structural change during reaction

Authors : Andrzej-Alexander Litwinowicz 1, Seiichi Takami 2, Daisuke Hojo 3, Nobuaki Aoki 3, Tadafumi Adschiri 2,3

Affiliations : 1 Graduate School of Engineering, Tohoku University; 2 Institute of Multidisciplinary Research for Advanced Materials, Tohoku University; 3 WPI-AIMR, Tohoku University

Resume : Nanoclusters of inorganic particles are expected to exhibit various optical, magnetic, and electrical properties that emerge from the periodicity and interaction of nanoparticles. We have synthesized cubic CeO₂ nanoassemblies comprising octahedral primary nanocrystals that shared the same crystallographic orientation. In this presentation, we report the structural change of CeO₂ nanoassemblies during their hydrothermal synthesis. Cerium oxide nanoassemblies were synthesized using a lab-scale plug-flow reactor. An

F.III.
2

aqueous solution of $\text{Ce}(\text{NO}_3)_3$ and glutamic acid was used as a reactant. The stream of the reactant was mixed with a pre-heated stream of water and instantaneously heated to $250\sim 300\text{ }^\circ\text{C}$. After passing an isothermal zone, the mixed stream was cooled by a jacket cooler. The residential time, that is, the reaction time, was changed in the range of $0.7 \sim 8.0\text{ s}$. The reaction pressure was 25 MPa . Secondary electron microscopy images of the products indicated that the products were spherical assemblies at the reaction time of 0.7 s . On the other hand, longer reaction time led to the formation of cubic products with ordered primary nanocrystals. These results suggested the two-step formation mechanism of ordered nanoassemblies. Firstly, the synthesized primary nanocrystals loosely agglomerate to form spherical products. Then, the nanocrystals ordered in the agglomerate and formed the ordered nanoassembly.

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17:00

Length Matters – How the Ligand Chain Length Affects Nanocrystal Size in the Hot Injection Synthesis

Authors : K. De Nolf, R. K. Capek, S. Abé, M. Sluydts, Y. Jang, E. Lifshitz, Z. Hens

Affiliations : Physics and Chemistry of Nanostructures, Ghent University; Schulich Faculty of Chemistry, Russell Berrie Nanotechnology Institute, Solid State Institute, Technion-Israel Institute of Technology; Center for Molecular Modeling, Ghent University

Resume : Colloidal semiconductor nanocrystals or quantum dots (QDs) are a very interesting class of nanomaterials since their properties can be tuned by their size due to quantum confinement. QDs are typically produced via a hot injection synthesis (HIS), which involves the injection of precursors in a hot mixture of a non-coordinating solvent and coordinating ligands such as carboxylic acids, thiols or phosphonic acids. For QDs to be implemented in a broad range of applications, a precise control over their size is essential. As a result, recent developments in the hot injection synthesis focus on producing QDs with predefined sizes, sharp size distributions and high reaction yields. In this study, we show that efficient size tuning at high reaction yield is possible by changing the chain length of the carboxylic acid. By combining an extended experimental reaction screening with reaction simulations, we demonstrate that the acid chain length affects the nanocrystal size by changing the diffusion coefficient and the solubility of the reactive monomers. In addition, we show that the relation between chain length and nanocrystal size can be used to assess the interaction of different coordinating species – including amines and phosphine oxides – with the reactive monomers. In this way, this work contributes to an enhanced, rational understanding of the widely used hot injection methods for the synthesis of colloidal nanocrystals.

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17:15

Synthesis of air and water stable Cobalt nanorods

Authors : Sergio Lentijo Mozo (1), Reasmey Tan (1), Teresa Hungria (1), Christophe Gatel (2), Benoit Cormary (1), Cécile Marcelot (1,2), Pierre-Francesco Fazzini (1), Marc Respaud (1), Katerina Soulantica (1)

Affiliations : (1) Université de Toulouse; INSA, UPS, CNRS, LPCNO 135 avenue de Rangueil, 31077 Toulouse, France. (2) Centre d'Elaboration de Matériaux et d'Etudes Structurales (CNRS), 29, rue Jeanne Marvig, 31055 Toulouse, France.

Resume : The synthesis of hybrid nanoobjects containing a magnetic core and a shell constituted by noble metals is investigated because of their potential use in different fields. In these nanoparticles, the magnetic core provides magnetic functionality and the noble metal shell offers a surface for biomolecules attachment and plasmonically active components. Co anisotropic nanoobjects such as nanorods and nanowires are of special interest for applications in which hard magnetic materials are required. However the development of a continuous shell of noble metal around Co nanoparticles is a challenge due to the immiscibility between the materials. We will describe the synthesis of new hybrid Co-metal core-shell nanorods of different shell composition and thicknesses. The growth of a complete shell is accomplished by introduction of a buffer layer between Co and the noble metal, compatible with the two otherwise immiscible materials. The complete shell protects the Co nanorods from oxidation, as demonstrated by the magnetic measurements and corroborated by HRTEM and EDX analysis. These measurements prove that the magnetic properties of Co, which are very sensitive to oxidation, are stable after exposition of the nanorods to the air for several weeks. When the metal shell is thick, it can provide oxidation protection of the Co-core in aqueous solutions for prolonged periods of time. After ligand exchange these nanorods can be transferred from organic solvents into aqueous solutions.

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17:30

Synthesis of HgTe QDs in the 1000-2500nm spectral range**Authors** : Laxmi Kishore Sagar^{1, 2}, Pieter Geiregat^{1, 2, 3}, Stijn Flamée^{1, 2}, Jonathan De Roo^{1, 2}, Yolanda Justo^{1, 2} and Zeger Hens^{1, 2}**Affiliations** : 1 Photonics Research Group, University of Ghent, Ghent, Belgium 2 Physics and Chemistry of Nanostructures group, University of Ghent, Ghent, Belgium 3 Center for Nano and Biophotonics, University of Ghent, Ghent, Belgium

Resume : HgTe is semi-metallic as a bulk material but when the crystal dimensions are reduced to the nanometer range, a band gap or HOMO-LUMO gap that is tunable throughout the IR region by the nanocrystal size opens up. The IR contains a number of technologically important wavelength ranges such as the 1300-1600 nm window used for telecommunication and the mid IR used for infrared spectroscopy. For these applications, HgTe quantum dots could be used for the emission, detection or modulation of light. In this study, we discuss a novel synthesis for HgTe QDs Using XRD and TEM, we show that the synthesis results in HgTe nanocrystals with the zincblende crystal structure and diameters of a few nanometer. Moreover, the HgTe QDs exhibit a clear absorption onset and a narrow photoluminescence spectrum corresponding to the quantum confined band gap transition. A detailed study of the reaction yield and the nanocrystal size as a function of time provides the insight in the reaction mechanism needed to tune the nanocrystal size and, concomitantly, the wavelength of absorption onset and photoluminescence. As a result, HgTe QDs with a spectrally narrow emission in the 1000 to 2500 nm range could be obtained. Our findings thus provide a thorough understanding of the mechanism of HgTe QD synthesis and result in materials that can be readily explored for applications such as photo detection and IR light emission.

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5[add to my program](#)[\(close full abstract\)](#)**Poster Session : Pascal André, Gordanna Dukovic, Mathieu Maillard, Laurence Motte, Richard Tilley**

17:50

Plasmonic enhancement of photocurrent in MoS₂ field-effect-transistor**Authors** : Jiadan Lin¹, Hai Li², Hua Zhang², Wei Chen^{1,3,4}**Affiliations** : 1Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore, 117542 ; 2School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798 ; 3Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, 117543 ; 4Graphene Research Centre, National University of Singapore, 2 Science Drive 3, Singapore, 117542

Resume : The two-dimensional material, molybdenum disulfide (MoS₂), has attracted considerable attention for numerous applications. Especially, benefiting from the strong absorption in the visible band, MoS₂ has been widely used in photocatalysis¹ and photodetection^{2,3} applications. However, monolayer or few-layer MoS₂ films turn into weak light absorber due to the thickness reduction. To address this issue, we demonstrate a significant plasmonic enhancement of photocurrent of MoS₂ field-effect-transistor by decorating its surface with gold (Au) nanoparticles (NPs). The localized surface plasmon in gold NPs⁴⁻⁷ largely improves the light absorption cross section of the MoS₂ layer underneath. We observed enhancement of the photocurrent for all the wavelengths shorter than 660 nm. It is also found that the gold-NPs decorated MoS₂ transistors possess a photocurrent response peaked at the plasmon resonant wavelength of around 540 nm. Therefore, it is possible to realize MoS₂ based wavelength-selectable photodetection by tailoring the size and shape of the coupled plasmonic Au or silver nanostructures. Our findings offer a possibility to realize wavelength selectable photodetection in MoS₂ based phototransistors. **Keywords**: MoS₂, plasmonic enhancement, photocurrent, transistor. (1)X. Zong, G. P. Wu, H. J. Yan, G. J. Ma, J. Y. Shi, F. Y. Wen, L. Wang, and C. Li, J. Phys. Chem. C **114**, 1963 (2010). (2)Z. Y. Yin, H. Li, H. Li, L. Jiang, Y. M. Shi, Y. H. Sun, G. Lu, Q. Zhang, X. D. Chen, and H. Zhang, ACS Nano **6**, 74 (2012). (3)Hee Sung Lee, Sung-Wook Min, Youn-Gyung Chang, Min Kyu Park, Taewook Nam, Hyungjun Kim, Jae Hoon Kim, Sunmin Ryu, and Seongil Im, Nano Lett. **12**, 3695 (2012). (4)T. J. Echtermeyer, L. Britnell, P. K. Jasnós, A. Lombardo, R. V. Gorbachev, A. N. Grigorenko, A. K. Geim, A. C. Ferrari, and K. S. Novoselov, Nat. Commun. **2**, 458 (2011). (5)Yuan Liu, Rui Cheng, Lei Liao, Hailong Zhou, Jingwei Bai, Gang Liu, Lixin Liu, Yu Huang, and Xiangfeng Duan, Nat. Commun. **2**, 579 (2011). (6) Keisuke Nakayama, Katsuki Tanabe, and Harry A. Atwater, Appl. Phys. Lett. **93**, 121904 (2008). (7)D. M. Schaadt, B. Feng, and E. T. Yu, Appl. Phys. Lett. **86**, 063106 (2005).

F.P. 1

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- 17:50 **Structural Properties of Gold Thin Films Deposited on Technologically Important Substrates by RF Magnetron Sputtering**
Authors : Moniruzzaman Syed1)*, Caleb Glaser2), Michael Schell2), Indrajith Senevirathne2)
Affiliations : 1Division of Natural and Mathematical Sciences, Lemoyne-Owen College, Memphis, TN38126, USA 2Department of Geology and Physics, Lock Haven University of Pennsylvania, Lock Haven, PA 17745, USA
Resume : In this study, Gold (Au) thin films were deposited on glass (SiO₂) and silicon (100) substrates at room temperature (RT) in an argon (Ar) gas environment as a function of sputtering time (Tsp). The structural properties of Au films have been studied using an Atomic Force Microscope (AFM). The results of this study indicate that the structural properties of the deposited Au film are related to the conductance of the substrate. AFM micrographs of Au films show that the films on nonconductive substrates show higher coalescence for longer sputtering times. Au films deposited on conductive silicon substrates show structures that show microvoids and to homogenous structures as the sputtering time increases. On the other hand, gold films deposited to nonconductive glass substrates showed homogenous structures that changed to cluster and island-type as a function of sputtering time.

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- 17:50 **EFFECT OF POLY(VINYL ALCOHOL) ADDITION ON RHEOLOGICAL PROPERTIES OF CERAMIC SLURRIES BASED ON YTTRIA AND NANOCOLLOIDAL BINDER**
Authors : Marcin Malek1, Pawel Wisniewski2, Hubert Matysiak2, Krzysztof Jan Kurzydowski1
Affiliations : 1Faculty of Materials Science and Engineering, Warsaw University of Technology, POLAND 2Functional Materials Research Centre, Warsaw University of Technology, POLAND * Corresponding author: marcin.malek@inmat.pw.edu.pl
Resume : This work characterize technological properties of ceramic slurries based on yttria fillers and binder with nanocolloidal particles of Al₂O₃, which are used in manufacturing ceramic shell molds for investment casting of superalloys. Two different granulation (200# and 325#) of yttrium III oxide was used in weight ratio 50÷50%. Polyvinyl alcohol in an amount of 6%, 10% and 15% as 10 wt.% solution was added as a liquefier. Solid phase content in ceramic slurries was 77 wt.%. Standard industrial parameters like: Zhan 4# cup, plate weight test, pH, density, viscosity and dynamic viscosity were investigated. In addition dipping test on wax model was done. For characterization yttria powders and binder with nano Al₂O₃ particles, grain size, scanning electron microscopy, chemical composition and Zeta potential were studied. Obtained results proved that yttria based slurries are stable vs. time and its properties are promising in further application in industrial scale. Key words: investment casting, ceramic slurries, yttria powders, nanocolloidal Al₂O₃, ceramic shell moulds, rheological properties. Financial support of Structural Funds in the Operational Programme - Innovative Economy (IE OP) financed from the European Regional Development Fund - Project "Modern material technologies in aerospace industry", No. POIG.01.01.02-00-015/08-00 is gratefully acknowledged.

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- 17:50 **3D anti-counterfeiting microtags of upconverting NaYF₄ colloidal nanocrystals by AFM nanoxerography**
Authors : Pierre Moutet*, Neralagatta M. Sangeetha*, Delphine Lagarde*, Gregory Sallen*, Bernhard Urbaszek*, Xavier Marie*, Guillaume Viau* and Laurence Ressler*
Affiliations : * Université de Toulouse, LPCNO, INSA-CNRS-UPS, 135 Avenue de Rangueil, Toulouse, 31077, France
Resume : Atomic Force Microscopy (AFM) nanoxerography is a powerful technique for directed assembly of colloidal nanoparticles. It relies on selective trapping of nanoparticles on the surface of patterned electrets by electrostatic interactions. This process is quick, inexpensive and versatile. Despite these advantages, the method suffered from a serious inconvenience: only monolayered (2D) assemblies of nanoparticles have been achieved until recently. In this presentation, recent efforts made to obtain three dimensional (3D) close-packed assemblies of lanthanide-doped hexagonal (β) NaYF₄ colloidal nanocrystals (NCs) will be described. NaYF₄ nanoparticles are popular as highly efficient upconverters of luminescence. Their 3D assembly can be controlled with some key experimental parameters: (i) surface potential of charged patterns, (ii) immersion time into the colloidal solution and (iii) concentration of the colloidal solution. By combining the unique capabilities of the AFM nanoxerography and NaYF₄ NCs, microtags were constructed with multiple beneficial features: improved luminescence intensity, two different luminescence

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from binary assemblies, topographically hidden messages. Ultimately, specific authentication is achieved by fine tuning of the luminescence properties of NaYF₄ NCs. AFM topographical imaging and spectral characterizations will be presented to demonstrate the strong capabilities of NaYF₄ NCs microtags for anti-counterfeiting and authentication applications.

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17:50

Can graphene quantum dots be used as photocatalysts?

Authors : Siobhan J. Bradley, Thomas Nann

Affiliations : Ian Wark Research Institute, University of South Australia, Mawson Lakes Blvd, Adelaide, SA 5095, Australia

Resume : Graphene quantum dots (GQDs) are nanometer-sized fragments of graphene where electronic transport is confined in all three spatial dimensions. They typically have diameters below 20 nm. As GQDs have more molecule-like character, they are much easier to handle compared to colloidal QDs, are non-toxic, in principle abundant and show the desirable optoelectronic properties of quantum dots.¹ It has been suggested that both the size and the edge groups contribute to the band gap of GQDs. This is useful for many applications as the band gap could be tuned simply through functionalisation. However the heterogeneous nature of quantum dots prepared using top-down methods makes it difficult to establish the structure-property relationships of GQDs. In this work we produced GQDs using a top-down approach and probe the electronic structure of the band gap of the GQDs to find out about their photocatalytic properties. References: 1. M. Bacon, S. Bradley and T. Nann, Part. Part. Syst. Charact. (Accepted Nov 2013)

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17:50

Synthesis and Phase Transfer of Monodisperse Iron Oxide (Fe₃O₄) Nanocubes

Authors : Melissa R. Dewi, William M. Skinner, Thomas Nann

Affiliations : Ian Wark Research Institute, University of South Australia, Mawson Lakes Blvd, Adelaide, SA 5095, Australia

Resume : Magnetic nanoparticles (MNPs) are used in various areas such as nanomedicine, sensing, information storage and catalysis. The properties and performance of the MNPs are strongly affected by their crystalline structure, particle shape, dimensions as well as uniformity. Monodisperse magnetic nanocubes (11-14 nm) have been synthesised via the effective monomer growth mechanism, followed by surface modification (hydrophobic to hydrophilic) without any notable increase of the nanoparticles' hydrodynamic diameter. Furthermore, the study of the magnetic properties has been carried out including the comparison of the magnetic properties of nanocubes and nanospheres to investigate the morphology/property relationship in this particular nanomaterial. We have observed that cube shaped MNPs offer superior magnetic properties in comparison with spherical MNPs. In addition, the cubic shape also allows for the investigation of the shape evolution during growth and how it affects the properties and performance of the MNPs. For many applications it is compulsory to disperse the MNPs in aqueous solution. A variety of methods exists to modify the surface of the nanocubes ranging from amphiphilic polymer coating to ligand exchange. We functionalised our MNPs via ligand exchange by using (a) nitrosonium tetrafluoroborate (NOBF₄) and (b) oxalic acid (C₂H₂O₄) to replace the organic ligands. Whilst water dispersible nanocubes were produced, the original size and shape of the nanoparticles has been preserved. In addition, this ligand exchange method also results in a very high colloidal stability of the nanocubes.

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17:50

Fast, microwave assisted synthesis of monodisperse refractory metal oxide nanoparticles

Authors : Jonathan De Roo, Katrien De Keukeleere, Jonas Feys, Petra Lommens, Zeger Hens and Isabel Van Driessche

Affiliations : Ghent University, Department of Inorganic and Physical Chemistry
Resume : Refractory metal oxides (HfO₂, ZrO₂, Ta₂O₅, Nb₂O₅) are particularly challenging to synthesize as monocrystalline, monodisperse nanoparticles (d < 10 nm) in a reproducible and economically feasible fashion. Niederberger et al. introduced the benzyl alcohol (BA) synthesis which is more environmentally friendly than surfactant-based syntheses. However, the synthesis takes several days and the resulting particles are aggregated. Here, we present a system which combines the advantages of both approaches. We focused on hafnium oxide as a model system and subsequently extended our synthesis method to other oxides. We use a cheap chloride precursor and the reaction mixture is heated via microwave heating in a closed vessel. The reaction attained full yield in three hours, which is comparable to hot injection syntheses. In the microwave

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synthesis, the ensemble of particles has a better size dispersion and a smaller average size (4 nm), as compared to the autoclave synthesis. The reaction mechanism was investigated and we found proof for an ether elimination process. Post-synthetic modification with a minimal amount of dodecanoic acid and oleylamine permitted the transfer of the synthesized particles from polar to nonpolar solvents. Concomitantly, aggregates are broken into the constituting nanoparticles, thus tackling the major disadvantage of the BA synthesis. Moreover, the thousand fold reduction in surfactant usage is an advantage over classical surfactant syntheses.

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17:50

Noble metal nanoparticles films: controlled synthesis by ultrasonic spray pyrolysis and catalytic effect

Authors : Yanpeng Fu, Yan Lu, Martha Ch. Lux-Steiner, Christian-Herbert Fischer

Affiliations : Helmholtz-Zentrum Berlin für Materialien und Energie

Resume : Metal nanoparticles (NPs) have many applications in areas such as photonics, sensing, medicine and catalysis. For colloidal NPs, capping groups on the surface are necessary in order to prevent aggregation. However, those can be harmful for applications by reducing access of light or chemicals for photosensitive or sensing and catalysis applications. Having long experience in metal compound nanodot films by ILGAR, now we report a simple yet versatile route to prepare substrate-supported Au NPs with naked surfaces (i.e., capping-free) by ultrasonic spray pyrolysis (USP). Particle size, density and morphology can be well controlled by the process parameters and substrate material. Au NPs on Mo substrates form spheres (size around 10 nm), while on Si icosahedra (edge length) or after addition of Cu ions to the precursor solution decahedra (edge lengths 15 nm or 10 nm, respectively). The catalytic activity of bare Au NP films and coated colloidal NPs was compared for the nitrophenol reduction by NaBH₄. Bare Au NPs showed the fastest reaction. By addition of various stabilizers their retarding effect was studied. Flow-through experiments showed the industrial potential of substrate supported Au NPs for continuous operation without aggregation and tedious separation from the reaction solution. The easy USP method for noble metal NP films and the morphology control of these Au NPs are also promising for solar cells (plasmonic enhanced absorption) and surface-enhanced Raman scattering.

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17:50

Quantum Confinement-Tunable Ultrafast Charge Transfer at the PbS Quantum Dot and PCBM Fullerene Interface

Authors : Ala'a O. El-Ballouli, Erkki Alarousu, Marco Bernardi, Shawkat M. Aly, Alec P. Lagrow, Osman M. Bakr, and Omar F. Mohammed

Affiliations : 1- Ala'a O. El-Ballouli; Erkki Alarousu; Shawkat M. Aly; Alec P. Lagrow; Osman M. Bakr; Omar F. Mohammed. Solar and Photovoltaics Engineering Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia 2- Marco Bernardi. Department of Physics, University of California at Berkeley, Berkeley, California 94720-7300, USA

Resume : Quantum dot (QD) solar cells have emerged as a promising low-cost alternative to existing photovoltaic technologies. Here, we investigate charge transfer and separation at PbS QDs and phenyl-C61-butyric acid methyl ester (PCBM) interfaces using a combination of femtosecond broadband transient absorption (TA) spectroscopy and steady-state photoluminescence quenching measurements. We analyzed ultrafast electron injection (EI) and charge separation (CS) at PbS QD/PCBM interfaces for different QD sizes, and as a function of PCBM concentration. The results reveal that the energy band alignment, tuned by quantum confinement, is the key element for efficient EI and CS processes. More specifically, only small-sized PbS QDs with a bandgap > 1 eV can transfer electrons to PCBM upon light absorption, due to the formation of a type-II interface band alignment, as a consequence of the size distribution of the QDs. The TA data indicates that electron injection from photoexcited PbS QDs to PCBM occurs within our temporal resolution of 120 fs for QDs with bandgaps that achieve type-II alignment, while virtually all signal observed in smaller bandgap QDs result from large bandgap outliers in the size distribution. Thus, our results clearly demonstrate that charge transfer rates at QD interfaces can be tuned by several orders of magnitude by engineering the QD size distribution. The work presented here will advance both the design and understanding of QD interfaces for solar energy conversion.

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- 17:50 **Understanding Different Single-Molecular ZnS Precursors for High Quality InP/ZnS Nanocrystal Synthesis**
Authors : Lifei Xi, Deok-Yong Cho, Martial Duchamp, Jun Yan Lek, Walter Tillmann, Astrid Besmehn, Christopher B. Boothroyd, Yeng Ming Lam, Beata Kardynal
Affiliations : Peter Grünberg Institute, Semiconductor Nanoelectronics (PGI-9), Microstructure Research (PGI-5) and ER-C, Central Institute for Engineering, Electronics and Analytics (ZEA-3), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany, CSCMR and FPRD, Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Republic of Korea, School of Materials Science and Engineering, Nanyang Technological University, 639798, Singapore, Institute of Technical and Macromolecular Chemistry/DWI an der RWTH Aachen e.V. and Institute of Materials in Electrical Engineering and Information Technology 2 (IWE2), RWTH, Aachen, D-52056 Aachen, Germany
Resume : A simple approach for synthesis of high quality InP/ZnS nanocrystals using single-molecular ZnS precursor is reported. The one-pot synthesis goes through heating of the solution of InP-Zn cores and the amount of powder Zn (S2CNR2) (where R = methyl, ethyl, butyl or benzyl) corresponding to a different shell thickness to 90-250 °C for 0.5-2.5 h. The role of different end groups of thiocarbamate, complex formation time, the reaction time, reaction temperature and the amount of single precursor have been fully studied with XPS, HR-TEM, HR-EELS, EDX, XRD, TGA, FT-IR, optical absorption and steady-state PL and time-resolved PL. We found that the end groups of thiocarbamate are crucial for the low temperature growth of high quality InP/ZnS nanocrystals. The different end groups have different polarity and steric effect, thus affect the capability of complex formation between the single-molecular ZnS precursor and amine, the reactivity of the complex, the decomposition temperature as well as the dispersibility of NCs after shell coating. We also found that the quality of the shell coating can be affected by the shell coating cycle number, the amount of single-molecular precursor, the reaction time and the reaction temperature. These findings would be useful for other types of core/shell growth and industrial large-scale production. F.P.
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- 17:50 **Controlled Preparation of Ultrafine Spherical LLM-105**
Authors : Juan Zhang*, Peng Wu, Feiyan Gong, Chun Liu, Yu Chi, Ping Wang
Affiliations : Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, Sichuan, China
Resume : 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) is a realistic high-performance energetic material. It is very thermally stable and insensitive to shock, spark and friction. These over-all properties enable it to raise great potential in several applications, including insensitive boosters, detonators, and possibly main charges in specially munitions. In this paper, ultrafine crystals of LLM-105 were produced by introducing ultrasonic treatment into solvent/antisolvent recrystallization process. The LLM-105 solute was dissolved in the solvent and subsequent sprays or drops into antisolvent with the aid of ultrasound. The effect of ultrasonic treatment on the crystal habit (shape and morphology) of explosive was studied by varying the amplitude and frequency using an ultrasonic probe and an ultrasonic bath. The final products were characterized for purity by HPLC analysis, morphology analysis by SEM. Particle size was tested by laser diffraction particle size analyzer and surface area by BET method in addition to XRD and thermal analysis. The results show that ultrasonic treatment is benefit to obtain ultrafine crystals of LLM-105, the ultrafine LLM-105 particles are spherical with a narrow particle size distribution and the particle size is in the range of 100nm~500nm. Spherical LLM-105 crystal has a surface area of 9m²/g and as the size of LLM-105 particles is in the submicro meter range, the XRD diffraction peaks become slightly broadened. F.P.
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- 17:50 **Stable NIR-absorbing Lanthanum Hexaboride Nanoparticle Formulations for Laser Welding Applications of Thermoplastic Polymers**
Authors : Claudia Rieser, Karin Peter, Martin Moeller
Affiliations : DWI – Leibniz Institute for Interactive Materials, Aachen, Germany
Resume : Commonly, thermoplastic materials don't absorb radiation in the Near Infrared Region (NIR). To make them applicable for laser welding it is necessary to use an NIR-absorbing additive. This can be a chemical compound, i.e. based on Perylenes, or a formulation of nanoparticles. Generally, the absorption of radiation by particulate materials is influenced essentially by the particle size and chemical composition [1]. The aim of our research is to create nanoscale particles of lanthanum hexaboride (LaB₆) - a widely used NIR-absorbing compound [2] - via a top-down approach in order to achieve a high absorption F.P.
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efficiency in the NIR-region (wavelength > 800nm). It was found, that the average particle size of LaB6 can be decreased to smaller than 60 nm by modifying the parameters of the grinding process. Simultaneously, the absorption is strongly increasing at wavelengths relevant for laser application. The correlation between particle size and absorption is demonstrated by the molar extinction coefficient ϵ . Comparing these values at various particle diameters with the absorption values of other inorganic NIR absorber, ground LaB6 nanoparticles feature as an efficient absorbing additive with high potential for laser applications. This efficiency could be demonstrated in laser welding of thermoplastic textiles. [1] Quinten, M., Optical Properties of Nanoparticles (John Wiley). Weinheim (2011). [2] Rosenberger, Silvia et al., PCT Int. Appl. (2006), DE102004045305 A1

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17:50 **Using Two Self-Assembling Materials to Hierarchical Structure and Non-Simple Nanopatterns**

Authors : Jin Wook Lee, Gu Hwan Jung, Jung Ki Lee and Seung Hyun Kim*

Affiliations : Division of Nano-Systems Engineering, Inha University

Resume : The fabrication of well-defined structures on the nanometer-scale is considerable interest for a wide range of applications in electronic, magnetic, chemical, and biological sensors. Nanostructure techniques, including electron beam lithography, micro contact printing, and self-assembly, etc. have been extensively exploited to generate and control the nanostructures. Among several possible alternatives, self-assembly has been recently recognized as a promising candidate for nanofabrication due to a simple and effective way in accessing complex structures on the nanometer scale and to the diversity of structure. In this work, we seek to find out new yet simple way to nanostructure via sequential applications of two different self-assembling materials. Block copolymer, one class of self-assembling materials, spontaneously self-assemble into various structures on the nanometer scale. Colloidal particles are another type of self-assembling materials, which produces highly ordered colloidal crystals via self-assembly driven by capillary force or convection flow. Colloidal particles are deposited on the substrate to form colloidal crystal, and then block copolymers are coated on colloidal crystals so that they are able to guide block copolymer self-assembly. Combination of two self-assembling materials with variation in characteristic size of templates was shown to lead to hierarchical structure and non-simple nanopatterns.

