International Conference of Fundamental Processes in Semiconductor Nanocrystals

Oxford, United Kingdom, 2014

edited by Efrat Lifshitz
You are invited to participate in the International Conference of Fundamental Processes in Semiconductor Nanocrystals, which will take place from 8 to 10 September 2014 in Oxford, United Kingdom.

Semiconductor nanocrystals (NCs), known for their tuneable electronic band structure, have been at the centre of significant interest over two decades, owing to potential application in various opto-electronic devices and biological platforms. NCs prepared via wet-chemical colloidal procedures are of particular current interest, due to cheap synthesis and scalable preparation of thin films. Despite intense research in the past decades, several basic fundamental issues are unknown. The nanoGe meeting will bring together speakers that will discuss current interest in this area.

<table>
<thead>
<tr>
<th>Invited Speakers</th>
<th>Institution/Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uri Banin</td>
<td>Hebrew University of Jerusalem, Israel</td>
</tr>
<tr>
<td>Christophe Delerue</td>
<td>IEMN, France</td>
</tr>
<tr>
<td>Alexander Eychmuller</td>
<td>Technical University of Dresden, Germany</td>
</tr>
<tr>
<td>Tom Gregorkiewicz</td>
<td>Universiteit van Amsterdam, Netherlands</td>
</tr>
<tr>
<td>Zeger Hens</td>
<td>Ghent University, Belgium</td>
</tr>
<tr>
<td>Arjan Houtepen</td>
<td>TU Delft, The Netherlands</td>
</tr>
<tr>
<td>Patanjali Kambhampati</td>
<td>McGill University, Canada</td>
</tr>
<tr>
<td>Christian Klinke</td>
<td>University of Hamburg, Germany</td>
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<tr>
<td>Todd Krauss</td>
<td>University of Rochester, United States</td>
</tr>
<tr>
<td>Liberato Manna</td>
<td>IIT, Italy</td>
</tr>
<tr>
<td>Rudolph Marcus</td>
<td>California Institute of Technology, USA</td>
</tr>
<tr>
<td>Alf Mews</td>
<td>University of Hamburg, Germany</td>
</tr>
<tr>
<td>David Norris</td>
<td>ETH Zurich, Switzerland</td>
</tr>
<tr>
<td>Arthur Nozik</td>
<td>University of Colorado, United States</td>
</tr>
<tr>
<td>Jonathan Owen</td>
<td>Columbia University, United States</td>
</tr>
<tr>
<td>Sandy Ruhman</td>
<td>The Hebrew University of Jerusalem, Israel</td>
</tr>
<tr>
<td>Laurens Siebbeles</td>
<td>TU Delft, The Netherlands</td>
</tr>
<tr>
<td>Dmitri Talapin</td>
<td>University of Chicago, United States</td>
</tr>
<tr>
<td>Daniël Vanmaekelbergh</td>
<td>The Debye Institute, The Netherlands</td>
</tr>
</tbody>
</table>
Monday 8th September 9.00 - 10.00
Single Molecule Intermittent Fluorescence Studies of Quantum Dots and in Initial Steps in Dye Sensitized Solar cells, Examples of Electron Transfers and Diffusion

R. A. Marcus
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Intermittently fluorescing single molecule systems are found in many materials, including dyes on crystal or nanoparticle film surfaces and semiconductor quantum dots (QD), among others. Experimental observations include a power law for the intermittency and, in the case of the “on” state of the QD’s, an exponential tail. We interpret the experiments in terms of a diffusion/electron transfer (ET) theory (“spectral” diffusion for the QD’s and particle diffusion for the semiconductor surfaces). The two theories differ in dimensionality, and so differ in their power (-1.5 versus -1.0) dependence. The ET’s are treated as resonant ET’s, and, for the QD’s at high incident light intensities that produce biexcitons, a Fermi Golden Rule ET (particle ejection) is used in treating it. It causes an exponential tail for the “on” state but no change in the power law behavior of the “off” state. The expected change of power at short “on” or “off” times, due to a building up of a concentration gradient near the “on-off” transition point, is also discussed. Experiment and theory on these many aspects are compared and desirability of additional theory-motivated experimental data is discussed.

Less studied than QD’s is single molecule dye-photoinjection of electrons or holes into semiconductors or semiconductor films of nanoparticles, of solar cell relevance. Here an injection can in principle be either into a conduction band (valence band in the case of hole injection) or into the band gap. We describe a diffusion/ET theory, leading to different kinetics for band and band gap injections and recombinations. Existing data are discussed.

Nanoparticles have been a boom for electron transfer enthusiasts, both for single molecule and ensembles studies. An active problem in electrochemistry and battery research has been looking for curvature in Tafel plots. An example using ensembles of nanoparticles is discussed. We had focused for QD’s on single molecule experiments, but illustrate the complementarity of ensemble studies with an example from QD’s.

Monday 8th September 10.00 - 10.30
Synthesis, Chemical Transformations and Assembly in Colloidal Nanocrystals

Liberato Manna
Istituto Italiano Di Tecnologia, Via Morego, 30, Genova, 16163, It

Colloidal inorganic nanocrystals (NCs) are among the most exploited nanomaterials to date due to their extreme versatility. Research on NCs went through much advancement in the last fifteen years, for example in the synthesis, which opened up the possibility to control their size and shape: this includes the ability to combine several materials in the same nano-object, with topological control, which has contributed to expand the functionality of NCs and the range of their applications considerably. An additional step forward was the creation of a wide range of superstructures from the assembly of such NCs, which can be clearly thought of as new types of artificial solids. Progress also came from the study of chemical transformations in nanostructures, most notably via cation exchange, which involves replacement of the sublattice of cations in a crystal with a new sublattice of different cations, while the sublattice of anions remains in place. New exciting directions have been uncovered recently through the development of plasmonic semiconducting nanoparticles and by the possibility to chemically adjust the density of free carriers in them. The present talk will highlight the recent progress by our group in the areas of advanced synthesis, assembly and in the study of chemical transformations in NCs, with focus on semiconducting/plasmonic nanomaterials.
Semiconductor Quantum Dots (QDs) are of great potential for optoelectronics applications like light-emitting devices, photovoltaic and photoelectrochemical cells. Charge transfer processes are ubiquitous in all these applications and their understanding is paramount for advancing in the construction of these devices. Despite these promising features, charge transfer between a QD and an acceptor, such as a metal oxide substrate like TiO$_2$ or another QD in QD solids, is in competition with deleterious processes like electron and/or hole trapping. In a recent work, we showed that fast electron trapping obstructs charge transport between CdTe and CdSe QD films. A similar behavior occurs in colloidal dispersion of CdTe QDs, in which the rate of electron trapping increases with increased number of washing steps.

