

Bad Honnef Physics School 2019

**Exciting nanostructures: Characterizing advanced confined systems**

*22 - 26 July 2019, Physikzentrum Bad Honnef*

Organized by Christian Klinke (University of Rostock) and Nikolai Gaponik (TU Dresden)

PROGRAM

***Sunday, 21 July 2019***

- 17:00 – 21:00 Registration
- 18:30 DINNER / Informal get together

***Monday, 22 July 2019***

- 08:00 BREAKFAST
- 08:45 – 09:00 Opening and welcome  
Prof. Christian Klinke and Prof. Nikolai Gaponik
- 09:00 – 10:15 *History of colloidal nanostructures*  
Prof. Alexander Eychmüller (TU Dresden)
- 10:15 – 10:45 COFFEE BREAK
- 10:45 – 12:00 *Can we synthesize colloidal quantum dots that are all the same size?*  
Prof. David J. Norris (ETH Zurich)
- 12:00 **Conference Photo (in the front of the Physikzentrum)**
- 12:15 LUNCH
- 14:30 – 15:45 *Two-dimensional nanostructures*  
Prof. Sandrine Ithurria (ESPCI Paris)
- 15:45 – 16:15 COFFEE BREAK
- 16:15 – 17:30 *Tutorial on 2D based nanodevices*  
Dr. Andres Castellanos (CSIC Instituto de Ciencia de los Materiales de Madrid)
- 18:30 DINNER

***Tuesday, 23 July 2019***

- 08:00 BREAKFAST
- 09:00 – 10:15 *The history of doping in semiconductor nanocrystals*  
Prof. David J. Norris (ETH Zurich)

10:15 – 10:45 COFFEE BREAK

10:45 – 12:00 *Chemical Transformation of Colloidal Nanomaterials*  
Dr. Vladimir Lesnyak (TU Dresden)

12:15 LUNCH

14:30 – 15:45 *Optical Properties of Colloidal Nanostructures*  
Prof. Alexander Efros (US Naval Research Laboratory)

15:45 – 16:15 COFFEE BREAK

16:15 – 17:30 *Hybrid Nanostructures*  
Dr. Vladimir Lesnyak (TU Dresden)

18:30 DINNER

19:30 **Poster session 1**

***Wednesday, 24 July 2019***

08:00 BREAKFAST

09:00 – 10:15 *Principles of optical spectroscopy of nanostructures*  
Prof. Sergey V. Gaponenko (Academy of Science Belarus)

10:15 – 10:45 COFFEE BREAK

10:45 – 12:00 *Probing Excitons and Mobile Charges with Terahertz (THz) - Spectroscopy*  
Dr. Jannika Lauth (University of Hannover)

12:15 LUNCH

14:00 – 18:00 Excursion & Café (hike in the vicinity, boat trip in case of rain)

18:30 DINNER (at the Physikzentrum)

***Thursday, 25 July 2019***

08:00 BREAKFAST

09:00 – 10:15 *Exciting Quasiparticles at the Nanoscale by Scanning Tunneling Microscopy*  
Prof. Roberto Otero (IMDEA Madrid)

10:15 – 10:45 COFFEE BREAK

10:45 – 12:00 *Spectroscopic electrochemistry with nanoparticles*  
Prof. Stephen Hickey (University of Bradford)

12:15 LUNCH

- 14:30 – 15:45 *The Chemistry and Physics of Nanoscale Surfaces*  
Prof. Zeger Hens (University of Gent)
- 15:45 – 16:15 COFFEE BREAK
- 16:15 – 17:30 *Luminiscence Nanothermometry with Semiconductor Nanoparticles*  
Prof. Beatriz H. Juarez (IMDEA Madrid)
- 18:30 DINNER
- 19:30 **Poster session 2**

***Friday, 26 July 2019***

- 08:00 BREAKFAST
- 09:00 – 10:15 *Advanced characterization of nanomaterials*  
Dr. Ute Resch-Genger (BAM Berlin)
- 10:15 – 10:45 COFFEE BREAK
- 10:45 – 12:00 *Spectroscopic electrochemistry with nanoparticles*  
Prof. Stephen Hickey (University of Bradford)
- 12:00 – 12:15 Poster awards and closing remarks  
Prof. Christian Klinke and Prof. Nikolai Gaponik
- 12:30 LUNCH
- End of the physics school and Departure

# History of colloidal nanostructures

**Alexander Eychmüller**

*Physical Chemistry, TU Dresden,  
Bergstrasse 66b, 01062 Dresden, Germany*

Some 35 years ago, the so-called size quantization in semiconductor nanocrystals has been found and explained correctly. Since then enormous progress has been made in various directions: quality of the materials (measured as size dispersity, crystallinity, compositional variability, surface functionalization, etc.), applications (in lighting, bioenvironments, solar cells, etc.), as well as basic theoretical understanding.

In my lecture, I will touch upon the tentative steps into the then new field in the early 80s of the last century, I will name a few of the founders of the field, and I will comment on some of the earlier scientific breakthroughs.

What you can expect: a personal view and assessment on selected topics related to semiconductor nanocrystals synthesized in colloidal solutions.

What you can't expect: neither a comprehensive history of colloidal nanostructures including the pre size-quantization era (this field is too large) nor a comprehensive presentation of the state-of-the-art of colloidal nanostructures (this field is also too large...).

## **Can we synthesize colloidal quantum dots that are all the same size?**

**David J. Norris**

*Optical Materials Engineering Laboratory,  
ETH Zurich, Zurich Switzerland.*

Nanometer-scale semiconductor particles, known as colloidal quantum dots, exhibit optical properties that are strongly dependent on their diameter. For example, this effect can be used to tune the wavelength range over which they absorb and fluoresce light. This phenomenon is useful for various applications including solar cells or light-emitting devices. However, during the synthesis of these particles, one inevitably obtains a distribution in particle sizes. This causes a broadening in their absorption and emission, which is detrimental for applications. In this lecture, we will discuss why real-world samples have a size distribution and the strategies that researchers have used to minimize it. We will describe the advantages and disadvantages of various synthetic approaches and then focus on the "hot-injection method." This latter synthetic methodology separates particle nucleation and growth, which has long been known as a strategy to obtain narrow size distributions. Ostwald ripening, and our ability to control its negative influences will also be discussed.

# **Two-dimensional nanostructures**

**Sandrine Ithurria**

École supérieure de physique et de chimie industrielles de la ville de paris (ESPCI),  
Laboratory of Physics and Material Studies, 75005 Paris, France

Changing the shape of the nanocrystals enables a change in the density of states and of the confinement. The growth in solution of anisotropic nanoparticles is not obvious since the precursors are submitted to Brownian motion. As a result, anisotropic synthesis needs to be driven by a process, which decreases the system energy.

In the lecture, I will give some examples of synthetic method leading to 1D nanowires and rods and to 2D objects such as nanosheets and nanoplatelets. I will show that most anisotropic growth can be sort over four class of mechanism: lattice induced anisotropy, ligand induced anisotropy, lattice defect induced growth and self-assembly of preformed nanocrystal. I will mostly focus on 2D nanoparticles with wurtzite, rock salt and zinc blende structures.

# **Tutorial on 2D based nanodevices**

**Andres Castellanos-Gomez**

*Instituto de Ciencia de los Materiales de Madrid (ICMM-CSIC)  
C/ Sor Juana Inés de la Cruz, 3  
28049 Madrid, Spain*

During the lecture, I will introduce and motivate the fabrication and study of electronic and optoelectronic devices based on atomically thin two-dimensional materials. At the beginning, the state of the art reviewed. This will help us to motivate the main reasons that has triggered the interest of the community on these nanodevices. Then, I will discuss the standard fabrication techniques and tools to implement such nanodevices and we will review few interesting figures of merit.

# **The history of doping in semiconductor nanocrystals**

**David J. Norris**

Optical Materials Engineering Laboratory,  
ETH Zurich, Zurich Switzerland.

Since the discovery of colloidal semiconductor quantum dots (nanocrystals) over 35 years ago, researchers have sought to incorporate intentional atomic impurities, or dopants, into these materials. This has been primarily motivated by three factors. First, researchers wished to study the impact of impurities on nanocrystals due to the critical role that dopants play in bulk semiconductor devices, such as the transistor. Second, impurities in nanocrystals should exhibit even more dramatic behavior than in bulk semiconductors because the dopants are confined to extremely small volumes. Finally, doping could in principle help address key problems in potential applications of nanocrystals (e.g., light-emitting diodes and solar cells). In particular, many applications utilize thin films of densely-packed nanocrystals. Electronically active impurities can provide extra electrical carriers, i.e. electrons or holes, to the particles and enhance the conductivity of these films. Due to these fundamental and technological motivations, nanocrystal doping has moved forward over the last thirty years. In this talk, we will review the progress and discuss some of the remaining challenges. In general, doping has followed the development of the broader field. Advances in nanocrystal synthesis have been exploited to understand the doping process (i.e. how impurities can be incorporated). Advances in optical and electrical characterization of nanocrystals have been utilized to understand the impact of impurities on their properties. During these efforts, interesting and important connections have also been made to related physical phenomena, such as charging, diffusion, and surface effects. Thus, researchers working on the “doping problem” have not only slowly developed a sub-class of nanocrystal materials that are important for future nanocrystal devices, but have contributed to a deeper understanding of nanocrystal behavior more broadly.

## **Chemical Transformation of Colloidal Nanomaterials**

**Vladimir Lesnyak**

*Physical Chemistry, TU Dresden,  
Bergstrasse 66b, 01062 Dresden, Germany*

This lecture will provide an overview of post-synthetic transformations of colloidal nanomaterials aiming at chemical modification of both their surface and inorganic cores. Basics of the surface capping, types of ligands, their influence on properties of nanostructures will be summarized. Thereafter, main approaches to adjust the surface, such as ligand removal, ligand exchange and ligand shell modification will be introduced. In the framework of the core transformations, alloy formation, Kirkendall effect, galvanic replacement, hollow nanostructures formation, cation and anion exchanges will be examined.

# Optical Properties of Colloidal Nanostructures

**Alexander L. Efros**

Naval Research Laboratory,  
Washington, DC, USA.

The optical properties of colloidal semiconductor nanostructures, such as nanocrystals (NCs), nanorods, nanowires, and nanoplatelets, depend strongly on their size and shape. The size dependence of NC optical properties was discovered independently more than 30 years ago in two different materials: in semiconductor-doped glasses by Ekimov et al (1981), and in aqueous solutions by Brus et al (1983). The first reliable technology for the growth of colloidal NCs with narrow size distribution and precise size control was reported by Murray, Norris and Bawendi (1993), and since the publication of this paper, practically all existing semiconductors have been prepared in the NC form, including Si, Ge, all A1B7, A2B6, A3B5 compounds and their alloys, and perovskites. Consequently, we have a solid theoretical understanding of NC size dependent optical properties, which was described initially by Efros et al (1982). This paper identified three confinement regimes in the size dependence. Future technological development allowed for controlling the colloidal nanocrystal shape. In 2000, Peng & Alivisatos showed that using some precursor one can grow strongly elongated NC (known as nanorods). Even more intriguingly, the controlled growth of nanoplatelets was reported by the Dubertret group in 2008. The growth of freestanding layers in aqueous solutions contradicts from my point of view of the common sense ideas on nanoparticle growth. These structures have the electronic properties of freestanding quantum wells. In my talk, I am going to discuss and compare the electronic and optical properties of all above-mentioned nanostructures. I will explain how the competition between spatial confinement of carriers and electron-hole Coulomb interaction generates the three confinement regimes, and how this idea works in one-dimensional (nanorods and nanowires) and two-dimensional (nanoplatelets) structures. I will also discuss the effect of dielectric confinement on the energy spectra and electron-hole coupling with light. The last phenomenon affects the radiative recombination rate in semiconductor nanostructures. I am also going to discuss two application-relevant issues: (i) the nonradiative Auger recombination, which is the central non-radiative relaxation process and negatively affects the performance of nanostructure-based devices. I will explain why it is enhanced in NCs and how we can suppress it. Secondly (ii) how the giant oscillator transition strength and some dielectric confinement geometries could bring the radiative decay times of nanostructures into the sub-nanosecond regime. Finally, I will discuss the optical properties of the recently discovered CPbX<sub>3</sub> (X=Cl, Br, I) NCs, which for the first time have a bright exciton ground state and consequently very short radiative decay times.

# **Hybrid Nanostructures**

**Vladimir Lesnyak**

*Physical Chemistry, TU Dresden,  
Bergstrasse 66b, 01062 Dresden, Germany*

This lecture will give an overview of composites made of colloidal nanoparticles integrated into various micro- and macro-structured matrices, such as polymers, silica, metal oxides, and others. A summary of different types of the composite materials, main preparation routes as well as important advanced properties will be provided. In particular, relations between resulting properties of the composites and their structure will be elucidated. Depending on the properties of these hybrid materials, their application potential will be assessed.

## ***Principles of optical spectroscopy of nanostructures***

**Sergey V. Gaponenko**

*National Academy of Sciences of Belarus,  
Minsk, Belarus*

Nanostructures represent a class of mesoscopic materials whose optical properties are basically formed by the parent bulky matter but are essentially size-dependent owing to quantum confinement phenomena. In this lecture, we briefly overview the essence of quantum confinement phenomena, their optical manifestations, and then will concentrate at experimental techniques used for nanostructure characterization and elaboration of design-oriented criteria. Basic introduction to optical properties of solids via electron energy spectrum will be provided, basic light absorption and light emission mechanisms will be discussed. Common optical characterization techniques like UV-vis spectroscopy, photoluminescence excitation and emission spectroscopy, vibrational spectroscopy will be introduced, and finally, special techniques for unveiling optical properties of nanostructures will be considered including size-selective spectroscopy, site-selective spectroscopy, surface enhanced Raman spectroscopy, and time-resolved photoluminescence spectroscopy.



# **Probing Excitons and Mobile Charges with Terahertz (THz) - Spectroscopy**

**Jannika Lauth**

Leibniz University Hannover, Institute of Physical Chemistry and Electrochemistry,  
Callinstraße 3A, 30167 Hannover, Germany.

Time-resolved spectroscopic methods including transient absorption and emission spectroscopy represent state-of-the-art techniques to characterize the (ultrafast) charge carrier dynamics in photoexcited (semiconductor) nanostructures. Optical pump–terahertz probe spectroscopy (OPTPS) represents a special case of pump–probe spectroscopy that e.g. allows for the distinction between the generation of free (and mobile) charges and bound excitons in photoexcited semiconductors. Additionally, one can deduce the transient THz conductivity/mobility of the samples as an important measure for assessing the charge carrier transport in the probed materials. I will focus on explaining the method and recent results on “exciting” semiconductor nanostructures.

# **Exciting Quasiparticles at the Nanoscale by Scanning Tunneling Microscopy**

**Roberto Otero**

*IMDEA Nanoscience,  
28049 Cantoblanco, Madrid, Spain*

Scanning Tunneling Microscopy (STM) is nowadays a well-established technique to resolve the atomic and molecular architecture of individual nanostructures supported on conductive substrates. Along with its capability to obtain atomic and molecular resolution images of the sample topography, STM can also be used to obtain spectroscopic information with unparalleled spatial resolution. While it was early realized that the intensity vs. bias voltage curves carry information about the electronic structure of the sample at the tip position, subsequent research has expanded the spectroscopic capabilities of STM, which can now be used to learn about the vibrations of individual molecules, the spin excitations of single magnetic adatoms, the localized surface plasmon modes at the optical picocavity between the tip and the sample, or the excitons in individual quantum emitters. From a general point of view, the elastic and inelastic tunneling processes that contribute to the tunneling current between the tip and the sample can be thought of as a source of individual quasiparticle excitations, and the measurements can thus be understood as the response of the nanoscale system to such well-defined excitations. In this lecture, I will review the general principles governing the behavior of STM, with emphasis on its uses to obtain spectroscopic information at the nanoscale. In particular, I will discuss the use of STM to investigate the interaction between electron and hole excitations in surface states with individual scatterers, the role of inelastic tunneling events to produce vibrational and spin excitations in individual adsorbates, and the emission of light from the tunnel junction due to plasmon and exciton creation induced by the tunneling current.

# Spectroscopic electrochemistry with nanoparticles

**Stephen G. Hickey**

School of Chemistry and Biomedical Sciences,  
University Bradford, UK.

If one intends to utilize colloiddally synthesized nanoparticles (NPs) as potential components in solid state devices, it is a requirement that they be attached to substrates so as to probe their performance characteristics. In order to achieve this a great deal of surface chemistry must be employed to i) exchange the initial ligand set present at the NP surface without altering the NP properties of interest and ii) to attach the NPs with their replacement ligand set to the device (be it a metal oxide, metal or metal like conductor). Here a review of some of the recent relevant literature will be presented and placed into context. Subsequently a number of strategies employed for achieving NP attachment to oxidic substrates will be presented and the electrochemical and optoelectrochemical techniques used to probe such interfaces will be introduced. Additionally some recent advances made concerning the determination of the conduction band positions of a series of NPs will be presented and discussed.

The information will be presented across two lectures. Lecture 1 will cover the fundamentals of electrochemical interfaces and their preparation and cover such topics as: the origin of the potential, metal and semiconductor interfaces, types of electrode, instrumental set-up for electrochemical measurement, the advantage of shining light onto such interfaces, electrochemistry of nanoparticles, substrate preparation, the role that linking molecules play in electrochemical systems and the electrochemical investigation of nanoparticle deposition. Lecture 2 will deal with advanced spectroscopic electrochemistry on nanoparticle systems and build on the information provided in lecture 1. As such this lecture will cover: how to probe complex systems, an overview of a number of different optoelectrochemical methods and will present two case studies (i) CdS nanoparticles on ITO (ii) CdSe nanoparticles on ITO.