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17:50 **Electrodeposition and Mechanical Properties of Porous Copper Using Colloidal Crystal Templating**

Authors : M. Mieszala, M. Hasegawa, J.M. Wheeler, R. Raghavan, J. Michler and L. Philippe

Affiliations : Empa - Swiss Federal Laboratories for Materials Science and Technology Laboratory for Mechanics of Materials and Nanostructures Feuerwerkerstrasse 39, Thun CH-3602, Switzerland

Resume : Colloidal crystal templating offers numerous exciting possibilities to synthesize three-dimensionally ordered micro/nano-porous materials of both scientific and technological interests, such as photonic crystals, catalyst, and sensors[1]. Porous materials also show unique mechanical properties. Especially, nano-porous materials are of great interest because such materials will exhibit enhanced mechanical strength despite being low density[2]. In this poster, we present the studies on electrodeposition of micro/nano-porous copper using polystyrene (PS) colloidal crystal templating aiming at achieving the high strength and low density material. A multilayer PS colloidal crystal was used as a template for porous Cu formation. Colloidal crystals of different PS sizes ranging from submicrometer to some micrometer of diameters were employed to synthesize porous Cu films with different pore sizes. Electrodeposition to completely fill interstitial space between PS particles was firstly investigated. Proper wetting of a template seems to be important in order to avoid insufficient infiltration of electrolyte into the narrow channels of template. By dissolving PS particles in toluene after electrodeposition, ordered porous structure with a controlled pore size was obtained. Further strengthening of porous Cu can be achieved by electrodeposition of nanocrystalline Cu[3] and nanotwin Cu[4] which exhibit improved mechanical strength. By adjusting plating parameters as well as the bath composition, we obtained Cu deposits with different grain sizes from several tens nanometer to a few micrometer on an unpatterned substrate. The application of such electrodeposition technique to a PS colloidal crystal template will be shown. Furthermore, mechanical properties of porous Cu electrodeposits with different pore sizes and crystal structure will be discussed.

F.P.
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References: 1. Stein, A. and Schroden, R.C., Colloidal crystal templating of three-dimensionally ordered macroporous solids: materials for photonics and beyond. *Current Opinion in Solid State and Materials Science*, 2001. 5(6): p. 553-564. 2. Biener, J., et al., Size effects on the mechanical behavior of nanoporous Au. *Nano Letters*, 2006. 6(10): p. 2379-2382. 3. Lu, L., M.L. Sui, and Lu, K., Superplastic extensibility of nanocrystalline copper at room temperature. *Science*, 2000. 287(5457): p. 1463-1466. 4. Hsiao, H.Y., et al., Unidirectional Growth of Microbumps on (111)-Oriented and Nanotwinned Copper. *Science*, 2012. 336(6084): p. 1007-1010.

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Synthesis and characterization of TiO₂ nano-colloid obtained by laser ablation in water

Authors : M. Zimbone b) G. Cacciato a), b), Ruy Sanz b), L. Romano a) ,R. Reitano a),V. Privitera b),c), M. G. Grimaldi a), b)

Affiliations : a) Dipartimento di Fisica ed Astronomia-Università di Catania, via S. Sofia 64, 95123 Catania, Italy b)MATIS IMM-CNR, via S. Sofia 64, 95123 Catania, Italy c)CNR-IMM, Stradale Primosole 50, I-95121 Catania, Italy

Resume : The development of industrial nanotechnologies is driven by the ability of manufacturing nanostructures with tunable size and properties, based on scalable and economically advantageous methodologies. Pulsed laser ablation in liquid (PLAL) is one of the most promising emerging technologies that fit these requirements. PLAL is applied for the synthesis of metal and oxide nano-colloids directly in liquid environment with unique properties as high purity, high surface activity, and the possibility of choosing different solvents depending on specific application. In order to tune the colloid properties, it is essential to understand how ablation parameters influence the formation, size and structure of nano-colloids. In the present work, we report on the synthesis of titanium oxides nano-colloid by PLAL in pure water by using a Nd:Yag laser at 1064 nm. We focus our attention on the titanium oxides nano-colloid properties, both in liquid and in dry environment. UV-Vis spectroscopy and dynamic light scattering are used for characterization in liquid. Scanning Electron Microscopy, Rutherford Back Scattering and X-Ray Diffraction were employed after drying. Spherical and stoichiometric TiO₂ nanoparticles of 34 nm in mean diameter, showing both amorphous and crystalline phases, have been found. The application of these nano-particles to photo-degradation of methyl-blue dye is also presented and discussed taking as reference the properties of commercial titanium nanoparticles.

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Characterization of Submicron HNIW Prepared by a Planetary Ball Milling Technology

Authors : Peng Wu*, Juan Zhang, Zhijian Yang, Zhiqiang Qiao, Jun Wang, Guangcheng Yang

Affiliations : Institute of Chemical Materials, China Academy of Engineering Physics

Resume : Due to tremendous surface-to-volume ratio and excellent performance, nano- and micro- energetic materials have great importance in military applications. 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, CL-20), known as a kind of high energy density materials (HEDMs), has the highest energy among HEDMs in use. In this study, submicron HNIW was prepared by a planetary ball milling technology. Scanning electron microscopy (SEM) was employed to characterize the appearance and size of submicron HNIW samples. It reveals that submicron HNIW particles have the shape of spheres or ellipsoids, and most of the particles are below 700nm. Fourier transform infrared spectroscopy (FT-IR) was used to identify the crystalline form of submicron HNIW. The FT-IR spectroscopy shows the submicron samples we obtained is epsilon-HNIW, which is the most promising form of HNIW. The five seconds explosion temperature of submicron HNIW is 3°C lower than that of raw HNIW, which shows the thermal stability of submicron HNIW is a little worse than raw HNIW. Impact sensitivity tests show that submicron HNIW was remarkably decreased in comparison to coarse HNIW.

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Preparation of superamphiphobic coating by combining fluoroalkyl silane with nano silica

Authors : Fang Wang, Zhongkuan Luo,Li Zhou, Puqi Chen

Affiliations : College of Chemistry and Chemical Engineering ,Shenzhen University

Resume : Superamphiphobic surfaces are promisingly applied in numerous fundamental and industrial applications. A transparent superamphiphobic coating was fabricated by combining fluoroalkyl silane copolymer(PFAS) with nano SiO₂. Firstly, Dodecafluoroheptylmethacrylate(DFMA) and γ-

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Methacryloxypropyl trimethoxy silane(KH-570) were used as monomer, tetrahydrofuran (THF) was used as solvent, fluoroalkyl silane copolymer(PFAS) was prepared by free radical polymerization. Then, a certain amount of SiO₂ nanoparticles were added to dispersed in PFAS to obtain a homogeneous hybrid sol. The hybrid sol was coated on glass surface by dip-coating method, and the resulting glass slide with coating was transparent and superamphiphobic. The visible light transmittance of the hybrid coating on the glass surface ranges from 87% to 92%. The contact angle(CA) of the coating for water or ethylene glycol is higher than 150°. It is proved that, surface roughness and low surface energy material are the two key factors to fabricate superamphiphobic coatings. If hydrolyzed tetraethoxysilane(TEOS) was added during the free radical polymerization of the PFAS, the coating exhibits a slightly decrease of contact angle for water or ethylene glycol, while its adhesion to the glass surface was improved obviously. This is a facile, cost-effective method to obtain transparent superhydrophobic and superoleophobic surfaces on larger area of various substrates.

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SATISFACTORY DESCRIPTION OF THE OPTICS IN A PHOTONIC CRYSTAL WITH A ONE-DIMENSIONAL STRATIFIED MODEL

Authors : Isabelle Maurin, Elias Moufarej, Athanasios Laliotis, Daniel Bloch

Affiliations : Laboratoire de Physique des Lasers, CNRS, UMR 7538, Université Paris 13, Sorbonne Paris-Cité, 99 avenue Jean-Baptiste Clément, 93 430 VILLETANEUSE, FRANCE

Resume : Opals, made of a compact arrangement of glass nanospheres deposited on a substrate, are a typical example of a photonic crystal prepared by soft chemistry. We approach here optics in an opal by describing it as a one-dimensionally (1-D) stratified medium, whose local effective index depends on the planar sphere/vacuum filling factor. Scattering, ignored by the model, is described by an ad hoc absorptive contribution to the 1-D layered index. Reflection and transmission coefficients are derived from optical transfer matrices. Our analysis allows understanding the specific contribution of the gap between the opal and the substrate which breaks the periodicity. Such a situation is very common for any kind of photonic crystal. Our simple calculations also yield quantitative predictions, including for the width and strength of the Bragg peak (in reflection) associated to the (bulk) opal periodicity. Defects in the opal periodicity are easily taken into account by our model. The model has also been extended to the situation of an infiltration - in the voids region- by a resonant medium, a situation that we had studied previously with gases [1]. Dedicated optical experiments with opals of various sizes, and our previous results [1], show that our modeling provides a satisfactory quantitative agreement in numerous cases. [1] P. Ballin et al., Appl. Phys.Lett, 102,231115 (2013)

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Reconstruction of nanosized tungstate structure from EXAFS spectra by evolutionary algorithm

Authors : J. Timoshenko 1, A. Anspoks 1, A. Kalinko 12, A. Kuzmin 1

Affiliations : 1 Institute of Solid State Physics, University of Latvia, Kengaraga street 8, LV-1063 Riga, Latvia; 2 Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette, France

Resume : Nanostructured tungstates CoWO₄ and CuWO₄ are very promising catalytic materials, particularly for photocatalytic oxidation of water. The high catalytic activity of tungstate nanoparticles is partially a result of their extremely small sizes, and, consequently, high surface-to-volume ratio. Thus the properties of such material strongly depend on the atomic structure, which, in turn, can significantly differ from that in the bulk. X-ray absorption spectroscopy is a powerful technique to study the local atomic and electronic structure of nanomaterials. In this study we employ the reverse Monte Carlo method based on a novel Evolutionary Algorithm (EA) for the analysis of the extended x-ray absorption fine structure (EXAFS) spectra from nanosized (smaller than 2 nm) CoWO₄ and CuWO₄ powders. The EA-EXAFS approach and simultaneous analysis of the W L₃- and Cu/Co K-edge EXAFS data allowed us for the first time to obtain a 3D structure model of tungstate nanoparticles and to explore in details the effect of size, temperature and transition metal type.

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Synthesis of 1D nanomaterials for transparent electrodes

Authors : Bastien BESSAIRE (1,2), Mathieu MAILLARD (1), Caroline CELLE (2), Jean-Pierre SIMONATO (2), Arnaud BRIOUDE (1)

Affiliations : (1) Université Lyon 1 – Laboratoire des Multimatiériaux et Interfaces – UMR 5615 (2) CEA Grenoble – DRT/LITEN/DTNM/LCRE

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Resume : In 2012, ITO is the mostly used Transparent Conductive Oxide (TCO), representing more than 90% of the world market in TCO. However, the quantity of indium on Earth is highly decreasing and the need of finding new ways to produce transparent, conductive and flexible electrodes is important. Some ways have been developed such as : metallic nanowires (mainly silver), graphene/carbone nanotubes or conductive polymers (PEDOT:PSS is one of the most famous). Herein, we present the synthesis and characterization of 1D nanomaterial, in order to replace ITO, using two different approaches. The first method, developed in the lab, is using soft chemistry in order to prepare gold nanowires. These syntheses require reduction of gold ions in solution following a three step growth process. This technique, followed by spray-coating could lead to the formation of large scale transparent electrodes. The second method we focused on is electrospinning. It consists in depositing solutions of polymer on substrates using high voltage. Its principal use is to disperse the polymer into nanofibers. Electrospinning is used for two approaches: one is including gold wires into a polymer matrix to orientate them in the fiber direction and thus lower the percolation threshold, for an improved conductivity. The other one is to prepare PEDOT:PSS nanofibers as a conductive template for a metallic electroplating.

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Synthesis and characterization of mixed ligand chiral nanoclusters

Authors : Zekiye Pelin Guven, Kellen M. Harkness, Hikmet Coskun, Francesco Stellacci, Ozge Akbulut

Affiliations : Sabanci University, EPFL

Resume : Nanoclusters became of interest due to their possible applications in biosensing, biolabeling, and optics. Here we report the synthesis and characterization of mixed ligand silver nanoclusters that exhibit chiral behavior. We have explored the occurrence of this behavior by changing the silver to thiol ratio and ratios of the ligands. We also show an increase in the chiroptical response of these clusters through a ligand exchange reaction.

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Laser-induced transient and permanent changes of absorption of gold nanorods in colloid solution

Authors : I.Dmitruk, Y.Shynkarenko, A.Dmytruk, C.Sönnichsen, Yu. Khalavka, A.Kotko, I.Blonskyi

Affiliations : Institute of Physics, National Academy of Sciences of Ukraine, Taras Shevchenko National University of Kyiv, Ukraine; Institute of Physics, National Academy of Sciences of Ukraine; Institute of Physics, National Academy of Sciences of Ukraine; Institute for Physical Chemistry, University of Mainz, Germany; Chernivtsi National University, Ukraine; Frantsevich Institute for Problems of Materials Science, Kyiv, Ukraine; Institute of Physics, National Academy of Sciences of Ukraine

Resume : Action of femtosecond laser irradiation on optical absorption of gold nanorods in colloid solution has been measured by pump-probe technique in spectral regions of both longitudinal and transverse modes of surface plasmons. Evolution of parameters of the plasmon absorption bands, namely, peak positions and band widths, after an impact of the pump pulse has been revealed by advanced data processing, accounting for a chirp of "white continuum" of the probe pulse. Under intense laser excitation both longitudinal and transverse plasmon peaks demonstrate broadening and spectral shifts. But direction of shift is different for two peaks, namely, transverse peak shifts to blue side and longitudinal – to red side of the spectrum. Observed kinetics of plasmon halfwidth fits hot electron relaxation theory. Besides, a significant increase of cross-phase modulation in the spectral range of surface plasmon absorption band has been found. Irreversible nanorod shape transformation (change of aspect ratio) has been observed after long term irradiation. Pump-probe measurements were performed at the Center for collective use of equipment "Femtosecond Laser Complex" of National Academy of Sciences of Ukraine.

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Synthesis and Properties of Pt@Ag Core@Shell Nanocolloids for Biosensing Applications

Authors : Anh T.N. Dao, Derrick M. Mott, Shinya Maenosono

Affiliations : School of Materials Science, Japan Advanced Institute of Science and Technology

Resume : Ag nanoparticles (NPs) show a wide range of colors corresponding to their localized surface plasmon resonance together with exceptionally high extinction coefficient associated with very high enhancement ability in Raman spectroscopy. These characteristics have made it an ideal candidate for use as a probe in sensing and bio-diagnostics applications. However, aqueous synthesis

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of Ag NPs still has several obstacles such as uncontrollable size and morphology of resulting NPs as well as extremely sensitive to oxidation. In our research, Pt is chosen as core material to create heterostructured Ag-based NPs in order to control size and shape of obtained core@shell NPs by seed-mediated growth mechanism. Ag in the shell is stabilized through electronic transfer effect yet still retains excellent surface plasmon resonance without compromising intensity. Our synthetic approach avoids the galvanic replacement reaction while overcoming lattice mismatch to successfully form Pt@Ag core@shell NPs which have tunable size and shell thickness. The Pt@Ag core@shell NPs are synthesized in aqueous environment and are characterized by using UV-Vis, XRD, HR-TEM, HADDF-STEM, EDS, XPS, and Raman spectroscopy.

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Fabrication of Micro and Nano Structure via Photo Resist-Free Process Using Polystyrene Beads for Solar Cell Application

Authors : Changheon Kim^{1,2}, Jonghwan Lee¹, Sangwoo Lim² and Chaehwan Jeong¹
Affiliations : 1. Applied Optics & Energy Research Group, Korea Institute of Industrial Technology, Gwangju 500-480, South Korea 2. Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, South Korea

Resume : The cylindrical micro and nano structure has been fabricated using polystyrene (PS) beads. Water-diluted 1, 2 and 4.5 micron-sized PS beads (purchased, Alfa Aesar) were mixed with ethanol to prepare the PS monolayer on substrates. The Chokralsky grown 200 μm -thick p-type (100) Si wafers (resistivity of 0.5-3.0 $\Omega\cdot\text{cm}$) were cut into 40 \times 40 mm² for substrates. The PS monolayer was formed on substrates after dipping into the PS solution and after the O₂ plasma treatment, PS beads were shirinked into smaller size. The sizes of 1micron-sized PS beads were gradually decreased to 500 nm following O₂ plasma treatment and 2 and 4.5 micron-sized PS beads showed same trend as well. This controllable sizing process gives opportunity for fabricating cylindrical wire shape with variable radii. The Ag thin film was deposited for the electrodeless etching process. The doping process was conducted using POCl₃ gas in diffusion furnace and electrodes for both front and rear side were fabricated following conventional screen printing method. These micro and nano structures were characterized using scanning electron microscope (SEM) and reflectivity of surfaces were measured using UV-Vis spectroscopy. The current-voltage (I-V) parameter of solar cell was measured under AM 1.5 G solar spectrum at 25 °C using solar simulator and external quantum efficiency (EQE) was examined using spectral response measurement system. This photoresist (PR)-free etching process can reduce the total cost for micro and nano structure fabricating. And the cylindrical structure could be applied for fabricating of nano and micro structured solar cells with low reflectivity.

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Preparation of microcapsules containing electrically tunable photonic crystal ink

Authors : Sujung Kim, Chul Am Kim, Hojun Ryu
Affiliations : Electronics & Telecommunications Research Institute

Resume : Responsive photonic crystals which change their reflection wavelength or intensity under external stimulus, have stimulated enormous research interest due to their applications in color displays, bio- and chemical sensors, photonic printing and decoration and anti-counterfeit labels. One of the focuses in these active research fields is to develop photonic crystals with a full color reflective display because they play a critical role in the development of high quality electronic papers and other information materials. In principle, one can achieve such a property by altering their periodicity and/or dielectric constants in response to an electrical, magnetic, or other stimulus. In practice, electrically responsive photonic crystals are more useful For use in full color reflective display, the photonic crystals should be modified to increase the suspension stability, solvent resistance and take on charges in nonpolar medium. In this study, we first improve the dispersibility of iron oxide particles in nonpolar solvents through surface modification of hydrophobic chains. The charge control agent was also added to the nanoparticle suspension in the dielectric medium to improve the mobility of the suspended photonic crystals. In addition, microcapsule containing colloidal photonic crystals was synthesized via a complex coacervation using gelatin and acacia gum as wall material to examine its potential application as e- skin devices.

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Superparamagnetic Iron Oxide Nanoparticles (SPION) labeled with Alexa Fluor® 750 as multimodal imaging agents - synthesis and physicochemical characterization

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Authors : Gabriela Kania, Weronika Górka, Szczepan Zapotoczny, Maria Nowakowska
Affiliations : Faculty of Chemistry, Jagiellonian University in Krakow, Ingardena 3, 30-060 Krakow, Poland

Resume : There has been observed growing interest in multimodal nanoparticles functioning as imaging agents. Magnetic Resonance Imaging (MRI) is a noninvasive technique commonly used in medical diagnostics. To improve visibility of internal structures, contrast agents are injected into the bloodstream. Another technique used in medicine is fluorescence microscopy. The combination of magnetic and fluorescent properties in one structure has some benefits. The most important advantage of MRI is practically unlimited tissue penetrating depth, whereas there is worse spatial resolution. On the other hand, fluorescence microscopy is a complementary technique to MRI with rather limited depth of imaging, but high spatial resolution [1]. In this report we present the synthesis and physicochemical properties of a novel contrast agent, SPION coated with ionically modified chitosans [2], which surface was modified by Alexa Fluor® 750 serving as a fluorescent probe. The obtained materials may be used as multimodal imaging agents for biomedical applications. References: [1] J Nanomater 2010, art. no. 894303 [2] J Nanopart Res 2013, 15:1372
Acknowledgements: This work was supported by the European Union from the resources of the European Regional Development Fund under the Innovative Economy Programme (grant coordinated by JCET-UJ, No POIG.01.01.02-00-069/09).

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Semiconductor quantum dots in homogeneous multiplexed FRET immunoassays

Authors : K. David Wegner, Xue Qiu, Niko Hildebrandt

Affiliations : NanoBioPhotonics, Institut d'Electronique Fondamentale, Université Paris-Sud, Orsay (France). www.nbp.ief.u-psud.fr

Resume : Semiconductor quantum dots (QDs) are well known for their superior photophysical properties. Their strong and spectrally broad absorption and their bright and narrow-band photoluminescence (PL) emission make QDs ideally suited for Förster resonance energy transfer (FRET). Combining QDs as FRET acceptors with luminescent terbium complexes (Tbs) as FRET donors offers exceptionally large Förster distances of more than 10 nm (detection of biological interactions over large distances), and time-gated PL detection for efficient suppression of autofluorescence and of PL from directly excited QDs (high sensitivity). The unique spectral properties of the Tb-QD FRET-pair allow the measurement of multiple biomarkers in a single sample (multiplexing). For the integration of multiplexed Tb-to-QD FRET into clinical diagnostics the technology needs to be applied in homogeneous sandwich immunoassays, which can be measured clinical fluorescence plate readers using small-volume serum samples. In this contribution we present multiplexed detection of the tumormarkers prostate specific antigen (PSA), neuron-specific enolase (NSE) and carcinoembryonic antigen (CEA) using FRET from Tb to different QDs. The homogeneous immunoassays were optimized using different types of antibodies (IgG, F(ab')₂ and F(ab) with molecular weights of ca. 150, 100 and 50 kDa, respectively), leading to picomolar detection limits for PSA, NSE and CEA in 50 µL serum samples. In addition to these QD-based in-vitro diagnostic tests, we performed a detailed study of the different FRET-systems using time-resolved spectroscopy. These investigations revealed the influence of the different antibodies on distance, functionality and sensitivity of the FRET immunoassays.

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Study on the Thermal Stability of Blue Phases by Addition of Mesogenic Thiol Ligand Modified Gold Nanoparticles

Authors : Jihye Lee[1], Sung-Kyu Hong[2] and Hyun Jung[1,*]

Affiliations : [1] Advanced Functional Nanohybrid Material Laboratory, Department of Chemistry, Dongguk University, Seoul-campus, 30 Pildong-ro 1-gil, Jung-gu, Seoul, 100-715, Korea; [2] Department of Chemical & Biochemical Engineering, Dongguk University, Seoul-campus, 30 Pildong-ro 1-gil, Jung-gu, Seoul, 100-715, Korea

Resume : Blue phases (BPs) have an enormous interest due to their unique optical properties and potential applications as self-assembling tunable photonic crystals and fast-response display. However, BPs have a limited thermal stability within a temperature range normally less than 1.0 oC due to the free energy cost of disclination lines. Therefore, we introduce surface modified gold nanoparticles in liquid crystal (mixture of 4-cyano-4'-pentylbiphenyl, JC-1041XX and chiral dopant) to decrease the free energy around disclination lines through the interaction between defect line and gold nanoparticles. In this regard, we modify the surface of gold nanoparticles with mesogenic thiol ligand (4'-(10-mercaptodecyloxy)biphenyl-4-carbonitrile, HS10OCB). The pristine gold

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nanoparticles were synthesized via Brust's two-phase reaction. The obtained gold nanoparticles were functionalized with the various ratios of dodecanethiol and HS10OCB. The obtained gold nanoparticles were characterized by high-resolution transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR). In order to searching the optimal interaction between the gold nanoparticles and disclination lines in BPs, we have studied the thermal stability of the BPs depending upon the addition amount of gold nanoparticles and the ratios of surface modifying ligands (dodecanethiol and HS10OCB) by polarizing optical microscopy (POM) and UV/vis spectrophotometry along with differential scanning calorimetry (DSC).

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Room temperature ferromagnetic response in CeO₂ and Cu doped CeO₂ nanocapsules crystallized under droplet confinement

Authors : Inderjeet Singh^{1,2}, Samet H. Varol², Katharina Landfester², Rafael Muñoz-Espí², Amreesh Chandra¹

Affiliations : 1 Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur 721302 West Bengal, India 2 Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Resume : It is shown that nanostructures of CeO₂ with capsular morphology can be obtained at ambient conditions by initiating the crystallization at the liquid-liquid droplet interface in inverse miniemulsions. The extent of interfacial crystallization can be modulated by varying the concentration of cerium precursor. This also allows the fabrication of CeO₂ nanocapsules with higher homogeneity and reproducibility. The size confinement forces the system to behave as an elongated grain and ferromagnetic type characteristic can be obtained at RT from CeO₂ nanocapsules. The ferromagnetic parameters are comparable or better than previous reports on CeO₂ nano-ceramics obtained using various thermal and pressure dependent synthesis routes. Doping of Cu in CeO₂ nanostructures induces appreciable enhancement in the ferromagnetic response. The frequency dependent dielectric response of CeO₂ nanoparticles also shows interesting features.

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TOXICOLOGY OF Fe₂O₃-SiO₂ CORE-SHELL NANOPARTICLES: ANALYSIS OF THEIR POTENTIAL THROMBOTIC, INFLAMMATORY AND HAEMOLYTIC EFFECTS

Authors : S. Grandi¹, C. Achilli², G.F. Guidetti², A. Ciana², E. Quartarone¹, D. Capsoni¹, G. Minetti²

Affiliations : 1 Dep. of Chemistry and INSTM, University of Pavia, V.le Taramelli 12, 27100 Pavia, Italy. 2 Department of Biology and Biotechnology "L. Spallanzani", Laboratories of Biochemistry, University of Pavia, Via Bassi 21, 27100 Pavia, Italy.