In this work, we perform atomistic simulations based on density functional theory (DFT) to unravel the origin of these trap states. In conjunction with a number of experiments on CdTe and CdSe QDs in which we control electrochemically the Fermi level, we are able to present a theoretical model that explains how the chemical processes occurring at the interface of these QDs is key in generating both electron and hole traps. Thanks to this new knowledge, we finally suggest a systematic way to remove trap states in an efficient way.

Monday 8th September 10.30 - 10.45
Modeling the Formation of Trap States in CdTe and CdSe Quantum Dots with Density Functional Theory
Simon C. Boehme$^b$, Jon M. Azpiroz$^a$, Arjan J. Houtepen$^b$, Ivan Infante$^a$

$^a$, Universidad del Pais Vasco, Kimika Fakultatea, Euskal Herriko Unibertsitatea, UPV/EHU , Donostia-San Sebastian, 20080, ES 
$^b$, Chemical Engineering, Optoelectronic Materials, TU Delft, Julianalaan 136, 2628 BL Delft, The Netherlands, NL

Single molecule fluorescence spectroscopy and scanning probe microscopy have been used to investigate small isolated clusters of CdSe/ZnS nanocrystalline quantum dots dispersed on insulating, conducting, and semiconducting surfaces. The aggregated quantum dots exhibit excited state energy transfer and charge transport which affects the time dependent autocorrelation of the photoluminescence (PL) emission intensity, photon counting statistics, blinking statistics, and PL lifetime, as observed by single molecule fluorescence spectroscopy. The structural arrangement of the nanocrystals and the electron transfer between the quantum dots and substrate can be investigated using atomic force microscopy, transmission electron microscopy, and scanning tunneling microscopy. These combined experiments provide novel perspectives on energy and electron transport in quantum dot higher order structures and the effects of structural arrangements, substrates, and attached ligands. These insights will enhance the development of technological applications of quantum dots, including bioimaging, display technology, and alternative energy technology.

Monday 8th September 10.45 - 11.00
Single Molecule Spectroscopy and Scanning Probe Microscopy to Investigate Excited State Energy Transport in Quantum Dot Higher Order Structures
Alan Van Orden$^a$, Kevin Whitcomb$^a$, Duncan Ryan$^b$, Martin Gelfand$^a$

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These combined experiments provide novel perspectives on energy and electron transport in quantum dot higher order structures and the effects of structural arrangements, substrates, and attached ligands. These insights will enhance the development of technological applications of quantum dots, including bioimaging, display technology, and alternative energy technology.
The interest in 2-dimensional systems with a honeycomb lattice and related Dirac-type electronic bands has exceeded the prototype graphene. Currently, 2-dimensional atomic and nanoscale systems are extensively investigated in the search for materials with novel electronic properties that can be tailored by geometry. I will show how atomically coherent honeycomb superlattices of rocksalt (PbSe, PbTe) and zincblende (CdSe, CdTe) semiconductors can be obtained by nanocrystal self-assembly, covalent attachment, and subsequent cation exchange. Atomistic theory and analytical predict that these artificial graphene systems combine Dirac-type electronic bands with the beneficial properties of a semiconductor, such as the presence of a band gap and strong spin-orbit coupling, leading to the quantum spin Hall effect. I will present the first experimental results on the opto-electrical characterisation of PbSe and CdSe honeycomb semiconductors.

**Monday 8th September 12.00 - 12.15**

Engineering of the Electronic Structure of Core/Shell Quantum Dots by In-Situ Alloying

Klaus Boldt\(^a\)\(^b\), Nicholas Kirkwood\(^b\), Kyra N. Schwarz\(^b\), Trevor A. Smith\(^b\), Paul Mulvaney\(^b\)

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We present a facile and robust synthetic method for the formation of graded multi-shell semiconductor nanoparticles. Epitaxial growth of a shell from a different material has been used extensively to improve the properties of quantum dots. The most common strategy is the type-I configuration, which employs a large band gap material to confine the exciton into the core and drastically improve photoluminescence quantum yield (PL QY). The staggered band alignment of a type-II structure in contrast induces a spatial charge separation, which is of interest for charge carrier extraction and stimulated emission, but often suffers from low PL QY.

We extend the CdSe/Cds synthesis published by Chen et al. to a range of core/shell and core/shell/shell structures. By adding cadmium or zinc oleate and octane thiol as precursors at elevated temperatures (260-310 °C) interface alloying between core and shell or between consecutive shells is induced. This process is used to engineer the electronic structure of the nanoparticles between the type-I and quasi type-II or type-II regime of charge carrier localisation.

Thus prepared CdSe/Cds/Zns particles exhibit very high fluorescence quantum yields close to unity and photo-stability when exposed to electron or hole scavengers. A blue-shift of the absorption and fluorescence spectrum caused by the alloying of Cds and Zns opens a new synthetic pathway to high quality green emitting quantum dots.