# The Chemistry and Physics of Nanoscale Surfaces

**Zeger Hens**

Ghent University, Chemistry Department  
9000 Gent, Belgium

Reducing the size of materials down to a few nanometer is a powerful approach to control material properties by design. A case in point are semiconductors, where size quantization leads to a size- and shape-dependent band gap once crystal dimensions become comparable or smaller than the exciton Bohr radius; an observation first made almost 40 years ago. Much more recent, however, is the idea that nanocrystal properties can be widely tweaked by adjusting nanocrystal surfaces.

This talk starts from the notion that about 50% of the atoms making up a 3 nm large crystallite are surface atoms. Especially in the case of colloidal nanocrystals, these surface atoms are readily accessible and standard analysis methods can give deep insight in the composition of nanocrystal surfaces and the impact of the surface on the chemical and physical characteristics of nanocrystals.

In a first part, we will highlight the main findings of about 10 years of research at Ghent University on the chemistry of nanocrystal surfaces. Here, the combination of elemental analysis and NMR spectroscopy has led to a detailed description of the nanocrystal surface chemistry, which has made that nanocrystals are currently classified by means of their surface termination.

These insights have made that a convincing connection has been developed more recently between experimental findings and the modeling of nanocrystal surfaces by means of density functional theory and molecular dynamics. Taking metal chalcogenide nanocrystals as an example, we will show that this has resulted in a detailed, atomistic description of the binding and packing of ligands on nanocrystal surfaces and the formation of surface defects that act as electronic trap states.

In a final part of the presentation, we will bring these elements together and explain how surface trap states can be used in the case of HgTe QDs to achieve almost thresholdless optical gain in the near infrared under CW optical pumping. This example is unique as it shows a research direction in which surface properties are not seen as an issue to be addressed, but as an immense source of novel and unmatched material properties that is waiting to be tapped.

# **Luminescence Nanothermometry with Semiconductor Nanoparticles**

**Beatriz H. Juárez**

Department of Applied Physical Chemistry and Condensed Matter Physics Center (IFIMAC),  
Universidad Autónoma de Madrid, 28049 Madrid, Spain

IMDEA Nanoscience, Faraday 9, Campus de Cantoblanco, 28049 Madrid, Spain.

One of the first signatures of the presence of many diseases and health dysfunctions is the appearance of temperature variations. In mammals, where it is essential to maintain body temperature, temperature variations are sometimes related to cellular dysfunctions and certain diseases. Most of these diseases that affect human health originate at the cellular level. Therefore, the first steps towards a complete understanding of the primary causes of diseases and / or tumors require knowledge at the cellular level, specifically in individual cells. The intimate knowledge of the local temperature can provide essential information about the cellular dynamics that govern certain diseases, as well as being a fundamental requirement for the application of hyperthermia therapies. In addition, more information is still needed to improve understanding of the relationship between temperature and function (dis) of different organelles within the cell and produce better diagnosis and treatment alternatives. Consequently, nanoscale thermometry is essential to monitor the precise dynamics of heat generation and propagation within cells and to obtain relevant information on cellular dysfunctions. This knowledge required for the design of novel strategies and therapies implies the development of new methods, materials and techniques to accurately map the temperature of living cells.

A promising approach in nanoscale thermal monitoring is luminescence nanothermometry. This simple method consists of using the optical signal of luminescent systems to monitor temperature changes in biological samples. This talk will review different measurement techniques providing high resolution in the nanometer range and will mainly focus on luminescence nanothermometry. The talk will provide an overview of the performance for temperature monitoring of different nanomaterials including semiconductor nanoparticles (NPs) operating in the visible range, and especially in the so-called second biological window, expanding from 1000 to 1300 nm. Especial emphasis will be given to systems related to Ag<sub>2</sub>S nanoparticles.

# **Advanced characterization of nanomaterials**

**Ute Resch-Genger**

*Federal Institute for Material Research and Testing (BAM),  
Division Biophotonics, D-12489 Berlin, Germany*

The rational synthesis and use of nanomaterials require the characterization of many different properties, ranging from particle size and size distribution over surface chemistry to more application-relevant features like optical, electrochemical, and magnetic properties. In the following, several methods for the characterization of functional groups on nanomaterials, like polymer and silica nanoparticles, semiconductor quantum dots, and lanthanide-based upconversion nanocrystals are presented. Additionally, procedures for the measurement of the key spectroscopic performance parameters of nanomaterials with linear and nonlinear photoluminescence, such as the photoluminescence quantum yield, are presented for the UV/vis/NIR/SWIR.

## Participant's Poster Contributions

### **Intraband mid infrared transitions in Ag<sub>2</sub>Se nanocrystals: potential and limitations for Hg-free low cost photodetection**

Junling Qu,<sup>1</sup> Nicolas Goubet,<sup>1,2</sup> Clément Livache,<sup>1,2</sup> Bertille Martinez,<sup>1,2</sup> Dylan Amelot,<sup>2</sup> Charlie Greboval,<sup>1</sup> Audrey Chu,<sup>1</sup> Julien Ramade,<sup>1</sup> Hervé Cruguel,<sup>1</sup> Sandrine Ithurria,<sup>2</sup> Mathieu Silly,<sup>3</sup> Emmanuel Lhuillier<sup>1\*</sup>

<sup>1</sup>*Sorbonne Université, UPMC Univ. Paris 06, Institut des NanoSciences de Paris*

<sup>2</sup>*Laboratoire de Physique et d'Etude des Matériaux, Sorbonne Université UPMC Univ Paris 06*

<sup>3</sup>*Synchrotron-SOLEIL, Saint-Aubin, France*

Infrared photodetection based on colloidal nanocrystals is a promising path toward low-cost devices. However, mid-infrared absorption usually relies on interband transitions of heavy metal-based materials (Pb and Hg typically), which poses toxicological concerns for mass market. In the quest of mercury-free infrared active alternatives, we here investigate Ag<sub>2</sub>Se nanoparticles presenting intraband transition between 3 and 15  $\mu\text{m}$ . With photoemission and infrared spectroscopy, we propose an electronic spectrum of Ag<sub>2</sub>Se in the absolute energy scale. We also find that the doping comes from a cation excess in Ag<sup>+</sup> form. We demonstrate photoconduction in this material under resonant excitation of the intraband transition. However, performances are currently quite weak with (i) a slow photoresponse (several seconds) and (ii) some electrochemical instabilities at room temperature.

A. Sahu et al., *J. Am. Chem. Soc.* **2011**, 133, 6509-6512

M. Park et al., *ACS Photonics* **2018**, 5, 1907-1911

J. Qu et al., *J. Phys Chem C* **2018**, 122, 18161-18167

### **Understanding novel Utrabithorax protein-derived film**

Valeria Italia, P. Bertoncello, A. Higgins, K. E. Meissner

Swansea University

Protein-based materials offer solutions to an extended range of potential applications. For instance, their natural biocompatibility can be used to improve implanted medical devices and they provide flexible platforms on which to create novel biosensors. In this work, we present a study of film formation at the air-water interface by a novel green fluorescent protein-Ultrabithorax (EGFP-Ubx) protein fusion. This investigation is the first step in applying rational design principles to production of Ubx-based materials for biomedicine.

### **Rheological properties and small-angle X-ray scattering studies of phosphate dust obtained from baghouse collectors**

Ikram Labtaini and Khalil El-Hami

University of Hassan 1st, Polydisciplinary Faculty of Khouribga,  
Laboratory of Nanosciences and modeling, Khouribga, Morocco

Baghouse dust collectors are employed as a part of the drying unit situated in Beni-Idir Khouribga Morocco, to retrieve phosphates particles from dust air drying before its expellation through the smokestacks. The phosphate dust samples used in this study were taken from the filtration chamber of the baghouse dust collectors. The first sample (S1) is untreated calcium phosphate dust, the second (S2) is the calcium phosphate dust from the

outside of filter media while the third one (S3) is the calcium phosphate dust from the inside of filter media which causes clogging depth. In this paper, the rheology and the small-angle X-ray scattering (SAXS) of three samples were investigated to elucidate the changes in terms of local structure, the viscosity and the shear stress parameters. The rheological behavior of the dust samples was investigated for a solid mass concentration ranging from 50 to 60 %, the three samples (S1) (S2) and (S3) had a solid mass concentration of C1= 60 %, C2= 55% and C3=50% and a shear rate in the range from 1 to 1000 s<sup>-1</sup>. The results indicated that during the filtration process, the pseudo-plastic behavior of the dust phosphate changed to that of Bingham. Comparing the results of the sample's viscosity, we found that the viscosity decreased during the process filtration. The SAXS results suggested that the dust phosphate samples possess a fractal surface structure of enormous dust particles with a rough surface interface. This study highlights the rheological behavior of grain phosphate which could be extrapolated to other mining powder.

## **Synthesis and Characterization of Iron-Hydroxyapatite nanoparticles for solar panels application**

Mohammed Eddy and Khalil El-Hami

University of Sultan Moulay Slimane, Polydisciplinary Faculty of Khouribga, Laboratory of Nanosciences and Modeling, Morocco

All over the world, people need more and more sources of energy, fossil, petroleum, electric... Sunlight is a long-lasting, non-polluting source of energy that can be captured by solar panels in the form electric or thermal energy. We tried, by this study, to find a new and adequate material, biodegradable ceramic based on hydroxyapatite (HAP) semiconductor material with high optical efficiency and friendly to the environment.

We suggest that the Iron-Hydroxyapatite (HAP-Fe) is the adequate candidate for this purpose. The HAP-Fe was synthesized by solid process using calcium carbonate as source of calcium and ammonium phosphate as source of phosphorus, and iron chloride as source of iron. All samples were characterized by X-ray diffraction (XRD), spectroscopy and UV-visible spectroscopy. The results show that our product retains its crystalline structure after iron doping and its optical efficiency has become greater than that its first state due to increases of light absorbance by 6% for HAP-Fe in the field of light between 550 nm and 800 nm. The absorbed light will be transformed into electrical energy by moving electrons between solar panel electrodes.

## **Photoluminescence properties of hybrid material based on semiconductor nanocrystals and gold nanorods under multiphoton excitation**

D.V. Dyagileva<sup>1</sup>, V.A. Krivenkov<sup>1</sup>, P.S. Samokhvalov<sup>1</sup>, I. Nabiev<sup>1,2</sup>, Yu.P. Rakovich<sup>1,3,4</sup>

<sup>1</sup>*National Research Nuclear University MEPhI, Moscow, Russian Federation*

<sup>2</sup>*Université de Reims Champagne-Ardenne, Reims, France*

<sup>3</sup>*Centro de Física de Materiales, San Sebastian, Spain*

<sup>4</sup>*IKERBASQUE, Basque Foundation for Science, Bilbao, Spain*

Semiconductor nanocrystals (SNC) quantum dots (QD), nanorods and nanoplates are able to generate two excitons simultaneously and also to proceed effective up-conversion in the multiphoton excitation mode [1]. These unique nonlinear optical properties made them promising materials for photovoltaic and optoelectronic applications. Moreover, these effects can be significantly enhanced by coupling SNC with plasmonic nanoparticles (PNP).



Due to the excitation of resonant localized plasmon modes, the electromagnetic field near the surfaces of metallic silver and gold PNPs is enhanced. Interaction of this enhanced field with the SNC leads to such physical effects as electromagnetically induced transparency [2], fluorescence and absorption enhancement, and amplified biexciton emission [3].

Additionally, the multiphoton absorption and luminescence near the surface of gold nanorods (GNRs) was shown to be strongly increased [4]. These nonlinear optical effects pave the way to biosensing and optoelectronic applications of the hybrid structures comprising the GNRs and SNCs. Thus, the photoluminescence properties and the optimal conditions of multiphoton excitation of GNR-SNC hybrid structures need to be elucidated if their practical applications are planned to be realized.

In this study, thin-film hybrid materials based on the CdSe QDs with ZnS and ZnS / CdS / ZnS shells, CdSe nanoplates, and GNRs with the plasmon resonance spectral position at the region of laser excitation or in the region of SNC fluorescence, were fabricated using the layer-by-layer deposition. In the two-photon excitation mode, the conditions of absorption saturation mode were determined, the optimal excitation intensities were selected, the photoluminescence lifetimes were measured, and the values of the two-photon absorption cross-sections and quantum yields were calculated. The results show that the fabricated SNC-GNR hybrid structures are fluorophores able to operate effectively under the two-photon excitation, what extends the perspectives of their application in the biosensing and optoelectronics.

This study was supported by the Ministry of Education and Science of the Russian Federation under the grant no. 14.Y26.31.0011.

[1] V.A. Krivenkov, P. S. Samokhvalov, D. Solovyeva, R. Bilan, A. Chistyakov, and I.R. Nabiev, *Optics Letters*, v.40, p. 1440 (2015).

[2] V.A. Krivenkov, S.A. Goncharov, I.R. Nabiev, and Yu. P. Rakovich, *Laser Photonics Rev.*, p. 1800176 (2018).

[3] S. A. Goncharov, V. A. Krivenkov, P. S. Samokhvalov, I.R. Nabiev, and Yu. P. Rakovich, *Optics and Spectroscopy*, No. 5, v. 125, p. 720 (2018).

[4] Xin Li, Fu-Jen Kao, Chien-Chin Chuang, and Sailing He, *Optics express*, No. 11, v. 18, p. 11335 (2010).

## **Crystallographically Textured SnSe Nanomaterials Produced from the Liquid Phase Sintering of Nanocrystals**

Mengyao Li<sup>1</sup>, Yu Liu<sup>1</sup>, Yu Zhang<sup>1</sup>, Yong Zuo<sup>1</sup>, Khak Ho Lim<sup>2</sup>, Doris Cadavid<sup>3</sup>, Ka Ming Ng<sup>2</sup>, Andreu Cabot<sup>\*,1,4</sup>

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We report on the thermoelectric performance of p-type nanocrystalline SnSe obtained from the liquid phase sintering of blends of SnSe nanocrystals and Te nanorods. A cycled hot press procedure at temperature above the Te melting point promoted the formation of crystallographically textured SnSe nanomaterials with relative densities up to 93%. After consolidation, part of this Te was found within the SnSe lattice and part remained as elemental Te between the SnSe grains. The presence of Te during the SnSe consolidation resulted in SnSe nanomaterials with higher electrical conductivities and lower Seebeck coefficients and thermal conductivities. By adjusting the amount of Te, thermoelectric figures

of merit (ZT) up to 1.4 at 790 K were measured in the direction of the uniaxial pressure, coinciding with the preferential a crystallographic axis. While this value matches the highest ZT value reported at this temperature for SnSe in the [100] crystal direction, ZT values of the consolidated SnSe along the bc plane were relatively lower due to moderately low thermal conductivities in this plane.

## OPTIMIZING THE PREPARATION OF QUANTUM DOT THIN FILMS FOR USE IN HYBRID LIGHT EMITTING DIODES

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Colloidal quantum dots (QDs) are a promising electroluminescent material for use in hybrid quantum dot light emitting diodes (QDLEDs). Volume and surface homogeneity, luminescence properties, and conductivity of condensed QD films, which serve as an active light-emitting material, play an important role in the efficiency of such devices. Despite the fact that modern QDs, in general, have a high luminescence quantum yield (QY) in solution, the preparation of QD thin films with high values of QY and fine conductivity remains challenging. Here we investigate the effect of variation of the type of QDs surface organic ligands and the parameters of thin film fabrication on the quality of surface and luminescence properties, as well as on conductivity of the obtained thin films.

QDs used in this study have a CdSe core with a diameter of 2.3 nm covered by three monolayer thick shell of ZnS, CdS and ZnS, one by one. We have chosen aliphatic amines - hexadecylamine (HDA), octylamine (OA); aliphatic and aromatic thiols - hexadecanethiol (HDT), octanthiol (OT), thiophenol (TP); and inorganic zinc chloride (ZnCl<sub>2</sub>) as the surface ligands to be varied in course of thin film preparation. Solutions of QDs with different ligands were characterized by measurement of the luminescence spectra and QY. QD films were formed on a glass substrate by spin-coating. During the manufacturing process we varied such parameters as substrate spinning rate, the condition of film annealing, the type of QDs solvent and concentration of QDs in solution. The quality of the obtained samples surface was monitored by atomic force microscopy (AFM). For all of the obtained QD films we have measured the luminescence spectra, relative QY and conductivity.

The experiments have shown that the QY of QD solutions and thin films significantly depended on the type of surface ligands. Thus, the solutions and films of QDs coated with thiol ligands have shown higher values of QY in comparison with QDs with amine ligands. In addition, QD films with thiol ligands had the lowest surface roughness. At the same time, we have found that the varying substrate spinning rate (1000 - 3000 rpm) didn't affect the surface roughness significantly, while the conductivity of these films had a strong dependence on this parameter. Thus, the higher the spinning rate was used, the greater the resistivity became. Apparently, this was due to an increase in the amount of volume defects in close packing of the quasispherical QDs, caused by a more rapid evaporation of the solvent from the thin film made at an increased spinning rate.