Resume : Nanostructured drugs, drug carriers and imaging agents are usually applied systemically, with blood first coming into contact with the injected nanoparticles. The various blood cellular components respond in a different and peculiar way to foreign material, depending on its chemical nature, dimensions and shape. Adverse effects of injected nanoparticles against erythrocytes may cause their lysis, producing jaundice and anaemia. Anomalous interaction with platelets can prompt their activation, with the formation of thrombi and the occlusion of blood vessels. Unwanted activation of neutrophils can also lead to oxidative and proteolytic damage to other blood components and blood vessels, and inflammatory reactions. Safety of intravenously administered nanostructured drugs is therefore a major issue, however, this aspect has been poorly investigated so far. The aim of this work was the investigation of haemocompatibility of core-shell nanoparticles (<150 nm diameter), which are of large interest for nanomedicine, in order to establish their safety for biomedical applications. Nanoparticles are constituted by a nanocrystal core of superparamagnetic Fe₃O₄ (obtained through thermal decomposition methods) coated with silicon dioxide by a sol gel process, and were characterized by means of Thermal Analysis, Infrared Spectroscopy, X-Ray Diffraction, Transmission Electron Microscopy and Dynamic Light Scattering. In vitro biochemical tests were performed on purified blood cells to evaluate platelet and neutrophil activation and erythrocyte lysis.

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Silver Nanoparticles Decorated DNA: An Ultrasensitive SERS Substrate

Authors : Dipanwita Majumdar, Achintya Singha, Prasanna Kumar Mondal, Subrata Kundu

Affiliations : Department of Physics, Bose Institute, 93/1, Acharya Prafulla Chandra Road, Kolkata 700009, India; Department of Physics, Bose Institute, 93/1, Acharya Prafulla Chandra Road, Kolkata 700009, India; Astroparticle Physics and Cosmology Division, Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata 700064, India;

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Electrochemical Materials Science (ECMS) Division, CSIR–Central Electrochemical Research Institute (CECRI), Karaikudi 630006, India

Resume : Detection of single-molecules is the ultimate sensitivity desired in chemical analysis, trace detection and biosensing .1,2 Surface Enhanced Raman Scattering (SERS) is a powerful analytical tool for acquisition of characteristic fingerprint at single-molecule level. Compared to normal Raman signals, SERS signals are ideally amplified 10¹³ to 10¹⁵ times when the probe molecules reside in the nanogaps (known as "hot-spots") between metal nanoparticles (NPs).3,4 The localized electromagnetic field, originating from the resonant coupling of the incident light with the surface plasmons, is the main reason for SERS enhancement. The plasmonic coupling effects at the "hot-spots" enable us to detect Raman active molecules with single-molecule sensitivity.5 The practical applications of SERS demand Raman signals to be reproducible and stable, and the substrate to be synthesized facilely. Recently, biomolecules have drawn enormous research attentions for their templating capacities to realize stable metal nanoclusters (NCs) with uniform interior nanogap. Here, by exploiting an easy and inexpensive route, we have fabricated a self-assembled wirelike silver-NCs (Ag-NCs) substrate with an inter-particle gap of 1.7 ± 0.2 nm using DNA as a template.6 The NPs are tightly immobilized by the DNA and have shown high performance as SERS platform with excellent reproducibility at single-molecule level.6 Here, DNA not only forms Ag-NCs but also plays an important role for the enhancement of the signals.6 In addition, the SERS signal is not highly dependent on the polarization of the excitation laser, as confirmed from both the experimental and theoretical simulation results.6 We believe that in future the DNA-based metal NCs might be useful as a potential SERS substrate for various applications like label-free biomedical sensing, Raman imaging etc. References: 1. X. S. Xie, J. K. Trautman, Annu. Rev. Phys. Chem., 1998, 49, 441–480. 2. F. Kulzer and M. Orrit, Annu. Rev. Phys. Chem., 2004, 55, 585–611. 3. S. Nie, S. R. Emory, Science, 1997, 275, 1102–1106. 4. K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari, M. S. Feld, Phys. Rev. Lett., 1997, 78, 1667–1670. 5. Q. Li, Y. Jiang, R. Han, X. Zhong, S. Liu, Z. Y. Li, Y. Sha, D. Xu, Small, 2013, 9, 927–932. 6. D. Majumdar, A. Singha, P. K. Mondal, S. Kundu, ACS Applied Materials and Interfaces, 2013, 5, 7798-7807.

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Preparation of Ag colloids by laser ablation in water: effect of target surface characteristics on nanoparticles distribution

Authors : A. Resano-Garcia, Y. Battie, A. En Naciri, N. Chaoui

Affiliations : LCP-A2MC, Institut Jean Barriol, Université de Lorraine, 1 Bd Arago, 57070 Metz, France

Resume : The most common route to prepare noble metals NPs consist of the reduction of metal salts in presence of stabilizers. Although, this technique offer some advantages such as simplicity and good control of the NP size and shape, the presence of reducing agent residues and/or stabilizers on the NP surface constitute its main disadvantage for applications in SERS, bio-medicine, or catalysis. Pulsed-Laser Ablation in Liquid (PLAL) appears as an alternative preparation method that addresses this drawback and allows to produce pure colloids, i.e. free of ligand (as long as a pure metal target is ablated in pure solvent). However, the too numerous processing parameters and their interdependence raise problems of reproducibility. In this presentation, the influence of the surface preparation and pre-treatment of the silver target on the NP population characteristics (size, shape and composition) is investigated. We aim to determine the extent to which the preparation of the target surface can influence the NP distribution obtained by PLAL. For that purpose, we present the results of several PLAL experiments, conducted in the same conditions with Ag target showing variable surfaces characteristics (degree of polish, freshly polished or aged target, pre-ablated target...). The extinction spectra of the colloids and their size distribution, obtained by TEM, are compared and put in relation with SEM observations of the ablated area of the target prior and after laser ablation.

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Fabrication of magneto-thermo-responsive microgels

Authors : Katharina Wiemer, Karla Dörmbach, Garima Agrawal, Andrij Pich, Ulrich Simon

Affiliations : Katharina Wiemer; Ulrich Simon Institute for Inorganic Chemistry of RWTH Aachen University, Landoltweg 1, 52074 Aachen Karla Dörmbach; Garima Agrawal; Andrij Pich Leibniz Institute of Interactive Materials DWI and Institute for Technical and Macromolecular Chemistry of RWTH Aachen University, Forckenbeckstraße 50, 52056 Aachen, Germany

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Resume : We report the synthesis of hybrid microgel particles loaded with magnetic nanoparticles (NPs) by using a solvent exchange method. Poly(N-vinylcaprolactam) microgels were transferred via dialysis from water into tetrahydrofuran (THF) solution and mixed with colloidal solutions of superparamagnetic 8.8 nm FePt NPs. FePt NPs are very hydrophobic due to the stabilization with oleyl amine and oleic acid ligands. By exchanging the surrounding solvent from THF to water again, the FePt NPs are forced to migrate into the microgels, whereby the uptake can accurately be controlled. These composite hybrid materials are colloidal stable in water and exhibit thermal responsiveness similar to un-loaded microgels. Furthermore, not only polymer features but also magnetic characteristics provided by FePt NPs can be observed for the hybrid material. Based on the thermal responsiveness of the loaded microgels a thermally induced volume phase transition (VPT) occurs. By applying of an alternating magnetic field these composite hybrid materials can magneto-thermally be heated above the VPT. Mentioned structures might find applications in medical field like Hyperthermia or drug delivery due to the biocompatibility of microgels and their responsiveness to external stimuli like temperature and magnetic field.

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CESIUM SALT OF 12-TUNGSTOPHOSPHORIC ACID AS NANO CATALYST

Authors : Elif AKBAY, Gülberk DEMİR

Affiliations : Anadolu Univ., Faculty of Eng., Dept. Of Chemical Eng.,Eskişehir, Turkey

Resume : Nanoparticles have emerged as sustainable alternatives to conventional materials, as robust, high surface area heterogeneous catalysts and catalyst supports [1]. Nowadays, studies for the synthesis of nano-catalyst increased but there are not more studies related to synthesis of nano scale heteropolyacid catalysis. Heteropolyacids of various heterogeneous catalysts have drawn attention due to their unique features such as well-defined structure, Bronsted acidity, high proton mobility, the ability to exchange electrons [2,3]. As a hetero-polyacid, 12-tungstophosphoric acid, H₃PW₁₂O₄₀, is known as a strong acid and it is considered within the class of super acid [4]. The substitution of protons such as Cs, K, Ag, and NH₄ can enhance the porosity and surface area as well as the insolubility. 12-tungstophosphoric acid cesium salt, Cs_{2.5}H_{0.5}PW₁₂O₄₀, exhibits high catalytic activity for various kinds of acid-catalyzed reactions [5-8]. Nano catalysts indicate both properties of homogeneous catalyst and heterogeneous catalyst. In this study, acidic cesium salts were prepared as nano catalyst by ultra-sound which was one of the synthesis methods of nano catalysis. All synthesized nano Cs-TPAs have been characterized by using XRD patterns and it is seen that crystal structure of Cs-TPA is maintained. The crystallite sizes of these samples were obtained by using Scherrer's equation using XRD data. It was found that the average crystallite size of all synthesized nano Cs-TPA is 13 nm. At the FT-IR analysis, it is seen that functional structure of Cs-TPA is maintained in nano Cs-TPAs and nano Cs-TPAs have Lewis and Brønsted acidity. SEM images given in Figure 1 indicate that the particles are fairly spherical. According to the XRF, it was found that the average value of W/Cs was 4.9. This value is very close to the stoichiometric W/Cs molar ratio of 4.8 for CsPW. TG analysis indicate that structure of nano Cs-TPA was maintained and all results proved that nano Cs-TPA was synthesized successfully. The particle size of catalyst was estimated from the surface area according to BET analysis. Particle sizes and BET surface areas of synthesized nano Cs-TPAs at different amplitudes are given Table 1. Green chemistry and nano-catalysis are most important areas of research at the present time. In this study, Cs-TPA was synthesized as nano particles and it was used in alkylation of benzene with dec-1-ene. The characterization of the synthesized nano Cs-TPA were examined by the XRD, FTIR, SEM, TG-DTG, particle distribution and crystallite size. The results show that Cs-TPA synthesized in nano scale and maintained all properties of Cs-TPA.

Acknowledgements The authors would like to thank The Anadolu University Scientific Research Projects Commission (Project No: 1207F112) for the financial support. **References** [1] V. Polshettiwar and R. S. Varma, The Royal Society of Chemistry, 12 (2010) 743-754. [2] L.E. Briand, G.T. Baronetti, H.J. Thomas, Appl. Catal. A Gen. 256 (2003) 37-50. [3] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171-98. [4] T. Okuhara, N. Mizuno, M. Misono, Appl. Catal. A Gen. 222 (2001) 63-77. [5] K. Na, T. Okuhara, M. Misono, J. Chem. Soc. Farad. Trans. 91 (1995) 367. [6] N. Essayem, G. Couudurier, M. Fourier, J.C. Védrine, Catal. Lett. 34 (1995) 223. [7] T. Okuhara, T. Nishimura, H. Watanabe, M. Misono, J. Mol. Catal. 74 (1992) 247. [8] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 103.

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- 17:50 **Synthesis of CdTe nanocrystals: ligand effect on morphological and functional properties**
Authors : Francesca Di Benedetto, Maria Lucia Protopapa, Luigi Bucci, Anna Grazia Scalone, Marilena Re, Luciana Algieri, Roberta Rosato, Maria Elena Mosca, Leander Tapfer
Affiliations : ENEA – Italian National Agency for New Technologies, Energy and Sustainable Economic Development – Technical Unit for Materials Technologies - Brindisi Research Center
Resume : High quality semiconductors nanocrystals (NCs) focus an increasing interest as promising materials for applications in the field of photonic crystals, LEDs, solar cells and bioimaging. [1] In this framework, the synthesis of the nanocrystalline CdTe by non-coordinating solvents could compete for quality and efficiency with other II-VI nanocrystals thanks to the pronounced quantum size effect and optical activity both in the visible and near infrared spectral regimes (with a bulk band gap of 1.44 eV at 300 K). The typical protocols used for the synthesis of colloidal nanocrystalline CdTe are based on the methods worked out by Y.A. Yang et al. [2] and J. Kolney-Olesiak et al. [3]. The ligands used as capping agent are phosphonic acid (ODPA) and fatty acid (oleic acid). In the present work we investigate the effects induced by other capping ligands on morphological and functional properties of CdTe NCs. In particular, the capping ligands chosen belong to the family of fatty acids saturated or unsaturated at long chain (C13 - C21). This family of ligands allows one to control the growth of crystals and also plays a fundamental role in the nanocrystalline structure of the CdTe. The effects of the several ligands on the microstructural, morphological and functional properties of NCs were studied by using wide and small angle X-ray scattering, transmission electron microscopy (TEM) and He-ion microscopy (HeIM), FTIR and photoluminescence and optical spectroscopy measurements. [1] Zhong H., Mirkovic T., Scholes G. D. Comprehensive Nanoscience and Technology, 2011, 5, 153. [2] Yang, Y.A.; Wu, H.; Williams, K. R.; Chao, Y. C. Angew. Chem. Int. Ed 2005, 44, 6712. [3] Kolney-Olesiak, J.; Kloper, V.; Osovski, R.; Sashchiuk, A.; Lifshitz, E. Surf. Sci 2007, 601, 2667

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- 17:50 **Study on the separation of nucleation and growth in silica nanoparticles microfluidic synthesis**
Authors : Bert De Roo, Alexander Schwamberger, David Jacob, Lutz Bruegemann, Jin Won Seo, Jean-Pierre Locquet
Affiliations : Department of Solid State Physics and Magnetism, KU Leuven, Belgium; Bruker AXS/TU Dortmund, Germany; Corduan Technologies, France; Bruker AXS, Germany; Department of Metallurgy and Materials Engineering, KU Leuven Belgium; Department of Solid State Physics and Magnetism, KU Leuven, Belgium
Resume : The use of nanoparticles is increasing in science, industry and medicine. In most applications, a very good knowledge of the properties of these nanoparticles is desired. To obtain a good control over these properties, we studied the effect of separating the nucleation and the growth of silica nanoparticles. In this study we used a microfluidic reactor at an elevated temperature to trigger the nucleation of silica nanoparticles. This reactor is connected to a capillary where the growth takes place. By varying the input flow of the different precursors, we can change the amount of silica nucleation. By varying the total input flow, we can control the total amount of time the precursors spend in the microreactor. When we have a large flow speed, the unwanted growth of silica nanoparticles inside the microreactor is negligible and the separation of the nucleation and growth has been accomplished. We monitored the growth of the silica in situ with a laboratory Small Angle X-ray Scattering (SAXS) instrument and Dynamic Light Scattering (DLS) device. Both were used as real-time monitoring tools. The results were then checked with transmission electron microscopy to confirm if the growth process was finished and to confirm the size and size distribution obtained from the SAXS data.

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- 17:50 **A study on the formation of luminescent and stable CdS nanoparticles using Pleurotus ostreatus**
Authors : M.N. Borovaya, A.P. Naumenko, Ya.V. Pirko, T.A. Krupodorova, A.I. Yemets, Ya.B. Blume
Affiliations : M.N. Borovaya, Ya.V. Pirko, T.A. Krupodorova, A.I. Yemets, Ya.B. Blume; Institute of Food Biotechnology and Genomics, Natl. Acad. of Sci. of Ukraine; A.P. Naumenko; Department of physics, Taras Shevchenko National University
Resume : CdS semiconductor nanoparticles have attracted great attention of scientists due to their highly interesting optical and electronic properties. Mentioned nanoparticles have a diverse range of applications. For example, they

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are employed as an alternative to traditional dyes since they have high levels of photostability and resistance to photobleaching. Also QDs are extremely promising targets for biosensing applications. Fluorescence resonance energy transfer (FRET) based on QDs is applied for monitoring some processes, such as DNA replication, telomerisation. A single QD-based nanosensor is able to detect extremely low concentrations of DNA (50 copies). In the present investigation fluorescent CdS QDs have synthesized using mycelium of the fungus *Pleurotus ostreatus* as biological matrix and cadmium sulfate solution as the source of cadmium. Mycelium was grown at the temperature 28 degrees Celsius. The absorption and luminescence spectra of such nanoparticles were investigated. It was found that the maximum in absorption spectrum correspond to the wavelength 453 nm. For samples containing CdS nanoparticles in luminescence spectrum were observed several distinct peaks at 431, 462, 486, 524 nm (excitation by a wavelength 340 nm). These peaks correspond to the excitonic band of various sizes nanoparticles. By the method of transmission electron microscopy was revealed that obtained quantum dots have spherical shape and size in the range from 5 to 8 nm. Resulting luminescent CdS nanoparticles are stable and promising for further biological applications.

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Optical Spectroscopy of Single Carbon Dots

Authors : Ming Fu , Jacek Stolarczyk, Jochen Feldmann, Yu Wang, Andrey L. Rogach
Affiliations : Photonics and Optoelectronics Group, Department of Physics and CeNS, Ludwig-Maximilians-Universität München, Amalienstrasse 54, D-80799 München, Germany; Photonics and Optoelectronics Group, Department of Physics and CeNS, Ludwig-Maximilians-Universität München, Amalienstrasse 54, D-80799 München, Germany; Photonics and Optoelectronics Group, Department of Physics and CeNS, Ludwig-Maximilians-Universität München, Amalienstrasse 54, D-80799 München, Germany; Department of Physics and Materials Science and Centre for Functional Photonics (CFP), City University of Hong Kong, Hong Kong SAR; Department of Physics and Materials Science and Centre for Functional Photonics (CFP), City University of Hong Kong, Hong Kong SAR;

Resume : The excitation-dependent PL behavior of carbon dots (CDs) can be useful in multi-color imaging applications, although their exact structure of the CDs is largely unknown. Through the single-particle spectroscopic measurements on individual CDs, we showed several interesting fluorescent phenomena which can not be observed in the ensemble of CDs. First, the studied CDs show almost the same PL spectral lineshapes and peak position irrespective of the size. Second, all the individual CDs studied showed stable fluorescence, which is free of PL blinking and bleaching effect. This indicates that an individual CD can not be treated as a single molecular emitter. Therefore, an individual CD may main contain many single molecular emitters with different frequency inside, which can be selectively excited at different wavelength and is responsible in the excitation-dependent PL behavior of CDs. These results provide insights into the internal structure of the CDs, in particular of their light emitting components, and will also help in applying the dots in wavelength-tunable nanolaser or light-emission diode.

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Synthesis, characterization and optical properties of graphene containing colloid material

Authors : S. Nedilko(a), S. Revo(a), V. Chornii(a), M. Nediuko(b), Yu. Sementsov(c)
Affiliations : (a) Taras Shevchenko National University of Kyiv, Volodymyrska Street 64/13, 01601, Kyiv, Ukraine; (b) E.O. Paton Electric Welding Institute of NASU, Kyiv, Ukraine; (c) Chuiko Institute of Surface Chemistry, NASU, Kyiv, Ukraine

Resume : Today various types of graphene preparation are well known. The mechanical exfoliation of HOPG graphite; nano-diamond – and SiC- based precursor methods, CVD growth using metal catalysts, such as Ni, Cu, etc. In spite that, development of new methods for fabrication of graphene – like structured materials is still under investigation, as a graphene families of materials prepared with different methods reveal somewhat different properties. We tried to use modified electro-chemical dispersion, called by us as electro-chemical exfoliation method, to prepare graphene containing material in the shape of colloid system. Raman spectroscopy, optical, AFM, STM, and SEM microscopy were applied for characterization of both freely suspended and extracted carbon particles sitting on various substrates (like glass, Si, quartz) as well. Luminescence studies were also performed for suspended particles and for flakes on glass or quartz substrates and for aggregated flakes too. We conclude that ensemble of particle consists of large particle those posses graphite structure and some quantity of graphene – type flaks. Dependences of the

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characteristics on the concentration, chemical treatment, size, and thickness of carbon micro- and nanoparticle stacking were obtained and analyzed.

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Hybrid ZnO:Polystyrene Nanocomposite for All Polymer Photonic Crystals

Authors : Paola LOVA 1,2,6, Luca BOARINO 3, Michele LAUS 4, Giulia URBINATI 5, Franco MARABELLI 5, Cesare SOCI 6, Davide COMORETTO 2

Affiliations : 1 Interdisciplinary Graduate School, Energy Research Institute at NTU (ERI@N), Nanyang Technological University, Singapore; 2 Department of Chemistry and Industrial Chemistry, University of Genoa, Italy; 3 National Institute of Metrological Research (INRIM), Italy; 4 Department of Life Sciences, University of Eastern Piedmont, Italy; 5 Department of Physics, University of Pavia, Italy; 6 Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore.

Resume : Polymer Distributed Bragg Reflectors (DBRs) are photonic crystals suitable for organic optoelectronic devices such as LEDs, lasers and sensors. They are usually prepared by spin coating of alternated orthogonal polymer solutions. Unfortunately, the orthogonality constraint, the relatively poor difference of polymers refractive index and the requirement of high transparency limit the available materials. 1 Polymers refractive index can be engineered preserving processability and transparency using oxides nanofillers. Here we report on high optical quality DBRs prepared alternating cellulose acetate ($n=1.46$) and ZnO:polystyrene (PS) nanocomposite layers engineered to increase PS refractive index ($n=1.58$). The new DBRs show a photonic band gap in the near infrared spectral region, an extended diffraction pattern up to the fifth order and the expected dependence on light polarization and incidence angle. Nanocomposite thin films are prepared loading into a PS solution ZnO nanoparticles grown by low temperature solvothermal synthesis after a graft reaction with a silane performed to reduce phase segregation in the non-polar matrix. Spectroscopic ellipsometry shows a 3% increase of PS refractive index upon ZnO loading of 5% v/v in agreement with effective medium theory. These results suggest a new strategy for the development of highly processable hybrid DBRs for photonic applications. 1 L. Frezza, M. Patrini, M. Liscidini and D. Comoretto, J. Phys. Chem. B 115 (40), 19939 (2011)

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Controlled growth of CdS nanoparticles in LTL colloidal zeolite

Authors : V. De Waele[a], A. Souici[b], K.-L. Wong[c], J. L. Marnignier[c], I. De Waele [a], M. Mostafavi[b] S. Mintova[c]

Affiliations : [a] LASIR, UMR8516 CNRS-Université de Lille 1, Cité scientifique, F-59655 Villeneuve d'Ascq, France [b] Laboratoire de Chimie Physique, UMR-8000, CNRS – UPS, Bat. 349, Orsay 91405, France ; Tel : 33 16915 7887 [c] Laboratoire Catalyse et Spectrochimie, ENSICAEN - Université de Caen – CNRS, 6, Boulevard du Maréchal Juin, 14050 Caen, France

Resume : The formation of CdS in LTL colloidal zeolite stabilized in the form of stable suspension is investigated by radiolysis. The growing process of CdS in the zeolite was induced using a gamma-ray irradiator (low dose rate) or using a pulse electron accelerator (high dose rate) and followed by UV-Vis spectroscopy. Two distinct stages during the formation of sub-nanometer sized CdS clusters in the LTL type zeolite are identified: (i) fast formation of dispersed small oligomers exhibiting a well-defined sharp absorption peak, which is shifted from 290 nm to 350 nm in the course of the growth process, and (ii) formation of interconnected CdS clusters along the zeolite channels by diffusion- assisted process. The final size and distribution of CdS is controlled by the irradiation dose. Additionally, the presence of sub-nanometer sized CdS clusters in the zeolite channels is confirmed by transmission electron microscopy (TEM). The colloidal zeolites were deposited in thin films and characterized by UV-Vis and FT-IR measurements. The sub-nanometer sized CdS clusters formed in the LTL type zeolite suspension exhibit a good stability under hydrous conditions.

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Synthesis and compositional control of size monodisperse SixGe1-x alloy nanocrystals for optoelectronic applications

Authors : Darragh P. Carolan, Keith Linehan, Hugh Doyle

Affiliations : Tyndall National Institute, University College Cork, Lee Maltings, Cork, Ireland

Resume : While the preparation of Group IV (Si, Ge) nanocrystals has been intensely researched, tuning of the band gap energies is not as well-developed as for III-V and II-VI semiconductor materials. Current approaches to modifying the composition of the NCs to improve their properties are based on either doping or alloying. While doping of NCs remains difficult, alloying involves

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mixing materials of the same electronic valency, to smoothly vary the properties from those of one material to another. Solution-phase synthesis and characterisation of size monodisperse alloy $\text{Si}_x\text{Ge}_{1-x}$ NCs dispersed in non-polar solvents with core diameters (d) between 1 -5 nm has been carried out. Alloy NCs were synthesised via the co-reduction of Si and Ge halide salts within reverse micelles. Composition of the silicon-germanium nanocrystals was carried out by varying the relative amounts of precursor. Covalent attachment of surface-bound monolayers produced NCs that stable under ambient conditions over a period of months. UV-Visible absorbance (UV-Vis) and photoluminescence spectroscopy (PL) showed strong significant quantum confinement effects, with moderate absorption in the UV spectral range, and strong emission in the blue, with photoluminescence quantum yields and lifetimes varying with nanocrystal composition.

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One pot two steps synthesis of water soluble functionalized gold nanoparticles

Authors : Romain Aupaure, Yoann Lalatonne, Laurence Motte and Erwann Guénin

Affiliations : Laboratoire CSPBAT (UMR7244) ; LPBS ; Université Paris 13 ; France

Resume : Water soluble gold nanoparticles (GNPs) own physical and chemical properties with a large scope of application in the biomedical research. Our project aims to develop new synthetic pathways for the direct synthesis of GNPs already possessing functionality allowing easy access to bio functionalization. This is achieved by using synthesized water soluble molecules. These molecules are bifunctional : One functional group is able to both reduce gold(III) chloride and to coat the surface of the obtained GNPs. The other functional group will remain inert during the NPs synthesis and will allow further chemoselective GNPs functionalization. Herein we will present the mechanism of this GNPs synthesis. We have demonstrated the related mechanism of this colloid formation and the interaction between our bifunctional molecules and the gold surface by classical analytical chemistry techniques. Optimization of the various synthesis parameters (temperature, concentration and pH) have been assessed to yield homogeneous GNPs of size ranging from 13-21 nm. Then reactions at the surface with the remaining, functional group have been characterized, confirming their chemoselective reactivity. These new GNPs are also used as a building block for sized controlled covalent assemblies preparation. The controlled size assemblies are water soluble and presents specific optical properties shifting from blue to NIR absorption yielding to promising in vivo applications such as hyperthermia.