When starting with ZnSe cores the resultant ZnSe/Cds and ZnSe/Cds/Zns particles have a type-II configuration. The PL can be tuned over a wide range of the visible spectrum from violet to orange, and closely packed films exhibit a low pump threshold for stimulated emission at room temperature. To our knowledge our method produces the highest published PL QY for such a structure, peaking at 75 % for ZnSe/Cds/Zns. The charge carrier overlap, Stokes shift, and fluorescence lifetime can be controlled via the shelling temperature, and have been monitored by nanosecond transient absorption and emission spectroscopy techniques.

**Monday 8th September 12.15 - 12.30**

Effect of Nanostructured TiO2 Morphology on Electronic Structure Studied by the Photoacoustic, Photoluminescence, and Photoelectron Yield Spectroscopy

Taro Toyoda\(^a\)\(^b\), Witoon Yindeesuk\(^b\), Keita Kamiyama\(^a\), Tsuyoshi Okuno\(^a\), Shuzi Hayase\(^b\)\(^d\), Qing Shen\(^a\)\(^b\)

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\(\text{TiO}_2\) is used in the numerous applications sensitized-solar-cells. A main factor for the photovoltaic performance is the morphology of \(\text{TiO}_2\) electrode for sensitizer assembly. Nanoparticulate (NP)-\(\text{TiO}_2\) electrodes have been used for sensitized-solar-cells. NP-electrode has high surface area to increase the loading of sensitizers. However, the recombination process is proportional to the electrode surface area. A balance between recombination and light harvesting is needed to maximize solar cell
performance. TiO₂ electrodes with a higher degree of order than NP-electrodes are desirable for higher conversion efficiency. An approach has been proposed using an inverse opal (IO)-TiO₂. There are several reports showing higher conversion efficiency in IO-case (mainly increase of open circuit voltage, V_{oc}) than that in NP-case. However, the key factors that determine the enhancement of conversion efficiency of IO-case still remain unclear. The fundamental studies of comparison of electronic structures in IO- and NP-TiO₂ is lacking. Photoacoustic (PA) spectroscopy is used for the optical absorption. Photoluminescence (PL) spectroscopy is used for defect state characterization. In addition to those measurements, photoelectron yield (PY) spectroscopy was applied to characterize the valence band maximum (VBM) position which is correlated with the conversion efficiency. Band gap value of IO-TiO₂ agrees with that of NP-TiO₂ (~ 3.2 eV) by PA measurements in good agreement with that of anatase TiO₂. Above the band gap region, the slope of exponential absorption in IO-TiO₂ is larger than that in NP-TiO₂, indicating the larger state density of IO-case than that of NP-case in the conduction band. The surface oxygen vacancies and bulk oxygen vacancies in IO-TiO₂ are lower than those in NP-TiO₂ from the PA measurements. PL measurements show that the self-trapped-exciton emission is dominant in IO-TiO₂, contrary to dominant emission from oxygen vacancy states in NP-TiO₂. The positions of VBM measured for IO- and NP-TiO₂ were -7.38 and -7.52 eV, respectively. The position of VBM of IO-TiO₂ is higher than that of NP-TiO₂, indicating the possibility of increase in V_{oc} in sensitized-solar-cells.

Monday 8th September 12.30 - 12.45
Patterned Thermal Doping by Vacancy Formation in Copper Sulfide Nanocrystal Arrays

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Doping semiconductor nanocrystals (NCs) is a highly pursued challenge, providing another means, along with size and shape, for controlling their electronic properties. We present a new impurity free method for NC doping by thermal treatment at moderate temperatures (T below 400K), thus creating vacancies leading to free charge carriers. This method is applied here for Cu₂S NCs, where Cu vacancies easily form, resulting in p-type doping. This thermal doping procedure is used here to controllably increase the conductance of Cu₂S-NC arrays, achieving up to 6 orders of magnitude enhancement, for which we extract the activation energy for Cu vacancy formation, ~1.6eV. The thermal doping effect manifests itself also in tunneling spectra by the emergence of in-gap states and ~280meV shift of the Fermi level towards the valence band, signifying p-type doping. The effect of vacancy formation was further verified via powder X-ray diffraction depicting a gradual irreversible switch between the Cu rich and Cu poor states of Cu₂S upon the thermal process. In addition, we demonstrated local thermal doping of the NC array via a focused laser beam serving as the heating source. This method yielded a similar increase in device conductance and further characterization obtained via Kelvin probe microscopy portrayed ~80meV increase in the potential of the NC array in the laser heated areas verifying that p-doping also takes place in the laser induced thermal process. This method opens an innovative route for low temperatures patterned doping of NC arrays.

Monday 8th September 12.45 - 13.00
2D Electronic Gas and Surface Effect in Ultrathin Colloidal Nanoplatelets

Mikäel Kepenekian a, Laurent Pedesseau b, Jacky Even b
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Due to their atomic flatness and strictly quantized thickness distribution, colloidal nanoplatelets (NPL) are ideal objects to understand quantum and dielectric confinement effects in well-defined ultrathin quantum wells. Previous simulations performed using empirical k.p or tight-binding models yield a first description of quantum confinement effects, with crude approximations for surface related properties. Density functional theory (DFT) as proposed in the present contribution, is well suited to better account for the influence of surface engineering. Various NPL surface morphologies are considered: surfaces passivated by carboxylic ligands or hydrogen atoms as well as 2x1 reconstructed...
surfaces. Quantum confinement effects are predicted but in addition, electronic densities of states and band diagrams exhibit a strong dependence on the surface states for ultrathin NPL.

Bare electron and hole monoelectronic states are well-known to exhibit a strong renormalization due to the “dielectric confinement” effect between the NPL and the surrounding medium, partially compensated by the increase of exciton binding. This self-energy effect was roughly taken into account in previous studies by considering abrupt dielectric profiles. A new method based on DFT calculations is proposed to compute dielectric constant and self-energy potential profiles in these nanoscale objects, beyond the abrupt interface model (AIM). Simulations are performed using local orbital representations of the electronic wavefunctions in presence of a static electric field. It allows calculations of local polarization and nanoscale dielectric constant profiles, taking into account lattice relaxations and chemical bonding at the surface. It shows that the AIM fails for ultrathin NPL.