Studies of the effect of variation of QDs concentration in the initial solution and conditions of annealing of the as-prepared thin film on the properties of the obtained QD films revealed a strong dependence on these parameters. The use of low-concentration solutions for the film manufacturing led to a redshift of the luminescence spectrum, while the use of a

highly concentrated solution led to a significant decrease in the film conductivity. The effect of varying of the annealing conditions strongly depended on the type of QD surface ligands. Thus, it could both improve (in the case of OT ligands) and worsen (in the case of  $\text{ZnCl}_2$ ) the morphology and quality of the annealed film.

It was also found that the choice of solvent of the initial solution used for spin-coating had a significant impact on the quality of the thin film. For thin films made from QDs with OT ligands, n-octane was found to be the optimal solvent for producing films with low surface roughness. This result may be due to the fact that this solvent has an optimal volatility and, in addition, its molecules are most structurally close to the ligand molecules (OT). Similarly, o-xylene was found to be ideal solvent for fabrication of thin films made of QDs with aromatic ligands.

To conclude, this study allowed us to reveal the main factors affecting the quality and properties of QD films and helped to understand their complex effects for the further development of high-performance QDLEDs based on condensed QD films acting as electroluminescent layers.

### **Half Metallic Character in chalcopyrites structures type: $\text{ZnXP}_2$ (X = Ge, Si) Chalcopyrites Doped with Mn**

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The electronic and the magnetic properties of  $\text{ZnXP}_2$  (X = Ge, Si) were studied using the Korring-Kohn-Rostoker (KKR) method combined with the coherent potential approximation (CPA). The total and partial density of state (DOS) are computed for different Mn concentrations. The total magnetic moment, FM and DLM energies, and their variation as well as Curie temperature are also given. It is shown that the substitution of X cations (X = Ge, Si) by Mn atoms in  $\text{ZnXP}_2$  chalcopyrites leads to half metallic ferromagnetic character with double exchange mechanism. Thus, the critical temperature can be controlled by varying the concentration of manganese impurity.

### **Rheological properties and small-angle X-ray scattering studies of phosphate dust obtained from baghouse collectors**

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Baghouse dust collectors are employing as a part of the drying unit situated in Beni-Idir Khouribga Morocco, to retrieve phosphates particles from dust air drying before its expellation through the smokestacks. The phosphate dust samples used in this study were taken from the filtration chamber of the baghouse dust collectors. The first sample (S1) is untreated calcium phosphate dust, the second (S2) is the calcium phosphate dust from the outside of filter media while the third one (S3) is the calcium phosphate dust from the inside of filter media which causes clogging depth. In this paper, the rheology and the small-angle X-ray scattering (SAXS) of three samples were investigated to elucidate the changes in terms of local structure, the viscosity and the shear stress parameters. The rheological behavior of the dust samples was investigated for a solid mass concentration ranging from 50 to 60 %, the

three samples (S1) (S2) and (S3) had a solid mass concentration of  $C1= 60 \%$ ,  $C2= 55\%$  and  $C3=50\%$  and a shear rate in the range from 1 to  $1000 \text{ s}^{-1}$ . The results indicated that during the filtration process, the pseudo-plastic behavior of the dust phosphate changed to that of Bingham. Comparing the results of the sample's viscosity, we found that the viscosity decreased during the process filtration. The SAXS results suggested that the dust phosphate samples possess a fractal surface structure of enormous dust particles with a rough surface interface. This study highlights the rheological behavior of grain phosphate which could be extrapolated to other mining powder.

### **On the stability of electrochemical doping of porous semiconductor films via room temperature freezing of the electrolyte solvent**

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Control over the charge density is very important for semiconductor applications. A promising method to dope porous semiconductor systems is via electrochemical doping, where the amount of injected charge can be controlled by the potential applied. However, a big challenge is to fix the injected charge inside the material after doping, and avoid unintentional relaxation back to the intrinsic state.

Here we investigate methods to increase the stability of injected charges in films of semiconductor nanocrystals (NCs), conducting polymers and fullerenes. The injected charge is stabilized by immobilizing the counter ions that act as dopant ions in the pores of the film. By choosing solvents with melting points above room temperature the charge stability at room temperature increases greatly, in some cases from few seconds to over an hour.

### **Structural Properties of a Fouling Deposit On Different Heat Exchanger Surfaces: Characterization by XRD and SEM Coupled with EDS**

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The cooling process of fluid in a heat exchanger is performed with a heat dissipation from the heated surface. During operation, the heat exchanging ability of the equipment is retarded with a higher pressure loss and extended pumping power due to the accumulation of the substance on the heated surface; which is referred to fouling. Therefore, scale deposition occurs when water contains ions of low solubility salts. Process conditions create super saturation in the presence of one or more of the sparingly soluble salts, which impose the potential for their precipitation as scale. In this light, an experimental setup of a novel hybrid cooling tower fouling test rig was built to inspect the mineral scale deposition on diverse heat exchanger pipe surfaces. The setup was installed in the Green Energy Park (GEP) research platform, located in Benguerir, Morocco, in the framework of the MinwaterCSP project (supported by EU H2020). A five- months long test was conducted to evaluate the progressive fouling deposition on different material (polymers and galvanized steel) surfaces under four

deluge water compositions. Calcium carbonate ( $\text{CaCO}_3$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), manganese sulfate ( $\text{MgSO}_4$ ), sodium chloride ( $\text{NaCl}$ ) and iron oxide ( $\text{FeO}$ ) were the mineral salts added to the deluge water with different amounts to maintain realistic cooling water. In this paper, we are highlighting the crystal morphology and the structural phases of the deposits particles. The phase identification was investigated by the XRD (X-ray Diffraction) technique while the morphology and the polymorphs were characterized by the SEM (Scanning Electron Microscopy) coupled with the EDS (Energy Dispersive Spectrometry). In this research, the artificial calcium carbonate deposit on different material surfaces is considered as it is one of the main elements of the most scales found in heat exchanging apparatus. The XRD analysis showed the presence of two phases in each deposit calcite and aragonite although the SEM images illustrate the calcium carbonate morphology and the EDS shows the main elements presented in each deposition scale. The results illustrated an upward trend for fouling deposition with time on the tested tubes. The deposition on the surfaces showed growth with the enhancement of the thermal conductivity of the surfaces. However, it is noted that the fouling deposition increases with the increase of the water concentration due to enhanced deposition.

### **Nanoplatelets of mercury chalcogenides**

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Among colloidal nanocrystals, 2D nanoplatelets (NPLs) of II-VI semiconductor are a special class with exceptionally narrow optical features. Our group have work to expand the reachable range of wavelength for these materials from visible in the case of cadmium chalcogenides to near and more recently short wave infrared using mercury chalcogenides material. The growth of these NPLs is obtained through an indirect method where a cation exchange process is performed from CdTe or CdSe NPLs. During the cation exchange process the absorption features strongly redshift from the visible to the near IR. The HgTe NPLs present the narrowest luminescence signal reported so far in the near IR range (1).

We have also worked on heterostructure based on mercury chalcogenides NPLs. This includes type I heterostructure of HgTe/CdS (2) and inverted type I of CdSe/HgSe (3). The potential of these materials for optoelectronic applications have been revealed by integrating them into field effect transistors (4) and photodetectors (2). I will also present recent developments relative to the surface chemistry of these NPL and how short surface chemistry compatible for both transport and bright luminescence can be implemented.

[1] Strongly confined HgTe 2D nanoplatelets as narrow near infrared emitter, E. Izquierdo et al, JACS 138, 10496 (2016).

[2] Impact of dimensionality and confinement on the electronic properties of mercury chalcogenides nanocrystals, C. Greboval et al, submitted (2019)

[3] Coupled HgSe colloidal quantum wells through a tunable barrier: a strategy to uncouple optical and transport band gap, E. Izquierdo et al, Chem Mat 30, 4065 (2018).

[4] Charge dynamics and optoelectronic properties in HgTe colloidal quantum wells, C. Livache et al, Nano Lett 17, 4067 (2017).

## **Formation of stainless steel nanoparticles using laser ablation in liquid technique**

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Laser ablation in liquids (LAL) used as a powerful technique for the synthesis of stainless steel nanoparticles (NPs). Consequently, there is a great interest in expanding the current knowledge not only about NPs formation mechanism and the properties of the plasma that formed during the interaction but also the suitable parameters to obtain the optimum interaction.

In order to improve the control on product structure and to extend the range of compositions accessible by this technique. Here we performed a systematic investigation on alloy NPs formation by Femtosecond LAL of Stainless steel with different compositions and. The experiments were carried out in water, which has effects on NPs formation. Results were analyzed with optical absorption spectroscopy, transmission electron microscopy since alloy NPs were obtained.

In all cases, our findings provide the evidence that the metals are mixed during particles formation. Besides, our results suggest that the probability of interaction between ablated matter and solution species is higher for the topmost layer of the target, i.e. the one closer to the solid/liquid interface. This provides useful insight for the synthesis of Nano alloys with new compositions, that are of interest in several fields, from catalysis to photonics and nanomedicine.

## **Towards stable and permanent electrochemical doping of quantum dots via photo-polymerisation**

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Quantum dots (QDs) have been attracting considerable attention over the past two decades as a result of their tunable optoelectronic properties. To utilize the full potential of QDs in some of the main applications e.g. solar cells, control over the charge carrier density is crucial since charges have been shown to play a key role in the properties of QDs. Because of the difficulties of introducing the charges into QDs in a reversible, non-destructive and controllable manner, the electronic doping of these materials has remained a significant challenge. One more recently provided successful method for doping of QDs is electrochemical doping. Here, electrons are injected in the QDs by externally changing the Fermi level of the sample using a potentiostat. As a result, counter ions are drawn into the voids of the QD film to prevent the rise of a net charge. However, the ions in the voids of the QD film can diffuse out when disconnecting the potentiostat, which results in a rapid loss of charge density. Here in this study, we explore ways to improve the charge stability. Preliminary results show that the charge stability can be enhanced by several orders of magnitude. We anticipate that this novel way of doping QDs will pave the way for new opportunities and potential uses.

## Short Wave Infrared Devices Based on PbS and HgTe Colloidal Nanocrystals

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Colloidal quantum dots (CQDs) are interesting materials for device applications such as displays, solar cells and detectors. In particular, nanocrystals are candidates for low cost infrared (IR) detection especially in the short-wave IR range (SWIR, 0.8-3 $\mu$ m). Because they have reached a high level of colloidal growth maturity, PbS [1,2] and HgTe [3] nanocrystals are the most promising candidates for SWIR photodetection. Here, I compare optical and electrical properties of HgTe and PbS in the telecom range of wavelength (*i.e.*  $\lambda$ =1.55 $\mu$ m). Using a combination of photoemission and transport measurements, we demonstrate that PbS is n-type material while HgTe is p-type. We observe that HgTe has a higher photoresponse which indicates that HgTe is a more promising material for SWIR photodetectors.

In the last part of my talk I will also present some development regarding the integration of the HgTe nanocrystals into photodiode for SWIR detection. We in particular report air stable properties thanks to low temperature process encapsulation [4] and development of unipolar to selectively filter one type of carrier [5]

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[2] Lead sulphide nanocrystal photodetector technologies, R. Saran et al, Nature Phot. 10, 81 (2016).

[3] Mid-infrared HgTe colloidal quantum dot photodetectors, S. Keuleyan et al, Nat Photon 5, 489 (2011).

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[5] Design of Unipolar Barrier for Nanocrystal Based Short Wave Infrared Photodiode, A. Jagtap et al, ACS Phot. 5, 4569 (2018)

## Shape and size tunability mechanism of colloidal 2D copper sulfide and its plasmonic properties in the NIR

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The family of copper sulfides presents promising materials for application in plasmon enhanced absorbers of near-infrared irradiation, especially the covellite phase with semi-metallic properties. We show and discuss shape and size control of colloidal CuS nanoprisms by variation of synthesis conditions being able to switch the shape between triangular and hexagonal nanocrystals in large range of sizes. We discuss the possible mechanism of the shape control in terms of interaction of different facets with ligand environment and support our findings with DFT calculations. Produced ultra-thin 2D nanocrystals of different sizes and shapes were characterized by optical absorption spectroscopy. We explain observed localized surface plasmon resonances and their tunability with the help of simulations based on Drude-Sommerfeld theory and Discrete Dipole Approximation.

## **The attempt of using GaAs (Cs:O) and GaN (Cs) as photocathodes in SRF photoinjector**

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The photocathodes determine the beam quality in linear accelerators and represent a key component for many accelerator projects. Free-electron lasers (FEL), synchrotron- and THz radiation sources require injector systems with high brightness electron beams.

High quantum efficiency, a long lifetime and good vacuum stability, fast response time and low thermal emittance are desirable parameters for a perfect photocathode used in accelerators. Semiconductors such as GaN and GaAs as novel materials for photocathodes are showing enormous potential.

GaAs is a well-known material for photocathodes. After activation with caesium and oxygen, it has a high QE for visible light (red or green). An advantage of GaAs is the opportunity of the layers to emit spin-polarized electrons.

GaN is a semi-conductive material and well known for its high QE when lighted with UV light. For improving the QE only caesium for activation is required.

At the moment GaN is used for photocathode-based detectors such as photomultipliers or phototubes and for LEDs. They have characteristics of low dark current, high-speed response and high sensitivity. It is very new for application in SRF Guns. It seems to be more robust and achieves higher QE than other photocathodes [1].

Crystallinity and surface parameters define the photoemission properties. Modern analytical methods are used for identification of impurities, dislocations and characterization of the crystallinity of the semiconductors and the right cleaning treatment as well as the right caesium rating.

[1] Uchiyama, Shoichi et al. 2011. "GaN-Based Photocathodes with Extremely High Quantum Efficiency" 103511(2005):1–4.

## **Electronic properties of core-shell mercury chalcogenide nanoplatelets and their use for shortwave infrared photodetection**

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Colloidal 2D nanoplatelets (NPLs) of II-VI semiconductors<sup>1</sup> present very interesting optical properties such as their bright and narrow photoluminescence in the visible. However, most of the reported NPLs are based on cadmium chalcogenides and have a bandgap in the visible. *Izquierdo et al.*<sup>2</sup> demonstrated that mercury based NPLs can be obtained by exchanging the Cd atoms by Hg ones which results in an absorption feature in the near infrared (900 nm). Here we show that a shell of CdS grown on HgTe NPLs leads to a shift of the optical absorption toward near infrared<sup>3</sup>. We use this material to investigate the effect of both dimensionality and confinement on the electronic spectrum and carrier dynamics in colloidal nanocrystals. We show that the material presents a p-type nature and the



confinement barrier added by the CdS shell strongly affects the majority carriers' dynamics. On the other hand, minority carriers are affected by the dimensionality of the material showing a longer lifetime for 2D NPLs than for similar bandgap QDs. Last, we show that such material can be used as an active material in a photodetector in the SWIR.

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(3) Gréboval, C.; Izquierdo, E.; Livache, C.; Martinez, B.; Dufour, M.; Goubet, N.; Moghaddam, N.; Qu, J.; Chu, A.; Ramade, J.; et al. Impact of Dimensionality and Confinement on the Electronic Properties of Mercury Chalcogenides Nanocrystals. *Submitted* **2019**.

## **Colloidal PbSe Nanoplatelets of Varied Thickness with Tunable Optical Properties**

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In this work, we report the synthesis of atomically flat colloidal PbSe nanoplatelets (NPLs) of different thicknesses via cation exchange (CE).

For this, lead bromide is dissolved in a non-coordinating solvent in the presence of oleylamine and CdSe NPLs are injected at 80°C. Size-tunable photoluminescence emission (1330 to 1550 nm) with quantum yields of around 15% was observed with remarkable stability in ambient atmosphere throughout several weeks. The low susceptibility to oxidation is attributed to surface passivation with bromide ions or PbBr<sub>2</sub> as X- and Z-type ligands, respectively. Electron microscopy confirms the retention of the anisotropic crystal shape throughout the CE process while the final crystal structure of the PbSe NPLs is the cubic rock-salt structure, as evidenced by XRD.

## **Electron emission spectra from gold-nanoparticles for dose estimation in radiation therapy**

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Cancer is the second most common cause of death in Germany and one of the top 10 worldwide [1,2]. Radiotherapy is one of the three standard methods of cancer treatment. It is based on the damaging effect of the ionizing radiation on tissue as a result of interactions with primary particles and secondary electrons. Since these interactions are not cell-specific, damage of healthy tissue also occurs [3,4]. By deposition of highly radiation-absorbing elements into the tumorous tissue, the effective dose for the healthy tissue is reduced and limited to the tumorous [4-6].

Studies have shown that the presence of gold nanoparticles during irradiation with X-rays or proton beams offer considerable advantages due to the enhancement of the radiation dose in the target volume. Monte Carlo track structure simulations are performed to quantify

such localized dose enhancement of secondary electrons [4-6]. These Monte Carlo codes are based on highly simplified theoretical scatter models. However, these lose their validity at electron energies below a few keV and extrapolations induce high uncertainties [6]. First experiments on electron spectrometry of gold nanoparticles have already been carried out to benchmark Monte Carlo simulations. Though, these experiments were limited to low keV energies of X-rays and showed a poor match with Monte Carlo simulations. It is necessary to include electron emissions at higher photon energies since these lead to long Auger cascades and simultaneously to a high number of low-energy secondary electrons [4,6]. It is also important to analyze the influence of the particle size, shape and structure on the energy loss or a possible self-absorption of the electrons by the nanoparticles [6]. The aim of the project is to determine the energy spectra of the electrons emitted by the gold nanoparticles. For this purpose, different ionizing radiation such as synchrotron X-rays and clinical X-ray sources and proton beam irradiation are examined. The present project should provide important fundamental data on dose distribution and dose enhancement of gold nanoparticles. This will allow a more accurate dosimetry for gold nanoparticles used as radiosensitizers in clinical research and for future treatment application [5,7].