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The effect of pressure on structural and electrical properties of nanocrystalline CdS

Authors : A. A. Ebnalwaled

Affiliations : Electronics & Nano Devices Lab, Physics Department, Faculty of Science, South Valley University, Qena, 83523 Egypt Corresponding author: e-mail: kh_ebnalwaled@yahoo.com

Resume : Among II-VI compounds, CdS with a direct band gap, $E_g = 2.40$ eV, is an important semiconductor with non-linear optical properties has potential applications such as solar battery, photoelectrocatalysis, Biological sensors and photodiodes. Many synthetic methods have been employed to prepare CdS nanoparticles including solid state reaction, sol-gel process and microwave heating. In the present work a simple chemical method is followed to grow CdS nanocrystals at room temperature. The effect of pressure on the microstructural and electrical properties of CdS nanocrystals was investigated in a pressure range 1.2 – 6.4 MPa for the first time in this work. The grown and compacted CdS nanocrystals were characterized for their electrical and structural properties using high resolution transmission electron microscopy (HRTEM), current-voltage measurements and X-ray diffraction patterns, respectively. It was determined from the results of these investigations that the electrical and structural properties of CdS nanocrystals considerably changed with pressure. The effect of crystallite size and microstrain on the electrical properties of CdS nanocrystals was investigated

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17:50

SUPERPARAMAGNETIC NANOPARTICLES FOR IMMUNO IMAGING OF BRAIN TUMORS BY MRI

Authors : Sophie Richard 1, Amaury Herbet 2, Marianne Boucher 3, Yoann Lalatonne 1, Sébastien Mériaux 3, Jean-Philippe Hugnot 4, Didier Boquet 2, Laurence Motte 1

Affiliations : 1 Université Paris 13, UMR 7244 CNRS, Bobigny, 93017, France; 2 CEA de Saclay, iBiTecS, LIAS, Gif sur Yvette, 91191, France; 3 CEA de Saclay, Neurospin, Gif sur

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Yvette, 91191, France; 4 Institut de Neuroscience de Montpellier, INSERM U1051, Montpellier, 34091, France;

Resume : Gliomas are the most common primary brain tumour in humans, affecting around 25000 people each year in Europe. To date, the only treatment of care consists of surgical removal of the tumour bulk, irradiation and chemotherapy, with finally a very poor prognosis. Literature and our personal works underline the significance to target endothelin receptor B (EDNRB) for imaging and/or eradicating glioma stem cells. Moreover, magnetic nanoparticles (MNPs) are excellent MRI contrast agents because of their transverse relaxation T2* property. MNPs can be also used for drug delivery coating the nanoparticle surface with therapeutic molecules. Hence, this hybrid nanosystem combines both MRI (diagnostic) and therapeutic applications. This strategy is referred to theranostic. The aim of this project is the experimental development of targeted multimodal medical imaging capable of achieving a high resolution, specificity and sensitivity in vivo MRI imaging through T2 contrast agent properties of iron oxide nanoparticles with a high specificity and sensitivity in vivo IR fluorescent imaging for guided surgery. To achieve this goal, we will develop the first antibodies-based dual-modality Fluorescent-MRI contrast agents, by combining iron oxide nanoparticles SPIOs with fluorescent nanoprobe with the first available antibodies (and fragments) directed and validated on EDNRB.

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[\(close full abstract\)](#)

17:50 **Graphene Complex Cellular Networks**

Authors : Suelen Barg, Felipe Macul Perez, Na Ni, Paula do Vale Pereira, Esther Garcia-Tuñon, Salvador Eslava, Cecilia Mattevi, Eduardo Saiz

Affiliations : Centre for Advanced Structural Ceramics, Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom

Resume : The development of many graphene-based technologies depends on our ability to assemble this two-dimensional building block into complex three-dimensional structures for practical devices. To achieve this goal it is necessary to develop fabrication approaches that enable an accurate control of chemistry and architecture at multiple length scales. In this work, we have developed a mesoscale self-assembly strategy for the manufacturing of ultra-light ($\rho \geq 1 \text{ mg cm}^{-3}$) chemically modified graphene CMG cellular networks. The approach is based on the use of soft templates and the controlled segregation of CMG to liquid interfaces allowing for manipulation of the structure at multiple levels from the densities (over two orders of magnitude from 1 to 200 mg cm^{-3}), cell shape (lamellar, polyhedral to spherical) and sizes (~ 7 to over 60 μm) at the micro-level to the cell walls topography, porosity and chemistry at the micro to nano-level. As a result we show it is possible to tune properties like surface area, elasticity, specific strength, energy loss coefficient, and conductivity. This opens up new opportunities to explore applications in numerous fields like in energy damping, compression tolerant super capacitors, catalysers or absorbers.

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17:50 **Hydrogenation of nanomaterials for high rate capability lithium ion batteries**

Authors : Jingxia Qiu, Evan Gray, Shanqing Zhang

Affiliations : Centre for Clean Environment and Energy Environmental Futures Centre Griffith School of Environment

Resume : Hydrogenation process could enhance conductivity of nanostructured semiconductors 1-3. Rutile TiO₂ powder and lithium Titanate (LTO) were hydrogenated under 40 bar H₂ pressure at 450 °C in this work. The hydrogenated LTO (H-LTO) and hydrogenated rutile TiO₂ (H-TiO₂) exhibit much improved performance compared with pristine LTO and rutile TiO₂. respectively as anode materials for lithium ion batteries (LIBs). We found that extend of the hydrogenation, i.e., crystalline properties (unit cell and volume) of the rutile nanorods, was enhanced by increase of the hydrogenation conditions (pressure, temperature, time). As shown in Fig. 1, the hydrogenated samples demonstrated significantly higher specific capacity and rate capacity than the pristine compounds. Furthermore, the rate capacity increased with the increase of treatment temperature and pressure. The significant improved performance of the hydrogenated blue samples over the white samples can be attributed to two reasons, the boosted electronic conductivity (i.e., reduced impedance) and the augmented TiO₂ lithium ion diffusion in the insertion/extraction process due to the partial removal of oxygen and formation of oxygen vacancy. The findings of this work provide guidance for the engineering of the properties of the metal oxide materials for LIBs via the hydrogenation processing. (1) Shin, J.-Y.; Joo, J. H.; Samuelis, D.; Maier, J., Chem. Mater. 2012, 24, 543-551. (2) Lu, Z. G.; Yip, C. T.; Wang, L. P.; Huang, H. T.; Zhou, L. M., Chempluschem 2012, 77,

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991-1000. (3) Xia, T.; Zhang, W.; Li, W.; Oyler, N. A.; Liu, G.; Chen, X., , Nano Energy 2013.

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PROGRAM VIEW : 2014 Spring

MY PROGRAM : 2014 Spring

Symposium : F

Established and emerging nanocolloids: from synthesis & characterization to applications

26 May 2014	27 May 2014	28 May 2014	29 May 2014	30 May 2014
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start at	Subject	Num.
	Bio-inspired Systems and Bio-Applications of nanoColloids : Laurence Motte, Erwann Guenin, Yoann Lalatonne, Florence Gazeau	
09:00	<p>Intracellular transformation of inorganic nanoparticles: how to conciliate theranostic efficiency with long term degradability in the organism? Authors : Florence Gazeau Affiliations : Laboratoire Matière et Systèmes Complexes, CNTS / Université Paris Diderot</p> <p>Resume : Many research efforts are presently focused on the life cycle and toxicity of nano-sized materials. While most toxicology studies warn about the effects of nanomaterials on biological functions (cytotoxicity, immunogenicity, genotoxicity...), the physical transformations of nano-objects in living environment are mostly unknown. Yet the mechanisms of biological transformations – aggregation, protein adsorption, degradation and elimination - determine the long term fate of nanoparticles in the body, their safety as well as their therapeutic outcome. Here we propose a multiscale methodology to examine the influence of intracellular lysosomal confinement on the structure and physical properties of magnetic nanoparticles that show outstanding properties for magnetothermal therapy and MRI detection. Our material science approach – combining nanoscale TEM observations of nanoparticle structure with the follow-up of magnetic properties in biological environment - opens up a new way to evaluate the life cycle of nanoparticles in the body and identify their biodegradation products. We will present several examples of magnetic nanostructures – iron oxide nanospheres, nanocubes, cooperative nanoflowers and iron oxide/gold dimers with different coating – and examine how cell-induced morphological degradation critically alters their magnetic properties, heating power and Magnetic Resonance relaxivity over time. Hence maintaining nanoparticles in the extracellular matrix of the tumor environment might be more advantageous for thermal therapy than favoring uptake by tumor cells. By contrast, specific internalization by the monocyte/macrophage system warrants the long term metabolization of particles and iron recycling. In the research for safe-by-design efficient nanoparticles for nanomedicine, one should control not only their synthetic identity, but also their ever-evolving context-dependent structure and properties. Controlling the balance between short term efficacy in the relevant biological context and long term degradability or elimination is an important challenge that may be overcome by chemical design of functionalized nanoparticles. References Lartigue L; Alloyeau, D; Kolosnjaj-Tabi, J; Javed, Y.; Guardia, P.; Riedinger, A.; Péchoux, C.; Pellegrino, T.; Wilhelm, C.; Gazeau, F. Biodegradation of Iron Oxide Nanocubes: High-Resolution In Situ Monitoring. ACS Nano 2013, 7, 3939-3952. Kolosnjaj-Tabi, J; Di Corato, R, Lartigue L; Guardia, P.; Luciani, N.; Flaud, P; Singh, JV, Decuzzi P, Pellegrino, T.; Wilhelm, C.; Gazeau, F. Heat Generating iron oxide nanocubes: subtle destructurators of the tumoral microenvironment. Submitted. Javed, Y.; Lartigue, Hugounenq P, Vuong QL, Gossuin Y, Bazzi R, Wilhelm C, Ricolleau C, Gazeau, F. Alloyeau, D. Biodegradation mechanism of iron oxide monocrystalline nanoflowers and tunable shield effect of gold coating. Submitted.</p>	F.IV. 1
	<p>add to my program (close full abstract)</p>	
09:30	<p>Silicon Carbide Quantum Dots: Properties and Application Authors : David Beke, Zsolt Szekrenyes, Istvan Balog, Katalin Kamaras, Balazs Rozsa, Istvan Palfi, Pál A. Maák, Adam Gali</p>	F.IV. 2

Affiliations : Wigner Research Centre for Physics; Institute of Experimental Medicine; Budapest University of Technology and Economics;

Resume : Visual analysis of biomolecules is an integral avenue of basic and applied biological research. Quantum dots (QDs) are semiconductor inorganic nanoparticles that are emerging as alternative or complementary tools to the organic fluorescent dyes currently used in bioimaging. Although these QDs have great potential as probes for bioimaging, certain limitations may restrict their applications. Cytotoxicity strongly influencing is one of the major limiting factors for the application of II-VI QDs in efficient in vivo imaging. We propose silicon carbide (SiC) QDs for bioimaging in order to eliminate numerous disadvantages of traditional QDs. SiC is a stable, chemically inert wide band gap indirect semiconductor. Biocompatibility of bulk SiC and SiC QDs has been proven by several research teams. We developed a two-step experimental routine of producing SiC QDs. First, microcrystalline SiC (SiC MCs) is formed by reactive bonding method which, principally, allows us to produce highly doped SiC MCs in order to modulate the optical properties of the prepared SiC QDs made from them. SiC QDs form by electroless wet chemical etching of the SiC MCs [1]. These SiC QDs are less than 3 nm in diameter and make stable colloid sol in water thanks to the surface termination that was studied by infrared spectroscopy. We developed a simple separation method to overcome of the relatively large size distribution of colloidal SiC QDs that could be suitable for two-photon study of neuron cells.

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09:45

Dextrin nanomagnetogels: in vivo performance as dual modality imaging bioprobe

Authors : Gonçalves, C.(a), Antunes, I. F.(b), Lalatonne, Y.(c), Ferreira, M.F.M.(d), Galdes, C.F.G.C.(e), Motte, L.(c), Martins, J.A.(d), de Vries, E. F. J.(b), Gama, F.M.(a)

Affiliations : (a) IBB-Institute for Biotechnology and Bioengineering, Centre for Biological Engineering, Minho University, Campus de Gualtar 4710-057, Braga, Portugal (b) Dept. of Nuclear Medicine and Molecular Imaging, University of Groningen, University Medical Center of Groningen, Hanzeplein 1, 9713 GZ Groningen, The Netherlands (c) CSPBAT Laboratory, UMR 7244 CNRS, Université Paris 13, Sorbonne Paris Cité, Bobigny, France (d) Chemistry Department, Minho University, Campus de Gualtar, 4710-057 Braga, Portugal (e) Departamento de Ciências da Vida, Faculdade de Ciência e Tecnologia, Centro de Neurociências e Biologia Celular e Centro de Química, Universidade de Coimbra, Portugal

Resume : Dual modality contrast agents, such as radiolabelled magnetic nanoparticles, are promising candidates for a number of diagnostic applications, since they combine two complementing imaging modalities, namely photon emission computed tomography (SPECT) and magnetic resonance imaging (MRI). The benefit of such combination lies on the ability to interpret more accurately abnormalities in vivo, by integrating the high sensitivity of SPECT with the superb spatial resolution and anatomical information provided by MRI. Superparamagnetic iron oxide nanoparticles (SPION) have been extensively studied as MRI contrast agents. SPIONs need to be coated in order to allow formulation in aqueous solutions and to increase in vivo stability. Dextrin nanomagnetogels consists on superparamagnetic iron oxide nanoparticles (γ -Fe₂O₃) stabilized within hydrophobized-dextrin nanogel (scheme 1). The nanomagnetogel formulation, with about 4 mM of iron and a diameter of 100 nm, presents relevant features such as superparamagnetic behaviour, high stability, narrow size distribution and potential for magnetic guidance to target areas by means of an external magnetic field [4]. The functionalization of the dextrin nanomagnetogel with a DOTA-monoamide γ -thiol metal chelator and radiolabelling with ¹¹¹In were used to ascertain its in vivo stability and behavior (blood clearance rate and organ distribution) after intravenous administration in mice model. The surface modification of the nanomagnetogel with PEG 5,000 was accomplished in an attempt to escape the phagocytic system. The unloaded radiolabeled dextrin nanogel (around 30 nm) showed lower uptake in the liver, spleen and kidneys than the nanomagnetogel loaded with SPIONs (around 110 nm). This difference in biodistribution profile can be ascribed to the differences in the particle size. Nanomagnetogel pegylation resulted in lower liver and spleen accumulation. The blood half-life obtained was approximately 4 hours for all formulations. A good correlation between the amount of polymer (quantified through radioactivity) and the amount of iron (ICP measurement) in the spleen was observed, indicating that leakage of iron from the nanomagnetogels after intravenous administration was negligible. The pilot imaging study demonstrated good performance of dextrin nanomagnetogels as dual modality imaging (MRI and SPECT) bioprobes as expected by the high transverse relaxivity (215-248 mM⁻¹s⁻¹) obtained in vitro, higher than those of commercial available

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3

formulations (160-177 mM-1s-1). The production of the nanomagnetogel is simple and easy to scale up, thus offering great technological potential. The authors acknowledge the program EuroNanomed and Fundação para a Ciência e a Tecnologia for funding through the project REBONE.

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10:00

Interactions of well-engineered nanoparticles and skin

Authors : Rute Fernandes(1), Neil R. Smyth (2), Simone Nitti (3), Michael R. Arden-Jones(2), Antonios G. Kanaras (1)

Affiliations : (1) Physics and Institute of Life Sciences, Faculty of Physical and Applied Sciences, University of Southampton, Southampton, United Kingdom, SO171BJ (2) Faculty of Medicine, University of Southampton, Southampton, United Kingdom, SO171BJ (3) Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy.

Resume : Understanding the interactions of nanoparticles with skin is of high importance for the development of new ways to deliver drugs efficiently but also in order to realize potential toxicity risks. The study of nanoparticle penetration through skin is a complex research task because it is associated with a number of experimental parameters that can not be easily controlled related to the complexity of the skin structure and the physicochemical characteristics of nanoparticles. In this presentation we follow a thorough analytical approach to answer key questions concerning these interactions. We will particularly focus on how the charge, shape and function of nanoparticles influence the penetration through skin. For our studies we chose to work with gold nanoparticles due to the ease of their surface modification. To gain a good understanding, we employ a number of techniques such as ICP-OES to quantitatively measure the penetration of nanoparticles, as well as two-photon spectroscopy and TEM cross sectioning to analytically detect the particles in the skin. Moreover we will hypothesize potential mechanisms of penetration.

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10:15

Discussion/Coffee Break

10:30

A Feasibility Study of NanoSERS Probe for Cancer Prognosis

Authors : Shuai He, Fahima Jaleel Khan, James Kah

Affiliations : Department of Biomedical Engineering, National University of Singapore, Singapore.

Resume : Protein phosphorylation is known to play a very important role in diseases such as cancer, where its occurrence has been shown to relate to dysregulation of protein phosphorylation in many cases. Based on the phosphorylation status of certain protein kinases, it is now possible to prognose certain cancer before the onset of tumour formation, thus allowing a better outcome of cancer treatment. However, real-time detection and monitoring of protein phosphorylation with adequate sensitivity is difficult to achieve using fluorescence or radioactive probes. Here we demonstrate a nanoSERS probe that make use of Surface-enhanced Raman spectroscopy (SERS) to detect subtle changes in protein conformation of a target peptide upon phosphorylation. Spiky gold-silver hybrid nanoparticles or nanostars were synthesized and characterized to form the core of the nanoSERS probe. Our in vitro results showed that the phosphorylation by a few protein kinases cancer markers can be detected by the nanostars conjugated to unique peptide substrates of the kinases. These changes were indicated by variations in SERS spectra before and after introduction of protein kinases. This study sheds light on the feasibility of using our nanoSERS probe to screen potential cancer patients at early stage.

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10:45

Diamond nanocolloid: synthesis, characterization, and biomedical applications

Authors : Naoki Komatsu, Li Zhao, Toku Yasuda, Hongmei Qin, Takahide Kimura

Affiliations : Shiga University of Medical Science

Resume : Biomedical applications of nanodiamond (ND) have been investigated extensively due to its low toxicity, non-bleaching fluorescence, and high extensibility of the surface functionality through covalent organic functionalization. For in vivo applications such as drug carrier and imaging probe, ND should form a stable hydrosol under a physiological environment. In this context, we recently found that polyglycerol (PG) functionalization is very effective to impart the sufficient solubility and stability to ND [1]. In addition, the stable hydrogel of PG-functionalized ND (ND-PG) enabled precise characterization of the chemical structure by solution phase NMRs. Quantitative analyses were also conducted by elemental and thermogravimetric analyses.

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The ND-PG was subjected to further organic transformations at a number of hydroxyl groups on the PG layer to add more functions. As a result, we successfully prepared the ND-based drug carrier with acid-responsive platinum drug [2] and MR imaging probe with gadolinium [3] and applied them to in vivo and in vitro evaluations. [1] L. Zhao, N. Komatsu, *Angew. Chem. Int. Ed.*, 50 (6), 1388-1392 (2011) [2] L. Zhao, N. Komatsu, X. Chen, submitted [3] L. Zhao, N. Komatsu, *J. Nanosci. Nanotechnol.* in press

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11:00

Air and Water Stable Gold Coated Gadolinium Metal Synthesized by Alkalide Reduction.

Authors : Michael J. Wagner, Ming Zhang

Affiliations : The George Washington University

Resume : Lanthanide metal nanoparticles are potentially superior materials for magnetic and biomedical applications. Of the lanthanides, Gd is of particular interest for application as a magnetic refrigerant and for biomedical imaging and therapeutic applications. Gd and its alloys display the largest magnetocaloric effects of any materials near room temperature. Stable Gd nanoparticles could serve as a MRI contrast agents but with a vastly greater spin density than currently used Gd chelates, or perhaps even used for magnetically guided tumor targeting and extraction following treatment. Multiple therapy options could be available including photon activation therapy, synchrotron stereotactic radiotherapy, ¹⁵⁹Gd radionuclide therapy and ¹⁵⁷Gd neutron capture therapy. ¹⁵⁷Gd has the largest neutron absorption cross section of any nucleotide, 66 times greater than the currently used ¹⁰B, thus potentially being more than an order of magnitude lower neutron flux for neutron capture have therapy. Finally, a number of Gd alloys and compounds have shown promise for hyperthermia treatment. Here we present the rapid chemical synthesis and characterization of Au@Gd nanoparticles and nanorods in high yield and small size dispersion. These nanomaterials are air and water stable (over a wide pH range), overcoming a significant roadblock to the exploration of applications of lanthanide metal nanoparticles. In addition, their evaluation as MRI contrast agents through relaxation studies will be presented.

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11:15

Weakly luminescent nanocrystals that make exceptional single-molecule probes

Authors : Daniel J. Gargas, Emory M. Chan, Alexis D. Ostrowski, P. James Schuck, and Bruce E. Cohen

Affiliations : The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Resume : Imaging cells at the single-molecule level reveals heterogeneities that are lost in ensemble imaging experiments. An ongoing challenge is the development of single-molecule probes with the requisite photostability, brightness, and continuous emission. Upconverting nanoparticles (UCNPs) overcome problems of photostability and continuous emission, and their upconverted emission can be excited with biologically benign NIR light at much lower powers than those required for conventional multiphoton imaging probes. The brightness of UCNPs, however, has been limited by open questions about energy transfer and relaxation within individual nanocrystals and unavoidable trade-offs between brightness and size. We have developed UCNPs with $d < 10$ nm that are over an order of magnitude brighter under single-particle imaging conditions than the brightest bulk compositions, allowing us to visualize single upconverting nanoparticles as small as fluorescent proteins. We use a combination of advanced single-particle characterization and theoretical modeling to find that surface effects become critical at $d < 20$ nm, and that the higher fluences used in single-molecule imaging fundamentally change the factors that determine nanocrystal brightness. We find that factors known to increase brightness in bulk experiments are unimportant at higher excitation powers, and that, paradoxically, the brightest probes under single-molecule excitation are barely luminescent at the ensemble level.

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11:30

Introduction to Magnetic Particle Spectroscopy and Imaging, its potential Applications, and the need for optimized and functionalized SPIO Contrast Agents

Authors : Jochen Franke

Affiliations : Bruker BioSpin MRI GmbH, Germany

Resume : In 2005 a novel tracer-based imaging method Magnetic Particle Imaging (MPI) has been presented [1], facilitating the direct quantitative detection of the 3D distribution of biocompatible coded superparamagnetic iron oxide (SPIO) nanoparticles with high sensitivity, high spatial and high temporal

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resolution and without any background signal and thus a high signal-to-noise ratio. In this contribution, a quick introduction to the technique of MPI will be presented, highlighting the basic principal of signal generation and reception as well as the hardware setup of state-of-the-art MPI scanners. Furthermore, potential medical imaging applications of MPI and the need of dedicated SPIOs as contrast agents will be discussed. Investigations of e.g. functionalized contrast agents open up further applications beyond cardio-vascular imaging. SPIO optimization in regard to their MPI performance has tremendous potential in increasing the spatial image resolution and image sensitivity. Such optimized SPIOs pave the way towards molecular imaging and cell labeling/tracking. [1] B. Gleich et al., Nature, vol. 435, no. 7046, pp.1214–1217, 2005

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11:45 Lunch Break

Colloidal nanoPlasmonics : Mathieu Maillard, Laurence Motte, Stephan Link

13:15

Collective Plasmon Modes in Nanoparticle Assemblies

Authors : Stephan Link

Affiliations : Rice University Department of Chemistry

Resume : In order to incorporate plasmonic nanoparticles into functional devices it is necessary to understand how surface plasmons couple as particles are arranged into ordered structures. Bottom-up assembly of chemically prepared nanoparticles facilitates strong plasmon coupling due to short interparticle distances, but also gives rise to defects in particle size, shape, and ordering. Single particle spectroscopy of plasmonic nanoparticle assemblies, especially when correlated with structural characterization using scanning electron microscopy, allows one to gain a detailed understanding about collective plasmon modes. We have used polarization sensitive dark-field scattering and extinction spectroscopy covering a broad spectral range from the visible up to 2000 nm and polarization dependent photothermal imaging to separately investigate radiative (scattering and luminescence) and nonradiative (absorption) properties of individual plasmonic nanoparticles and coupled one-dimensional nanoparticle assemblies. Furthermore, we have developed a fluorescence based method to visualize plasmon propagation in one-dimensional nanostructures. This far-field microscope technique, called bleach-imaged plasmon propagation (BIIPP), allows us to image the plasmon propagation by exploiting the photobleaching behavior of photoluminescent dyes coated on top of the plasmonic waveguides.

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13:45

Size dispersion effect on plasmonic responses of Au and Ag nanocolloidal solutions.

Authors : Y. Battie, A. Resano-Garcia, N. Chaoui, A. En Naciri

Affiliations : LCP-A2MC, Institut Jean Barriol, Université de Lorraine, 1 Bd Arago, 57070 Metz, France

Resume : The optical properties of metallic spherical nanoparticles embedded in host liquid matrix are studied. Extended Maxwell-Garnett-Mie formulation which accounts for size dispersion, the intrinsic confinement and extrinsic size effect, is proposed for the calculation of the effective dielectric function and absorption coefficient of size dispersion of colloidal solution of Au and Ag nanoparticles in water. We demonstrate that the size distribution induces an inhomogeneous broadening and an increase of the amplitude of the plasmon band. A large redshift of the plasmon band is also observed for silver nanoparticles. Compared to the conventional Maxwell Garnett theory, we demonstrated that this model gives better description of the measured absorption spectra of colloidal gold solutions.

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14:00

Chiral Nanoparticles for Visible and Ultraviolet Plasmonics

Authors : Kevin M. McPeak,¹ Christian D. van Engers,¹ Mark Blome,^{2,3} Jong Hyuk Park,^{1,4} Sven Burger,^{2,3} Miguel Angel Gosálvez Ayuso,^{5,6} Ava Faridi,¹ Yasmina R. Ries,¹ Ayaskanta Sahu,¹ David J. Norris ¹

Affiliations : ¹ Optical Materials Engineering Laboratory, Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland; ² Zuse Institute Berlin, 14195 Berlin, Germany; ³ JCMwave GmbH, 14050 Berlin, Germany; ⁴ Photo-Electronic Hybrids Research Center, Korea Institute of Science and Technology, Seoul 136-791, South Korea; ⁵ Donostia International Physics Center, San Sebastian 20018, Spain; ⁶

F.V. 3

Centro de Física de Materiales, University of the Basque Country, San Sebastian 20018, Spain

Resume : Chiral plasmonic nanoparticles have been predicted to exhibit both strong circular dichroism in the visible spectral range and non-linear optical effects. These properties open up applications for chiral nanoparticles in sensing, enantiomer separations, and non-linear optics. Unfortunately, to date the fabrication of colloidal nanoparticles with chiral shape (shapes not superimposable on their mirror image) has posed a significant challenge due to a very limited ability to transfer chirality from chiral template molecules to nanoparticles. Here we report a simple and general route to chiral nanoparticles. We exploit anisotropic etching of high-index silicon wafers to prepare metallic nanopyramids with a specific handedness. The resulting particles, which are easily dispersed into liquids, present chiral pockets for molecular binding whilst their tips allow exploration of superchiral electromagnetic fields. If fabricated from gold, colloids with record molar circular dichroism ($>5 \times 10^9 \text{ M}^{-1} \text{ cm}^{-1}$) at red wavelengths are obtained. Further, we demonstrate chiral colloids from aluminum, a plasmonic metal suited to ultraviolet wavelengths. Because these aluminum nanopyramids have chiral optical signatures resonant with many biomacromolecules, new methods for detecting structural chirality in chemistry and biology become possible.

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14:15 **Template-assisted self-assembly of Gold nanoparticles into helicoidal superstructures**

Authors : J. Cheng, 1 E. Pouget, 1 S. Lecomte, 1 P. Barois, 2A. Aradian, 2 Marie-Hélène Delville³ and Reiko Oda 1

Affiliations : 1CBMN-IECB 5248, Chimie et Biologie des Membranes et Nano-objets, Institut Européen de Chimie et Biologie, 2 Rue Robert Escarpit, 33607 Pessac France; 2CRPP Centre de Recherche Paul Pascal, Centre de Recherche Paul Pascal.115 Avenue Schweitzer, 33600 Pessac France; 3ICMCB 9048, Institut de Chimie de la Matière Condensée de Bordeaux, 87 Av du Dr Schweitzer, 33608 Pessac France.

Resume : Plasmonic nanoparticles are widely considered potential structural and functional building-blocks for many optical usages depending not only on the size and the composition of the nanoparticles but also on the arrangement of the nanoparticles with respect to each other. Herein, we report a template-based methodology with silica nanohelices and twisted ribbons to prepare a diverse collection of helical gold nanoparticle(GNPs) superstructures having controllable handedness and structural metrics by using different sizes of GNPs varying from 3.5nm-6nm as the building blocks, and the silica nanohelices or twisted ribbons as the templating matrix. The synthesized materials exhibited well-defined chiral arrangement of GNPs following the chirality of the silica helices by employing electrostatic interactions as the driving force. A clear surface plasmon resonance was observed in UV visible range. Decorations with various surface charged GNPs and silica nanohelices were investigated respectively. These novel nanohybrid systems will provide a new sustainable approach for photonic applications such as chiral metamaterials and optical sensors based on the 3D network of GNPs.