Monday 8th September 14.30 - 15.00
Properties and Dynamics of Cooling Charge Carriers in Lead Sulfide Quantum Dots
Pieter Geiregat\textsuperscript{a, b}, Arjan Houtepen\textsuperscript{a, c}, Dries Van Thourhout\textsuperscript{b}, Christophe Delerue\textsuperscript{a}, Zeger Hens\textsuperscript{a}
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\textsuperscript{b} Department of Information Technology, Photonics Research Group, Ghent University, BE
\textsuperscript{c} Department of Chemistry, Opto-electronic materials section, Delft University of Technology, The Netherlands
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Following above band gap photoexcitation of semiconductor materials, a high energy exciton rapidly dissipates its excess energy to end up as a band edge exciton with the electron and the hole occupying the lowest conduction band and highest valence band levels. Very often, hot exciton relaxation is seen as a loss channel, competing with processes that better preserve the free energy of the high energy exciton such as multiple exciton generation or charge transfer of hot charge carriers. On the other hand, the high rate of intraband relaxation may render the process useful for applications relying on a fast change or modulation of materials properties. In both cases, application development would benefit from a better understanding of the properties and dynamics of cooling charge carriers.

In this contribution, we use hyperspectral transient absorption spectroscopy to map the properties of cooling charge carriers in lead sulfide quantum dots. First, we show that, depending on the energy of pump and probe photons and on the pump-probe time delay, different phenomena dominate the transient absorption spectrum. Whereas around the bandgap transition, the well-documented bleach and Coulomb-shift of the bandgap exciton dominate, a short lived transient bleach feature appears at probe photon energies corresponding to the critical point in the energy band diagram along the Σ direction. This temporary slowing-down of the cooling exciton is present in PbS nanocrystals of different sizes, suggesting that this cooling bottleneck is intrinsically related to the PbS band structure. In fact, as the critical point along the Σ direction is a saddle point, the cooling exciton arriving at the critical point must change the direction of its k vector to continue cooling towards the band edges around the L point. Apparently, this results in a temporary accumulation of the exciton around the critical point. Moreover, we argue that this slow cooling via the Σ direction saddle point is the dominant cooling pathway for high energy excitons. This conclusion stresses the importance of the bulk band structure for understanding cooling dynamics of hot charges in semiconductor nanocrystals.

At probe wavelengths below the bandgap, we observe an ultrafast and broadband photo-induced absorption feature that reflects the changing cross section for intraband absorption of the cooling exciton. Interestingly, the wavelength at which this photoinduced absorption matches the bleach of the bandgap transition stays put after exciton cooling. Hence, at this matching wavelength, photo-excitation results in a short, 1-2 ps burst of photoinduced absorption after which the sample has the same absorbance as the original, unexcited sample. We find that this burst photoinduced absorption is linear in the excitation power, both in the single and multi-exciton regime. Moreover, excitation pulses separated by only 2.2 ps give rise to a sequence of absorption bursts, showing that PbS quantum dots could be used for the ultrafast (500 Gb/s), all-optical conversion of data signals between two wavelengths.
In quantum dots (QDs), quantum rods (QRs) and unique molecular chromophores that undergo singlet fission (SF) the relaxation pathways of photoexcited states can be modified to produce efficient multiple exciton generation (MEG) from single photons. Efficient MEG in PbSe, PbS, PbTe, and Si QDs and efficient SF in molecules that satisfy specific requirements for their excited state energy levels has been studied and observed at NREL for many years. MEG has been studied in close-packed QD arrays where the QDs are electronically coupled in the films and thus exhibit good transport while still maintaining quantization and MEG. Simple, all-inorganic QD solar cells that produce large short-circuit photocurrents and respectable power conversion efficiencies via both nanocrystalline Schottky junctions and nanocrystalline p-n or p-i-n junctions have been produced. These solar cells also show for the first time external quantum yields (QYs) for photocurrent that exceed 100% in the photon energy regions of the solar spectrum where MEG is possible (i.e., energy conservation is satisfied); the photocurrent internal QYs from MEG as a function of photon energy match those determined via time-resolved spectroscopy and settles controversy concerning MEG. Very efficient SF in thin films of molecular crystals of 1,3-diphenylisobenzofuran with quantum yields of 200% at the optimum SF threshold of 2Eg (HOMO-LUMO for T1-S0), reflecting the creation of two excited triplet states from the first excited singlet state, has also been observed. Various possible configurations for novel solar cells based on MEG in QDs and SF in molecules that could produce high conversion efficiencies will be presented, along with progress in developing such new types of solar cells. Recent analyses of the dramatic effects of solar concentration combined with MEG or SF on the conversion efficiency of solar cells to both solar electricity and fuels will also be discussed. The properties required for nanocrystals and SF molecules to achieve the high solar conversion efficiencies predicted by theory will be discussed. Regarding production of solar fuels, the most efficient systems must have the following features: (1) two photosystems arranged either in a Z-scheme analogous to biological photosynthesis, or two tandem p-n junctions connected in series where sufficient photopotential (1.23 V + overvoltage for H2O splitting) is generated to drive the redox reactions; (2) strong absorption of solar photons; (3) efficient separation of the photogenerated e-h pairs; (4) efficient transport to and collection of the separated carriers at electrocatalytic surfaces; (5) low overvoltages; (6) appropriate alignment of the redox potentials in the photoelectrodes with those of the fuel-producing reactions; and (7) resistance to dark-and photo-corrosion achieving long-term photostability. Progress in this application will also be discussed.
We demonstrate that the combination of the honeycomb geometry and the strong spin-orbit coupling leads to the formation of bands with nontrivial topology. Model systems are studied in order to understand the origin of these unconventional properties.