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## **THE OPTIMAL PROPERTIES OF COLLOIDAL SEMICONDUCTOR NANOCRYSTALS FOR OPTICAL ENCODING OF POLYELECTROLYTE MICROCAPSULES**

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Quantum dots (QDs) are colloidal fluorescent semiconductor nanocrystals characterized by wide absorption spectrum and a narrow size-tunable emission spectrum, high photostability, quantum yield value close to 100% and bright fluorescence that makes them and also nano-micro-tools based on their use, advanced photonic probes for biological applications [1-3]. The use of polyelectrolyte microcapsules (PMCs) as microcontainers for delivery and controlled release of pharmaceutical substances, fluorescent sondes, plasmon and magnetic nanoparticles, has been demonstrated as a promising approach in development of novel theranostics agents. PMC optical labelling or encoding has been widely performed using classical organic dyes. Application of the QDs for this purpose yields highly fluorescent PMCs and provides an opportunity for multiplexed imaging using differently sized QDs for PMCs encoding [4,5]. PMCs may be obtained via layer-by-layer assembly of alternatively charged polyelectrolytes that is normally performed in aqueous media. Originally, synthesized QDs are hydrophobic and insoluble in aqueous media due to the tryoctylphosphine oxide (TOPO) coating. Here, we have demonstrated a technique for QD transferring into the aqueous phase and evaluation of their colloidal properties for further optical PMCs via layer-by-layer assembling approach.

After the synthesis, CdSe/ZnS core/shell QDs were purified from TOPO and transferred to the water phase by means of successive two steps ligand exchange on QD surface: the attachment of D,L-cysteine and replacing it with carboxylated thiol containing polyethylene glycol derivative. Hydrodynamic diameter and  $\zeta$ -potential of the QDs were measured by

dynamic light scattering and laser Doppler micro-electrophoresis, respectively. QD-encoding was performed by adsorption of water-soluble QDs onto PMCs consisting of calcium carbonate cores covered by the polyanion and polycation layers. Efficiency of QD entrapment onto PMC surface was estimated spectrophotometrically. The QD-encoded PMC detection and optical characterization was performed using fluorescence microscopy.

The obtained water-soluble QDs were characterized by a wide absorption spectrum and a narrow fluorescence spectrum with an emission maximum of 590 nm. The hydrodynamic diameter of the QD was  $32.3 \pm 0.2$  nm. The solubilized QDs possessed negative surface charge ( $-29.9 \pm 2.3$ ) mV, which ensured their efficient adsorption between polycation layers during the PMC encoding procedure. It was demonstrated that the efficient PMC-encoding may be obtained even with low QD quantities. The prepared QD-encoded PMC have been characterized as the individual micro-sized objects with bright fluorescence.

Obtained data present the procedure of modification of the QD surface with polyethylene glycol derivative to ensure water-soluble QD optimal dispersivity and surface charge. The prepared water-soluble QDs could be effectively entrapped within the PMC polymer matrix by electrostatically driven adsorption using layer-by-layer technique. The QD-containing PMC could be used as the tools for the drug delivery [6] and fluorescent labels with practically unlimited number of optical codes.

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## **Amphiphilic Gold Nanoparticles in Chloroform for Nanoplasmonics**

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Recently decades, gold nanoparticles are of great interest because of their fascinating properties that are strong different from properties of a bulk material. Unique optical properties, their high stability, the passivity and non-toxicity for biological objects determine their wide application in optoelectronic devices, *in vitro* and *in vivo* biomedical diagnostics, as well as in therapeutics. Moreover, ligands on the nanoparticle surface play an important role in their properties. There are a lot of relatively simple methods for the synthesis of gold nanoparticle in aqueous solutions that allow controlling their size and shape, as well as provide a large choice of ligands. However, nanoparticles in organic phase can be also perspective for various applications, including hydrophobic composites with polymers, self-

assembled thin film formation etc.<sup>i,ii</sup> Additionally, nanoparticles, which are able to overcome the cell membrane barrier, are very perspective in therapeutics. Hydrophobic nanoparticles due to hydrophobic interactions with the cell membrane can be a perfect tool for this purpose.<sup>iii</sup> However, by the increasing of the hydrophobicity, the solubility of nanoparticles in aqueous solution is decreasing that reduces their possible applications. Therefore, it is important to synthesize amphiphilic nanoparticles that are able to participate in hydrophobic interactions and be dissolved in the aqueous solution.

In this work, the new simple synthesis of amphiphilic gold nanoparticles capped polyvinylpyrrolidone (PVP) was developed. PVP is nontoxic agent that widely used in medicine and pharmaceuticals in particularly as a binder in tablets. Due to its lactam ring, PVP can be dissolved in polar solvents. On the other hand, non-polar alkyl chains provide its ability to hydrophobic interactions. Gold nanoparticles synthesized in chloroform suppose a spontaneous transfer into an aqueous solution without any external influence. Moreover, these nanoparticles can be re-dissolved in various organic solvents, that makes them useful in many applications

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## Combined High Catalytic Activity and Efficient Polar Tubular Nanostructure in Urchin-like Metallic NiCo<sub>2</sub>Se<sub>4</sub> for High Performance Lithium Sulfur Batteries

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Lithium-sulfur batteries (LSBs) have been regarded as a promising candidate for next generation energy storage systems to overcome the dissatisfying low-energy density of traditional lithium-ion batteries (LIBs). However, the serious volumetric expansion, the shuttle effect of lithium polysulfides (LiPS), the electrical insulating character of sulfur, and the sluggish redox kinetics of LiPS severely limit the practical application of LSBs. Toward overcoming these limitations, we synthesized urchin shaped NiCo<sub>2</sub>Se<sub>4</sub> (u-NCSe) nanostructures by a simple hydrothermal reaction, and explored them as effective sulfur host in LSBs. u-NCSe provides a beneficial hollow structure to relieve volumetric expansion, a superior electrical conductivity to improve electron transfer, a high polarity to promote absorption of LiPS, and outstanding electrocatalytic activity to accelerate their conversion kinetics. Owing to these excellent qualities as cathode in LSBs, S@u-NCSe delivers outstanding initial capacities up to 1403 mA h g<sup>-1</sup> at 0.1 C, and retains 626 mAh g<sup>-1</sup> at 5 C with exceptional rate performance. More significantly, even after 2000 cycles, a reversible

capacity of  $480 \text{ mA h g}^{-1}$  is retained at high current rates of 3 C. DFT calculations demonstrate u-NCSe strongly adsorbs LiPS. This work not only demonstrates that transition metal selenides can be promising candidates as sulfur host materials, but also provides a strategy for the rational design and the development of LSBs with long-life and high-rate electrochemical performance.

## **Synthesis of multidimensional CdSe/CdS Core/Shell Systems and their optical characterization**

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Shown here is a new and easy method to grow elongated and in thickness controllable CdSe/CdS core/shell nanoparticles. The particles hold a very high extinction coefficient in comparison to common core/shell structures.

The wurtzite shell is grown on top of a cubic core. So an elongated growth is realized without a wurtzite structured templating core.[1] The presented synthesis is realized using a combination of coordinating surfactants and non coordinating solvents as well as a two step heating method. For further studies the synthesis parameters were varied to determine the effect on the product. The Cd:S ratio turned out to be a main factor for the aspect ratio of the resulting particles. This results can be way guiding for the synthesis of elongated, cadmium free systems which most do not have a templating core.

## **Optical spectroscopy of type-II semiconductor ZnSe/CdS dot-in-rod nanostructures**

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In type-II semiconductor heterojunctions the band offset leads to a spatial separation of electrons and holes. This charge separation makes type-II systems particularly useful, e. g., as light-harvesting materials in photovoltaic devices. Nanoparticles consisting of a spherical ZnSe core surrounded by a rod-shaped CdS shell, so-called dot-in-rods (DRs), represent a quantum system with an intrinsic type-II band alignment at the core/shell interface. Here, photogenerated electrons can delocalize within the shell, while holes are strongly localized in the core. The recombination energy of electrons and holes is mainly determined by the spatially indirect band gap at the interface. The type-II band structure should allow for an efficient manipulation of exciton properties by, e.g., external fields.

We wet-chemically synthesize highly luminescent type-II ZnSe/CdS DRs via a hot-injection method. Transmission-electron micrographs of the DRs reveal a radiused cylindrical geometry with average diameters and lengths of 7.3 nm and 29.9 nm, respectively. In solution, our ZnSe/CdS DRs exhibit an ensemble fluorescence energy of 2.16 eV with quantum yields above 35%. For comparison, the original ZnSe dots, acting as nucleation seeds for the CdS growth, fluoresce at 3.3 eV.

We use time-, energy-, and space-resolved confocal fluorescence spectroscopy at room and cryogenic temperatures to investigate individual ZnSe/CdS DRs. The DRs show a high photostability while emitting linearly polarized light. Compared to the more conventional type-I CdSe/CdS DR system [1], ZnSe/CdS DRs exhibit increased fluorescence lifetime. At 8 K, the lifetime is decreased compared to room temperature measurements. Furthermore, at low temperature, we observe abrupt spectral shiftings of the emission line over time, superimposed on smoother spectral diffusion processes. The spectral diffusion covers a larger range in energy than for type-I CdSe/CdS DRs, indicating the larger susceptibility of type-II structures to external stimuli, like surface charges.

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## **Structural and electrical transport properties of (1-x) La<sub>0.7</sub>Sr<sub>0.3</sub>Mn<sub>0.95</sub>Co<sub>0.05</sub>O<sub>3</sub> (LSMCO)+(x) ZnO (x = 0%, 6%, 9%, 12%, 15% & 18%) composites**

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In this communication, we report the structural and electrical transport properties of (1-x) La<sub>0.7</sub>Sr<sub>0.3</sub>Mn<sub>0.95</sub>Co<sub>0.05</sub>O<sub>3</sub> (LSMCO)+(x) ZnO (x = 0%, 6%, 9%, 12%, 15% & 18%) composites. For the preparation of (1-x) LSMCO+(x) ZnO (x = 6%, 9%, 12%, 15% & 18%) composites, sample of LSMCO was prepared by the auto combustion technique /inexpensive modified sol-gel technique and ZnO (99.99%) procured from Sigma Aldrich was used. The results of Rietveld refined XRD data show that LSMCO sample possesses a rhombohedral structure with the R-3c space group whereas ZnO compound remains with hexagonal structure with the P6<sub>3</sub>mc space group in all the composite samples. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) show that no any extra unwanted phase was observed in each composite excluding the LSMCO and ZnO phases. ZnO is mostly distributed at the grain boundaries and on the surface of the LSMCO grains. Elemental presence and ratio was confirmed through the EDX analysis. The electrical resistivity of LSMCO and each composite was measured in the temperature range of 2 K to 319 K at 0 Oe, 10 kOe, 50 kOe & 90 kOe magnetic field. The results indicate that the ZnO addition increases the resistivity of all the composites compare to that of pure LSMCO. The electrical resistivity explored by the theoretical model below TMI and fitting enlightenment for the observed behavior is transmitted here in detail.

## **Synthesis and durability investigation of InP/ZnE (E = S, Se, Te) Quantum Dots for LED lighting applications**

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In the race for miniaturization of optical systems like lighting or display devices, the development of luminescent nanoparticles with high quantum yields and covering a wide colour-range represents a tremendous issue. Fluorescent colloidal

semiconductor nanocrystals, commonly called “Quantum Dots” (QDs), seem to meet all the conditions for such applications. QDs have generally a diameter lower than 10 nm and exhibit size-tunable optical properties. QDs having currently the best stability under continuous irradiation (UV) and the highest optical performances contain cadmium (Cd), a strongly toxic chemical element. The purpose of this work was to develop a Cd-free QDs family by thermolysis method allowing an accurate control of the stoichiometry and the final diameter of QDs with a narrow size distribution. To this aim, we have synthesized indium phosphides (InP) QDs from indium halide and aminophosphine precursors [1]. Three types of shell were grown onto InP cores, ZnS [1], ZnSe [1,2] and ZnTe, in order to enhance their stability and their optical efficiency. By modifying the InP core growth time, the nucleation/growth temperature or the nature of halide precursors, QDs covering wavelength from 480 to 680 nm were synthesized. QDs have been characterized structurally (XRD), morphologically (HAADF-STEM) elementally (EDX, ICP-OES) and optically (quantum yields, excitation/emission spectra, fluorescence decays). The surface composition has been analyzed too ( $^{31}\text{P}$ ,  $^1\text{H}$ ,  $^{13}\text{C}$  MAS NMR, IR, XPS). Furthermore, the durability of QDs and thus the long-term stability of their optical performances were assessed upon photonic/thermal stresses.

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## **Setting things straight: Alignment of CdSe@CdS Nanorods on Conductive Surfaces**

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Semiconductor nanostructures such as CdSe@CdS nanorods have already proved to be ideal photosensitizers for photocatalytic applications. Not only do their high absorption coefficients allow for efficient harvesting of solar light, but also their structure promotes efficient and long-lived charge separation: Upon photon excitation, an electron-hole pair is generated with the hole quickly localizing in the CdSe core and the electron at the CdS tip. A catalyst coupled to the nanorod tip could in turn use this electron in the reduction of hydrogen. [1,2] We are currently focusing our efforts on aligning CdSe@CdS nanorods on a transparent, conductive surface, i.e., ITO glass, for the construction of a photoelectrode in a full watersplitting cell: While the electron is transferred to the catalytic center located at the nanorod tip and used for hydrogen reduction, the hole could be transferred to a counter electrode, where it may oxidize water to generate molecular oxygen. To this end, the nanorods have to be directly aligned on the surface under retention of their anisotropic parameters. Several different approaches such as electrophoretic deposition or interfacial self-assembly are discussed and compared.

Additionally, the interaction of nanorods with a redoxactive, conductive polymer matrix, namely polydopamine, is presented. Embedment in such an environment could not only improve the mechanical stability of a nanorod layer, but also protect it from oxidative or reductive stress during photocatalysis. In particular, the influence on

the optical properties, i.e., emission intensity and excited state lifetimes, under different pH values is investigated.

This work is funded by the Deutsche Forschungsgemeinschaft (SFB/TRR 234 "CataLight", TP-B4).

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## **Porous NiTiO<sub>3</sub>/TiO<sub>2</sub> Nanoneedles for Photocatalytic Hydrogen Evolution**

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Our group is working on a synthetic method to produce needle-like NiOx/TiO<sub>2</sub> and NiTiO<sub>3</sub>/TiO<sub>2</sub> nanostructures through the controlled oxidation of a nickel-doped TiO<sub>2</sub> precursor. The NiOx composites were obtained by annealing in nitrogen and NiTiO<sub>3</sub> obtained by annealing in air, afterwards hollow-needle structure was observed. This hollow NiTiO<sub>3</sub>/TiO<sub>2</sub> exhibited superior photocatalytic activity toward hydrogen generation. With low content of NiTiO<sub>3</sub> in the TiO<sub>2</sub>, high hydrogen generation specific rate of 10 mmol·h<sup>-1</sup>·g<sup>-1</sup> was achieved at room temperature, this rate is almost 3 times higher than the pure anatase TiO<sub>2</sub>. Moreover, hollow structure in the composites improved their structure stability. This synergistic strategy proposes simple, efficient and versatile blue-prints in synthesizing NiTiO<sub>3</sub> composites in anatase TiO<sub>2</sub> for photocatalytic application.

## **Metal–organic framework derived CoTe<sub>2</sub> encapsulated in nitrogen-doped carbon nanotube frameworks: a high-efficiency bifunctional electrocatalyst for overall water splitting**

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Developing highly active electrocatalysts with low cost and high efficiency for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is essential for water splitting. In this work, we for the first time report a high-efficiency electrocatalyst cobalt telluride encapsulated in nitrogen-doped carbon nanotube frameworks (CoTe<sub>2</sub>@NCNTFs) derived from metal–organic framework ZIF-67, which was synthesized via a straightforward telluride process under a hydrogen atmosphere. Notably, benefiting from the hollow polyhedron carbon nanostructure with large surface area, high conductivity, fast electron transport, and open channels for effective gas release, the as-synthesized electrocatalysts exhibit remarkable catalytic activity, with overpotentials of 330 mV and 208 mV toward the OER and HER at a current density of 10 mA cm<sup>-2</sup> in 1.0 M KOH solution, respectively. Moreover, when



CoTe<sub>2</sub>@NCNTFs was fabricated as an alkaline electrolyzer in basic solution, overall water splitting was achieved with high efficiency, which was comparable to the integrated performance of the commercial IrO<sub>2</sub> and Pt/C catalyst couple. Our work provides a way for developing efficient noble-metal-free catalysts via rational surface engineering.

### **Electrically tunable quantum emitters in an ultrathin graphene - hexagonal boron nitride van der Waals heterostructure**

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The recent discovery of solid-state single-photon emitters in two-dimensional host systems has unveiled a huge potential for quantum information processing and integrated nanophotonics.

In this context, hexagonal boron nitride (h-BN), owing to its unique optical properties, has emerged as a highly promising candidate for exploring atomic defect-related quantum emission. However, the presence of inhomogeneous energy distribution and spectral diffusion of the zero-phonon line (ZPL) makes it difficult to achieve the emission of indistinguishable photons as required for many applications. Stark effect-induced spectral tuning of the ZPL is able to compensate intrinsic local strain and electrostatic fields, which constitute the main sources of inhomogeneity and instability in the emission from individual h-BN defects.