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14:30 **Enhanced dipolar coupling evidenced in 2D assemblies of silver and gold nanoparticles**

Authors : Y. Liu, S. Begin-Colin, B.P. Pichon, C. Leuvrey, D. Ihiwakrim, M. Rastei, G. Schmerber, M. Vomir, J.Y. Bigot

Affiliations : Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504, CNRS, Université de Strasbourg, 23, rue du Loess, 67034 Strasbourg Cedex

Resume : Localized surface plasmon resonance (LSPR) associated to Ag and Au nanoparticles (NPs) have attracted remarkable attention due to their potential applications. Highly ordered arrays are expected to be applicable to deposit onto arbitrary substrates over macroscopic length scales. It is reported that the strength of dipolar interactions in these assemblies is generally related to the interparticle distances. However investigations of the collective properties of magnetic NPs in powdered, 2D and 3D assemblies have shown the appearance of a shape anisotropy induced by the 2D assembly leading to enhanced dipolar interactions. Therefore one may wonder if stronger dipolar interactions could be also observed in 2D assemblies of Ag and Au NPs due to a shape anisotropy? Thus the synthesis of Ag and Au NPs has been optimized and these NPs have been then assembled on large scales in ordered 2D arrays by Langmuir-Blodgett technique and in 3D films by drop casting. The NPs size and the interparticle distances have been tuned by submitting LB arrays to a thermal annealing. These different films have been characterized and the SPR band shift compared

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to diluted NPs in suspension has been related to the interparticle distances and dimensionality in assemblies. The evidence of the occurrence of a shape anisotropy in 2D arrays of metallic NPs was supported by modeling. Previous results of magneto-acoustic application would be demonstrated.

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14:45

Silver-containing colloidal zeolites: a promising materials for plasmonic chemistry

Authors : V. De Waele[1], Biao Dong[2], S. Mintova{2}, F. Kawtharani[1], R. Retoux[3], O. Poizat[1], G. Buntinx[1]

Affiliations : 1 Laboratory of Infrared and Raman Spectroscopy (LASIR), CNRS-University of Lille1, 59650 Villeneuve d'Ascq, France, e-mail: vincent.dewaele@univ-lille1.fr 2 Laboratory of Catalysis and Spectroscopy (LCS), ENSICAEN, CNRS, University of Caen, 6 Bd Maréchal Juin, 14050 Caen, France 3 CRISMAT, ENSICAEN, CNRS, University of Caen, 6 Bd Maréchal Juin, 14050 Caen, France

Resume : Efficient plasmonic nano-colloids for catalytic applications require materials exhibiting a large surface area, an intense photoresponse in the UV-Vis, and an efficient coupling between the metal and the reactants. We report here on the facile preparation by chemical reduction of highly dispersed silver metal nanoparticles into the porous volume of colloidal zeolites stabilized in aqueous suspension. The formation of small nm-sized silver nanoparticles is confirmed by UV-Vis spectroscopy and HRTEM images. The plasmonic response of the silver-zeolites colloides was investigated by femtosecond transient absorption spectroscopy. The dynamics of the hot-electrons generated by an ultrashort optical excitation in resonance with the plasmon band of the metal nanoparticles was measured. The kinetics of the electrons-phonons relaxation is analyzed in the frame of the two -temperatures model. The results suggest that a significant part of the energy initially injected in the conduction band is transferred to the surrounding media of the particle directly from the hot-electrons. Our study let anticipate the silver-containing colloidal zeolites as good candidates for hot-electron driven chemistry applications.

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15:00

Single Au nanorods and nanorod arrays for optical Hg detection

Authors : Carola Schopf, Alfonso Martín Ruano, Daniela Iacopino

Affiliations : Tyndall National Institute, University College Cork, Cork, Ireland

Resume : Great efforts have been undertaken in the development of sensors for mercury due to its well-known toxicity, employing various sensing methods and platforms. As a potential platform, gold nanostructures have received widespread attention due to their optical properties arising from surface plasmon resonance (SPR). Among gold nanostructures, gold nanorods exhibit a narrow SPR band that is a function of nanorod composition, size, shape, aggregation state and environment. This feature of the SPR can be utilised for sensing based on a shift of the nanorods' optical signatures upon changing of any of the factors listed above. To observe the SPR of single nanostructures, dark field microscopy/spectroscopy has emerged as a powerful method and has been employed in this work. We fabricated gold nanorods of various aspect ratios as well as 2D arrays thereof to explore the relationship between their structure and their optical properties, correlated with electron and optical microscopy. Furthermore, both structures proved very suitable for mercury detection in water down to nanomolar concentrations with no further functionalization necessary. Upon amalgamation of gold nanorods with mercury, a pronounced blue shift of the SPR can be observed; a result of the combined effect of the change of composition and shape of the nanorods. Also, polarisation resolved spectroscopy shows decreasing polarising behaviour of the nanorods as the shape changes from rod towards an optically isotropic sphere.

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15:15

Gold nanoparticles for electron emission cancer treatment

Authors : Mattias Vervaele 1, Cédric Spaas 1, Bert De Roo 1, Jin Won Seo 2, Jean-Pierre Locquet 1

Affiliations : 1 Dept. of Physics and Astronomy, KU Leuven, 3001 Leuven, Belgium 2 Dept. of Metallurgy and Materials Engineering (MTM), KU Leuven, 3001 Leuven, Belgium

Resume : A key challenge in modern radiation therapy remains the localization of its toxicity. In this project, we consider to use gold nanoparticles (GNP) as radiosensitizers to enhance the effectiveness, thus localization of ionizing radiation. By means of simulations we investigate the spatial energy distribution of electrons and photons produced by a GNP which is irradiated with keV photon beams. Monte Carlo simulations implemented with the Geant4 toolkit allow us to examine, in 3D, the effects on the microscopic energy deposition when varying primary beam energy, GNP size and coating. The highest energy deposition is

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found for lower photon beam energies and larger GNP radii. Subsequently, various GNP cores are synthesized and functionalized with polyethylene glycol (PEG). It allows us to examine the different microscopic dose enhancement factors on organic materials, such as supercoiled DNA(scDNA), in the vicinity of the irradiated GNPs. By varying the thickness of the PEG surface coating, the distances of the scDNA relative to the GNP core are adapted. Gel electrophoresis reveals the amounts of linear and circular DNA after irradiation. By experimentally supported simulations, the most effective GNP complex can be chosen for further experiments on cells and other biologic material.

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15:30

Synthesis of Spiky Ag – Au Octahedral Nanoparticles and Their Tunable Optical Properties

Authors : Srikanth Pedireddy, Anran Li, Michel Bosman, In Yee Phang, Shuzhou Li, Xing Yi Ling*

Affiliations : Nanyang Technological University, Singapore

Resume : Spiky nanoparticles exhibit higher overall plasmonic excitation cross sections than their nonspiky peers. In this work, we demonstrate a two-step seed-mediated growth method to synthesize a new class of spiky Ag – Au octahedral nanoparticles with the aid of a high molecular weight poly (vinylpyrrolidone) polymer. The length of the nanopikes can be controlled from 10 to 130 nm with sharp tips by varying the amount of gold precursor added and the injection rates. Spatially resolved electron energy-loss spectroscopy (EELS) study and finite-difference time-domain (FDTD) simulations on individual spiky Ag – Au nanoparticles illustrate multipolar plasmonic responses. While the octahedral core retains its intrinsic plasmon response, the spike exhibits a hybridized dipolar surface plasmon resonance at lower energy. With increasing spike length from 50 to 130 nm, the surface plasmon of the spike can be tuned from 1.16 to 0.78 eV. The electric field at the spike region increases rapidly with increasing spike length, with a 10^4 field enhancement achieved at the tips of 130-nm spike. The results highlight that it is important to synthesize long spikes (>50 nm) on nanoparticles to achieve strong electric field enhancement. A hypothesis for the formation of sharp spikes is proposed based on our studies using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and high resolution transmission electron microscopy (TEM).

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15:45

Discussion/Coffee Break

Surfaces and Interfaces at nanometer Scales from Electronic to Catalysis : Richard Tilley, Erwann Guenin, Justin Holmes

16:00

Shape-Sensitivity of Pd Nanocatalysts in Carbon-Carbon Coupling Reactions

Authors : Gillian Collins, Michael Schmidt, Colm O'Dwyer, Gerard P. McGlacken and Justin D. Holmes

Affiliations : Department of Chemistry, University College Cork, Ireland, Cork

Resume : Understanding the shape sensitivity of a catalyst can facilitate the optimal design of nanoparticles for specific catalytic reactions. This presentation describes the catalytic performance of Pd nanocrystals with cubic, cuboctahedral and octahedral morphologies in Suzuki coupling reactions, one of the most industrially utilised carbon-carbon bond forming processes. Superior catalytic reactivity was observed for Pd nanocrystals with {100} surface facets compared to {111} facets. The origin of the facet-dependant reactivity was probed by combining TEM analysis of the nanocatalysts before and after reaction, XPS analysis to identify changes to the catalyst surface chemistry and ICP analysis to assess the heterogeneity and homogeneity of the reactions. Furthermore, by conducting reaction rate studies under air and in an inert atmosphere, we observed that an oxidative environment enhanced the catalytic performance. Overall, a number of factors were found to determine shape sensitivity in Suzuki reactions including, the percentage of surface defect atoms, the nature of surface facets, surface oxidation and oxygen activation.

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16:30

Synthesis, Optical Properties and Applications of Plasmonic Ag/Au Nanoprisms

Authors : Mohammad Mehdi Shahjamali, Can Xue*

Affiliations : School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

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Resume : Noble metal nanostructures have attracted extensive research attentions due to their intriguing optical properties. In particular, silver nanoprisms are of great interest due to their size-dependent surface plasmon resonance bands that are tailorable in the visible and near-IR range. However, the poor stability of silver nanoprisms against oxidation and etching restricts their applications. Herein we demonstrate a simple process of gold-coating on silver nanoprisms. The resulting Ag@Au core-shell structure preserves the optical signatures of nanoprisms and offers versatile functionality and better stability against oxidation. Further, by slightly modifying the gold-coating process, we can obtain various functional Ag/Au bimetallic structures, such as Ag@Au-framed prisms and ultrathin nanoframes. [1,2] These interesting Ag/Au nanostructures are capable of showing high sensitivity in refractive sensing and strong enhancement of polaron yield in organic photovoltaics. Reference: [1] M. M. Shahjamali, M. Bosman, S. W. Cao, X. Huang, X. H. Cao, H. Zhang, S. S. Pramana, C. Xue*, *Small* 2013, 9, 2880-2886. [2] M. M. Shahjamali, M. Bosman, S. W. Cao, X. Huang, S. Saadat, E. Martinsson, D. Aili, Y. Y. Tay, B. Liedberg, S. C. J. Loo, H. Zhang, F. Boey, C. Xue*, *Adv. Funct. Mater.* 2012, 22, 849-854.

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16:45

Bioinspired nanomaterials: synthesis, assembly and applications

Authors : Siddharth V. Patwardhan,* Khalid M. Alotaibi, Sher-Leen Goh, Lorraine T. Gibson, Claire Forsyth, Craig Drummond

Affiliations : University of Strathclyde, Department of Chemical and Process Engineering, Glasgow G1 1XJ.

Resume : Nanomaterials, in particular silica-based nanomaterials, are used in wide applications such as in catalysis, food and drug technology, biomedical materials, water purification, tyres and paints. The laboratory or industrial production of such nanomaterials often utilises harsh conditions and/or produce toxic wastes. In contrast, biological organisms, through biomineralisation, produce elaborate and ordered nanomaterials under physiological conditions. Taking inspiration from organisms, we have developed green routes for the controlled synthesis and assembly of nanostructured silica with bespoke properties.1 Our results demonstrate that these materials are suitable for applications in carbon capture,2 environmental remediation,3 catalysis,4 biocatalysis and drug delivery.1 This presentation will illustrate how such bioinspired materials can be designed and fine-tuned for each of these applications of bioinspired silica. The results suggest that these materials provide an exciting new platform and can rival more expensive meso-silica materials. References: www.svplab.com 1. S. V. Patwardhan, *Chem. Commun.*, 2011, 47, 7567. 2. C. Forsyth, T. W. S. Yip and S. V. Patwardhan, *Chem. Commun.*, 2013, 49, 3191. 3. A. M. Ewlad-Ahmed, et al., *Environ. Sci. Technol.*, 2012, 46, 13354. 4. C. Forsyth and S. V. Patwardhan, *J. Mater. Chem. B*, 2013, 1, 1164.

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17:00

Monodisperse AuM (M=Pd, Rh, Pt) Bimetallic Nanocrystals for Enhanced Electrochemical Detection of H₂O₂

Authors : Tingting Han, Yuan Zhang, Jiaqiang Xu*

Affiliations : College of Science; Shanghai University

Resume : Monodisperse AuM (M=Pd, Rh, Pt) bimetallic nanoparticles were synthesized in claymine media and studied for electrocatalytic oxidation and sensing of hydrogen dioxide (H₂O₂). The catalysts activities, expressed as onset potential of AuM catalysts towards H₂O₂, reduced in the order Au (0.45 V) < AuPt (0.33 V) < AuRh (0.29 V) < AuPd (0.21 V). Among these bimetallic nanocrystals generated, monodisperse AuPd nanocrystals, exhibited an enhanced sensitivity of 195.27?A mM⁻¹ cm⁻² at a relatively low test potential (0.25V) and a great anti-interference performance. Especially, the AuPd nanocrystals showed the best catalytic properties for H₂O₂ with the detection limit reaching 8.4?M. These results demonstrated that the monodisperse AuPd bimetallic catalyst with the uniform shape and high electrocatalytic activity could be a promising sensing material used for screen printed electrochemical platform for biomedical, environmental and industrial analyses.

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17:15

SELF-ASSEMBLING AND ELECTROCHEMICAL PROPERTIES OF CdSe – CdS DOT-IN-RODS NANOPARTICLES

Authors : Benoît Boichard, Cyrille Hamon, Thomas Bizien, Alexandre Ciaccava, Pascale Even-Hernandez, Elisabeth Lojou, Franck Artzner, Valérie Marchi

Affiliations : Université Rennes 1, Institut des Sciences Chimiques de Rennes, CNRS UMR 6226, Campus de Beaulieu, 35042 Rennes, France ; Université de Rennes 1, Institut

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de Physique de Rennes, CNRS UMR 6251, Campus de Beaulieu, 35042 Rennes, France ; Bioénergétique et Ingénierie des Protéines, Institut de Microbiologie de la Méditerranée, CNRS-AMU, 31 Chemin Aiguier, 13009 Marseille, France

Resume : Although the self-assembly of anisotropic particles remains a challenge in nanotechnology, we here introduce an original method to generate, on a macroscopic scale, three-dimensional supracrystals made of quantum rods (QRs). In a first step, they are transferred in an aqueous phase thanks to the substitution of the original capping layer by peptidic ligands. In a second step, water evaporation in a microstructured environment (C.Hamon et al. ACS Nano. 2012) yields superstructures in which rods obey a smectic B arrangement, as shown by electron microscopy. Bulk drying in a capillary tube generates a similar local order, as evidenced by small angle X-ray scattering. We thus validate the use of peptidic ligands as a generic chemical platform allowing one to finely control the organization in solid phase of semiconductor (T.Bizien et al. Submitted) originally dispersed in an aqueous media. This aqueous media and the chemical functionality of the ligands allows peptidic coupling between QRs and molecules that has been demonstrated for O₂-tolerant hydrogenase (C.Hamon et al. Chem. Commun. ASAP). Under visible irradiation, the QR-hydrogenase complex presents an enzymatic activity mediated by methylene blue at potentials where the unbound enzyme is normally inactive. If the electrochemical intrinsic behavior of the QRs is better understood, and in a hydrogen-based-energy context, these semiconductor nanoparticles may lead to new photosensitive materials with promising applications.

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Immobilization of Palladium Nanoparticles on Three-Dimensionally Ordered Hierarchically Porous Tin Dioxide Inverse Opals for Catalytic Applications

Authors : Gillian Collins, Martin. Blömker, Michael. Osiak, J. D. Holmes, Michael Bredol, and C. O'Dwyer

Affiliations : Department of Chemistry, University College Cork, Cork, Ireland; Micro & Nanoelectronics Centre, Tyndall National Institute, Lee Maltings, Cork, Ireland; Centre for Research on Adaptive Nanostructures and Nanodevices, Trinity College Dublin, Dublin 2, Ireland; Materials and Surface Science Institute, University of Limerick, Limerick, Ireland; Department of Chemical Engineering, Münster University of Applied Sciences, Stegerwaldstraße 39, 48565 Steinfurt, Germany

Resume : Immobilization of colloidal nanoparticles on support materials is a critical aspect to many catalytic and electrocatalytic applications. Hierarchical porosity of 3 dimensionally ordered systems are beneficial for heterogeneous catalytic applications as they provide small pores for nanoparticle immobilization and the presence of larger pore networks reduces mass transport limitations. We report the synthesis of monodisperse Pd nanoparticles and their immobilization onto hierarchically porous oxide networks, resulting in thin films with functional catalytic and electro catalytic behaviour. The Pd NP dispersion is controlled by utilizing weak ligand-metal interactions and strong metal-oxide interactions for the immobilization step. The resulting oxide Pd IOs were investigated by X-ray photoelectron spectroscopy indicating electronic interactions between the Pd and SnO₂ and alterations to NP surface chemistry. Cross-sectional SEM and EDX was used to assess the distribution profile of the Pd nanoparticles through the IO thin film. Pd nanoparticles assembled with excellent dispersion on the ordered oxide IOs show superior catalytic performance for liquid phase chemical reactions and allow easy removal of the catalyst substrate post reaction. Higher mass electrocatalytic activity is also demonstrated for formic acid oxidation, superior to commercial Pd/C catalysts due to great access to catalytically active sites.

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17:45

Atomically Well Defined Thiolate Gold Nanoclusters for Heterogeneous Catalysis

Authors : Christophe Lavenn,¹ Florian Albrieux,² Alain Tuel¹ and Aude Demessence*¹

Affiliations : 1. Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256, CNRS / Université Lyon 1 - Villeurbanne, France. 2. Centre Commun de Spectrométrie de Masse, UMR 5246, CNRS / Université Lyon 1 - Villeurbanne, France.

Resume : Gold nanoparticles, less than 5 nm, exhibit a catalytic activity in many chemical processes. However polydisperse particles obscure the interesting size-dependent catalytic activity of nanogold. Recently, atomically well defined thiolate-capped Au nanoclusters (denoted as Au(SR)_m) have been successfully isolated and their catalytic properties have been demonstrated. These monodispersed functionalized clusters, with gold core between less than 1 nm and more than 2 nm, hold promises as a new generation of catalysts. More importantly, these nanoclusters permit in-depth studies on the subtle correlation of structure and catalytic activity, since they are well defined and their

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crystallographic structures start to be solved. To investigate the influence of the size, the type of ligands at the surface and also the support effect, different nanoclusters have been synthesized. New clusters made of 4-aminothiophenol (HSPhNH₂) have been synthesized, such as Au₂₅(SPhNH₂)₁₇, and fully characterized by mass spectrometry, X-ray diffraction and XPS. Moreover these clusters exhibit absorption bands related to their molecular state. Catalytic activity for oxidation of alkene and alcohol derivatives of these colloidal or supported clusters were investigated and compared to the commonly used Au_n(SCH₂CH₂Ph)_m nanoclusters. At the opposite of the bare gold nanoparticles, the presence of the ligands around the clusters leads to a much better selectivity of the product.

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18:00

One-Dimensional Hybrid Metal-Metallic Oxide Composite Nanofibers Synthesis by Electrospinning and Applications

Authors : Xiaojiao YANG; Vincent SALLES; Mathieu MAILLARD; Arnaud BRIOUDE

Affiliations : Université Lyon 1 – Laboratoire des Multimatériaux et Interfaces – UMR 5615

Resume : The hybrid metal-metal oxide composite nanofibers are promising new materials for photocatalysis applications. In this study, an electrospinning technique coupled with sol-gel chemistry is applied to produce one-dimensional (1D) hybrid metal-metal oxide composite nanofibers. Metallic nanoparticles are formed within nanofibers using two methods: metal ions are introduced either before or after electrospinning and then reduced within fibers using various treatments. All the methods used induce metallic nanoparticles formation on the surface or inside the hybrid composite nanofibers. Structures, morphologies of nanofibers and photocatalysis activity can be readily tuned as a function of the electrospinning process parameters and metal nanoparticles content and morphology. The growth mechanism and relation between structure and electrochemical and photocatalysis properties are discussed in details.

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18:15

Hydrogen Sensing on Single Gold Nanorods by Surface Plasmon Spectroscopy

Authors : M Cittadini 1, S. Collins 2, P. Mulvaney 2, A. Martucci 1

Affiliations : 1 Industrial Engineering Department, University of Padova, Padova, 35131, Italy; 2 School of Chemistry and Bio21 Institute, University of Melbourne, Parkville, Victoria 3010, Australia.

Resume : The direct optical monitoring of electron exchange on single plasmonic nanoparticles, involved in chemical reactions with gas molecules, is one of the main challenges in the heterogeneous catalysis and gas sensing fields. The present work shows how the use of Dark Field Microscopy (DFM) coupled with surface plasmon spectroscopy, enables the direct observation of the kinetics of H₂ gas interaction with single gold nanorods (NR) coupled with Pt nanoparticles (NPs). The plasmonic particles, gold NRs, act as optical probes, and enable the monitoring of the electron exchange through the measurement of their surface plasmon resonance (SPR) band shift. To improve the redox reaction kinetics, the Au NRs have been coupled with Pt NPs and embedded also into a TiO₂ low scattering matrix. Both the Au NRs and the Pt and the TiO₂ NPs have been synthesized by colloid chemistry. Several samples made of bare Au NRs, or Au NRs coupled with only Pt NPs or with Pt and TiO₂ NPs have been deposited by spin coating on silica substrates. The longitudinal Au SPR band shift has been monitored by DFM looking at the variation of the scattering spectrum of a single Au NRs in the presence of H₂. Time-resolved measurements have been also conducted looking at the plasmon band shift, in wavelength, in order to monitor the kinetics of the H₂ reaction. With such measurements it was possible to elucidate the importance of the adsorbed oxygen and the TiO₂ matrix on the H₂ reaction with the Pt NPs.

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PROGRAM VIEW : 2014 Spring

MY PROGRAM : 2014 Spring

Symposium : F

Established and emerging nanocolloids: from synthesis & characterization to applications

26 May 2014	27 May 2014	28 May 2014	29 May 2014	30 May 2014
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start at	Subject	Num.
Emerging Nanoscale Materials : Richard Tilley, Pascal André, Amanda S. Barnard		
09:00	<p>Exploring the probability and population of high index morphologies in metal colloids</p> <p>Authors : Amanda S. Barnard Affiliations : CSIRO Materials Science and Engineering Resume : Theoretical predictions and experimental observations of the structures present in colloidal samples of metal nanoparticles are often at odds. Theory and computer simulation are very efficient at finding the most stable, lowest energy structure, and it is often interpreted as meaning all particles should adopt this morphology. However, characterization of colloidal samples reveal a range of shapes, including structures with high index, high energy facets. This conundrum is usually attributed to competing thermodynamic and kinetic influences, and the high energy shapes are assumed to be a result of kinetic effects driving the system out of equilibrium. However, a strong kinetic driving force would also results in well defined and preferred morphologies, as opposed to the diverse ensembles that are often observed. In this presentation this issue will be explored, and it will be shown that a diverse ensemble of metal colloids can be explained entirely using thermodynamics and statistical mechanics; without needing to censure kinetics. We will see that high index (high energy) morphologies have a predicable probability of observation, and at large sizes there will actually be a surprisingly low population of the thermodynamically preferable (low energy) shape. The relationship between stability, probability and population will be discussed.</p>	F.VII. 1
	add to my program	(close full abstract)
09:30	<p>Individualized colloidal Nanohelices SiO₂ and SiO₂@MxOy: new nanostructures for applications in NEMS devices</p> <p>Authors : Dymtro Dedovets^{1,2}, Satyabrata Si¹, Emilie Pouget², Sabrina Habtoun³, Said Houmadi³, Chistian Bergaud³, Reiko Oda², Marie-Hélène Delville^{1*}, Affiliations : 1 ICMCB/CNRS, Université de Bordeaux, Pessac, France; 2 Chimie et Biologie des Membranes et des Nano-objets, allée de St Hilaire, 33600 Pessac, France 3 CNRS, LAAS, 7 avenue du Colonel Roche, F-31400 Toulouse, France *e-mail: delville@icmcb-bordeaux.cnrs.fr Resume : In the field of emerging nanoscale materials with switchable properties chiral structures like helices or twisted ribbons are of great interest because of their intrinsic optical and mechanical properties. In this contribution, we present a study about the mechanical properties of SiO₂ and SiO₂@MxOy nanotubes and helical nanosprings synthesized by an original and simple technique from organic nanotubes through inorganic transcription. These nano-objects have potential applications in nano-electromechanical systems (NEMS), ranging from physical sensing and signal processing to ultra-low power radio frequency signal generation, thanks to their striking features. NEMS have been generally based on 1D nano-objects, such as carbon nanotubes [1] or silicon nanowires [2]. However, the use of 3D nanostructures such as nanohelices would allow a significant improvement the electromechanical performances of functional nanodevices, due to their specific properties. The originality of our synthesis method consists in the possibility to obtain 3D nanostructures with specific morphology and properties. In the present work, functional hybrid nano-helices are synthesized by use of amphiphilic organic chiral self-assemblies forming very well defined helix or ribbons structures and exploits them as</p>	F.VII. 2

templates for inorganic nanomaterial formation [3]. A bio-inspired mineralization of these self-assemblies allows creating silica nano-helices with very well controlled morphologies. We focus particularly on the formation of short helices (length control), individualized and well-dispersed in solution. Using this method, NTs and helical nanosprings with controlled dimensions were fabricated using inorganic materials usable in functional nanodevices such as sensors, actuators and resonators. To the best of our knowledge, nothing has been published concerning the mechanical properties of inorganic nanotubes or nanosprings templated from organic self-assemblies. Their elastic properties were determined by performing three-point bending tests on suspended NTs and nanosprings over micro-cavities using an atomic force microscope (AFM).. The SiO₂ nano-objects were subjected to a load f at midpoint using an AFM tip by performing force vs. distance (F-d) curve measurements. The elastic modulus E was then determined using the beam bending theory of clamped-clamped beam [4], that gives the relationship between E and the elastic deformation of a suspended and clamped cylindrical beam or tube. For all tested NTs the average value of the elastic modulus E was determined to be 73.3 ± 6.7 GPa, which is comparable to that of bulk SiO₂ [5] as well as amorphous SiO₂ nanowires obtained using chemical vapor deposition [6]. On the other hand, the average value of E measured for helical nanospring was 70 ± 7 GPa, which is in very good agreement with the result obtained for the NTs. This is of paramount importance because the nanospring exhibit unconventional physical properties and can be advantageously used as building blocks in functional nanodevices. The first advantage concerns their helicity and periodicity that can be varied to tune the spring constant. In addition, due to their structural flexibility, the helical shape is also ideal for inducing polarization effects under mechanical stress [7]. The obtained results demonstrate that the proposed synthetic route for obtaining inorganic NTs is robust and reproducible.