**Monday 8th September 16.00 - 16.30**

**Multiexciton Generation and Decay in Two-dimensional Nanosheets**

Laurens Siebbeles  
*TU Delft, Julianalaan 136, Delft, 2628, NL*

We have determined the Auger recombination kinetics of electrons and holes in colloidal CdSe-only and CdSe/CdS/ZnS core/shell nanoplatelets by time-resolved photoluminescence measurements. At high excitation density Auger recombination can be described by second-order kinetics. From this we infer that the majority of electrons and holes are bound in the form of neutral excitons, while the fraction of free charges is much smaller, in agreement with our terahertz conductivity measurements. The biexciton Auger recombination is not diffusion-controlled and is more than one order of magnitude smaller than for quantum dots and nanorods of equal volume. The latter is of advantage for application in lasers, light-emitting diodes and photovoltaics. The generation of two or more electron-hole pairs for the absorption of a single energetic photon is of interest for development of highly efficient (up to 44%) solar cells. The efficiency of this carrier multiplication (CM) process depends on several factors, including the competition with cooling, the Coulomb interaction between the hot charge carrier and the final trion density of states. All these factors depend on nanocrystal dimensionality. Previously carrier multiplication has been investigated in lead chalcogenide quantum dots (0D), nanorods (1D) and bulk (3D). We investigated the efficiency of carrier multiplication in two-dimensional PbS nanosheets of 4 to 7 nm thickness using ultrafast optical pump-probe spectroscopy. The efficiency of carrier multiplication in nanosheets is much higher than for quantum dots, nanorods and bulk material. In thin PbS nanosheets virtually the entire excess photon energy above the CM threshold is used for CM, in contrast to quantum dots, nanorods and bulk lead chalcogenide materials.

**Tuesday 9th September 8.30 - 9.00**

**Electronic Impurity Doping of Colloidal Quantum Dots**

David Norris  
*ETH Zurich, Universitaetstrasse 6, Zurich, 8092, CH*

Doping is extremely important for controlling the electronic conductivity of bulk semiconductors. However, very few examples exist where impurities that have been incorporated into colloidal semiconductor quantum dots have affected their electronic properties. Here we will discuss the challenges in this area and recent progress. In particular, we will describe the use of arrested cation exchange to lightly dope quantum dots with a controllable number of electronic impurities. The physical characterization of these materials then shows that the addition of even one impurity per quantum dot has a dramatic effect on their optical properties. Furthermore, studies of the electrical transport through films of these quantum dots show complex non-monotonic behavior in the Fermi level as a function of dopant concentration. To explain these trends, we have recently developed a microscopic model of impurity incorporation that is also consistent with the process of cation exchange, which, in addition to doping, is becoming an increasingly important tool for the preparation of new quantum-dot materials.

**Tuesday 9th September 9.00 - 9.30**

**Fluorescent and Magnetic Nanocrystals in Materials and Life Sciences**

Horst Weller  
a, Hamburg University, Inst. of Physical Chemistry, Grindelallee 117, Hamburg, 20146, DE  
b, Center for Applied Nanotechnology Hamburg (CAN), DE  
c, Interdisciplinary Nanoscience Center Hamburg (INCH), DE  
d, The Hamburg Center for Ultrafast Imaging (CUI), DE
We report on the precision synthesis of CdSe/CdS/ZnS core-shell-shell nanocrystals using a preparative flow reactor. Experimental design is used to determine the crucial parameters and their influence on particle growth and size distribution.

In the second part of the talk, we will present applications of nanocrystals. In particular, we will report on the development of quantum dot quantum rod particles with fluorescence quantum efficiencies close to unity and applications in lighting and display technology. For biomedical applications we will present a biocompatible encapsulation technique based on amphiphilic poly(isoprene-block-ethylene oxide) (PI-b-PEO) diblock copolymers. We varied block lengths, structure and functional terminal end groups and investigated the effect on unspecific uptake. Fluorescence quenching experiments with encapsulated quantum dots show that best behavior in respect to unspecific cellular uptake is realized in those systems, in which the polymer shell yielded best protection against quenching molecules from the surrounding medium. Combination of micelle encapsulation with block copolymers and seeded emulsion polymerization finally leads to biolables for which unspecific uptake could be almost completely suppressed even under in-vivo conditions. We present various techniques for bio-conjugation with recognition molecules and show examples for specific cell and tissue targeting. In-vitro and in-vivo fluorescence and MRI data will be discussed.

Tuesday 9th September 9.30 - 10.00
To be announced
Jonathan Owen

Tuesday 9th September 10.00 - 10.15
Near-infrared Paramagnetic Manganese-doped PbS Nanocrystals
Lyudmila Turyanska\textsuperscript{a}, Moro Fabrizio\textsuperscript{a}, Andrew N Knott\textsuperscript{a}, Oleg Makarovsky\textsuperscript{a}, Amalia Patane\textsuperscript{a}, Michael W Fay\textsuperscript{a}, Alan Meaney\textsuperscript{c}, Peter C M Christianen\textsuperscript{c}
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\textit{b, The University of Nottingham, Nottingham Nanotechnology and Nanoscience Centre, NG7 2RD, GB}
\textit{c, High Field Magnet Laboratory, Radboud University, Nijmegen 6525 ED, The Netherlands}

The controlled incorporation of dopant impurities in a single colloidal nanocrystal (Quantum dot, QD) is a challenging field of research with potential for numerous applications in nanotechnology. Of particular interest is the incorporation of 3d transition metal ions (Mn, Co, etc) whose d-shell electronic configurations imprint the nanocrystal with unique magnetic and optical properties.

Here we report the successful incorporation of Mn in colloidal PbS nanocrystals and demonstrate Mn-induced electronic and optical properties of fundamental and technological interest. Our “one pot” synthesis approach produces nanoparticles that combine within one structure, paramagnetic properties of transition metals with efficient and tuneable photoluminescence (PL) emission in the near-infrared (NIR) wavelength range (850-1200 nm).