Here, we investigate the Stark tuning of quantum emitters in few-layer h-BN sheets by means of low-temperature confocal photoluminescence spectroscopy. The required vertical electric field is implemented using a graphene top contact. The emitters can be effectively and reproducibly tuned, revealing a high robustness under repeated gate voltage sweep cycles. Moreover, we demonstrate an electric field-induced modulation of the emission intensity and fluorescence lifetime.

### **The Subtle Balance between Surface Coordination and Core Transformations in Colloidal CsPbBr<sub>3</sub> Nanocrystals**

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The surface chemistry of inorganic lead halide perovskites is a crucial, albeit poorly understood aspect towards the effective development of this promising class of semiconductor materials. Here we contribute to a comprehensive description of the surface

of colloidal CsPbBr<sub>3</sub> nanocrystals (NCs), as archetype of the perovskite system, and its relevance for photo-induced luminescence properties. To this aim, we probed the surface chemistry of two different CsPbBr<sub>3</sub> NCs, natively terminated with either oleylammonium ion pairs or Cs-oleate complexes, respectively, with a ligand library, which comprises amines (and their conjugated acids) featuring different basicity, chain length, and steric encumbrance. We demonstrate that the post-synthesis addition of such species leads either to an improved NC passivation, as a result of the stable surface coordination by stoichiometric amounts of ligands, or to ligand-induced transformations of the inorganic cores, related to the effective solvation of metal halide salts constituting the perovskite lattice by an excess of ligands. These phenomena are more prominent for ligands that are strong bases, with sufficient surfactant capabilities, and minor steric hindrance and show a marked dependence on the acidity of the environment. The beneficial role of stoichiometric amounts of amine (ammonium) ligands for the colloidal and structural stability of CsPbBr<sub>3</sub> NCs is demonstrated, leading to long-term preservation of their bright photoluminescence under standard conditions.

## **Spin and recombination dynamics of exciton confined in CdSe nanocrystals in glass matrix**

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Surface state of inorganic nanocrystals (NCs) play an important role in determining their structural, thermodynamic, transport and optical properties. Comparing with colloidal NCs prepared with wet chemical method, those grown in glass matrix are quite different, especially their surface state. NCs in glass matrix are completely free from passivation and their surfaces are dominated by dangling bond orbitals which sharply modify their magneto-optical properties. In this work, we studied CdSe nanocrystals grown in glass matrix with diameter range from 2.8 to 6.2 nm. Temperature and magnetic field dependence of photoluminescence (PL) decay measurement confirmed the exciton nature of optical transitions. The longest component of PL decay shortens with increasing magnetic field and temperature, which can be well explained within the three-level model. Exciton spin relaxation time is very short comparing to the recombination time, therefore only tiny difference is observed between the equilibrium and inequilibrium degree of circular polarization (DCP). PL decay curves measured under low temperature, 2.2 K, can be well fitted by four exponential functions corresponding respectively to dark exciton, multiple dark exciton, bright exciton and multiple bright exciton states. Time-resolved technique with three laser pulses (pump, orientation, and probe) was also carried out, and the basic measurements at room temperature show that electron g factor decreases but dephasing time increases with the increasing NC size.

## Design and preparation of Copper based materials and their application in Lithium-Sulfur Batteries

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Copper based materials as efficient sulfur hosts are synthesized to overcome the limitations of lithium sulfur batteries (LSBs) simultaneously. Copper sulfide provides a beneficial hollow structure to relieve volumetric expansion, a superior electrical conductivity to improve electron transfer, a high polarity to promote absorption of LiPS, and outstanding electrocatalytic activity to accelerate LiPS conversion kinetics. This work may not only demonstrates that transition metal sulfide can be promising candidates as sulfur host materials, but also provides a strategy for the rational design and the development of LSBs with long-life and high-rate electrochemical performance.

## Excitons and Optical Transitions in *quasi*-0D $\text{Cs}_3\text{Bi}_2\text{I}_9$ Nanoplatelets

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Lead halide perovskites possess fascinating optoelectronic properties, but the toxic nature of the constituent lead drives the quest for more benign alternatives. Bismuth-based perovskites are of particular interest because of the isoelectronic structure of  $\text{Bi}^{3+}$  and  $\text{Pb}^{2+}$ . In this context, we report the preparation of hexagonal  $\text{Cs}_3\text{Bi}_2\text{I}_9$  nanoplatelets with thickness of 8-10 nm and lateral sizes up to half a micrometer. We further apply a combination of first-principles density functional theory (DFT) and Green's function-based many-body perturbation theory calculations as well as timeintegrated and time-resolved optical measurements to elucidate the unusual properties of this material and explain the reasons for its weak photoluminescence. Moreover, we identify a strong excitonic transition in the absorption spectrum and discuss the origin of its large exciton binding energy. The study demonstrates that bismuth-based perovskites offer unique optical and electronic properties, distinct from their lead-based counterparts, yet promising for future applications.

## Synthesis and optical properties of near infrared-emitting PbS nanosheets

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One of the key discoveries concerning nanomaterials was that nanostructures of the same chemical composition can show dramatic differences depending on their morphology. This is a feature often provided by the different dimensionality of quantum confinement. Two-

dimensional nanomaterials are thus a trending topic, especially from the position of optoelectronics and photovoltaics where 2D geometry is preferred for the devices. Among the important materials in that field are lead chalcogenides. For obtaining colloidal two-dimensional PbS successfully applied routes include cation exchange from nanoplatelets of other compositions [1] and decomposition method [2]. However, the first one requires a preliminary synthesis of nanostructures and the second - first creating a complex compound of narrow usability. Our goal was to develop simple and reproducible procedure where the best choice is the colloidal synthesis from lead and sulfur precursors. As in the case with cadmium compounds in our previous works [3] our goal was to breach the minimal thickness limitation of the existing procedures and obtain structures with most prominent impact of one-dimensional quantum confinement. Scientific literature yields the thinnest nanosheets with estimated thickness of 1.2 nm that correspond to the PL band of 1470 nm or energies 0.84 eV [4]. The common practice for obtaining nanocrystals of smaller size or thickness is to lower the reaction temperature. It was reported that chloroalkane compounds play vital role in the formation of PbS nanosheets, so the temperature scalability is connected to the choice of a chloroalkane compound with suitable boiling temperature. It was reported that a successful formation of PbS nanoparticles can be observed at room temperatures already [5]. We decided to substitute commonly used chloroform with dichloromethane that has a boiling point of 39.6 degrees and lower the reaction temperature to the interval of 60-80 °C. As a result, we obtained thin PbS nanosheets with the lateral size of 200-400 nm and the PL band at 1340 nm or 0.92 eV. This is the new ultrathin population of nanosheets never observed before. Estimated size using the fitting curves is around 1.0 nm. We demonstrate the close study of the optical parameters of nanosheets by the means of absorption and photoluminescence spectroscopy. Additionally, we look into their behavior in solution and address the possible issues with stability, underlying processes and prevention routes.

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## **Superionic phase transition in single Ag<sub>2</sub>Se nanowires**

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One-dimensional nanowires synthesized via the well-established solution-liquid-solid method (SLS) allow for easy integration into nano-electronic devices. Tailoring the properties of the nanostructures, e.g. by exchanging the cations to a desired extent, offers a wide field of application. At this, silver selenide (Ag<sub>2</sub>Se) shows highly interesting properties due to a

straightforward cation exchange, leading to nanowires with conductivities up to  $105 \Omega^{-1}\text{m}^{-1}$  and temperature driven crystallographic phase transition at moderate temperatures.

Here, cadmium selenide nanowires are grown directly on substrates [1] for easy fabrication of single nanowire devices. Complete exchange to silver selenide is achieved by a wet-chemical approach with methanolic silver nitrate and confirmed via transport measurements. Field-effect transport measurements validate the n-type character of the nanowires. Switching from the low-temperature orthorhombic phase to the high-temperature cubic phase in  $\text{Ag}_2\text{Se}$  can be observed at temperatures below  $100^\circ\text{C}$ , resulting in an enhanced conductivity of up to 50 %. Hence, the electrical properties of these devices can be tailored for the desired application by adjusting the degree of cation exchange as well as the operating temperature.

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## Scaling up the production rate of size-selected clusters

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Size-selected clusters have a wide range of potential applications in many areas such as catalysis, plasmon, and biomedicine. However, the main limitation of nanocluster production is maintaining high precision of cluster size while increasing the rate of production. Here we provide a solvent-free cluster source Matrix Assembly Cluster Source (MACS). Argon and metal vapor are solidified together on a cold finger to form a “matrix” by cooling down the temperature to 20K, and then clusters are produced by enhancing the collision between the metal atoms inside a matrix with an ion beam [1]. This method is able to produce elementary

or alloyed clusters with a narrow mass distribution at a high rate of 1g/h. It is possible to carry

out research of elementary or alloyed cluster catalysis which meets quantity demand.

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## Chemical Cutting of Perovskite Nanowires into Single-Photon Emissive Low-Aspect-Ratio $\text{CsPbX}_3$ ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) Nanorods

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Halide perovskite nanocrystals (NCs) have received significant research interest owing to their extraordinary optical properties as well as their appeal as efficient light sources for technological applications. The optical properties of perovskite NCs are tunable by their dimensions as well as halide composition. Here, we report the shape transformation of  $\text{CsPbBr}_3$  perovskite nanowires (NWs) into low aspect ratio  $\text{CsPbX}_3$  ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ ) nanorods (NRs) by the reaction with lead halide ( $\text{PbX}_2$ )-ligand complex. Through control experiments it was found that the ligands present in the  $\text{PbX}_2$  precursor solution induced the fragmentation of NWs into NRs. The shape transformation resulted in an increase of photoluminescence (PL) efficiency owing to a decrease of non-radiative decay rates. The

increase of PL efficiency is attributed to the separation of NWs having traps from the non-defective ones when the NW breaks into NRs, otherwise the excitons are likely to find a trap owing to large exciton diffusion lengths of perovskites. Interestingly, we have found that these low aspect ratio NRs serve as quantum light sources at room temperature as revealed by photon antibunching measurements, while this behavior is not observed in the parent NWs. This work not only reports on the ligand-induced shape-transformation of perovskite NCs, but also expands our current understanding of shape-dependent light-emitting properties of perovskite nanocrystals.

## **Synthesis and Characterization of Elongated Type-II ZnSe/CdS Core-Shell Particles**

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Colloidal semiconductors nanoparticles, consisting of a spherical core and an elongated shell (DotRod), show great potential for optoelectronic devices because of their tunable emission wavelength and high stability to environmental influences. In a type-II semiconductor like ZnSe/CdS, excitation with light leads to the formation of an exciton, in which electron and hole are spatially separated due to the band alignment. The recombination of the charge carriers takes place at the interface between ZnSe and CdS and is strongly influenced by its composition.

Here, wet chemically synthesized ZnSe/CdS DotRods with a type-II band alignment are presented. The DotRods fluoresce red light with a quantum yield of about 30 % and fluorescence lifetimes up to 80 ns. The length of the particles is tunable in the range from 20 nm to 60 nm, adjusted by the amount of Cadmium in the reaction solution. As the growth of the elongated CdS-shell is slow in the first minutes of the hot-injection synthesis, cation exchange occurs because core and shell consist of different ions. This leads to the formation of an alloyed  $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$  core, which strongly influences the band alignment and thereby the optical properties like fluorescence wavelength and lifetime. Different synthetic approaches are used to control the composition of the core and the interface between core and shell.

## **Targeting ultra broadband autocorrelation via novel 2D semiconductors**

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We investigate II-VI semiconductor nanoplatelet Two-Photon Absorption (TPA) based broadband-autocorrelators as an alternative to common second harmonic generation techniques. The as compared to bulk material giant enhancement of two photon absorption in these 2D structures results in very efficient two photon absorption-based autocorrelation detected via fluorescence. We compare the results with wurtzite CdS bulk-material and SHG autocorrelation in  $\beta$ -Barium-borate.

Both, CdSe nanoplatelets and CdS bulk allow a precise pulse-width determination in line with the BBO based determined 171 fs pulse width of our 800 nm Titan-Sapphire-Laser. We verify

our approach and the usability of CdSe platelet based efficient broadband TPA autocorrelation by further power dependent measurements. Our results suggest that ultra broadband autocorrelation with more than 100 nm bandwidth and high sensitivity is feasible with II-VI nanoplatelet based autocorrelators. We further determine the two photon absorption cross section of the used nanoplatelets and demonstrate the mechanism for the observed strong enhancement of the nonlinearities resulting in considerably higher TPA cross section per unit volume as compared to bulk.<sup>[1,2]</sup>

## **Magnetic Circular Dichroism and Excitonic *g*-factors of CdSe Nanoplatelets**

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When a sample is exposed to a magnetic field with the lines parallel to the light beam, absorbance of left and right circularly polarized light becomes different. This phenomenon is known as magnetic circular dichroism (MCD) and it is valid for any kind of substance [1].

At room temperature, two major effects give rise to MCD: Zeeman splitting and mixing of states. The first one means lifting the degeneracy of states by magnetic field. It provides information on symmetry, splitting energy and *g*-factors of the charge carriers. The second one comes from the mixing of wavefunctions of close-lying states when magnetic field is applied.

MCD measurements have already been made for several types of semiconductor nanostructures. For example, for InGaAs quantum wells and colloidal CdSe quantum dots the analysis of MCD spectra helped to determine the *g*-factors of excitons and to evaluate the Zeeman splitting energy [2,3]. At the same time, for CdTe nanoparticles the only presence of paramagnetic mixing effect was found [4].

By summarizing positive results of these works we concluded that MCD could be a powerful tool for characterization of other types of nanostructures. Among them – colloidal two-dimensional CdSe nanoplatelets (NPLs). Their advantages are narrow-line emission and very short lifetimes. Convenient 2D geometry, along with the ability to control nanoplatelets thickness on the atomic scale, made them a promising material for various photonic applications [5].

As far as we know, MCD studies of colloidal CdSe nanoplatelets have not been reported yet. Within this work we measured magnetic circular dichroism of CdSe NPLs of three thicknesses: 4, 5 and 6 monolayers. We diluted the samples in hexane and put the solutions into fused silica cuvettes. We registered MCD spectra on the Jasco J-1500 CD spectrometer (Japan) with applied magnetic field of +1.5 T.

We have made spectral decomposition of both absorbance and MCD spectra in the following way. In the absorbance spectra of the NPLs we distinguished two major types of transitions: excitonic and interband transitions. We described excitonic transitions from

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<sup>1</sup> J. Planelles et al. *ACS Photonics*, **2018**, 5, 9, 3680-3688.

<sup>2</sup> R. Scott et al. *Nano Lett.*, **2015**, 15, 4985-4992

heavy- and light-hole subbands of the valence band by Lorentz functions. At the same time, interband transitions were described by the density of states of the two-dimensional electron gas, which could be given by a “broadened” Heaviside step. In approximating the MCD spectra, we assumed that magnetic field could result in both Zeeman splitting and mixing of the exciton states. In case of the interband transitions, we assumed that the contribution from Zeeman effect is negligible compared to that from the mixing of states.

Conducted decomposition revealed the presence of magnetic dipole transitions in the MCD spectra of nanoplatelets, with the intensity comparable to that of electric dipole transitions. Both heavy- and light-hole transitions exhibit derivative-like MCD lines resulting from Zeeman splitting, analogous to those observed in epitaxial quantum wells. The effective *g*-factors of excitons were calculated directly from the spectra for all three nanoplatelets samples.

Our research demonstrates that the magnetic circular dichroism is a powerful tool for a deeper analysis of colloidal nanoplatelets. We hope that this experimental technique will help in a better understanding of other existing and future types of nanostructures.

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## **Gold Superparticles with Significantly Red-Shifted Plasmon Resonance**

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The feasibility to agglomerate colloidal nanoparticles into superparticle structures is an avenue to new nanomaterials. One of the key superparticle features is the preservation of the nanoparticle building blocks in size and shape, while interesting physical properties such as collective plasmonic excitations are observed.[1][2] Coin metal nanoparticles were synthesized by a single phase approach according to literature.[3][4] A bifunctional linking agent replaces part of the initial ligands and triggers the controlled agglomeration process, to specific ensemble sizes as investigated via transmission electron microscopy.

A red-shift of the nanoparticle plasmonic band in the visible range of the electromagnetic spectrum occurs after assembling, indicated by a colour change of the colloidal solution from wine-red to dark blue. From time-resolved transient absorption spectroscopic measurements, we can disentangle and infer that the red-shifted plasmon resonance of the superparticle ensemble apparent in steady-state absorption spectra is composed of coupled plasmonic excitations in the single nanoparticles and the superparticle composite.



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## **Optical gain in colloidal III-V quantum dots: trapping and photoinduced absorption in core/shell InP/ZnSe.**

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Colloidal III-V quantum dots (QDs) promise the development of optoelectronics that are free of heavy metals such as Pb or Cd with size tunable emission between 0.45 to 3  $\mu\text{m}$ . Due to synthetic difficulties, III-V QDs development lagged behind the II-VI materials. However, the recent integration of aminophosphines as phosphorus precursor provided a simple and economic method to its synthesis. Despite the synthetic efforts to provide bright and size tunable particles, obtaining optical gain in III-V QDs still remains a challenge. In this work, using Transient Absorption Spectroscopy (TAS) and Photoluminescence Spectroscopy (PL), we analyze InP/ZnSe core/shell QDs optoelectronic properties to understand carrier dynamics and gain build up in III-V QDs with the goal of understanding the absence of gain in this material.