[1] K. Jensen, K. Kim, A. Zettl, *Nature Nanotechnology*, (2008) 3, 533 - 537.
 [2] Lih J. Chen *J. Mater. Chem.*, (2007) 17, 4639-4643. [3] T. Delclos, C. Aimé, E. Pouget, A. Brizard, I. Huc, M.-H. Delville, R. Oda, *Nano Lett.* (2008), 8, 1929 - 1935, [4] J. M. Gere, S. P. Timoshenko, *Mechanics of Materials*, PWS-KENT, Boston, Massachusetts, (1990) Third Edition [5]. B. Bhushan, *Handbook of Nanotechnology* (Springer, Berlin, 2007) 2nd edition, p. 1040 [6] H. Ni, X. Li, H. and Gao, *Appl. Phys. Lett.* (2006) 88, 043108 [7]. J.P. Singh et al. *Applied Physics Letters* (2004) 84, 3657.

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09:45

Increased stability of hollow gold nanospheres stabilized with mono-, bi- and tridentate PEG thiols

Authors : Julie Ruff, Ulrich Simon

Affiliations : Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany

Resume : Hollow gold nanospheres (HGN) are promising contrast agents for photoacoustic tomography due to their strong and tunable absorbance in the optical window of biological tissues between 600 and 900 nm. HGN are obtained via reduction of tetrachloro auric acid by sodium borohydrid, in the presence of citrate as capping ligands, on cobalt nanoparticles as sacrificial templates. For increased stability and possible biocompatibility that allow in vivo applications of HGN, PEGylation via a ligand exchange with PEG (polyethylene glycol) ligands bearing thiols as anchor groups (PEG thiols) needs to be performed. We report the synthesis of HGN with 38 nm diameter, a shell thickness of 4,6 nm, an absorbance maximum at 816 nm, and their stabilization by mono-, bi- and tridentate PEG thiols. Therefore, novel bi- and tridentate PEG thiols were synthesized comprising methoxy end groups and having similar molecular weights of around 5000 Da. The stability of these PEGylated HGN was explored in three different aspects: (1) stability towards competition reactions with the strong binding ligand dithiothreitol (DTT), (2) resistance towards Au dissolution with potassium cyanide, and (3) colloidal stability, tested by addition of salt. These studies revealed improved colloidal stability for all PEGylated HGN compared to citrate stabilized ones and increasing stability with increasing number of thiol anchor groups.

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10:00

Mixed ferrite nanoparticles for T1, T2 magnetic resonance imaging contrast agents

Authors : E.G. Petrova, D.A. Kotsikau, V.V. Pankov

Affiliations : Belarusian State University

Resume : Despite the fact that contrast agents based on iron oxides are widely used in MRI, further attempts are made to improve the sensitivity in getting

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images. For such purpose ferrites with spinel structure can be used because of uncompensated magnetic moment appearing due to the interaction between ions located in tetrahedral and octahedral sites. Conventional doping ions include Mn^{2+} , Co^{2+} , Zn^{2+} etc. A number of spinel structure ferrites with compositions of $Mg_{0,5}Mn_{0,5}Fe_2O_4$, $MnFe_2O_4$, $CoFe_2O_4$ and Co-doped Fe_2O_3 (2,6 % Co) were synthesized, converted into soluble form with a concentration of 50 mg/ml and stabilized with dextrane. Proton relaxation time values for the resulting solutions were found to be lower by 2 orders than this of pure water. The MRI images in T1- and T2-modes were then taken and compared with those of pure water and obtained using traditional iron oxides. The proton relaxation times in these cases were For T1-mode non-magnetic amorphous Co and Mn ferrites showed the best contrasting properties, while for T2-mode $Mg_{0,5}Mn_{0,5}Fe_2O_4$ and Co-doped Fe_2O_3 demonstrated better contrasting ability. However, varying concentration of the contrast agent allow to use it in both modes – while the signal of 50 mg/ml Co-doped Fe_2O_3 solution was absent in T1-mode, it appeared after 6 times dilution of the initial solution. This demonstrates there is a limit of ferrite solution concentration which determines the possibility to use it as a contrast agent it in T1- or T2-mode.

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10:15 Discussion/Coffee Break

10:30 **Synthesis and Characteristics of Cu-Zn-S Nanoparticle Materials for Sustainable Thermoelectrics**

Authors : Derrick Mott, Maninder Singh, Shinya Maenosono

Affiliations : Japan Advanced Institute of Science and Technology, School of Materials Science, 1-1 Asahidai, Nomi, Ishikawa, 923-1211, Japan

Resume : Thermoelectric materials with high efficiency are currently being highly sought for their advantageous applications in energy conversion or targeted cooling. While many new materials have been developed that rely on nanotechnology towards enhancing efficiency, many of the best examples rely on elements such as Bi, Sb, Te, and Pb, which are all either rare or toxic, limiting the sustainability of the resulting thermoelectric materials. In response we have developed a new chalcogenide nanoparticle system composed of Cu, Zn and S, elements which are abundant and sustainable in nature. The presentation will focus on our recent results in the synthesis and characterization of this new class of copper zinc sulfide nanoparticle with thermoelectric properties. The particles composition and Janus structure have a remarkable tailorable nature that could be exploited for enhanced sustainable thermoelectrics. The studies give insight into how to design and manipulate the properties of sustainable materials for thermoelectrics. Results will be discussed using characterization techniques such as XRD, XPS, TEM, STEM-HAADF, EDS Elemental Mapping and others.

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[\(close full abstract\)](#)

10:45 **Lanthanide doped core-shell alkaline-earth fluoride colloids: interesting optical probes for biomedical applications**

Authors : M. Pedroni, A. Speghini

Affiliations : Dipartimento di Biotecnologie and INSTM, Unita' di Verona, Universita' di Verona, Strada le Grazie 15, 37134 Verona, Italia

Resume : Alkaline-earth fluorides nanoparticles doped with Er^{3+}/Yb^{3+} or Tm^{3+}/Yb^{3+} lanthanide ions are efficient upconversion materials [1] that can find use in various technological fields, in particular in biomedical diagnostic. A recent paper describes the possibility of using upconverting Er^{3+}/Yb^{3+} or Tm^{3+}/Yb^{3+} codoped CaF_2 nanoparticles for cellular imaging [2]. In this contribution, we describe the synthesis of water dispersible core-shell alkaline-earth fluoride nanoparticles and the study of the spectroscopic properties of the prepared nanostructures upon near infrared excitation. A hydrothermal procedure has been developed to prepare core-shell $SrF_2:Nd^{3+}/Tm^{3+}/Yb^{3+}@SrF_2:Nd^{3+}$ nanoparticles with hydrophilic capping agents. The behavior of the Tm^{3+} and Yb^{3+} ions luminescence upon excitation in the near infrared region and the $Nd^{3+} - Yb^{3+}$ energy transfer processes have been investigated also as a function of the temperature for possible use of the nanoparticles as optical probes and nanothermometers. [1] M. Pedroni, F. Piccinelli, T. Passuello, S. Polizzi, J. Ueda, P. Haro-Gonzalez, L. M. Maestro, D. Jaque, J. Garcia-Sole, M. Bettinelli and A. Speghini, Cryst. Growth Des., 2013, 13, 4906-4913. [2] N. N. Dong, M. Pedroni, F. Piccinelli, G. Conti, A. Sbarbati, J. E. Ramirez-Hernandez, L. M. Maestro, M. C. Iglesias-de la Cruz, F. Sanz-

F.VII.
6

Rodriguez, A. Juarranz, F. Chen, F. Vetrone, J. A. Capobianco, J. G. Sole, M. Bettinelli, D. Jaque and A. Speghini, ACS Nano, 2011, 5, 8665-8671.

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[\(close full abstract\)](#)

11:00

Tuning the physical properties of Sr²⁺ doped BiFeO₃ multifunctional ceramics

Authors : S K Mandal, and Amreesh Chandra

Affiliations : Department of Physics and Meteorology, Indian Institute of Technology Kharagpur, Kharagpur-721302, West Bengal, India.

Resume : Multiferroic system that possess both ferroelectric (FE) and ferromagnetic (FM) properties with coupling between them are broadly classified as magneto electric (ME). The physical properties of such ME materials can be appreciably tuned as a function size confinement. BiFeO₃ is a well known multiferroic but possess low coupling coefficient at room temperature. The intrinsic problem of high leakage current also limits the use of pure BiFeO₃. To overcome these limitations, the use of dopants (both divalent and trivalent) is being widely investigated. In this paper, we report significant physical property variation in one such doped system viz., Bi_{1-x}Sr_xFeO₃. It is shown that the particle morphology can be changed from spherical to pillar like by carefully controlling the calcination temperature. The particle growth mechanism can be explained on the basis of minimization of the surface energy compared to the volume energy term. As a function of particle shape, large scale tunability in the photoluminescence property could be obtained. Using dielectric, XRD, and SQUID data, it is shown that doping allows a method to tune the low temperature phase transitions of the BiFeO₃ host matrix.

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11:15

Molecular strategies toward original nanomaterials: sub-oxides and boron-based compounds

Authors : Vasana Maneeratana,⁴ Weiwei Lei,⁵ Julien Chaste,⁶ Dominique Mailly,⁶ Markus Antonietti,⁴ Clement Sanchez,^{1,2,3} David Portehault^{1,2,3,*}

Affiliations : 1 Sorbonne Universités, UPMC Univ Paris 06, UMR 7574, Chimie de la Matière Condensée de Paris, F-75005, Paris, France; 2 CNRS, UMR 7574, Chimie de la Matière Condensée de Paris, F-75005, Paris, France; 3 Collège de France, Chimie de la Matière Condensée de Paris, 11 place Marcelin Berthelot, 75231 Paris Cedex 05, France; 4 Max-Planck Institute for Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, 14424 Potsdam, Germany; 5 Institute for Frontier Materials, Deakin University, Waurin Ponds, Victoria 3216, Australia; 6 Laboratoire de photonique et de nanostructures, CNRS UPR 20, Route de Nozay, 91460 Marcoussis, France

Resume : Reactions between molecular species are often the most suitable for cost effective fabrication of materials with controlled crystal structure, nano-, meso- and micro-structures. Such chemical pathways are studied for nanostructured metals, chalcogenides and oxides of metals with high oxidation state, but other compounds were only scarcely, if ever, reported at the nanoscale. These systems show at the bulk scale mechanical, catalytic and electronic properties without equivalent among common compounds. Corresponding nanostructures could lead to important changes of existing properties, emergence of new behaviours and novel processing possibilities. We will demonstrate that accurate control of experimental parameters such as the solvent nature or the temperature provides access to new compounds families at the nanoscale. We will focus on 3 systems: reduced titanium oxides, so-called Magnéli phases, where innovative nanostructuring impacts the thermoelectric and the electrical properties; the first ever reported synthesis of metal-boron alloys nanocrystals will be shown; finally, boron-carbon-nitrogen graphene analogs will be presented with tunable band gap, hydrogen sorption, electrochemical energy storage, and water remediation properties.

Maneeratana, Portehault, Chaste, Mailly, Antonietti, Sanchez, Adv. Mater. In press, 2014. Carenco, Portehault, Boissiere, Mezailles, Sanchez, Chem. Rev. 113, 7981, 2013. Lei, Portehault, Dimova, Antonietti, J. Am. Chem. Soc. 133, 7121, 2011

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[\(close full abstract\)](#)

11:30

Formation and properties of SiC nano-particles colloids in non polar liquids

Authors : Hamza Hazzaji 1, Sergei Alekseev 2, David Philippon 3, Gérard Guillot 1, Philippe Vergne 3, Jean-Marie Bluet 1

Affiliations : 1 Université de Lyon, CNRS, UMR 5270, INSA-Lyon, INL, F-69621 Villeurbanne, France 2 Chemistry Faculty, Kiev National Taras Shevchenko University, 01601 Kiev, Ukraine 3 Université de Lyon, CNRS, UMR5259, INSA-Lyon, LaMCoS, F-69621 Villeurbanne, France

Resume : The goal of this work is to form SiC nanoparticles colloids in non polar liquids toward temperature sensing application in lubricant. The formation of stable SiC colloids in polar liquids like water or ethanol has been

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demonstrated and explained by their surface chemistry resulting in a negative zeta potential [1, 2]. The strong fluorescence emission of these colloids led to application as a non toxic bio label [3]. Here, we will present surface functionalization of SiC nanoparticles by long chain amines (nonylamine, octadecylamine) in order to disperse them in non polar liquids like alkane or alkene. The SiC nanoparticles have been obtained by two different top-down technology : the first is electrochemical anodization of polycrystalline SiC in an hydrofluoric acid-ethanol mixture, the second is chemical etching of micrometer size SiC particles in a hydrofluoric -nitric acid mixture. Chemical (FTIR, Raman), structural (TEM, DLS) and optical characterization (fluorescence and fluorescence lifetime) of the resulting colloids will be presented. [1] J. Botsoa, J.-M. Bluet, V. Lysenko et G. Guillot, J. of Appl. Phys. 102 (8), p. 083526 (2007). [2] Yu. Zakharko, J. Botsoa, S. Alekseev, V. Lysenko, J.-M. Bluet, O. Marty, V. A. Skryshevsky, and G. Guillot, J. of Appl. Phys. 107, 013503 (2010). [3] J. Botsoa, V. Lysenko, A. Geloën, O. Marty, J.M. Bluet and G. Guillot, Appl. Phys. Lett. 92, 173902 (2008).

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11:45 Lunch Break

Photonic Properties & Spectroscopy of nanoColloids : Mathieu Maillard, TBC, Gabriele Rainò

13:45 Core/Shell Semiconductor Quantum Heterostructures with Tailored Optical Properties

Authors : G. Raino (1), T. Stoeflerle (1), I. Moreels (2), Z. Hens (3), and R. F. Mahrt (1)

Affiliations : 1- IBM Research ? Zurich, S?umerstrasse 4, 8803 Rueschlikon (Switzerland), 2 - Istituto Italiano di Tecnologia, via Morego 30, IT-16163 Genova, (Italy), 3 - Physics and Chemistry of Nanostructures, Ghent University, Krijgslaan 281-S3, B-9000 Gent (Belgium)

Resume : Colloidal semiconductor quantum nanostructures allow controlling the confinement of charge carriers through material composition and geometry. In addition, complex heterostructures can be synthesized expanding this range of possibilities further. This enables the design of nanoscale quantum light sources with tailored optical properties. As an example of such extraordinary control, here we report on our recent results on precisely engineered core/shell nano-heterostructures allowing to control and tune the quantized energy levels and their radiative rates. Moreover, by wavefunction engineering, the band-edge fine structure splitting energy can be accurately adjusted. This allowed us to study the exciton dynamics and unveil a so called -phonon bottleneck-. Such peculiar behavior has not been observed so far in colloidal QDs due to the presence of additional and efficient relaxation paths such as electron/hole Auger cooling, coupling to surface ligands and defect mediated relaxation, masking the phonon-mediated relaxation. The flexibility offered by core/shell heterostructures (material composition, combination, shape) is crucial at the single particle level. Indeed, this enabled the development of blinking-free, stable and narrow emission linewidth single quantum core/shell heterostructures. This level of control of nanoscopic material could pave the way towards temperature-insensitive laser devices, novel single photon sources or sensitive local probe at the nanoscale.

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14:15 Excitation intensity dependent blinking statistics and quantum yield of Si/SiO₂ and CdSe/ZnS QDs

Authors : Benjamin Bruhn (1), Ilya Sychugov (2), Fatjon Qejvanaj (2), Jan Linnros (2), Tom Gregorkiewicz (1)

Affiliations : (1): Van der Waals-Zeeman Institute, University of Amsterdam, 1098XH Amsterdam, The Netherlands (2): Materials and Nanophysics, KTH Royal Institute of Technology, 16440 Stockholm, Sweden

Resume : Blinking, a cyclic transition between a bright and a dark state, is a fundamental property of quantum emitters. Quantum dots in the bright state support radiative exciton recombination, whereas light emission is quenched in the dark state, reducing the emitter's quantum efficiency. Important insights into the blinking mechanism can be obtained from ON- and OFF-interval length histograms. These are commonly described by (truncated) power-law distributions, whereas mono-exponential blinking statistics have only been reported in well passivated silicon quantum dots at high pumping. This

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observation of purely exponential decays at comparatively low excitation raised the question whether excitation intensity itself can completely alter the blinking statistics, and not only introduce a truncation in the ON-time distribution. In order to answer that question, a comparison between blinking statistics of silicon and cadmium selenide nanocrystals throughout a large range of excitation power densities will be presented. ON- and OFF-time distributions and temporal correlation of neighboring intervals will be investigated. Since blinking is intimately related to quantum yield, the duty cycle (ON-time fraction) is also examined as a function of excitation power, and the results are cross-correlated.

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14:30

Intraband transitions in butyl-terminated Ge quantum dots

Authors : Chris de Weerd, Katerina Dohnalova, Tom Gregorkiewicz

Affiliations : UvA-WZI

Resume : Although Si is widely used for photovoltaic and electronic applications, light emission from Si is in general poor due to its indirect bandgap. Apart from Si, also Ge makes a good candidate for electronic devices. It has a rather large exciton Bohr radius (~18 nm) and bulk Ge has a direct bandgap of 0.8 eV. Therefore, Ge should also make a good candidate for QD-based devices. As reported in past literature, emission from (oxidized) Ge QDs is in general weak. Here, we discuss high-intensity PL emission bands from colloidal butyl-terminated Ge QDs. The PL bands blueshift with increasing excitation energy, indicating an ensemble of QDs with a broad size distribution. We observed PL lifetimes on a sub-nanosecond timescale. In addition, we discuss the intraband transitions in butyl-terminated Ge QDs. For that purpose, we use ultrafast transient induced absorption spectroscopy. The time-dependent evolution of absorption spectra provides information on relaxation and recombination processes within the excited states of QDs. This is done by probing intraband transitions of free carriers generated by the pump pulse. We demonstrate that the features observed by experiment agree well with theoretical modeling. We discuss implications of these findings for new applications of these bright emitting colloidal Ge QDs for photovoltaic and light emitting devices.

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14:45

Controlling the Emission Rate and Oscillation Strength via Shape-Control in 2D Colloidal Nanocrystals

Authors : Sotirios Christodoulou,1 Hongbo Li,1 Rosaria Brescia,1 Mirko Prato,1 Giovanni Bertoni,1,2 Liberato Manna,1 and Iwan Moreels1

Affiliations : 1 Istituto Italiano di Tecnologia, via Morego 30, IT-16163 Genova, Italy ; 2 IMEM-CNR, Parco Area delle Scienze 37/A, IT-43124 Parma, Italy.

Resume : Colloidal nanocrystals (NCs) are well known for their excellent optical properties such as a high optical stability and a wide tunability of the emission peak, making them applicable for lasing, LEDs, or as quantum emitters. Control over the NC exciton lifetime is a crucial aspect in these devices, and in NC heterostructures we already obtained a significantly longer lifetime by manipulating the electron delocalization. Here we demonstrate that we can also obtain faster recombination rates, by controlling the local field factor fLF and the intrinsic oscillator strength of the band-edge transition. Key is to tune the shape and lateral dimensions of the nanocrystal. Firstly, using flat CdTe quantum disks we show that fLF can be enhanced, typically reducing the PL lifetime from 20-25 ns in spherical CdTe NCs to about 12 ns in disks with an aspect ratio of 3-4.[1] Secondly, synthesizing 2-D CdSe nanoplates of variable lateral size, we demonstrate that we can additionally boost the emission rate in such flat structures, by delocalizing the exciton wave function in the two lateral directions over an increasing number of CdSe units. The resulting giant oscillator strength enables us to reach lifetimes of less than 10 ns, further decreasing to sub-ns values at 4K. We conclude that shape-engineering finally brings about the full control over the NC optical properties, from the position of emission peak to the corresponding lifetime. [1] H. Li et al., J. Am. Chem. Soc 2103, 135, 12270

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15:00

Amplified spontaneous emission from water-soluble CdSe/CdS quantum dot-in-rods

Authors : Francesco Di Stasio, Joel Q. Grim, Angelo Accardo, Vladimir Lesnyak, Francesco De Donato, Iwan Moreels, Roman Krahné

Affiliations : Istituto Italiano di Tecnologia, Via Morego 30, IT-16163 Genoa, Italy

Resume : We discuss the optical properties of highly luminescent CdSe/CdS quantum dot-in-rods synthesized by seeded growth(1) and then transferred to

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water using a simple ligand-exchange method employing mercaptopropionic acid (MPA)(2). From a device fabrication point of view, water-soluble nanocrystals (NCs) are most desirable since they enable the preparation of multi-layer structures by exploiting orthogonal solvents, as well as the use of organic materials for the fabrication of a variety of photonic structures. Nevertheless, obtaining water-soluble CdSe/CdS NCs possessing similar optical properties to organic soluble ones has represented a major challenge. The water-soluble MPA-capped NCs here investigated possess a CdS rod with a diameter that is significantly larger than the CdSe core. The larger CdS rod prevents surface defects formed during the ligand-exchange reaction to affect the photophysics of the system, hence MPA-capped NCs show similar optical properties to the pristine (organic soluble) octadecylphosphonic acid functionalized NCs. More importantly, we demonstrate amplified spontaneous emission from the core or shell states(3) of films made from water-soluble CdSe/CdS dot-in-rods, providing further evidence that the desired properties are preserved after the ligand-exchange reaction. References: 1 Carbone L, et al. Nano Letters 2007, 7, 2942 2 Wuister S F, et al. Nano Letters 2003, 3 3 Krahn R, et al. Appl. Phys. Lett. 2011, 98, 063105

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15:15

Size-dependent Phonon Confinement in Colloidal Si Nanoparticles Revealed via Raman Spectroscopy

Authors : Pengfei Zhang, Yu Feng, Gavin Conibeer and Shujuan Huang

Affiliations : School of Photovoltaics and Renewable Energy Engineering (SPREE), the University of New South Wales (UNSW), Sydney 2052, NSW, Australia

Resume : By introducing a variable confinement factor into a well-known phenomenological phonon confinement model (PCM) developed by Richter et al, decent fitting is achieved to downshifted and asymmetrically-broadened Raman spectroscopies of free-standing colloidal Si nanoparticles (NPs) of different sizes from 2.2nm to 6.3nm. Comparative study on these Raman spectroscopies reveals an apparent positive correlation between this defined phonon confinement factor and the size of Si Nanoparticles (NPs). Considering this confinement factor determines the degree of phonon confinement from the Gaussian envelop function in PCM, for the first time, the phonon confinement and the sizes of NPs are connected in a specific relationship. Based on the trend of fitted value of this confinement factor, we demonstrated the probability amplitude of first-order optical phonon is larger at the edge of smaller NPs, which means that it is easier to detect a phonon at the boundary of smaller NPs. This finding is consistent with the relaxation rule of Raman scattering within nano-structures. From this study, the quantum confinement effect is systematically proved to exist from the aspect of lattice vibration, namely, phonon.

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15:30

Study of InAs quantum dots in silicon obtained through ion implantation

Authors : M.A. Sortica [1; 2], B. Canut [1], M. Hatori [2], P. L. Grande [2], J.F. Dias [2], N. Chauvin [1], O. Marty [3]

Affiliations : [1] Université de Lyon; Institut des Nanotechnologies de Lyon INL-IMR5270, CNRS, INSA de Lyon, Villeurbanne, F-69621 Villeurbanne, France; [2] Instituto de Fisica, Universidade Federal do Rio Grande do Sul (IF-UFRGS), Av. Bento Gonçalves 9500, 91501-970, Porto Alegre (RS), Brazil; [3] Université de Lyon, Institut des Nanotechnologies de Lyon INL-IMR5270, CNRS, Université Lyon 1, Villeurbanne, F-69621 Villeurbanne, France

Resume : Nanocrystals of III-V compounds embedded in a semiconductor matrix with higher band gap are of great interest for optoelectronic devices since the pronounced quantum confinement effects of such materials allow tuning their light emission by controlling the size of the nanocrystals. Molecular beam epitaxy (MBE) is the most used technique to produce such nanostructures. Another technique to form this kind of nanocrystals is the combination of ion implantation and thermal annealing. In this work, we study the formation of InAs quantum dots by sequential implantations of As and In in silicon with subsequent Rapid Thermal Annealing (RTA) of the implanted samples. Two sets of samples were produced with fluencies of $2 \times 10^{16} \text{ cm}^{-2}$ and $5 \times 10^{16} \text{ cm}^{-2}$. The specimens were implanted at 500 °C with energies of 250 keV for As and 350 keV for In. The samples were annealed with different maximum temperatures and durations in order to optimize the light emission from InAs nanocrystals embedded in Si. Besides photoluminescence (PL), the samples were characterized with complementary techniques like RBS-C, SEM and TEM, thus providing further structural information. After RTA treatment, InAs precipitates are evidenced and a strong increase of photoluminescence

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yields were observed. From RBS analysis, no significant losses of implanted ions due to diffusion processes took place.

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15:45 Discussion/Coffee Break

16:00 PLENARY SESSION

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PROGRAM VIEW : 2014 Spring

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Symposium : F

Established and emerging nanocolloids: from synthesis & characterization to applications

26 May 2014	27 May 2014	28 May 2014	29 May 2014	30 May 2014
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start at	Subject	Num.
	nanoColloidal Hybrid Systems : Pascal André, Laurence Motte, Michel Calame	
09:00	<p>Emerging functionality in nanoparticles arrays Authors : Michel Calame Affiliations : Physics Department and Swiss Nanoscience Institute, University of Basel Klingelbergstrasse 82, 4056 Basel, Switzerland michel.calame@unibas.ch Resume : Arrays of metal nanoparticles interlinked by an organic matrix have attracted a lot of interest due to their diverse electronic and optoelectronic properties [1]. By controlling the nature of the matrix material and the interparticle distance, the electronic behavior of the nanoparticle array can be substantially tuned and controlled [1,2]. We have recently shown that nanoparticle arrays form a useful architecture to build networks of molecular junctions. Here, the nanoparticles act as electronic contacts to the molecules and a molecular functionality can be used to induce an overall functionality at the array scale. Using this approach, we have build nanoarticles arrays exhibiting for instance redox [3] and optical [4] switching behaviors. The later is made possible thanks to the excitation of surface plasmons in the nanoparticles. Thanks to this particular configuration, the molecules can easily be accessed by optical means. A resonant excitation of the molecules within the array will thus leads to a photoconductance enhancement at the array level [5]. Nanoparticle arrays thus represent an interesting architecture opening possibilities for the development of novel molecular scale electronic and optoelectronic devices. Their possible implementation as an information storage platform or even as computing networks thanks to a defect-tolerant architecture is currently under investigation [6]. References 1. M.A. Mangold et al., Nanoparticles arrays, to appear in the Springer Handbook of Nanoparticles (2014). 2. M. Calame, Molecular junctions: from tunneling to function, <i>Chimia Int. J. Chem</i>, 64 (6), 391-397 (2010). 3. J. Liao et al., Cyclic conductance switching in networks of redox-active molecular junctions, <i>Nano Letters</i>, 10 (3) , 759–764 (2010). 4. S. van der Molen et al., Light-controlled conductance switching of ordered metal-molecule- metal devices, <i>Nano Letters</i>, 9 , 76-80 (2009). 5. M. A. Mangold et al., Resonant Photoconductance of Molecular Junctions Formed in Gold Nanoparticle Arrays, <i>J. Am. Chem. Soc.</i>, 133 (31) , 12185–12191 (2011). 6. G. Wendin et al., Synaptic Molecular Networks for Bio-Inspired Information Processing, <i>Int. J. Unconv. Comp.</i>, 8 , 325-332 (2012).</p>	F.IX. 1
	<p>add to my program (close full abstract)</p>	
09:30	<p>Memory with Colloidal Si-SiO₂ nanoparticles embedded in Hybrid organic-inorganic Dielectrics Authors : Caiming SUN, Xiaohua CHEN, Jun DU Affiliations : Nano and Advance Materials Institute (NAMI) Limited, Units 608-9, 6/F, Lakeside 2, No 10 Science Park West Avenue, Hong Kong Science Park, Shatin NT, Hong Kong Resume : The global market for the printed electronics (PE) totaled US\$2.2 billion recently. In reducing cost of these printed devices, printed memory and logic functions are urgently required and will drive the future development of PE market. Memory card based on traditional Si microelectronics costs US\$2-10 per piece. Very tiny Si chips must be assembled into the large-area plastic card and the assembly cost is larger than the chip itself. Printed memory devices don't need complicated assembly and are expected to cost below US\$0.5 per piece. In this work, Si-SiO₂ core-shell nanoparticles (<5nm) are formulated into colloidal</p>	F.IX. 2

inks and embedded into dielectric layers, acting as floating gate for non-volatile memory transistors. And hybrid organic/inorganic dielectrics is developed by UV curable Sol-Gel methods. 10nm-100nm thick dielectrics is formed by dip-coating with dielectric strength >2MV/cm. Then 50nm thick dielectric layer can work up to 10V and this voltage is consistent with low-voltage operation below 10V. The interconnections between different layers (source, drain and gate) are formed by laser ablation of the dielectric layer followed by silver overprinting. Gold nanoparticles (Au NPs) are extensively used as floating gate in printed memory transistors, but poor Au-to-dielectrics interfaces made retention time limited to <1 year. Si-SiO₂ core-shell NPs demonstrated significant improved durability, with retention time up to 10 years.