We present electron spin resonance (EPR) studies revealing magnetic resonance transitions between states that are split by the hyperfine interaction between d-shell electrons and the nuclear spins of individual Mn$^{2+}$ ions in the QDs. We investigate the spin dynamics of the Mn-impurities by pulsed EPR spectroscopy and achieve long spin coherence times ($\sim 1$ ms at 5K) and Rabi oscillations.

Finally, we use high magnetic fields (up to 30T) to investigate the effect of an increasing Mn-content in the QD on the degree of circular polarization of the QD PL emission and show that Mn-impurities provide a tool for engineering the effective exciton g-factor. The observation of quantum oscillations and tuneable g-factor makes these new nanocrystals attractive candidates for spin manipulation studies and quantum information applications. Dual functionality, i.e. NIR luminescence and paramagnetism, of PbS:Mn also opens up exciting prospects for their future exploitation as imaging labels for combined fluorescence and magnetic resonance imaging.

Tuesday 9th September 10.15 - 10.30
Highly Coupled Nanocrystal Arrays that Reveal Sharp Decays in Band Tail States, Delocalized Coherent Exciton Formation and High Carrier Mobility
Ryan Crisp\textsuperscript{a}, Justin Johnson\textsuperscript{a}, Rebecca Callahan\textsuperscript{a}, Peter Erslev\textsuperscript{a}, Joseph Luther\textsuperscript{a}
Semiconductor nanocrystals (NCs) are promising materials for next-generation photovoltaic technologies and other various optoelectronic applications. NCs can be coupled yet still quantum confined into arrays with intriguing optoelectronic properties utilizing recent developments on surface ligand manipulation. Despite being organized into highly disordered arrays, the charge carrier transport characteristics have been characterized as bulk-like while still maintaining discrete excitonic optical transitions. Thus, understanding the peculiarities of the optoelectronic properties of coupled quantum dot (QD) arrays will further enable unique applications for NCs. In this talk, I will describe recent work where we have measured carrier trapping occurring in band tail states extending from the band edges into the gap. The band tails have surprisingly low characteristic energies near 14 meV, similar to those found in larger grain, polycrystalline bulk semiconductors, rather than the large Urbach energies normally associated with amorphous, or porous nanocrystalline films. Then, utilizing ultrafast cross-polarized transient grating (CPTG) spectroscopy we measured electron–hole wave function overlap in CdSe QD films with chemically modified surfaces for tuning inter-QD electronic coupling. By comparing the CPTG decays with those of isolated QDs, we find that excitons coherently delocalize to form excited states more than 200% larger than the QD diameter. Furthermore, we have used transient microwave conductivity experiments to measure charge carrier mobilities within isolated NCs in solution. We find that the (optical frequency) mobility and lifetime of photo-induced carriers are controlled by the NC shape and dimensions. When cast into films, carrier mobilities are highly dependent on the capping ligand for the CdTe NCs measured. We identify specific Te-based ligands that improve transport characteristics (i.e. diffusion lengths) over that of bulk CdTe films. The combination of these unique energetic and pump-probe techniques further the understanding of such complex materials and provide new insight into coupling strategies.

**Tuesday 9th September 11.00 - 11.30**

**Photo Luminescence of Individual CdSe Quantum Nanowires**

 Alf Mews  
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CdSe-based quantum nanowires (QNWs) are chemically synthesized using similar “TOPO” methods as for nanocrystals, but with additional Bismuth particles acting as catalysts to initiate one dimensional growth. By using this so-called solution-liquid-solid method, the diameter of the wires can be reduced to values well below the exciton dimension, while the length of the wires can exceed several micrometers. Hence, these wires can be viewed as ultra-long nanorods, where the optical properties such as the fluorescence wavelength or the absorption threshold are dictated by confinement effects in radial direction. On the other hand the photo generated charge carriers or excitons can move in length direction and can be trapped at different sites along the nanowires.Here we present a detailed structure-property relationship by combining confocal single QNW PL measurements with TEM studies on the same individual QNWs. After a brief discussion on the preparation of such QNWs we will show several results of room temperature PL in combination with EFM measurements to monitor the charge distribution upon local illumination. The main part of the talk will cover time-resolved low-temperature confocal PL spectroscopy to observe interesting features of the QNWs which are hidden at room temperature. For example we observe a manifold of spectral lines which show a blinking behavior on different time scales. The interpretation of the spectra is based on quantum mechanical models which include structure effects as well as the presence of donor and acceptor states.

**Tuesday 9th September 11.30 - 12.00**

**Back to the Future: Mechanistic Insights into Semiconductor Nanocrystal Syntheses**

 Todd Krauss, Leah Frenette, Kelly Sowers, Amanda Preske, Brett Swartz  
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For over 30 years semiconductor nanocrystals (NCs) have been the subject of much interest for fundamental and applied studies. The synthesis of NCs has developed and matured over this time such that production of monodisperse, photostable NCs with close to an exact size and shape are readily achievable. However, an understanding of the chemical reaction mechanism behind the synthesis of
NCs has lagged the ability to synthesize high quality nanoparticles. In this presentation, NC synthetic mechanisms that have been proposed for metal-chalcogenide (ME) semiconductor NCs, particularly CdE and PbE, will be discussed. Specifically, for PbE NCs synthesized under relatively low temperatures (< 200 °C) it was found that secondary phosphate chalcogenides are the primary reactive species that determines the formation of NC nuclei. Tertiary phosphate chalcogenides are completely unreactive at these temperatures. Small quantities of secondary phosphate impurities in the conventional tertiary phosphate based synthesis thus play an important role in determining the number of NCs formed and the rates of the reaction. For NCs synthesized under much higher temperatures (generally > 250 °C), such as CdE NCs, several other mechanistic pathways start to dominate the reactivity. In particular, strong evidence exists for the formation of highly reactive metal-alkyl species in situ, which fundamentally bears a striking resemblance to some of the original CdSe NC syntheses developed over 20 years ago. Also to be discussed will be how an understanding of fundamental reaction mechanisms can lead to improved NCs with controllable surface chemistry and with tailored optical properties.