## **Energy Deposition and Charging Effects in Colloidal Spherical Quantum Wells Nano-Scintillator**

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The increasing requirements for radiation detection materials led to the continuously extensive research on scintillators. Colloidal quantum dots (QDs), due to the fast luminescence decay time, tunable emission across the visible spectrum, chemical stability and the relatively facile synthesis, are considered as potential candidates. However, the energy deposition and excitation mechanisms under X-rays or electrons excitation in nanoparticles for which most of the characteristic distances are larger than the particle size are still ambiguous. Hu et al have studied the multi-excitons emission of semiconductor nanocrystals under the intense pump lasers and high-energy photon excitation[1]. Enormous efforts have been made to improve the quantum efficiency of multi-excitons emission by tuning the structure and size of QDs[2-3]. Nonetheless, the giant core/shell structure which conduce to relax energy and generate multi-excitons, is detrimental to release the stress between the interfaces, increasing the possibility of QDs' charging effects and causing the non-radiative

Auger recombination. Spherical Quantum Wells (SQW) CdS/CdSe/CdS with near-unity photoluminescence quantum yield has been proposed to significantly avoid the defects at the hetero-structure interface, beneficial to the synthesis of large-size nanoparticles[4].

This subject is to first synthesize different-size SQW and compare their behavior under high fluency visible light excitation and under X-ray radiation. These results are confronted to simulations of multiexcitonic generation under ionizing radiation in these nanocrystals. This will provide a better understanding of the mechanism of nanoparticles scintillation properties and hopefully develop new and highly efficient nano-scintillators.

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## **Pulsed PECVD of Nanostructured Carbon Nitride with Enhanced Photocatalytic Activity**

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One of the most promising materials for eco-friendly energy generation is the organic semiconductor graphitic carbon nitride ( $C_3N_4$ ). Typically,  $C_3N_4$  is synthesized via thermo-polymerization, which leads to an amorphous powder with low processability. To make use of carbon nitride, e.g., as an active layer in a photoelectrode, it is highly favorable to deposit carbon nitride directly on solid substrates. This can be realized by performing chemical vapor deposition. However, the precise gas-phase deposition of organic polymers, especially  $C_3N_4$ , is still a significant challenge.

We report on a novel approach for the large-area deposition of crystalline carbon nitride films via plasma-enhanced chemical vapor deposition (PECVD) using a solid-state precursor. The films are characterized via XRD, SEM, TGA and XPS. A band gap of 2.1 eV was estimated via photoluminescence spectroscopy, which makes our carbon-nitride films usable as a photocatalyst for light-induced water splitting. We demonstrate the enhanced catalytic activity of the deposited carbon nitride by the photoreduction of methylene blue.

## **Large scale synthesis of semi-conductor nanocrystals from lead chalcogenides**

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Semiconductor nanocrystals (SNCs) have attracted much attention from researchers owing to their desirable optical features especially tunable absorption and emission ranging from ultraviolet to infrared (IR) regions by varying the size, shape, and composition of the SNCs. In addition, SNCs exhibit high photoluminescence (PL) efficiency, narrow PL spectral bandwidth and high thermal stability.

SNCs are significant for their use as light absorbers or emitters in solar cells, in third generation photovoltaics and sensing devices. However, for such devices, there is a need of large production of mono-dispersed SNCs to provide narrow and well-controlled absorption and emission. A simple, feasible and cost effective method is to produce such SNCs by colloidal synthesis which is a well-established method. The advantage of colloidal methods in the laboratories is the production of narrow size distributed SNCs. But, the main drawback of the laboratory scale is the yield of production, using a 50 ml flask, is around 100 milligrams. This amount of SNCs is not sufficient for the commercial use. Thus, scale-up of the synthesis is the need of the hour.

The momentum transport, energy (heat) transport, and mass transport are key variables for large-scale synthesis. The understanding and control of the above variables are essential to obtain high-quality nanocrystal quantum dots as well as achieving higher yield. Obtaining mass and heat transfer, which controls the final size and shape of the SNCs are the major challenges for the increasing the yield of SNCs production. In my research, I address this problem by focusing on developing a methodology for up-scaling the production of SNCs (particularly lead chalcogenides). The optical activity in the IR, a range where a few materials are optically active, makes lead chalcogenides fascinating materials in light-absorber and IR emitter devices.

### **Polymer Brushes as Biomimetic Hybrid Materials for Switchable Colours**

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Different plants, algae<sup>[1]</sup> and animals like peacocks and silverfish<sup>[2]</sup> obtain their brilliant colouration due to structural colours. Those structural colours appear as a result of the interaction between light and a periodic nanostructure, so called photonic crystals.<sup>[3]</sup>

The skin of a chameleon consists of such photonic crystals based on guanine crystals embedded into cytoplasm and different pigments. Emotions of the chameleon evoke a variation in colour by changing the crystal distances, and thus the interference pattern.<sup>[4]</sup>

The processes of the chameleon skin will be mimicked with the help of polymers (biomimetic equivalent to cytoplasm) and gold nanoparticles (biomimetic equivalent to guanine crystals).<sup>[5]</sup> The gold nanoparticles are chosen because of their plasmonic behaviour. As the switching parameter polymer brushes are used due to their swelling properties. The polymer brushes can be obtained via Atom Transfer Radical Polymerization (ATRP) and combined with spherical gold nanoparticles as introduced by the *von Klitzing* group.<sup>[5]</sup>

The aim is to fabricate innovative biomimetic hybrid materials with the help of the above-mentioned systems to combine plasmonics with piezoelectricity.

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# **Accurate positioning of quantum dots by means of dielectrophoresis**

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Semiconductor quantum dots (QDs) attract a lot of interest due to their tunable light emission, high efficiency and single-photon characteristics. Combining them with optical antennas can not only lead to strong coupling [1] but further enhance the emission and directionality of the radiation. To achieve that the QDs have to be positioned accurately which, in the past, has been realized by complex and time consuming processes [2,3].

Here we report on a much simpler process, utilizing dielectrophoresis, to load the gap of an electrically connected antenna with colloidal QDs.

The dot-in-rod QDs align along the 30-nm gaps of the dimer antennas, show strong photoluminescence and are promising for electro-optical applications. This method is not restricted to the dimer antennas and allows accurate preparation of QD-antenna-systems within a few minutes.

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## **Optical Properties of Colloidal InSb Quantum Dots**

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InSb possesses the narrowest bandgap (0.17 eV), the highest room-temperature electron mobility (78000 cm<sup>2</sup>/Vs), the lowest thermal conductivity, and the smallest exciton binding energy (0.5 meV) among all binary semiconductors. The small effective masses of the charge carriers result in a very large exciton Bohr radius (~60 nm). Consequently, strong quantum confinement is achieved at larger nanocrystal sizes than for other semiconductors, allowing great flexibility in bandgap engineering through size control, making it possible to tune the bandgap of InSb quantum dots (QDs) from the mid- to the near-IR spectral window. These properties render colloidal InSb QDs extremely interesting for a number of applications, including infrared detectors, high-frequency electronics, and thermoelectric power conversion. They are also possible alternatives for colloidal PbSe QDs in solution-processed thin-film solar cells. Despite its great potential, the synthesis of colloidal InSb QDs is still lagging behind compared to that of many other binary semiconductors [1, 2].

We recently developed a viable synthetic route to crystalline, stoichiometric, colloidal InSb QDs in the 3 to 7 nm diameter range with small polydispersity, displaying size-dependent band edge absorption and luminescence from ~1.1 to 0.8 eV.

The optical properties of the QDs were studied with steady-state absorption, photoluminescence and transient absorption spectroscopy. The latter technique showed that the lifetime of the band-edge bleach is ~2 ns, which is two orders of magnitude longer than previously reported for InSb QDs of similar size [3].

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## **Highly oriented stable thin films of $\gamma$ -CsPbI<sub>3</sub>: fabrication from MoS<sub>2</sub> induced sonochemically synthesized colloidal nanocrystals and the degradation studies**

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CsPbI<sub>3</sub> is known to exhibit the most suitable low band gap for photovoltaic application among all-inorganic lead halide perovskites. However stabilizing the cubic  $\alpha$ -phase of CsPbI<sub>3</sub> has been a challenge in the photovoltaics research as it readily transforms into non-perovskite orthorhombic  $\delta$ -CsPbI<sub>3</sub>. Recently, an intermediate metastable perovskite black phase  $\gamma$ -CsPbI<sub>3</sub> is being reported with stability higher than its alpha analogue due to its lower surface free energy. Herein, we report a facile synthesis of  $\gamma$ -CsPbI<sub>3</sub> colloidal nanocrystals induced by MoS<sub>2</sub> with ultrasound mediated process. The presence of MoS<sub>2</sub> significantly influences the nanocrystal formation. A substantial phase-stability of  $\gamma$ -CsPbI<sub>3</sub> is obtained in the colloidal solution. The thin film fabricated from the solution by simple one-step spin coating process also showed high stability of over 1 month under nitrogen atmosphere. The degradation profile (conversion from  $\gamma$ - to  $\delta$ -CsPbI<sub>3</sub>) under ambient air of the thin films were studied with absorbance, Raman, SEM, and photoluminescence (PL) measurements. The absorbance and Raman degradation patterns illustrated significant variations in the morphology and crystal structure. Besides, the effect of substrate temperature on the spin coating is demonstrated and observed to differ. The present study is a first report using transition metal chalcogenide (TMD) to promote the formation and stabilize the phase of lead halide perovskites, which can open new research platforms in this direction.

## **Time-resolved spectroscopic characterization of Au nanoclusters**

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The photoluminescence (PL) of bulk metal films is known to be very weak with quantum yield (QY) on the order of only 10<sup>-10</sup> for gold<sup>1</sup>. When the size of the metal nanoparticle is getting comparable to the de Broglie wavelength of electrons (~0.7 nm for gold), the energy

band gap opens and molecule-like properties are gained: discrete energy levels, absorption bands and appearance of PL with high QY. These extremely small size scale nanoparticles are often called nanoclusters. Especially gold nanoclusters (AuNCs) attracted attention of researchers during the last decade due to their excellent stability after proper passivation, mostly via thiolated ligands<sup>2</sup>. AuNCs show PL, good photostability, high emission rates, large Stokes shift, extremely high surface-to-volume ratio and low toxicity. The emission wavelength can be tuned by changing number of Au atoms in the cluster from UV to near-infrared (NIR) region<sup>3</sup>. We have studied optical properties of thiolate-passivated AuNCs emitting in red region with peak at 725 nm. The decay kinetics are strongly non-exponential and expectedly<sup>3</sup> slow (in  $\mu$ s-range). Employing PL modulation technique<sup>4</sup>, we estimated absorption cross-section of AuNCs to be  $7 \times 10^{-18} \text{ cm}^2$ . The absolute QY was measured in integrating sphere and occurred to be around 15% for UV excitation. That is worth to mention that though bulk gold is a metal, the optical properties of AuNCs are very similar to semiconductor quantum dots like PbS<sup>5</sup> or Si<sup>4</sup>.

<sup>1</sup> A. Mooradian, Phys. Rev. Lett. **22**, 185 (1969).

<sup>2</sup> R. Jin, Nanoscale **2**, 343 (2010).

<sup>3</sup> J. Zheng, C. Zhou, M. Yu, and J. Liu, Nanoscale **4**, 4073 (2012).

<sup>4</sup> M. Greben, P. Khoroshyy, I. Sychugov, and J. Valenta, Appl. Spectrosc. Rev. **0**, 1 (2019).

<sup>5</sup> M. Greben, A. Fucikova, and J. Valenta, J. Appl. Phys. **117**, 144306 (2015).

## **Biodetection with Whispering Quantum Dots**

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Quantification of specific biomarkers is an important diagnostic tool. Many models require extensive washing steps and amplification signaling, which limits the ability to perform, and increases the efficiency and the likelihood of replication, in particular when the biomarker of interest is only present at very low concentrations. Non radiative energy transfer (or FRET) has been used to design one-step bioassays which do not require washing steps, where the biomarker enables the formation of a sandwich complex involving donor-labeled and acceptor-labeled antibodies. FRET then provides an optical signature of the complex formation, hence of the biomarker of interest. However, the large size of this complex limits the effectiveness of energy transfer, preventing sensitive detection. Recent improvements in energy transfer efficiencies have been reported using plasmonic nanostructures but these structures remain ill adapted to the design of a simple and portable device. In this project we propose to improve the efficiency of energy transfer through the use of solution-phase optical microcavities. To this aim we will first design structures in which fluorescent colloidal quantum dots are precisely located within dielectric microspheres to enable strong coupling of their fluorescence emission with the whispering gallery modes of the microspheres. We will then characterize the coupling and energy transfer between these methods and acceptor molecules present in the evanescent field, within a few 10s-100s nms of the interface. We will finally impart biospecificity to the microspheres with a surface chemistry recently to detect specific biomarkers. In this configuration energy transfer will occur over distances much larger and more efficiently than with standard FRET. We will take benefit of this

strong coupling to design novel biodetection schemes presenting the advantages of simplicity (no washing steps), portability and sensitivity.

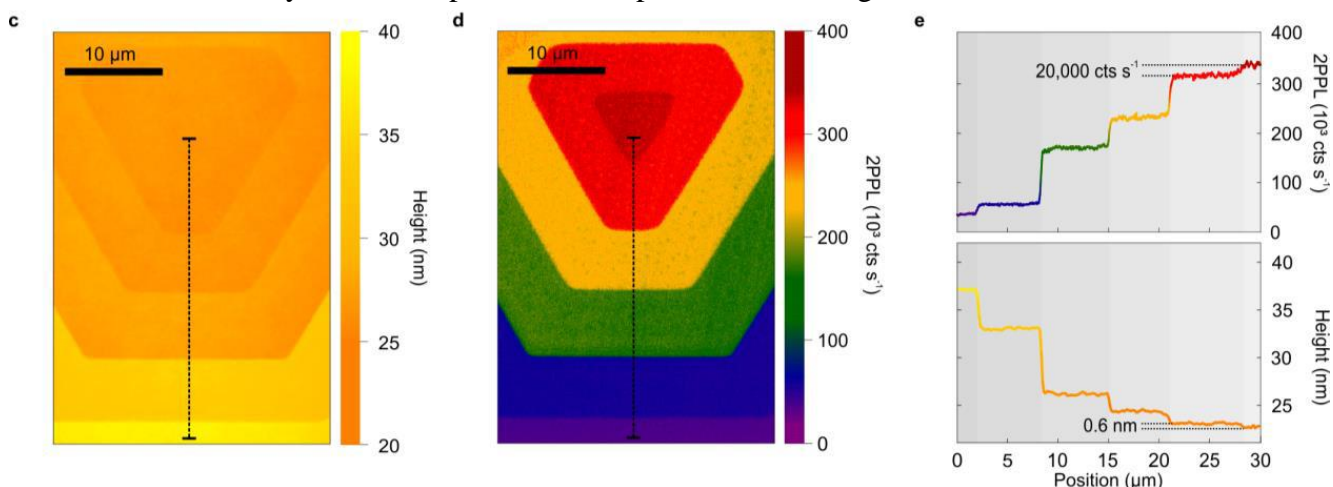
## Two-dimensional properties of thin single-crystalline gold films

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Gold nanostructures such as nanowires can strongly enhance and confine optical fields while also providing excellent electronic contacts to functional elements.[1]

Thin films of single-crystalline gold also ensure well-defined experimental conditions for precision metrology and sensing.[2] In all these cases the electronic properties of gold either affect the functionality or the interpretation of experimental findings.



**Figure 1. Thickness dependence of the two-photon photoluminescence.** *a*, Atomic force micrograph of a terraced microplatelet. *b*, Two-photon photoluminescence scan image of the same platelet as in *a*. *c*, Comparison between the height profile marked in *a* and the intensity profile from *b*.

Here, we report notable changes in the electronic structure of gold occurring already for film thicknesses of 30 nm by studying atomically flat 2D single-crystal gold platelets of variable thickness. When the gold thickness reduces below 30 nm deviations from bulk electronic properties reveal themselves in a 100-fold increase of the nonlinear two-photon photoluminescence signal.

Our findings are supported by density functional theory calculations and also allow us to optically resolve single-unit-cell steps.

[1] J. Kern et al., *Nature Photonics* **9**, 9 (2015)

[2] E. Krauss et al, *Crystal Growth & Design* **18**, 1297-1302 (2018).

## Optical and thermophoretic control of plasmonic Janus particles

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We present how Janus microparticles, which are made of silica microspheres that are half-coated with a thin gold layer, can be trapped and manipulated with optical tweezers. In a laser trap the gradient forces acting on the dielectric sphere confine the Janus particle in the laser focus. At the same time, plasmonic heating of the metal side results in a temperature gradient along the particle axis that gives rise to an upward directed thermophoretic force.

Balancing these optical and thermal forces by controlling the laser power allows to move and position the Janus microspheres along the beam axis with high accuracy<sup>1</sup>, which cannot be achieved with a regularly trapped particle. Importantly, the presence of ions in the surrounding solution has a further influence on this Janus movement. We find that adjusting the ion concentration or using different electrolyte solutions allows a fine-tuning of the Janus particle movement due to thermo-osmotic and thermo-electric effects<sup>2</sup>. Finally, we give examples how this strategy for the light-controlled manipulation of plasmonic Janus particles with optical tweezers can be used for biological applications such as photo-poration of living cells<sup>3</sup> or force measurements on single biomolecules<sup>2</sup>.