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09:45

Physical reasons of emission variation of CdSeTe/ZnS quantum dots at the bioconjugation

Authors : T. V. Torchynska¹, G. Polupan²

Affiliations : 1ESFM– National Polytechnic Institute, México D. F. 07738, México 2ESFM– National Polytechnic Institute, México D. F. 07738, México

Resume : Core/shell CdSeTe/ZnS quantum dots (QDs) with emission at 800 nm (1.60 eV) have been studied using the photoluminescence (PL), its excitation power dependence and Raman scattering in nonconjugated states and after the conjugation to three types of antibodies (Ab): i) mouse monoclonal [8C9] human papilloma virus (HPV), anti-HPV 16-E7 Ab, ii) mouse monoclonal [C1P5] human papilloma virus, HPV16 E6 + HPV18 E6 Ab, and iii) pseudo rabies virus (PRV) Ab. The transformation of PL and Raman scattering spectra, stimulated by the antibodies, has been studied in bioconjugated QDs. CdSeTe/ZnS QD energy diagrams were designed that helps to analysis of the PL spectra and their transformations at the bioconjugation. It is revealed that the core in CdSeTe/ZnS QDs has the type II quantum well that permits to explain the near IR optical transition (1.60 eV) and its transformation at the bioconjugation with appearing the high energy PL bands (1.88-1.94 eV). A set of physical reasons has been analyzed for the explanation of PL spectrum transformation at the bioconjugation, such as: i) emission of the antibody molecules or the PBS buffer, ii) a compressive strain applied to QDs at the bioconjugation, iii) core/shell material intermixing or oxidation at the bioconjugation, iv) the quantum-confined Stark effect stimulated by the electric charge of antibodies, v) dominated emission of excitons localized at the excited QD states, vi) the change of energy band profile at the application of electric field of charged Abs, vii) the quantum confined effect owing to the shift of QD energy levels stimulated by the change of electric potential at the QD surface or by decreasing the effective QD size in bioconjugated QDs. Finally it is shown that the change of energy band profile and the shift of QD energy levels for the strong quantum confinement at the bioconjugation of QDs to charged antibodies are the dominant reasons of emission transformation. The effect of PL spectrum transformation is useful for the study of QD bioconjugation with specific antibodies and can be a powerful technique in early medical diagnostics.

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10:00

From semiconductor nanocrystals to artificial graphene and topological insulator

Authors : E. Kalesaki, C. Delerue, C. Morais Smith, W. Beugeling, G. Allan, D. Vanmaekelbergh

Affiliations : IEMN-Department of ISEN, UMR CNRS 8520, 59046 Lille, France ; Physics and Materials Science Research Unit, University of Luxembourg, 162a avenue de la Faiënerie L-1511 Luxembourg, Luxembourg ; Institute for Theoretical Physics, University of Utrecht, 3584 CE Utrecht, Netherlands ; Debye Institute for Nanomaterials Science, University of Utrecht, 3584 CC Utrecht, Netherlands

Resume : Recent advancements in colloidal chemistry indicate that two-dimensional single-crystalline sheets of semiconductors forming a honeycomb lattice can be synthesized from semiconductor nanocrystals [1]. We perform atomistic tight-binding calculations of the band structure of CdSe sheets with such a nano-geometry [2]. We predict in the conduction band Dirac cones at two distinct energies and nontrivial flat bands and, in the valence band, topological edge states. These edge states are present in several electronic gaps opened in the valence band by the spin-orbit coupling and the quantum confinement in the honeycomb geometry. The lowest Dirac conduction band has s-orbital character and is equivalent to the pi bands of graphene but with renormalized couplings. The conduction bands higher in energy have no counterpart in graphene; they combine a Dirac cone and flat bands because of their p-orbital character. These systems emerge as remarkable platforms for

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studying complex electronic phases starting from conventional semiconductors.
 [1] W. H. Evers, B. Goris, S. Bals, M. Casavola, J. de Graaf, R. van Roij, M. Dijkstra, and D. Vanmaekelbergh, *Nano Lett.* 13, 2317 (2013). [2] E. Kalesaki, C. Delerue, C. Morais Smith, W. Beugeling, G. Allan, D. Vanmaekelbergh, *Phys. Rev. X*, in press.

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10:15 Discussion/Coffee Break

- 10:30 **Chemical Stability Enhancement via Electron Transfer Phenomenon in Core@Shell Heterostructured Nanoparticle System**
Authors : Anh T. N. Dao, Prerna Singh, Aparna Wadhwa, Daisuke Hotta, Derrick Mott, Shinya Maenosono
Affiliations : School of Materials Science, Japan Advanced Institute of Science and Technology
Resume : Metal nanoparticles (NPs) have long been utilized for various types of chemical and/or biological sensing applications exploiting their localized surface plasmon resonance (LSPR) and/or surface enhanced Raman scattering (SERS) properties. At the same time, much of the knowledge being gained for manipulating NP structure or composition has focused on multimetallic type NPs. Such systems can display multiple properties arising from the individual components, but it is the observation of synergistic phenomena that is the most intriguing. Recently, we have synthesized various binary core@shell type NPs such as Au@Ag, Pt@Ag, Au@Fe and Au@Cu NPs. In all cases, it has been demonstrated that electron transfer from core to shell materials takes place and it modifies electronic/chemical states of shell materials. This synergistic effect enhances strengths and eliminates weaknesses of the shell element which is not achievable by alloying strategy. For example, Ag has superior SERS properties than Au, however Ag is easy to be oxidized. If one makes Au-Ag alloy NPs, both LSPR/SERS properties and oxidation resistivity would be in between those of Au and Ag NPs. In the case of Au@Ag NPs, however, we can combine LSPR/SERS properties of Ag and chemical stability of Au into single NPs. The electron transfer phenomenon has been confirmed for various core@shell NP systems by XPS and many other analytical techniques. We attempt to provide a unified explanation for those observations.

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[\(close full abstract\)](#)

- 10:45 **Atomistic Simulations of the Surface Coverage of Large Gold Nanocrystals**
Authors : Takieddine Djebaili (a,b), Johannes Richardi (a,b), Stéphane Abel (c) and Massimo Marchi (c)
Affiliations : (a) Sorbonne Universités, UPMC Univ Paris 06, UMR 8233, MONARIS, F-75005, Paris, France (b) CNRS, UMR, MONARIS, F-75005, Paris, France (c) Commissariat à l'Energie Atomique et aux Energies Alternatives, DSV/iBiTEC-S/SB2SM/LBMS & CNRS UMR 8221, Saclay, France.
Resume : The adsorption of alkanethiolates on gold nanocrystals with diameters up to 10 nm is studied by Molecular Dynamics simulations. Nanocrystals of various shapes such as icosahedra, octahedra and cubes are investigated. The surface coverage of the nanocrystals obtained in the simulations is in good agreement with experimental data. For icosahedral and octahedral shapes, we observe two different molecular organizations of the thiolates on the edges and in the centers of the nanocrystal facets. The incompatibility between both organizations explains the fact that the formation of self-assembled monolayers usually observed on flat Au(111) surfaces is hindered for nanocrystals smaller than 6 nm. We also show that the organization of thiolates on the edges is at the origin of the lower average surface per adsorbed thiol found for nanocrystal. Reference: T. Djebaili, J. Richardi, S. Abel, M. Marchi, *J. Phys. Chem. C* 117, 17791 (2013).

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[\(close full abstract\)](#)

- 11:00 **Role of surface passivation on radiative properties of Silicon quantum dots – study by single quantum dot spectroscopy**
Authors : B. van Dam, B. Bruhn, K. Dohnalova
Affiliations : Van der Waals-Zeeman Institute, University of Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands
Resume : Silicon quantum dots (Si QDs) are promising alternative to toxic, rare and expensive QDs of other materials that nowadays are being researched for or used in optoelectronics, photonics and bio-imaging. Radiative rates, though, are comparatively low, owing to the indirect bandgap nature of Si. Deeper understanding of the processes involved can be achieved from single QD

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7

spectroscopy, allowing study of individual quantum emitters, while avoiding ensemble averaging effects. Comparison of single QD characteristics with those of the ensemble gives insight into the microscopic processes that underlie ensemble photoluminescence (PL) and quantum yield (QY). As generally in all quantum emitters, the QY is critically influenced by blinking (PL intermittency), a cyclic transition between an emissive bright and a non-radiative dark state, that emerges on a microscopic level. The mechanism behind the blinking process is not yet fully understood, but could arise from charging of the QD or trapping into a nearby defect state. Surface states assume a major role in both models, but also influence the radiative rates through modification of the electron and hole wavefunctions. By single QD spectroscopy, as well as complementary ensemble measurements, we examine the effect of carbon- and silica oxide-based surface capping on blinking and PL of colloidal Si QDs, which will help the development of Si QDs for application in lighting technologies.

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11:15

Chalcogenol ligand toolbox for CdSe nanocrystals and their influence on exciton relaxation pathways

Authors : Jannise J. Buckley, Elsa Couderc, Stephen E. Bradforth, and Richard L. Brutchey

Affiliations : Department of Chemistry and the Center for Energy Nanoscience, University of Southern California, Los Angeles, California 90089, United States

Resume : We have employed a simple modular approach to install small chalcogenol ligands on the surface of CdSe nanocrystals. This versatile modification strategy provides access to thiol, selenol, and tellurol ligand sets via the in-situ reduction of R₂E₂ (R = tBu, Bn, Ph; E = S, Se, Te) by diphenylphosphine (Ph₂PH). The ligand exchange chemistry was analyzed by solution NMR spectroscopy, which reveals that reduction of the R₂E₂ precursors by Ph₂PH directly yields active chalcogenol ligands that subsequently bind to the surface of the CdSe nanocrystals. Thermogravimetric analysis, FT-IR spectroscopy, and energy dispersive X-ray spectroscopy provide further evidence for chalcogenol addition to the CdSe surface with a concomitant reduction in overall organic content from the displacement of native ligands. Time-resolved and low temperature photoluminescence measurements showed that all of the phenylchalcogenol ligands rapidly quench the photoluminescence through a hole localization mechanism. The greatest quenching efficiency was achieved using the selenol and tellurol ligands due to their greater driving forces for hole transfer. The hole transfer process could lead to engineering long-lived, partially separated excited states.

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11:30

High-yield synthesis of nanocolloids with valence

Authors : A. Désert¹, C. Hubert², L. Moulet¹, J. Majime¹, A. Thill³, E. Bourgeat-Lami⁴, M. Lansalot⁴, E. Duguet¹, S. Ravaine²

Affiliations : 1 CNRS, Univ. Bordeaux, ICMCB, UPR 9048, 33600 Pessac, France 2 CNRS, Univ. Bordeaux, CRPP, UPR 8641, 33600 Pessac, France 3 DSM/IRAMIS/SIS2M/LIONS, UMR CEA/CNRS 3299, 91191 Gif-sur-Yvette, France 4 Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, LCPP group, 69616 Villeurbanne, France

Resume : In the last decade, interest for colloidal particles with anisotropic composition has considerably increased due to the potential benefits of these entities in multiple areas of materials science. Indeed, controlling the morphology and/or the composition of colloidal particles is an absolute necessity if one intends to master their physico chemical properties. We have reported the synthesis of large quantities of binary colloidal molecules that consist of a central silica core surrounded by a precise number of polystyrene (PS) nodules [1,2]. In this presentation, we will first show that we have considerably improved the synthesis of these so-called "colloidal molecules" during the last year, so that the tetrahedral, hexagonal, octagonal,..., colloidal structures can now be produced in large quantities with a yield higher than 90% versus the number of silica seeds. These binary entities can be considered as patchy silica particles bearing a controlled number of well-located hydrophobic PS patches[3]. We will also show that we succeeded in promoting the growth of the silica core of these colloidal molecules. While growing, the silica surface conforms to the shape of the PS nodules. After removal of the latter, large quantities of silica particles with a precise number of concave patches – which can be regarded as a valence state- are produced. Since it is possible to specifically functionalize the silica surface before removing the organic nodules, the patchy particles are capableIn the last decade, interest for colloidal particles with anisotropic composition has considerably increased due to the potential benefits of these entities in multiple areas of materials science. Indeed, controlling the

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morphology and/or the composition of colloidal particles is an absolute necessity if one intends to master their physico chemical properties. We have reported the synthesis of large quantities of binary colloidal molecules that consist of a central silica core surrounded by a precise number of polystyrene (PS) nodules [1,2]. In this presentation, we will first show that we have considerably improved the synthesis of these so-called "colloidal molecules" during the last year, so that the tetrahedral, hexagonal, octagonal,..., colloidal structures can now be produced in large quantities with a yield higher than 90% versus the number of silica seeds. These binary entities can be considered as patchy silica particles bearing a controlled number of well-located hydrophobic PS patches[3]. We will also show that we succeeded in promoting the growth of the silica core of these colloidal molecules. While growing, the silica surface conforms to the shape of the PS nodules. After removal of the latter, large quantities of silica particles with a precise number of concave patches – which can be regarded as a valence state- are produced. Since it is possible to specifically functionalize the silica surface before removing the organic nodules, the patchy particles are capable of directional interactions with other ones. Their assembly into precise and predictable structures can be now envisaged. [1] A. Perro et al., Angew. Chem. Int. Ed., 2009, 48, 361 [2] E. Duguet et al., Chem. Soc. Rev., 2011, 40, 941 [3] A. Désert et al., Polym. Chem., 2012, 3, 1130

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11:45 Lunch Break

Energy Conversion and Storage : Gordanna Dukovic, Mathieu Maillard, Tim Lian

13:15 Photo-driven charge separation and H2 generation in multifunctional colloidal nanorod heterostructures

Authors : Tianquan Lian

Affiliations : Department of Chemistry, Emory University, Atlanta, GA 30322, USA

Resume : Quantum confined semiconductor nanocrystals have been widely investigated as light harvesting and charge separation components in photovoltaic and photocatalytic devices. The efficiency of these semiconductor nanocrystal-based devices depends on many processes, including light harvesting, carrier relaxation, charge separation and charge recombination. The competition between these processes determines the overall solar energy conversion (solar to electricity or fuel) efficiency. Compared with single component quantum dots (QDs), semiconductor nanoheterostructures, combining two or more materials, offer additional opportunities to control their charge separation properties by tailoring their compositions and dimensions through relative alignment of conduction and valence bands. Further integration of catalysts (heterogeneous or homogeneous) to these materials form multifunctional nanoheterostructures. Using CdSe/CdS/Pt, dot-in-rod nanorods (NRs) with Pt tips, as a model system, we are examining the mechanism of long-lived charge separation and H2 generation in the presence of sacrificial electron donor. The rates of electron transfer, hole transfer and charge recombination are directly monitored by transient absorption and time-resolved fluorescence spectroscopy. In this talk, we will discuss the mechanism of exciton dissociation and the dependence of the rates of elementary charge transfer processes on the dimension (size and length) and band alignment in these materials.

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13:45 Plasmon-enhanced thin film solar cells with self-assembled colloidal metal nanosphere arrays

Authors : Manuel J. Mendes(1), Seweryn Morawiec(1,2), Francesca Simone(2), Francesco Priolo(1,2,3), Isodiana Crupi (1)

Affiliations : 1) MATIS CNR-IMM, via S. Sofia 64, 95123 Catania, Italy 2) Dipartimento di Fisica e Astronomia, Università di Catania, via S. Sofia 64, 95123 Catania, Italy 3) Scuola Superiore di Catania, Università di Catania, via Valdisavoia 9, 95123 Catania, Italy

Resume : Novel plasmonic back reflector (PBR) structures were developed, using metal nanoparticles (NPs) synthesized in colloidal solution, to enhance the optical path length of the near-infrared (NIR) light in thin film silicon (Si) solar cells (SCs). Such light trapping structures were realized with spherical gold (Au) colloids due to their high monodispersity in size and shape as well as chemical and environmental stability. A scalable, low-cost and low-temperature wet-coating method was developed[1] to self-assemble uniform arrays of Au NPs with improved physical properties relative to the NPs formed with typical PBR

F.X. 2

fabrication methods by physical dewetting. The strong scattering properties of the optimally-designed colloidal nanostructures match those determined analytically with Mie theory, and allow the production of PBRs with remarkable light diffusion similarly to the best state-of-the-art PBRs fabricated with conventional methods. Nevertheless, with the colloidal approach presented here, this is achieved with a much lower MNP surface coverage and process temperature (<120C) which is a key technological advantage since it allows integrating the PBRs after (and on top of) the Si SCs. The light trapping effects of colloidal PBRs are analyzed by incorporating them in thin film Si SCs fabricated by PECVD. The NIR photocurrent enhancement produced in the cells by plasmon-assisted scattering is correlated with the PBRs optical spectra. [1] M.J. Mendes et al. Nanotechnology (2013)

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[\(close full abstract\)](#)

14:00

Photovoltaic-Quality PbS Quantum Dots Synthesized in a Continuous Flow Reactor.

Authors : Irina Lokteva a), Katharina Poulsen a), Dominique Ehlert a), Jan Niehaus a), Christoph Gimmler a), Horst Weller b)

Affiliations : a) CAN (Center for Applied Nanotechnology) GmbH, Grindelallee 117, 20146 Hamburg, Germany; b) University of Hamburg, Institute of Physical Chemistry, Grindelallee 117, 20146 Hamburg, Germany

Resume : Colloidal quantum dots (QDs) prepared in solution are interesting due to their unique physical and chemical properties both for fundamental research and possible optoelectronic applications. Up-scaling and automated synthesis of high-quality nanomaterials is a prerequisite for their implementation in large-scale production and devices. Here we report a strategy for a flow synthesis of PbS nanocrystals with excitonic peaks from 1000 to 1600 nm and demonstrate their performance in photovoltaic devices. The synthesis in a continuous flow reactor allows the production of monodisperse, spherical nanoparticles in large quantities (10 grams per day) with high reproducibility and control over the optical properties, and is applicable to a wide range of high-quality semiconducting nanocrystals. The regulation of particle growth with desired properties by varying temperature, flow speed and precursor parameters will be discussed. Furthermore, we study the application of PbS QDs as an active layer in solar cells using different synthesis conditions and post-synthetic ligand exchange procedures, as well as cell architectures. The fabricated solar cells exhibit power conversion efficiencies comparable to those with small-scale batch-synthesized nanoparticles. The influence of oxygen doping and external conditions during film formation is investigated.

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14:30

Transport properties of CdSe nanocrystal superlattice

Authors : Pierre Capiod*(1), Maxime Berthe(1), Bruno Grandidier(1), Wiel Evers(2), Daniel Vanmaekelbergh(3)

Affiliations : 1 Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN), CNRS, UMR 8520, Département ISEN, 41 bd Vauban, 59046 Lille Cedex, France 2 Kavli Institute of Nanoscience & Chemical Engineering department, Delft University of Technology, 2600 GA Delft, The Netherlands 3 Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, University Utrecht, Princetonplein 1, 3584 CC Utrecht, The Netherlands

Resume : Two-dimensional materials exhibit exotic electronic properties and high specific surface areas that make them unique to investigate novel physical phenomena. In addition, their two-dimensional geometry is directly compatible with established design and processing approaches from the semiconductor industry and such an asset has motivated numerous applications in sensing, catalysis and energy storage. Recent achievements in wet-chemical semiconductor fabrication have demonstrated that two-dimensional single crystalline sheets can be synthesized from nanocrystalline colloids, where the nanocrystal facets are atomically bonded. As a result, the sheets show a super periodicity with a square or a honeycomb geometry, that make their electronic structure quite unique. Here, we report on the investigation of the transport properties of CdSe sheets with multiple probe scanning tunneling microscopy in ultra high vacuum. By performing four-point probe measurements, we are able to determine the conductivity of the sheets with dimensions exceeding a few micrometers. We also find a change of the conductivity as a gate voltage is applied to the underlying substrate. Key transport parameters, such as the free carrier concentration and the mobility are deduced from these measurements and their magnitude will be discussed in light of the structural properties of the sheets.

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14:45

PbS nanocrystals in hybrid systems for solar cells applications

Authors : C. Borriello *, A. Bruno, R. Diana, T. Di Luccio, P. Morvillo, R. Ricciardi, F. Villani, C. Minarini

Affiliations : ENEA - Italian National Agency for New Technologies, Energy and Sustainable Economic Development Research Centre Portici Portici (NA) I-80055 Italy

Resume : Recently, much research efforts are focused on lead chalcogenides nanocrystals (PbS and PbSe) to harness energy from near or mid-infrared (IR) wavelengths by controlling nanocrystals size-dependent absorption. Indeed, an important approach toward the realization of significant improvements to solar cell performance is to extend the spectral sensitivity of cells to near-infrared wavelengths, which contains as much as half of the energy of the solar spectrum. In this work we present the synthesis and characterization of PbS nanocrystals absorbing at 1185 nm. The nanocrystals have a cubic crystal structure as found by X-ray diffraction analysis. The nanocrystals Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) potentials have been obtained by Cyclic voltammetry measurements and are -4.6 and -3.8 eV, respectively. PbS nanocrystals were combined with poly(3-hexylthiophene) (P3HT) and P3HT:PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) to obtain binary P3HT:PbS and ternary P3HT:PCBM:PBs blends. The concentration of PbS was changed in both systems and in the ternary blends at fixed P3HT:PCBM weight ratio. Photoluminescence measurements performed on the two sets of samples showed an efficient quenching of P3HT signal at increasing PbS concentration. These results are very promising for the application of both donor-acceptor systems in hybrid solar cells.

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15:00

Nanocolloids of Titanium Oxides as interfacial layers in photovoltaics

Authors : Mireille Richard-Plouet, Luc Brohan, H el ene Terrisse, Solenn Berson*, St ephane Guillerez *

Affiliations : Institut des Mat eriaux Jean Rouxel, Universit e de Nantes CNRS, 2, rue de la Houssini re, BP 32229, 44322 Nantes Cedex 03, France *CEA, LITEN, Laboratoire des Modules Photovoltaiques Organiques, INES 50 avenue du Lac L eman, 73375 Le Bourget du lac, France

Resume : The photoactive properties of titanium dioxide are very attractive allowing many applications in the environmental domains. Its integration in hybrid organic solar cells, especially, requires the elaboration of layers to optimize collection and transport of photogenerated electrons. Solvothermal process allows us to adjust the size and variety of titanium dioxide by tuning pH or by using organic solvents. Depending on the chosen way, the hydrolysis-condensation is controlled; sols, gels and crystalline colloids can be prepared. Choosing to perform the synthesis in suitable solvents is a key parameter to obtain colloidal solutions, with the required physico-chemical properties for chemical solution deposition. In order to remain compatible with low temperature processes on plastic substrates, crystalline colloids are processed as thin film because no further annealing at high temperature is required. Their integration as interfacial layers allowed us to lengthen the lifetime of organic bulk heterojunction solar cells over 6500 hours, with a loss in photon conversion efficiency limited to less than 17% [1]. [1] Karpinski, A.; Berson, S.; Terrisse, H.; Mancini-Le Granvalet, M.; Guillerez, S.; Brohan, L.; Richard-Plouet, M. Solar Energy Mater. & Solar Cells 116, 27-33, 2013

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15:15

Colloidal PbS Quantum Dots with Low Cost and High Quality

Authors : Jun Pan, ‡ Ala'a O. Ballouli, ‡ Lisa Rollny, § Oleksandr Voznyy, § Edward H. Sargent, § and Osman M. Bakr ‡ *

Affiliations : ‡ Division of Physical Sciences and Engineering, Solar and Photovoltaics Engineering Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia, § Department of Electrical and Computer Engineering, University of Toronto, 10 King's College Road, Toronto, Ontario, M5S 3G4, Canada

Resume : Colloidal quantum dots (CQD) are attractive materials for optoelectronics, sensing devices and photovoltaics, due to their low cost, tunable bandgaps, and solution processability. This makes them attractive candidate materials for cheap and scalable roll-to-roll printable device fabrication technologies. However, the cost-effective mass production of CQDs with high quality is still a major challenge. Herein, we use PbS CQDs as an example, to demonstrate the scalable and automated synthesis of high quality monodisperse nanocrystals via a dual-temperature-stage flow reactor. Separate stages for nucleation and growth allow a high degree of control over the monodispersity of the CQDs. High photoluminescence quantum yield (50 %) and narrow full width-half max values were achieved for the optimized dual-stage

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flow-synthesized CQDs. Solar cells fabricated from the flow-synthesized PbS CQDs achieve on-par performance with that of small-scale batch synthesized CQDs at a power conversion efficiency of 4.1%. The dual-stage flow reactor approach, with its versatility and rapid screening of multiple parameters, combined with its efficient materials utilization, offers an attractive path to automated synthesis of CQDs for photovoltaics and, more broadly, active optoelectronics.

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15:30 Discussion/Coffee Break

Emerging & Doped nanoColloids : Pascal André, Mathieu Maillard, Celso De Mello Donega

15:45 Tailoring Colloidal Nanomaterials via Cation-Exchange: a versatile route to Hetero-structuring, Alloying, and Doping of Nanocrystals

Authors : Celso de Mello Donega

Affiliations : Debye Institute for Nanomaterials Science, Utrecht University, Netherlands

Resume : Colloidal semiconductor nanocrystals (NCs) are a new class of versatile nanomaterials, whose properties are determined by their size, shape, and composition. Semiconductor NCs comprising two (or more) different materials joined together by heterointerfaces, i.e., heteronanocrystals (HNCs), offer even more exciting possibilities regarding property control. The spatial localization of charge carriers in HNCs can be manipulated by controlling the offsets between the energy levels of the materials that are combined at the heterointerface. Doping of NCs and HNCs enables further control over their electronic, optical, transport, and magnetic properties. Moreover, colloidal NCs and HNCs are coated with a layer of organic ligand molecules, which further extends their functionality, since it allows for easy surface manipulation and solution processing. These characteristics have turned colloidal semiconductor NCs and HNCs into promising materials for a myriad of applications, motivating extensive research into their synthesis. In this talk, we will discuss a synthesis approach that has been attracting increasing attention in recent years, and is establishing itself as a versatile strategy to fabricate shape-controlled NCs, HNCs, and doped NCs that are not attainable by conventional methods: Cation Exchange.