**Tuesday 9th September 12.00 - 12.15**
High-Quality Quantum-Confined Colloidal Indium Nitride Nanocrystals
Basudeb Chakraborty, Zhihui Liu, Benjamin Schaus, Remi Beaulac
Department of Chemistry, Michigan State University, 578 S. Shaw Lane, East Lansing, 48824, US

Group-III nitrides form an attractive class of materials in view of their chemical stability, high heat and electrical conductivities, and large variation of optical bandgaps. There are nevertheless few methods at the moment that allow the direct synthesis of high-quality, free-standing colloidal nitride nanomaterials. We describe here a new approach to synthesize indium nitride that yields colloidal nanoparticles matching the quality of II-VI nanomaterials obtained through state-of-the-art hot-injection approaches. An interesting aspect of these new materials is that they clearly do not exhibit any features of impurity-based doping that are prevalent in other forms of nanocrystalline InN previously studied, as seen from the absence of the large Burstein-Moss shifts and surface plasmon resonance signatures typically reported. Instead, as expected for pristine semiconductor nanomaterials, the samples obtained through our approach exhibit unambiguous size-dependent electro-optical effects that are consistently explained by the trend expected from Brus equation for strong-confinement regimes, with effective optical bandgaps that can be tuned from 0.7 eV to above 1.0 eV for quantum dot diameters varying between 3 nm and 10 nm. These samples furthermore are bright emitters in the near-infrared, with microseconds recombination lifetimes and photoluminescence quantum yields around 10%, making them attractive candidates for imaging and detection applications. We also show that the shape of these nanocrystals can be altered from quasi-spherical to disc-shaped structures by simple modifications of the general synthetic scheme.

**Tuesday 9th September 12.15 - 12.30**
Confined Acoustic Phonon Modes Mediating Relaxation between Fine-structure Levels in Single Core-Shell Quantum Dots
Johannes Haase‡, Florian Werschler‡, Tjaard de Roo§, Stefan Mecking§, Alfred Leitenstorfer§, Denis V. Seletskiy‡

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Core shell quantum dots possess size-dependent (tunable) electronic and optical properties together with large dipole moments. Their colloidal characteristics are ideal for experiments in the domain of quantum optics. For our recent studies, we embed single CdSe/CdS core/shell quantum dots into PMMA particles via miniemulsion polymerization. These hybrid particles exhibit high quantum yields and single photon emission together with long-term photochemical stabilities.

At cryogenic temperatures, we observe fine-structure emission originating from the two band edge excitons (i.e. the low energy “dark” and the high energy bright exciton) of the CdSe/CdS system. The fluorescence decay time consists of a long and a short component. These components are dependent on the relaxation rate between the two fine-structure states and the relaxation of each of them to the ground-state, at a given temperature. By employing a three level temperature-dependent rate-equation
model, we fit the relaxation rate between the fine-structure states. This rate strongly depends on the existence of acoustic phonon modes. In nanoscale objects, acoustic phonons are confined modes with eigen-energies in the range of a few meV. The examination of hybrid particles with similar size and different degrees of fine-structure splitting allows us to map the energy spectrum of the confined acoustic phonon modes. In addition, we are able to observe these modes as pronounced peaks in the photoluminescence spectra. Our theoretical analysis of the vibrational eigen-modes of an elastic sphere is in excellent agreement with the measurements.

**Tuesday 9th September 12.30 - 12.45**

Ultrafast Biexcitonic Signatures in Single Quantum Dot Pump-probe Spectroscopy

Christopher Hinz, Johannes Haase, Christian Traum, Stefan Lohner, Denis Seletskiy, Alfred Leitenstorfer

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II-VI semiconductor quantum dots with high confinement potentials and large Coulomb correlation energies provide promising systems for quantum optical experiments. Recently we were able to observe ultrafast Coulomb renormalization and single photon gain in negatively charged CdSe/ZnSe dots. Here we report on two-color femtosecond pump-probe measurements on a single self-assembled CdSe/ZnSe quantum dot. The fundamental trion (X-) emits at 2.168 eV. Two additional emission lines at 2.160 eV and 2.156 eV (XX1- & XX2-) are identified as charged biexcitons via polarization resolved PL spectroscopy. PLE measurements and theoretical calculations enable us to identify the two lowest energetic resonances as the 1D_{3/2} to 1S_{1/2} and the 1P_{3/2} to 1P_{1/2} transitions. The system was resonantly pumped on the 1P_{3/2} to 1P_{1/2} transition with a 660 fs laser pulse of 5 meV spectral width. The charge carrier dynamics of the system was spectro-temporally investigated across both the trion line and the biexcitonic emission lines with a probe pulse duration of 200 fs and a spectral width of 17.8 meV. Differential transmission spectra for time delays between -100 ps and +200 ps were acquired. For negative delays an absorption feature at the position of the trion line is clearly identified. This consists of the perturbed free induction decay component and possibly fine-structure splitting due to a long-lived nuclear spin polarization, which is currently under investigation. After hot exciton creation by the pump, for positive time delays the trion resonance exhibits an initial bleaching followed by stimulated emission, which occurs after relaxation to the ground state. Additionally, negative pump-probe features emerge on the low-energy side of the X- line. We attribute those to an induced absorption into the biexciton states, switched on by the Coulomb renormalization of the X- ground state due to the excitation by the pump. This picture is corroborated by matching transient absorption and photoluminescence emission lines. Exciting the system on the 1D_{3/2} to 1S_{1/2} transition instead leads to a suppression of the absorption lines due to the full occupation of the S-level.