<sup>1</sup>S. Nedev, *et al.*, *ACS photonics*, 2, 491 (2015)

<sup>2</sup>S. Simoncelli, *et al.*, *Small* 12, 2854 (2016) and *ACS Photonics* 4, 2843 (2017)

<sup>3</sup>C. Maier, *et al.*, *Nano Letters* 18, 7935 (2018)

## Thermoelectric properties of aerogels of PbS nanoplatelets

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The increasing power consumption all over the world and the challenges of climate change lead to an increasing demand of energy-efficient processes. Thermoelectrics provide an approach to capitalize on a surplus of heat which is already generated by both renewable sources such as solar power as well as conventional fossil fuels or engines. Unfortunately, current materials rarely reach the figure of merit needed to allow a widespread use. The nanostructuring of materials for thermoelectric devices is a promising approach to advance this type of energy harvesting as it allows the reduction of the thermal conductivity while retaining the electric conductivity.<sup>1,2</sup>

In this work, a solid-state assembly of nanoparticles for the use in a thermoelectric generator is presented. The colloidal synthesis of the two-dimensional nanoplatelets was performed by oriented attachment of PbS nanoparticles.<sup>3</sup> A self-supporting network of these anisotropic nanoplatelets from a colloidal solution was formed by slow destabilization by altering the pH value. Supercritical drying of such gel-type networks resulted in aerogels. These aerogel materials exhibit mesoporosity, extremely low density and high surface to mass ratio. The physical properties were characterized by transmission electron microscopy, scanning electron microscopy and N<sub>2</sub>-physisorption measurements. The thermoelectric properties around room temperature were measured with a hot probe setup. Therefore, multifunctional probes which were able to simultaneously measure the temperature difference and the thermovoltage were utilised<sup>4</sup>. The material features the nanostructural benefits of aerogels while retaining the Seebeck coefficient of the bulk phase, enabling promising approaches for the use in thermoelectrical devices.

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## **Polarization switching between parallel and orthogonal collective resonances in arrays of metal nanoparticles**

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We discuss the excitation of orthogonal and parallel collective resonances in rectangular arrays of aluminum nanoparticles and switch between them with a change of the array dimensions or polarization. We study the difference of the far-field interactions in the array for both homogeneous and heterogeneous refractive index environment and their influence on the coupling direction in arrays. The rate of the parallel coupling depends on the interparticle distance which allows us to control the intensity of the coupled mode. The high quality plasmonic resonances with spatial and frequency control are promising in molecular sensing and enhanced spectroscopes.

## **PHOTOREDUCTION OF SILVER NANOSTRUCTURES WITH DIFFERENT SHAPES AND THEIR CHARACTERIZATION**

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Recently using of electromagnetic radiation for producing nanoparticles with different morphology are especially perspective. Light is most purity and nontoxic tool for the formation of silver nanostructures due to their ability to absorb radiation with certain wavelength.

In presented study the effectiveness of electromagnetic radiation for the formation of spherical silver nanoparticles in aqueous solution and yeast water extract is studied. Laser radiation with a wavelength of 445 nm was used for the silver nanoparticles forming by photostimulated reduction of Ag ions in silver salt aqueous solution stabilized by sodium citrate. The obtained silver colloids were exposed to irradiation by LEDs to change the nanoparticles geometrical parameters. It was found that irradiation of the silver colloids by blue light usually leads to the formation of decahedral nanostructures. Prismatic nanostructures are mostly formed under the influence of red and green photon flows.

The morphology of obtained spherical, prismatic and decahedral silver nanostructures were confirmed by TEM-imaging. Optical properties of formed monodisperse silver nanostructures in yeast water extract and aqueous solution were evaluated by UV-VIS spectrometry. Dynamic light scattering (DLS) distribution and polydispersity index for the resulting Ag nanoparticles have been evaluated. Thus, we can confirm that electromagnetic radiation is an effective tool for synthesis silver nanostructures with different shapes.

## **Nonlinear properties of the hybrid Au-Si sponge nanoparticles**

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Plasmon sponge nanostructures have occupied a special role in the field of plasmonics and nanophotonics: sensors and advanced source of white emission. If the pores of a golden spongy nanostructure are filled with silicon, the result will be a

promising source of broadband radiation, with high efficiency due to the localization of the field by a structure with a high surface-to-volume ratio. This paper presents the results of photoluminescence generation with multiphoton absorption and second-harmonic generation obtained from hybrid sponge Si/Au nanoparticles. The particles have been fabricated by femtosecond laser ablation at room temperature in the air. Experiments have shown the ability to generate broadband photoluminescence in the range of 500 – 800 nm (0.93 eV). The obtained results can be applied for creation of white light luminescent metasurfaces and advanced nanophotonic spectroscopy devices.

## **Electrically Driven Optical Antennas Featuring Ultrasmall Gaps**

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Optical antennas could be used to control and enhance light-matter interaction on a nanometer scale and are therefore interesting for e.g. spectroscopy and optical sensing applications. When they are electrically driven, the antennas get appealing for on-chip optical communication [1]. However, an ultrahigh fabrication accuracy – especially in the gap region – is needed for stable light emission, high field enhancements or reliable surface-enhanced Raman spectroscopy. Standard nanofabrication techniques including electron beam lithography or focused ion beam (FIB) milling using gallium (Ga) ions in combination with a polycrystalline metal film achieve minimum feature sizes of only 10 nm. The combination of Ga-FIB and helium ion microscope (HIM) based milling improves on that and allows to fabricate gap sizes down to 6 nm [2].

We present a Ga-FIB/HIM based milling approach combined with single-crystalline gold flakes, which already showed great improvements for pure Ga-FIB milling [3]. Thus we are able to achieve gap sizes < 3 nm for electrically driven optical antennas.

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## **Photoinduced Modifications of CdSe Nanowires in Flow Channels**

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Semiconducting nanowires have unique characteristics due to their one-dimensional structure. The photoluminescence (PL) properties of nanowires strongly depend on their chemical environment. In order to investigate the relationship between PL properties and chemical environment, confocal fluorescence spectroscopy measurements were performed on semiconducting nanowires in flow channels, which allow for the controlled exchange of the gaseous surroundings of the nanowires. The measurements were conducted in different gases on CdSe nanowires with a diameter of 7.7 nm, synthesized by a solution-liquid-solid method.

For nitrogen, we do not observe any photoinduced effects on the PL emission. In contrast, for air and oxygen we measure a photoinduced PL enhancement accompanied by a blueshift of the emission wavelength.

Here, extent and speed of the PL enhancement depend on both the excitation power and the oxygen content in the environment. These observations suggest a mechanism in which unpassivated Se anions at the nanowire surface react

photoinduced with oxygen, leading to an enhancement of the PL intensity as the rate of non-radiative recombination via surface trap states decreases. Furthermore, a strong influence of the PL properties of CdSe nanowires on the presence of gaseous propylamine was observed. With an excess of propylamine in the nanowire environment, strong photoinduced quenching effects, accompanied by large intensity fluctuations, occur. In subsequent measurements in pure oxygen, however, faster and more intense photobrightening than before could be observed. A mechanism is suspected in which the PL decreases with an excess of propylamine in the gas phase, since propylamine is oxidized and holes are thus neutralized, which prevents recombination of the charge carriers. The subsequent observation of the intense rapid PL increase could be explained by a better passivation of surface defects by the remaining propylamine molecules on the surface.

## **Multi component nanocrystals with catalytic and plasmonic properties**

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This project is dealing with the synthesis and characterization of nanocrystals in organic and aqueous media. The combination of metal and noble metal components or other components which show plasmonic properties with materials like metal oxides and metal chalcogenides with possible catalytic activity. Our interest is the investigation of the change of the plasmonic behavior according to the combination with other materials and according to the controlled variation of particle parameters like shape and composition. The synthesis of nanocrystals and nanocrystal components which show catalytic activity in organic chemistry reactions is another focus of the project. To synthesize the nanocrystals we mainly use hot-injection methods in high boiling solvents and aqueous CTAB based syntheses. Also cation exchange reactions are tools in the creation of our nanoparticles. To achieve a good comparability we are investigating also methods to phase transfer the synthesized nanocrystals to other solvents. The characterization methods we commonly use include TEM imaging, Dynamic Light Scattering and Zeta-Potential measurements, UV/Vis Spectroscopy and X-Ray Diffraction.

The resulting nanocrystals could find their application as catalysts of reactions in Solution.

## **Near-infrared plasmon-exciton interactions in colloidal nanostructures**

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Near-infrared emitting colloidal semiconductor nanocrystals draw a lot of attention due to various fields of their potential application, such as bio-imaging, photovoltaics, photodetectors, light emitting diodes, and optical amplifiers for telecommunication systems. Due to the fact that brightly emitting colloidal quantum dots consist mainly of toxic materials, while low-toxic alternatives typically show lower photoluminescence quantum yields, strategies to increase their quantum yields are of

paramount importance for their further application. One of the means to improve fluorescence of quantum dots is their coupling with structures exhibiting localized surface plasmon resonance. As has been demonstrated for the visible active nanostructures, plasmon-exciton interactions can enhance photoluminescence of CdSe and CdTe QDs.

In this work, we study the influence of electromagnetic field of plasmonic copper chalcogenide-based semiconductor nanocrystals on the photoluminescence of quantum dots in the near-infrared region, aiming not only at the fluorescence enhancement but also at its modulation, such as control of the radiative lifetimes via energy transfer.

## **Localized Surface Plasmon Resonance in Nickelsul\_de Nanostructures**

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Localized surface plasmon resonance (LSPR) is a phenomena best known from noble metal nanoparticles, but can also be observed in other materials with a high free charge carrier density. In this project the optical properties of different nickel sulfide nanostructures were investigated regarding the occurrence of a LSPR. After the synthesis of monodispers  $\text{Ni}_3\text{S}_2$  and  $\text{Ni}_3\text{S}_4$  nanoparticles, the phase purity was confirmed with X-ray diffraction and the size and shape control was observed via transmission electron microscopy. The occurrence of a LSPR could be shown with UV/Vis spectroscopy in media with different permitivities and via transient absorption spectroscopy. As the shape of the nanoparticles has a big influence on the plasmonic behavior rod shaped  $\text{Ni}_3\text{S}_4$  nanaoparticles with two different aspect ratios were synthesized. As expected the LSPR band changed and got a broad shoulder resulting from the longitudinal LSPR while the transversal LSPR stays distinct. Lastly heterostructured core-shell nanoparticles were synthesized. Here  $\text{Ni}_3\text{S}_2$  shells were grown onto Au nanoparticles. As both materials are plasmonic this results in a shift of the plasmonic band between the plasmon bands of the pure materials dependent on the shell thickness.

## **Synthesis of HfO<sub>2</sub> Nanoparticles for Resistive Switching Experiments**

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The recent developments in big data and the Internet-of-Things are accompanied by an exponentially growing demand for data storage. Resistive switching random access memories (ReRAM) based on metal oxides display particular features that enable non-volatile and fast data processing. Those features make them prominent candidates for next generation data storage technologies.[1] Hafnium dioxide is a well-established component in complementary metal oxide semiconductors (CMOS). It is one of the most promising insulating materials within the metal-insulator-metal (MIM) memristor configuration in ReRAMs.[2] Typically, the fabrication of MIM

devices is realized by top-down processes, e.g. pulsed laser- or sputter deposition. In order to circumvent the associated size limitations and crystal phase ambiguities, we present a bottom-up approach for HfO<sub>2</sub> nanoparticles. We synthesized those highly crystalline particles in wet chemical synthesis routes and characterized them by using transmission electron microscopy (TEM) techniques, i.e. negative spherical aberration corrected high-resolution imaging and selected area electron diffraction (SAED). We are able to adjust the crystal phase of the nanoparticles via the synthesis protocol and received the monoclinic and the tetragonal crystal structures. Additionally, we could synthesize sub-10 nm particles of spherical morphology for both crystal systems. This is essential for the consistent assembly of nanoparticle monolayers, which is a prerequisite for in situ switching experiments within a three dimensionally confined memristor architecture. Thereby, we want to deepen our understanding of conductive filaments against the background of a variable Hf/O composition ratio. [1] R. Waser, *Advances Materials*, 2009, 21, 2632-2663, [2] M. Lanza, *Materials*, 2014, 7, 2155-2182

## **Synthesis and Optical Properties of Colloidal Quantum Well Heterostructures**

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**Abstract.** Colloidal quantum wells, also commonly known as nanoplatelets (NPLs), have emerged as a highly favorable class of semiconductor nanocrystals especially attractive as nano-emitters. Owing to their tight 1D-confinement and quasi-2D atomically flat structure, the NPLs exhibit distinct strong excitonic features. Additionally, by forming their heterostructures (in core/crown and core/shell architectures), these excitonic properties can be further enhanced and tailored, and/or new properties can be imparted, for example, to obtain different types, combinations and degrees of electronic band alignments in a single quantum heterostructure. As a result, tunable outstanding optical properties can be attained, which make these hetero-NPLs highly promising for light-generating applications including lasers and LEDs.

To synthesize different heterostructures of NPLs, various methods are implemented. Using the combination of colloidal atomic layer deposition (c-ALD) and hot-injection (HI) shell coating techniques, composition and structure of such atomically flat coating layers can be precisely controlled and tuned while successful passivation is obtained. The resulting core/shell heterostructures, particularly enabled by the use of HI method alone or in combination with c-ALD, exhibit extremely high quantum yields (QY) (reaching near unity in various cases), accompanied with high colloidal stability. Here we will review these combinations of multiple synthesis routes we use to produce such hetero-NPLs with superior features."

## Stepwise Growth of Ruthenium Terpyridine Complexes on Au Surfaces

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Integration of functional molecules into complementary metal-oxide-semiconductor circuit is a promising approach to combine bottom-up with top-down processes to generate novel electrical devices. [1,2] Of particular interest is the integration of terpyridines, which are suited to coordinate a variety of transition metal ions to form molecular wires by end-to-end complexation of metal ions between terminal terpyridine groups. Such wires have already been applied in nanoelectrode configurations and exhibited conductance switching properties.[3] Here we report the stepwise growth of layers consisting of molecular wires, starting from a surface bound terpyridine (4'-mercaptophenyl-2,2':6',2''-terpyridine) forming a densely packed monolayer. After monolayer formation, the reactive metal ion precursor ((Ru(acetone)3)(PF6)2) and a bisterpyridine ligand (1,4-Bis(2,2':6',2''-terpyridin-4-yl)benzene) were added in turns. Infrared reflection absorption spectroscopy (IRRAS) and surface enhanced Raman scattering (SERS), combined with DFT calculations were utilized to document the elementary steps of Ruthenium terpyridine wire formation. The orientation of the resulting layers was evaluated by comparing the bulk and surface spectra. Further, we correlated the orientation of the molecules derived from the spectroscopic analyses with the layer thickness of each growth steps, which was monitored by variable angle spectroscopic ellipsometry (VASE). The combination of these analytical methods allows proving the successful formation of the desired complexes in situ and will thus support our efforts to integrate terpyridine-based molecular wires into nanoelectronic circuitry. [4]

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## CdS based nano hybrid photocatalysts for overall water splitting

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Nowadays, fossil fuel is still the main source energy in the world, the problem of air pollution and limited amount initiates the exploration of clean and renewable energy source. Unlimited and clean solar energy can be converted and stored as hydrogen energy via the process of photocatalysis.

In our lab, near 100 % quantum efficiency for hydrogen generation of water splitting has been realized by adopting CdSe embedded CdS nanorod with Pt tip as

photocatalyst with the assistance of isopropanol as the sacrificial agent in the basic environment. To realize overall water splitting is our next target. Pt tipped CdS rod can achieve excellent charge separation, however, the generated hole can't oxidize water to generate oxygen, our solving method is to introduce metal oxide with lower valence band that has enough ability to oxidize water. In addition, the catalyst will be synthesized via the colloidal protocol.

In the nanostructure of metal tipped CdSe embedded CdS rod, exciton migration, dissociation and transfer refer to the deep mechanism and also have a great effect on the photocatalytic efficiency. We have demonstrated that metal size on the rod tip can affect the time scale of electron transfer via Coulomb blockade and Schottky barrier. But the detail of exciton migration and dissociation in the rod is not clear. In our research, rods with varied length were synthesized via control of temperature, source amount. Exciton behavior inside rods is investigated by the method of transient absorption technique.

### **„Novel inorganic hole transport materials for inverted Sb<sub>2</sub>S<sub>3</sub> ETA solar cells“**

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To comply with the rising demand in green energy, new durable photovoltaic devices, which use earth abundant, non-toxic and affordable materials, are required. Novel all solid state ETA solar cells with inverted architecture are made with Sb<sub>2</sub>S<sub>3</sub> as light-absorber. In contrast to TiO<sub>2</sub> based devices the inverted architecture offers a larger versatility of employable hole conducting materials, avoiding organic semiconductors which deteriorate fast. Very thin layers of different transition metal oxides and sulphides are examined as new potential hole conducting materials (eg.: MoS<sub>2</sub>, MoO<sub>3</sub>, NiO, V<sub>2</sub>O<sub>5</sub>). ALD is utilized to ensure a defect free deposition of the hole conductor and absorber layers on the transparent contact. Other deposition methods such as reactive sputtering are considered. The characteristics of the deposited two dimensional layers and their applicability for photovoltaic devices are investigated.