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16:15 Chemistry in nanoreactors: nanocrystalline inorganic compounds via miniemulsion

Authors : Paolo Dolcet[a], Maurizio Casarin[a], Silvia Gross[a,b]

Affiliations : [a] Dipartimento di Scienze Chimiche, Università degli Studi di Padova, via Marzolo, 1, I-35131, Padova, Italy; [b] Istituto per l'Energetica e le Interfasi, IENI-CNR and INSTM, UdR, via Marzolo, 1, I-35131, Padova, Italy

Resume : Colloidal systems are highly appealing to achieve a good control on inorganic nanoparticles size, size distribution, crystallinity and shape. Among them emulsions play a leading role and, in more detail, miniemulsions (MEs) represent a promising way to achieve a good control on the final material characteristics. Thanks to the high shear forces applied during homogenization, these systems reach the minimum droplet size possible, diffusion and collision phenomena are hindered, and droplets maintain their identity. A ME thus represents an ensemble of 10¹⁸-10²⁰ independent droplets, where a reaction can take place in a parallel fashion. In these last years we exploited inverse MEs for the syntheses of a wide variety of inorganic materials. For example, ZnO nanostructures were obtained at RT, through an easy and reproducible route, which also enabled controlled doping (Eur. J. Inorg. Chem. 2013, 2291; J. Mater. Chem. 22, 1620). A similar approach was applied to the preparation of other lanthanide-doped binary and ternary systems, i.e., hydroxides, sulphides and halogenides. These materials showed good doping control, interesting luminescence properties and low cytotoxic effects, leading to appealing systems with potential bioimaging applications. The ME approach was also exploited for the photodecomposition in confined space of a tailored single-source Au/TiO₂ precursor, enhancing catalytic properties with respect with the same materials prepared in a bulk (Nanoscale, 5, 10534).

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- 16:30 **Synthesis and surface characterization of CuInS₂ colloidal nanocrystals**
Authors : Ruben Dierick, Freya Van Den Broeck, José Martins, Zeger Hens
Affiliations : Physics and Chemistry of Nanostructures, NMR and Structure Analysis, Ghent University, Belgium
Resume : Colloidal semiconductors nanocrystals of I-III-VI₂ materials (Cu (In,Ga)(S,Se)₂ (CIGS) and related compounds) are interesting alternatives to well-established Cd and Pb chalcogenide nanocrystals for opto-electronic applications. Advantages include a lower toxicity and the possibility of band gap engineering both by using quantum confinement and altering material composition. Moreover, CIGS is a well-known absorber material for high efficiency thin-film photovoltaics, and the use of nanocrystals as precursor inks is an interesting route to decrease the production cost of CIGS solar cells. In this work, we report on the colloidal synthesis of CuInS₂ nanocrystals with a focus on characterizing the surface chemistry. By using ¹H solution Nuclear Magnetic Resonance spectroscopy (NMR), we show that oleylamine, which is widely used in CIGS nanocrystal synthesis, is surprisingly strongly bound to the nanocrystal surface. We demonstrate in-situ NMR heating-up experiments which allows us to conclude that oleylamine is bound to the nanocrystal surface as a two electron donating species (L-type). The observation of strongly bound L-type amines is in contrast with amines bound to Cd- and Pb based chalcogenides and points towards a unique and unexplored surface chemistry of CuInS₂ colloidal nanocrystals. In addition, we investigate possible ligand exchange procedures towards carboxylic acids and thiols, to build a complete picture of the CuInS₂ nanocrystal/ligand system. The understanding of the ligand chemistry of CIGS nanocrystals is of critical importance towards tailoring these systems towards applications.
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- 16:45 **High performance cadmium-free luminophores: synthesis, characterization and application of AgInS₂/ZnS nanocrystals.**
Authors : Théo Chevallier, Gilles Le Blevennec, Frédéric Chandezon.
Affiliations : CEA, LITEN, F-38054 Grenoble; CEA, LITEN, F-38054 Grenoble; CEA, INAC, F-38054 Grenoble.
Resume : AgInS₂/ZnS (AIZS) solid solution nanocrystals are luminescent semiconductor nanoparticles that are good candidates for the development of new white light emitting diodes. These materials exhibit high absorption coefficients and are much less toxic than classic cadmium-containing quantum dots. Moreover, their synthesis is easily scalable as precise control of the size of the crystallites is not needed. Emissions spectra from the green to the near-infrared region are obtained depending on the composition of the nanocrystals. Indeed, the luminescence of AIZS nanocrystals comes from donor-acceptor pairs recombinations of carriers localized in the intrinsic defects of the material. In the present work, we describe the recent results of our investigations on the synthesis, fluorescence properties and aging performances of AIZS nanocrystals. A better understanding of their synthesis allowed us to target compositions with suitable emission spectra and maximum efficiencies. In addition to quantum yield measurements, time resolved emission spectroscopy was used to probe the photoluminescence process. These studies emphasize the crucial role played by the structural defects in the absorption, photoluminescence emission and efficiency of the material. Using a modified synthesis and a new surface passivation method, nanocrystals with internal luminescence quantum yields up to 80% were synthesized and tested in white-LED devices in order to test their final performances.
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4
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- 17:00 **Synthesis of magnetic nanoparticles with adjustable anisotropy energy**
Authors : Veronica Gavrilov-Isaac, Sophie Neveu, Vincent Dupuis, Valerie Cabuil
Affiliations : Laboratoire PHENIX (UMR 8234), Université Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris, France
Resume : Magnetic nanoparticles with spinel structure MFe₂O₄ (M = Fe, Co, Mn, Zn, Ni, Cu...) have been extensively studied for their various magnetic applications ranging from information storage to biomedical applications¹. One way to synthesize ferrite nanoparticles is thermal decomposition of metal precursors, which has demonstrated to be a convenient method to control the size and the morphology of ferrite nanoparticles². We'll describe the elaboration of core-shell bimagnetic nanoparticles with adjustable magnetic anisotropy energy. These particles are a combination of a hard phase (e.g. CoFe₂O₄) and a soft phase (e.g. MnFe₂O₄ or Fe₃O₄). They have unique magnetic characteristics³. To prove the original properties of the core-shell structure, we compared magnetic properties (blocking temperature and coercivity) of the core
- F.XI.
5

and of the core-shell particle. Figure 1 illustrates the modulation of coercivity in bimagnetic core-shell Fe₃O₄@CoFe₂O₄ nanoparticles compared to magnetic soft phase Fe₃O₄ nanoparticles and magnetic hard phase CoFe₂O₄ nanoparticles. Such particles are expected to have a good efficiency in magnetic hyperthermia. References [1] N.A. Frey, S. Peng, K. Cheng, S. Sun, Chem. Soc. Rev. 2009, 38, 2532-2542. [2] S. Sun, H. Zeng, D.B. Robinson, S. Raoux, P.M. Rice, S.X. Wang, G. Li, J. Am. Chem. Soc. 2004, 126, 273-279. [3] O. Masala, D. Hoffman, N. Sundaram, K. Page, T. Proffen, G. Lawes, R. Seshadri, Solid State Sci. 2006, 8, 1015-1022. [4] J.-H. Lee, J.-T. Jang, J.-S. Choi, S.H. Moon, S.-H. Noh, J.-W. Kim, J.-G. Kim, I.-S. Kim, K.I. Park, J. Cheon, Nature Nanotechnol. 2011, 6, 418-422.

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17:15

Synthesis and doping of CuInS₂ quantum dots for optical and medical applications

Authors : Krzysztof Gugula*, Piotr J. Cywinski[^], Thomas Jüstel*, Michael Bredol*

Affiliations : *Münster University of Applied Sciences, Department of Chemical Engineering, Stegerwaldstraße 39, 48565 Steinfurt, Germany; [^]NanoPolyPhotonics, Fraunhofer- Institute for Applied Polymer Research, Geiselbergstrasse 69, 14476 Potsdam-Golm, Germany

Resume : I-III-VI ternary semiconductors have proven to be an efficient and low-toxic alternative to Cd-, Pb- and Hg- containing binary semiconductors. With a large Stokes-shift and long luminescence lifetimes these materials are good candidates for in-vivo imaging, while wavelength-tunable broadband emission may find applications in white LEDs and color converters in displays. Notably, CuInS₂ quantum dots (QDs) have a band gap suitable for near- infrared (NIR) emission with wavelengths tunable from green to the NIR. Recently, highly transparent luminescent polymer nanocomposites (PNCs) comprising CuInS₂/ZnS QDs have been demonstrated [1]. To obtain PNCs with good optical properties, proper reaction and purification conditions have to be established. Relative precursor reactivities and ligand interactions have to be considered to obtain dispersions fully stabilized in liquid as well as in solid media. These QDs can also serve as host crystals for various dopants. With cubic chalcopyrite crystal structure, similar to zinc blende in II-VI materials, they are an excellent material for homo- as well as heterovalent doping. The present work elucidates the QD stabilization mechanisms with respect to optical properties in solid matrices and aims to identify suitable methods for doping QDs with magnetic ions i. e. Mn²⁺, Fe³⁺ to enable the dots to act as bi-functional luminescent in-vivo probes and MRI contrast agents. [1] K. Gugula, M. Bredol, Z. Naturforsch. B, 2014, 69b, in press

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17:30

Tunable band structure in core-shell quantum dots through alloying of the core

Authors : Antoine Guille (1,2), Arjan Houtepen (3), Rik van Deun (4), Edouard Brainis (1,2), Zeger Hens (1,2)

Affiliations : (1) Physics and Chemistry of Nanostructures, Ghent University, Belgium ; (2) Center for Nano- and Biophotonics (NB-Photonics), Ghent University, Belgium ; (3) Opto-electronic Materials, Delft University of Technology, The Netherlands ; (4) Luminescent Lanthanide Lab, Ghent University, Belgium ;

Resume : Integrated optics have a wide range of applications in telecommunications, information treatment and lab-on-chip analysis. Nowadays, light is in most cases generated outside of the photonic device, coupled with it through optical fibers. The integration of reliable light sources would make these devices more efficient, more robust and would allow the creation of active components. In that view, core-shell quantum dots (QDs) show unique properties: their emission wavelength can be tuned, they present high quantum yield and their integration in photonic devices is based on classical fabrication process. Moreover, the band structure of core shell QDs give rise to interesting features. In type II QDs, such as CdS/ZnSe, one type of charge carrier is confined in the core and the other in the shell, what allows single exciton gain. On the contrary, in type I QDs, such as CdSe/ZnSe, both charge carriers are strongly confined in the core, what results in high emission quantum yield and single photon emitter behaviour. Here, we present an original method to finely tune the band structure of visible emitting core-shell QDs between type I and type II. We study CdSe(1-x)Sx/ZnS QDs with various compositions of the alloyed core and we show that, by changing the ratio between sulfur and selenium, one can shift continuously from type I to type II. Based on transient absorption spectroscopy measurements, we also analyse the evolution of gain with the proportion of selenium in the core.

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PROGRAM VIEW : 2014 Spring

MY PROGRAM : 2014 Spring

Symposium : F

Established and emerging nanocolloids: from synthesis & characterization to applications

26 May 2014

27 May 2014

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start at

Subject

Num.

Optoelectronic & Hybrid Devices based on nanoColloids : Gordanna Dukovic, Pascal André, Aurora Rizzo

09:00

All-Inorganic Colloidal Nanocrystal based Solar Cells**Authors :** Aurora Rizzo, Anna Loiudice, P. Davide Cozzoli, Giuseppe Gigli**Affiliations :** National Nanotechnology Laboratory (NNL), CNR-Istituto Nanoscienze, c/o Distretto Tecnologico, via per Arnesano km 5, 73100 Lecce, Italy, CBN - Center for Biomolecular Nanotechnologies - Italian Institute of Technology - Energy Platform - Via Barsanti sn, 73010 Arnesano (Lecce), Italy, Dipartimento di Matematica e Fisica ?E. De Giorgi?, Universit? del Salento, via Arnesano, 73100 Lecce, Italy

Resume : In the search for high-efficiency and cost-effective solar cell solutions, wet-chemically prepared nanocrystals (NCs) have also drawn much interest.[1] Among these, the most efficient system for photovoltaic application consists of a low band gap PbS quantum dots (QDs) as light harvester coupled with transition-metal oxide TiO₂ as electron acceptor. PbS(QDs)/TiO₂ based devices have been developed into various configurations reaching a state of the art power conversion efficiency of 7%. [2] Despite the tremendous improvement in performance achieved over other donor/acceptor NC system, PbS QDs/TiO₂ solar cells remain far less appealing for potential implementation into flexible plastic technology and large-scale industrial manufacturing because the preparation of the relevant TiO₂ acceptor film usually requires harsh high-temperature processing. In this frame we developed different approaches for the fabrication of high-efficiency all-inorganic solar cells which involve processing of colloidal PbS QDs and anisotropic TiO₂ NCs. In our work preformed-anatase TiO₂ NCs are used as building blocks to construct thin films that function as the electron-acceptor layers in the design of depleted bulk heterojunction solar cells. In one approach, we exploit the use of anatase TiO₂ NCs to avoid the application of a high-temperature annealing step to achieve the oxide in the required crystalline form.[3,4] Through this procedure we have realized solar cell devices that achieve a power conversion efficiency of ~4% on glass and ~1.8% on PET substrates, which is the highest ever reported for entirely inorganic-NC-based solar cells on plastic support. In the second approach, we take advantage of the self-assembly properties of open-split skeleton with double-fantail morphology branched TiO₂ NCs to fabricate three-dimensional mesoporous scaffold favorable for effective absorption and charge extraction. [5] Remarkably, we fully exploit the potential of colloidal semiconductor nanocrystals NCs, which offer many opportunities in the assembly of nanoscale-controlled devices by the bottom-up paradigm and allow attributing enhanced functions crucial to design of advanced optoelectronic devices. Overall, our results fully meet one of the major and intensively pursued goals in the design and fabrication of photovoltaic NC-based materials, that is the development of a facile and mild-room temperature solution-based route to the assembly of solar cells via utilization of inorganic-inks that combine the advantages of low-temperature solution-processable organic compounds and the chemical-physical properties of colloidal semiconductor NCs. [1] M. C. Beard, J. M. Luther, O. E. Semonin, J. A. Nozik, *Acc. Chem. Res.* 46, 1252 (2013); [2] A. H. Ip, S. M. Thon, S. Hoogland, O. Voznyy, D. Zhitomirsky, R. Debnath, L. Levina, L. R. Rolny, G. H. Carey, A. Fischer, K. W. Kemp, I. J. Kramer, Z. Ning, A. J. Labelle, K. W. Chou, A. Amassian, E. H. Sargent *Nature Nanotech.* 7, 577 (2012); [3] A. Loiudice, A. Rizzo, G. Grancini, M. R. Belviso, M. Corricelli, M. L. Curri, M. Striccoli, A. Agostiano, P. D. Cozzoli, A. Petrozza, G. Lanzani, G. Gigli, *Energy*

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Environ. Sci. 6, 1565-1572 (2013); [4] C. Giansante, L. Carbone, C. Giannini, D. Altamura, Z. Ameer, G. Maruccio, A. Loiudice, M. R. Belviso, P. D. Cozzoli, A. Rizzo, G. Gigli, J. Phys. Chem. C 117, 13305 (2013); [5] A. Loiudice, G. Grancini, A. Taurino, M. Corricelli, M. R. Belviso M. Striccoli, A. Agostiano, M. L. Curri, A. Petrozza, P. D. Cozzoli, A. Rizzo, G. Gigli, Three-Dimensional Self-Assembly of Networked Branched TiO₂ Nanocrystal Scaffolds for Efficient Room-Temperature Processed Depleted Bulk Heterojunction Solar Cells Submitted Manuscript

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09:30

Synthesis and Characterization of Self-assembled BaTiO₃ nanocubes for Resistive Random Access Memory

Authors : Xi Lin, Adnan Younis, Dewei Chu, and Sean Li

Affiliations : School of Materials Science & Engineering, University of New South Wales Sydney NSW 2052 Australia

Resume : Nanosized barium titanate, one of the important perovskite oxide nanomaterials, is essential for future nanoelectronics, such as gate insulators, high-k capacitors, and random access memories. Among various nanostructures, barium titanate nanocubes are one of the most promising candidates for electronic industry since their distinct geometry would exhibit excellent dielectric properties with a narrow dispersion of capacitance. This property is extremely important for the design of the next generation memory technology, such as resistive random access memory (RRAM). In this work, a novel and facile approach is used to fabricate well dispersed BaTiO₃ nanocubes and to assemble them into ordered thin films for resistive switching memory devices. Besides, the mechanism of resistive switching properties BaTiO₃ nanocubes based devices was discussed.

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09:45

Investigation of Seebeck coefficients in DMSO based Ferrofluids – Application for thermo-electric devices

Authors : B.T. Huang, M. Bonetti, M. Roger and S. Nakamae¹

Affiliations : 1 Service de Physique de l'Etat Condensé, CEA-IRAMIS-SPEC (CNRS-MPPU-URA 2464) CEA-Saclay, F-91191 Gif-sur-Yvette Cedex, France botao.huang@cea.fr

Resume : Thermogalvanic heat conversion is currently attracting much attention as an alternative path to produce electricity from low-grade waste heat [1]. Recently, it has been implied that in charged colloidal suspensions, such as ferrofluids (i.e., liquid suspensions of magnetic nanoparticles), the Seebeck voltage induced by the thermodiffusion of colloidal particles can further enhance the overall thermoelectric effect [2]. Here we present the Seebeck coefficient (Se) measurements of DMSO based ferrofluids (FF) with ferrocene (Fc)/ferrocenium(Fc⁺) inorganic redox couple. The volume fraction (ϕ) of maghemite nanoparticles (NP) was varied between 0 and 1% while the Fc/Fc⁺ redox couple concentration was fixed at 2 mM/4 mM respectively. The mean temperature within the cell was kept between 30°C to 50°C. The results revealed that at low volume fractions ($\phi < 0.1\%$) the values of Se becomes 15-20 % higher than that of DMSO without nanoparticles but tends to decrease at higher ϕ values. The observed phenomena are analyzed in terms of competing thermogalvanic (Fc/Fc⁺) and thermodiffusion (NP) effects. Further investigations on optimizing the thermoelectric conversion efficiency by tuning the solvent and NP properties are currently underway. [1] A. Gunawan et al. Nanoscale and Microscale Thermophysical Engineering 17 304 (2013). [2] J. Morthomas and A. Würger, Eur. Phys. E 27 425 (2008)

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10:00

Discussion/Coffee Break

10:30

Graphene enabled gate-controlled fluorescence of colloidal quantum-dots

Authors : Omer Salihoglu, Osman Balci, Emre O. Polat, Coskun Kocabas*

Affiliations : Bilkent University Department of Physics

Resume : Controlling light-matter interactions at the nanometer length scale is a central goal of With exceptional electronic and gate-tunable optical properties graphene provides new possibilities for active nanophotonic devices. Requirements of very large carrier density modulation, however, limit the operation of graphene based optical devices in the visible spectrum. In this talk we will present a unique approach that avoids these limitations and implements graphene to optoelectronic devices working in the visible spectrum. The approach relies on controlling nonradiative energy transfer between colloidal quantum-dots and graphene through electrical tuning of the charge density of the graphene. Using the approach, we demonstrated a new class of

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optoelectronic devices including fluorescence display and voltage-controlled color-variable devices working in the visible spectrum.

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10:45

Anchoring of colloidal nanocrystals on substrates for electronic characterisation

Authors : Stefan Kudera(a,b), Tu Hoang(a), Christoph Becker Freyseng(a), Joachim P. Spatz(a,b)

Affiliations : (a) Max Planck Institute for Intelligent Systems, Dept. New Materials and Biosystems, Heisenbergstr. 3, 70565 Stuttgart, Germany; (b) University of Heidelberg, Dept. of Biophysical Chemistry, Heidelberg, Germany

Resume : Semiconductor colloidal nanoparticles offer a wide spectrum of electrical properties.[1] However, incorporating such particles into electronic devices is still a tedious process. Either single particles are addressed with dedicated lithographic approaches or larger ensembles of such particles are investigated. Here, we will present a method for the controlled deposition of semiconductor nanoparticles from a dilute solution onto regular arrays of nanoparticles and apply the same technique for the incorporation of such nanoparticles into integrated circuits. The regular arrays on the substrate consist of gold nanoparticles arranged with distances in the range of 50-100 nm and show a quasi-hexagonal pattern.[2] The semiconductor nanoparticles are anchored on these substrates with a nanowelding approach.[3] To this aim the semiconductor nanoparticles need to be decorated with gold domains; by selectively etching this gold and a counterpart on the substrate, the semiconductor nanocrystals can be anchored at the site pre-defined by the array. In this approach also different metals can be used for the anchoring sites, in particular metals that are relevant for the industrial chip production. We will finally show how the nanosoldering approach can be used to incorporate the semiconductor nanoparticles into an integrated circuit. [1] Krahne et al. Physics Reports 2011 501, 75–221 [2] Glass et al. Nanotechnology. 2003 14, 1153–1160 [3] Figuerola et al. Adv. Mat. 2009 21, 550–554

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11:00

Design and develop metal oxide nanomaterials for gas sensing applications

Authors : Xuchuan Jiang, Aibing Yu

Affiliations : School of Materials Science and Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

Resume : Energy and environment have emerged as the most critical challenges to the sustainable global development in the 21st century. Nanomaterials have attracted much more attention because of their unique functional properties and broad applications in the energy and environment. This presentation aims to talk about environmental nanomaterials, focusing on their gas sensing applications. Our efforts are mainly concentrated on the development of synthesis strategies of metal oxide nanomaterials with shape, size and surface control, fundamental understandings of particle growth and relationships between structure and functions, and exploration potential applications in environmental monitoring and detection. We have devoted more efforts to the research on gas sensing materials, such as ZnO, SnO₂, and noble metal doped nanocomposites, which shows higher sensitivity and higher selectivity towards various gas species, which may be explored for different applications in environment monitor and control.

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11:15

Synthesis, characterization and emission tuning of I-III-VI₂ semiconductor nanocrystals as color converting alternatives for white LEDs

Authors : Sofie Abé, Philippe. F. Smet, Zeger Hens

Affiliations : Physics and Chemistry of Nanostructures, Ghent University, Krijgslaan 281-S3, 9000 Ghent, Belgium; LumiLab, Ghent University, Krijgslaan 281-S1, 9000 Ghent, Belgium

Resume : Colloidal I-III-VI₂ semiconductor nanocrystals form a versatile family of nanomaterials with similar properties as Cd-containing quantum dots (QDs), but with lower toxicity. Their interesting and tunable optical properties have resulted in their use in a variety of applications, ranging from biolabeling over solar cells to white LEDs. For an optimal performance each of these applications requires the QDs to show specific optical properties. The relatively narrow emission of Cd-based QDs can easily be tuned over the visible range at a high chemical yield by adjusting specific synthesis conditions[1,2]. However, the typical broad emission of Cu-In-Zn-S QDs has proven to be more challenging to tune and requires a different strategy. We propose a study on the one-pot synthesis and characterization of Cu-In-Zn-S QDs with efficient and broad emission. A careful preparation of the precursors and control of the reaction time is required to synthesize CuInS₂ and Cu-In-Zn-S QDs reproducibly. We

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discuss the limited emission tuning obtained by changing reaction conditions (e.g. precursor concentrations). More successfully, we have expanded the emission range by composition tuning, where In can for instance be replaced by Ga or Al and Cu by Ag. Finally, we address the potential of the resulting materials as alternative color convertors for white LEDs[3]. 1)S. Abe et al., ACS Nano, 2012, 6, 42. 2)S. Abe et al., ACS Nano, 2013, 7, 943. 3)P.F. Smet et al, J. Electrochem. Soc., 2011, 158, R37

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11:30

Synthesis and characterization of novel ZnS and ZnSe hybrid polymer nanocomposites for optoelectronic applications

Authors : Katarzyna Matras-Postolek¹, Karolina Gorcka², Michael Bredol², Dariusz Bogdal¹

Affiliations : ¹Cracow University of Technology, Faculty of Chemical Engineering and Technology, Chair of Biotechnology and Physical Chemistry, Warszawska 24 St. 31-155 Cracow, Poland, e-mail: matras@chemia.pk.edu.pl ²Münster University of Applied Sciences, Department of Chemical Engineering, Stegerwaldstraße 39, 48565 Steinfurt, Germany

Resume : In the last few years significant attention has been paid to the adjustment of optical properties of polymer nanocomposite materials by the employment of functionalized semiconductor inorganic nanocrystals (NCs). Zinc sulfide (ZnS) and zinc selenide (ZnSe) with band gap respectively about 3.6 eV and 2.8 eV are very good candidates as nanofillers for polymer systems because of their intense luminescence, narrow emission, broad absorption and chemical stability. Additionally, those materials due to the large band gap can be used as an efficient semiconductor hosts to dope different transition metal ions such as Mn²⁺. ZnS NCs doped with Mn²⁺ ion have been one of the best efficient electroluminescent phosphor materials in use. On the other hand, ZnSe NCs by having the smaller band gap is an attractive and suitable material for hybrid photovoltaic devices. In this work we report the fabrication and study of novel and transparent ZnSe:Mn/ZnS/PMMA and ZnS:Mn/PMMA hybrid nanocomposite thin films, including preparation techniques of colloidal ZnSe:Mn/ZnS and ZnS:Mn nanoparticles, their surface modification and the integration process with PMMA system in different solvents, as well as the consequences for their luminescence. Transparent ZnS:Mn/ZnS/PMMA and ZnS:Mn/PMMA nanocomposite materials via a film casting were obtained. Resulting colloidal nanocrystals and nanocomposite were characterized with respect to their optical and structural properties and their stability under ambient conditions. Additionally, in this work we present the latest research on preparation of one-dimensional (1D) ZnS and ZnSe NCs under microwaves irradiation and their surface modification as a potential component for polymer system.

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11:45

Hydrogenated nanostructured TiO₂ electrodes for sensing organic compounds in waters under visible light illumination

Authors : Shanqing Zhang,[1]* Feng Peng [2]

Affiliations : [1] Centre for Clean Environment and Energy, Griffith School of Environment, Gold Coast Campus, Griffith University, QLD 4222 (Australia) ; [2] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong, 510640 (China)

Resume : A series of nanostructured TiO₂ sensors and photoelectrochemical cells have been developed in our group for photoelectrochemical determination of organic compounds, leading to a series of commercialized patents [1] and commercial products. This sensing mechanism is based on photoelectrocatalytic oxidation of organic compounds in waters under UV radiation [2-4]. Recently, a hydrogenated nanostructured TiO₂ photoanode was prepared by hydrogenating TiO₂ nanorod arrays (H-TNRs) electrode. Hydrogenation is an efficient and effective means to extend light absorption to visible light region and improve electron conductivity of TiO₂ via introduction of oxygen vacancy and mid-gap levels in TiO₂ lattice. The H-TNRs photoanode was used as a sensor for organic compound detections under visible light illumination for the first time. Preliminary experiments demonstrate that the H-TNR electrode is able to sensitively determine various organic compounds in water with satisfactory stability. This suggests that the hydrogenation nanostructured TiO₂ electrodes are promising in sensing organic compounds in waters and further to be further developed into commercial products. References: 1. Zhao, H., Zhang, S., Improved water analysis. PCT Int. Patent. (2008) WO 2008077191 2. Qiu J., Zhang S., Zhao H., Recent Applications of TiO₂ Nanomaterials in Chemical Sensing in Aqueous Media, Sensors & Actuators: B. Chemical, 2011, (2011); 160: 875-890 (Review) 3. Zhang S., Li H., Zhao H.,

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12:00 **Lunch Buffet**

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