### **Observing a Hierarchy of Modes in a 1D Strongly Correlated Non-Linear Luttinger Liquid**

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It is notoriously hard to study theoretically interacting quantum systems outside the Luttinger-liquid regime, particularly when considering higher-energy excitations in finite-length 1D systems, as its key assumptions no longer hold. Recent theoretical work has focused on extending this theory to include such regimes [1]. It is predicted that, for higher-order excitations, 'replica' parabolic dispersions with higher momenta or negative effective mass should be observed, in addition to the simple parabolic

dispersion, and that a hierarchy of modes should therefore emerge [2,3], controlled by system length and separated in amplitude by powers of  $R^2/L^2$ , where  $R$  is the interaction length-scale and  $L$  is the length of the system.

Our work focuses on the experimental detection and quantification of these higher-order excitations.

We measure momentum-resolved tunnelling of electrons to and from an array of wires formed within a GaAs heterostructure, and map the dispersion of the system both in the equilibrium and nonequilibrium regimes. We will present recent experimental data obtained at 300mK for systems ranging from 1-5 $\mu$ m where both first- and second-order replica modes, in addition to the lowest 1D subband itself, can be seen. The momentum dependence of the observed structure will also be discussed and compared to what is predicted by theory. Independent interaction parameters are obtained from other well-known 1D features observed at low energy, such as the spin-charge separation and the zero-bias anomaly [4].

[1] O. Tsyplatyev et al., Phys. Rev. Lett. 114, 196401 (2015).

[2] M. Moreno et al., Nat. Comm. 7, 12784 (2016).

[3] O. Tsyplatyev et al, Phys. Rev. B 93, 075147 (2016).

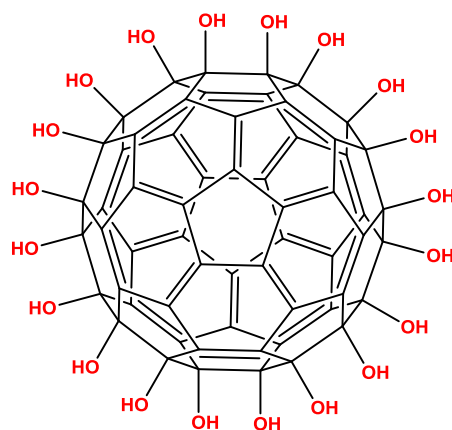
[4] Y. Jompol et al., Science 325, 597-601 (2009).

## Preparation and Extensive Characterization of Fullerenol $C_{60}$

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Recently, functionalization processes onto the outer surface of Fullerenes such as  $C_{60}$  and  $C_{70}$  with various groups attracted large interesting from scientists, which including convert  $sp^2$  hybridization carbon atoms to  $sp^3$  hybridization that aim for enhancing its solubility in an organic polar solvent. This work converts the fullerene  $C_{60}$  successfully to hydroxyl functionalized fullerene which called fullerenol  $C_{60}$ .



Fullerenol  $C_{60}$

The hydroxyl functionalized Fullerene  $C_{60}$  nano-product was characterized using FTIR,  $^1H$ -NMR,  $^{13}C$ -NMR, AFM, SEM, TEM, EDX, TGA, and XRD examinations, they proved the fullerenol  $C_{60}$  structure and demonstrated the remarkable change in fullerene  $C_{60}$  topography from un-uniform particles to shape like spherical with high aggregation.



## **Time-resolved photoluminescence anisotropy from diverse silicon nanocrystals**

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Silicon nanocrystals (Si-NCs) represent potential non-toxic alternative to commercial lighting emitters. Choice of the surface passivation could affect band structure and emission dynamics. In this work, the technique of time-resolved photoluminescence (TRPL) anisotropy is used to discern between radiative transitions from degenerate band-like and localized defect-like states. In this experiment, Si-NCs are excited by a polarized ps-pulsed laser and the degree of emission polarization is measured. The possible depolarization pathways could be through several channels: degenerated transition levels, transfer to an emissive defect site, hot carrier relaxation, particle diffusion, etc. The results show non-zero TRPL anisotropy, which indicates that radiative transition occurs from a discrete state. The smaller Si-NCs appear to have higher intrinsic anisotropy which could be related to higher degree of energy levels discretization.

## **3D TI / graphene – based devices**

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The presented work aims at the nanofabrication and characterization of spintronic devices based on 3D and 2D topological insulators (TIs).

The goal is to exploit the strong spin-orbit coupling (SOC) in a 3D TI to enhance the band gap in graphene, thus rendering the latter into a 2D TI whose intriguing spin transport properties can be experimentally accessed. Such interface-induced SOC shall be achieved, for instance, by combining graphene and the 3D TI Bi<sub>2</sub>Te<sub>2</sub>Se into a heterostructure.

The poster summarizes the results that have thus far been obtained, along with a description of the fabrication methods and experiments planned for the near future.

## **Highly Luminescent and Water Resistant Nanocrystals Coordinated with PMMA**

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Hybrid lead halide perovskite nanomaterials exhibit tunable bandgaps, high extinction coefficient, solution preparation, and superior charge-transfer properties have aroused

extensive interest in optoelectronic applications, such as solar cells, low-threshold lasers, photodetectors and LEDs. However, moisture, air instability and thermal decomposition limit their applications. In this work, we propose a solution for this problem by utilizing partially hydrolyzed poly(methyl methacrylate) (h-PMMA) as ligand stabilizing the nanocrystals (NCs). The hydrophobic polymer of h-PMMA imparts excellent film-forming properties and water stability to the resulting NC–polymer composite. Consequently, the PL intensity of the PNC–polymer film remains at 80% of its original value after storing for 40 days in water. These superior properties allowed us to fabricate a proof of concept thin film OLED with the NCs as easily processable, narrowly emitting color conversion material.

## **The tempered fractional equation for conductance distribution of quasi-fractal quantum wires**

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Several experiments and numerical simulations indicate that disorder in mesoscopic systems (e.g. in quantum wires) can be of fractal (self-similar) type. In this case, statistics of quantum conductance can not be described by the Dorokhov-Mello-Pereyra-Kumar (DMPK) equation of the random transfer matrix approach. Here, tempered Levy stable distributions of scatterers along x-axis is considered to model a quasi-fractal quantum wire. The generalized DMPK-equation containing tempered fractional derivative on length is derived. Solution of this equation provide conductance distributions expressed via the tempered Levy stable laws. These solutions describe evolution from the anomalous conductance distribution for a relatively short wire to the Dorokhov function for a long wire. In addition to the weak scattering regime, we consider sequential tunneling through quasi-fractal wires containing barriers with widely distributed resistances. To confirm analytical solutions, numerical simulations based on the tight-binding model is performed.

## **Improving the stability of Silver Nanowires for electrodes *via* surface modification**

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The future electronic devices will be soft, flexible and even stretchable to be more human-friendly in the form of wearable computers and gadgets. Transparent conductors (TCs) in large-area touch screens, thin-film solar cells, and organic light emitting diodes (OLEDs) are currently made from a sputtered film of indium tin oxide (ITO) due to its high transmittance (95%T) at low sheet resistances ( $50 \Omega \text{ sq}^{-1}$ ).<sup>1</sup> However, in the last decade, silver nanowires (Ag NWs) networks have shown the highest performance of any solution-coatable alternative to ITO with optoelectronic performance that exceeds that of ITO.<sup>2</sup> Despite significant advantages and progress in Ag NWs, they are still suffering from inherent drawbacks.

In this context, we are planning to develop a highly reproducible method of homogeneous silver nanowires synthesis with further surface functionalization by ligand exchange of organic ligands to inorganic ligands. We believe, that this ligand exchange of original NWs surface ligands (PVP) can provide better interwire charge transport as well as material stability. Next, this modified Ag NWs will be investigated both in film and solution. To explore the influence of ligand exchange on electrode functionality, the Ag NWs will finally be implemented in a solar cell or LED devices as an electrode.

The recent progress consists of a modified polyol synthesis resulting in Ag NWs with average diameters of 50 nm and length up to 20  $\mu\text{m}$ . High-performance transparent electrodes require thin diameter and high aspect ratio as two key structural traits that determine their film performance.

[1] Ye al., *Adv. Mater.* 2014, 26, 6670.

[2] Li et al., *Nano Lett.* 2015, 15, 6722–6726

## Highly Conductive Copper Selenide Nanocrystal Thin-Films for Advanced Electronics

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Investigating the influence of the nanocrystal (NC) surface ligands on the electronic and optoelectronic properties of the thin-films devices is essential and sets the fundamental for applications. Here, macroscopic superlattices of copper selenide ( $\text{Cu}_2\text{-xSe}$ ) nanocrystals (NCs) were prepared by self-assembly at the liquid/air interface accompanied by simultaneous ligand exchange with the inorganic  $\text{S}^{2-}$  as well as organic 1,2-ethanedithiol (EDT), 1,4-butanedithiol (BDT), 1,6-hexanedithiol (HDT), and 1,8-octanedithiol (ODT) ligands. By using X-ray photoelectron spectroscopy (XPS) and optical absorption spectroscopy, we demonstrated that the newly introduced ligands largely replaced native surfactants on the  $\text{Cu}_2\text{-xSe}$  NC surface and acted as cross-linkers between neighboring particles. Transport measurements, specifically focusing on the effect of the size of the ligand, revealed a ligand-dependent increase in electrical conductance by 5-9 orders of magnitude with decreasing the size of the ligands from ODT to inorganic sulfide ions, suggesting that the newly introduced species provide efficient electronic coupling for adjacent  $\text{Cu}_2\text{-xSe}$  NCs. Finally, the vapor sensitivity of chemiresistors was investigated by dosing the sensors with 4-methyl-2-pentanone (4M2P), toluene, 1-propanol, and water in the concentration range of 100–5000 ppm at 0% relative humidity. The nanocrystal superlattices were found to respond with an increase in resistance to these analytes.

## LARP technique for obtaining stable lead-free perovskites for photovoltaic devices

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Metal and organometal halide perovskites, an emerging class of direct bandgap semiconductors, have attracted great attention for applications in optoelectronic devices. Lead halide perovskite quantum dots (QDs) were recognized as promising candidates for

future lighting applications, due to their high quantum yield, narrow full width at half maximum (FWHM), and wide color gamut. Nonetheless, the toxicity of lead induces new approaches such as obtaining lead-free perovskites and further investigation of their stability and optoelectronic properties.

Now the most popular candidates to replacing lead are tin(II) (ABX<sub>3</sub> structure)[1], tin(IV) in double perovskites [2], bismuth(III) [3] and antimony(III) [4] in triple (A<sub>3</sub>B<sub>2</sub>X<sub>9</sub>) and double hybrid perovskites (A<sub>2</sub>B'B''X<sub>6</sub>) [5]. The most promising approach, that attracted attention in last few years, is co-LARP technique because of the simplicity, economic advantage and ability to differentiate the composition of precursors due to a wide range of suitable solvents. By this method could be obtained nanostructures that were recognized as the non-received by the classical hot-injection method. Moreover, most of the syntheses do not require a Schlenk line, an inert atmosphere, heating to high temperatures and careful control of the temperature and time parameters of the synthesis. Because of the simplicity, co-LARP method has a great opportunity to solve the problem of accessibility of perovskites and devices with perovskites that broadens new horizons from the economical side of viewing. In our research we obtain nanocrystals with different composition and structure and investigate their properties and stability for the further usage in lighting application.

[1] Synthesis and Optical Properties of Lead-Free Cesium Tin Halide Perovskite Nanocrystals. Tom C. Jellicoe, Johannes M. Richter, Hugh F. J. Glass, Maxim Tabachnyk et al. *Journal of the American Chemical Society* 2016 138 (9), 2941-2944 DOI: 10.1021/jacs.5b13470

[2] Controlled Synthesis of Lead-Free and Stable Perovskite Derivative Cs<sub>2</sub>SnI<sub>6</sub> Nanocrystals via Facile Hot-Injection Process. Aifei Wang, Xingxu Yan, Mian Zhang, Shibin Sun et al. *Chemistry of Materials* 2016 28 (22), 8132-8140 DOI: 10.1021/acs.chemmater.6b01329

[3] Synthesis and Optical Properties of Colloidal M<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> (M = Cs, Rb) Perovskite Nanocrystals. Jaya Pal, Amit Bhunia, Sudip Chakraborty, Suman Manna et al. *The Journal of Physical Chemistry C* 2018 122 (19), 10643-10649 DOI: 10.1021/acs.jpcc.8b03542

[4] High Quantum Yield Blue Emission from Lead-Free Inorganic Antimony Halide Perovskite Colloidal Quantum Dots. Jian Zhang, Ying Yang, Hui Deng, Umar Farooq et al. *ACS Nano* 2017 11 (9), 9294-9302 DOI: 10.1021/acsnano.7b04683

[5] The Making and Breaking of Lead-Free Double Perovskite Nanocrystals of Cesium Silver–Bismuth Halide Compositions. Yehonadav Bekenstein, Jakob C. Dahl, Jianmei Huang, Wojciech T. Osowiecki et al. *Nano Letters* 2018 18 (6), 3502-3508 DOI: 10.1021/acs.nanolett.8b00560

## **Spectral and Lifetime Encoding of Polymer Particles with Cd-free Ternary Semiconductor Quantum Dots for Flow Cytometry with Time Resolved Fluorescence Detection**

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Multiplexed encoding schemes of nano- and micrometer sized polymer particles with fluorescent dyes or quantum dots (QDs) and their optical detection, are of increasing interest for applications in the life sciences, for example in flow cytometry. Almost all strategies utilizing fluorescence focus on spectrally distinguishable emission bands or colors and different intensity levels as fluorescence codes. In this work the goal is to perform multiplexing with encoding fluorophores with different fluorescence lifetimes (LTs). In comparison to the spectral multiplexing strategies this has the advantage, that the different fluorescence LT codes can be measured with the same excitation and emission wavelength,

thus reducing instrumental costs. Moreover, LTs should not depend on emitter concentration. Unlike organic dyes, the LTs of which are typically  $<10\text{ns}$ , the fluorescence LTs of ternary semiconductor QDs which represent a “green” alternative to conventional Cd-containing QDs are in the range of several hundred ns, independent of oxygen concentration, and can be tuned to a certain extent by chemical composition and surface chemistry. This presents a time region that can barely be covered by other emitters that have either much shorter or longer lifetimes. In this project, different encoding strategies will be assessed, and the encoded particles will then be used for fluorescence assays for the analysis of several targets in parallel. Therefore, the encoded particles will be functionalized with different target-specific bioligands and read out with a specifically designed flow cytometer enabling time-resolved fluorescence detection. With this instrument, the particles will be discriminated by their fluorescence LTs in one detection channel while the analytes will be quantified by fluorescence labels in a second channel in the intensity domain.

### **Non-local spin transport in topological insulator nanowire**

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The momentum and spin of charge carriers in the topological insulators are constrained to be perpendicular due to strong spin-orbit coupling.  $\text{Sb}_2\text{Te}_3$  is one of the topological insulator materials with a bulk band gap of 0.28 eV and simple surface states consisting of a single Dirac cone in the band gap. We have synthesized single crystalline  $\text{Sb}_2\text{Te}_3$  nanowires using low pressure catalytic chemical vapor deposition, via vapor-liquid-solid growth mechanism. Two levels of aligned E-beam lithography were used to pattern non-magnetic outer Au leads and two magnetic tunnel junction inner leads on individual  $\text{Sb}_2\text{Te}_3$  nanowires. The tunnel junction leads consist of a free Py ( $\text{Ni}_{80}\text{Fe}_{20}$ ) layer, whose magnetization determines the magnitude and direction of spin current injected into the  $\text{Sb}_2\text{Te}_3$  nanowire.

Measurements of the device resistance between the two Au leads reveal that the Au/ $\text{Sb}_2\text{Te}_3$  has ohmic contacts. The two-point resistance measured through the topological channel as a function of magnetic field shown exhibits positive magnetoresistance, originating from weak anti-localization of carriers in the  $\text{Sb}_2\text{Te}_3$  nanowire induced by spin-orbit interaction. The weak anti-localization signal serves as evidence of a strong impact of spin orbit interaction on transport in the  $\text{Sb}_2\text{Te}_3$  nanowire system. Furthermore, we have also measured a non-local spin valve signal in  $\text{Sb}_2\text{Te}_3$  nanowire channels. The symmetry of this non-local spin valve (NLSV) signal is dramatically different from that of a NLSV with a channel that lacks spin-momentum locking (such as graphene). Two parallel states of the injector and detector magnetic moments give rise to different non-local voltage values, which is never observed in conventional NLSVs. This unusual symmetry is a clear signature of the spin-momentum locking in the  $\text{Sb}_2\text{Te}_3$  nanowire topological surface state.

## **LATERAL MICROSTRUCTURING Metal-Insulator-Metal PHOTONIC AND PLASMONIC CAVITIES**

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Metal-Insulator-Metal (MIM) nanocavities have shown great potential due to their high field confinement and strong coupling capabilities without the need of any momentum matching techniques. The resonance wavelength of these cavities that exhibit Epsilon near zero (ENZ) modes can be tuned by changing the thickness of the layers. Carefully embedding photon-emitting nanoparticles in these cavities allows additional tuning of their photo-physical properties. Also, confining the geometry of the layers to the micro regime can alter the properties of these modes. We investigate on how different geometries affect the photonic and plasmonic modes of MIM structures in micro and nano regime.

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