**Tuesday 9th September 12.45 - 13.00**

Exciton and Bi – Exciton Fine Structure of CdTe/CdSe Colloidal Quantum Dots in Weak and Extremely Weak Confinement Regime

Jenya Tilchin, Maya Isaev, Itai Meir, Efrat Lifshitz, R.J.A. (Relinde) Moes, Daniel Vanmaekelbergh

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Colloidal quantum dots (CQDs) implementation in optoelectronics is limited by internal material imperfections such as a fluorescence intermittencies (blinking) and its spectral stability (spectral diffusion). Both the effects originate in the material ability of extra energy exclusion from the system and closely packed charges. A turning point occurred when a few distinctive systems with blinking free behavior were reported in CQDs with either type – I, type – II or quasi – type – II core/shell configurations. The particular interest gains the “giant” CQDs with quasi – type – II configuration such as CdSe/CdS3. This “giant” particle size enables to decrease the charged carriers interaction. The later results in reduction of the non – radiative Auger and paves the way for non – blinking material. However, the increase of the particles size above bulk exciton Borh radius decries the strength of quantum confinement. In this work we explore the effect of weak and extremely weak quantum confinement on exciton (X) and bi-exciton (BX) fine structure in CdTe/CdSe “giant” CQDs. The particles under consideration were covered with two monolayers of CdSe on top of CdTe core with total particle diameter of 9.5 nm (Sample A) and 25.5 nm (Sample B). The major difference between two samples lies...
in CdTe core size which is less than its bulk exciton Bohr radius (7.3 nm) in sample A and significantly excites it in sample B. Both of the samples possess an efficient BX formation along with almost complete suppression of X emission line (BX formation due to substantial filling). In extremely weak confinement regime (sample B) X and BX do not exhibit any well resolved polarization dependent fine structure leading only slight elliptical cross polarization of both the emission bands. The exchange interaction induced excitonic fine structure was not resolved even with increase of external magnetic field strength leading to overall emission line broadening due to Zeemann of the sub bands. On the other hand, the weak confinement regime (sample A) both of the bands possesses well resolved cross polarized emission lines from their energy fine structure already at zero Tesla magnetic field strength. This was further splitted at higher magnetic field powers.

**Tuesday 9th September 14.30 - 15.00**
Optoelectronic Properties of Individual PbS Nanosheets
Thomas Bielewicz, Sedat Dogan, Christian Klinke
*Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, Hamburg, 20146, DE*

Two-dimensional, solution-processable semiconductor materials are appealing for low-cost electronic applications, such as transistors and solar cells. In the talk I will discuss the synthesis of colloidal lead sulfide nanosheets. The formation mechanism is based on oriented attachment of small nanoparticles. The final structures possess a lateral size of several microns. I will show how their size, shape and height can be tuned by the variation of the synthesis parameters. As a consequence of the adjustability of the nanosheets’ thickness between 2 to more than 20 nm charge carriers are in quantum confinement, which has a decisive impact on their electronic properties. This is demonstrated by their use as conduction channel in field effect transistors. The experiments show that the performance in terms of On current, field-effect mobility, On/Off ratio, and sub-threshold swing is tunable over a large range. Furthermore, I will show the function of individual nanosheets as solar cells.

**Tuesday 9th September 15.00 - 15.30**
Dimensionality Matters: Dimensionality Effects on Optoelectronic Behavior of Semiconductor Nanocrystals
Uri Banin
*Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

Studying the transition of properties of nanostructures as they develop from the zero-dimensional to the one-dimensional regime is significant for unravelling the modifications that occur in the electronic structure of the particle as its length to width aspect ratio is increased. Such understanding can lead to better design and control of the particle properties, with relevance for a wide range of technological applications. The ongoing improvements in the control of shape and morphology of nanoparticles in colloidal synthesis, which allows forming structures of similar composition but of different dimensionalities and shapes, open the way for probing such dimensionality effects. We will present several effects involving the 0D to 1D transition in CdSe/CdS core/shell nano heterostructures of different morphologies including “sphere in a sphere”, “sphere in a rod” and “rod in a rod”. In addition, a recently discovered new architecture of “nanorod couples” will be introduced.

Both ensemble and single particle based measurements were used to decipher these effects providing complementary viewpoints. The first dimensionality related aspect involves the modification of emission and absorption polarizations, as the dimensionality of the particles and of their cores changes. The second aspect relates to the function of these nanocrystals as donors in energy transfer processes to multiple dye molecules bound on their surfaces and functioning as acceptors (see schematic of the FRET process in the figure below). We will show how the dimensionality of the particles’ core and shell affects the donor’s time dependent survival probability, as well as the behavior of FRET to multiple acceptors on single particle level. The opportunity to tailor the systems dimensionality with multiple acceptors on the surface results in enhanced FRET efficiencies with relevance for optical, sensing and energy funneling applications.
Tuesday 9th September 15.30 - 16.00
High Charge Carrier Mobility Enables Exploitation of Carrier Multiplication in Quantum-Dot Films
C.S. Suchand Sandeep\textsuperscript{a}, Syben Ten Cate\textsuperscript{a}, Jueon Schins\textsuperscript{a}, Tom Savenije\textsuperscript{a}, Y. Liu\textsuperscript{b}, Matt Law\textsuperscript{b}, Sachin Kinge\textsuperscript{c}, Laurens Siebbeles\textsuperscript{a}, Arjan Houtepen\textsuperscript{a}
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Carrier Multiplication (CM), the generation of multiple electron-hole pairs by a single photon, is of great interest for solar cells as it may enhance their photocurrent. This process has been shown to occur efficiently in colloidal quantum dots, however harvesting of the generated multiple charges has proved difficult. Here we show that by tuning the charge carrier mobility in quantum-dot films, CM can be optimized and may show an efficiency as high as in colloidal dispersion.

We vary the charge carrier mobility in PbSe quantum-dot films by using ligands of varying lengths and varying anchor groups as well as infilling with alumina via atomic layer deposition. Carrier multiplication is observed and quantified in both time-resolved microwave photoconductivity studies and ultrafast transient absorption measurements. These results indicate that the number of surviving free charge carriers that result from CM increases with increasing charge carrier mobility.

Our results are explained quantitatively by the competition between dissociation of multiple electron-hole pairs and Auger recombination. For low mobility materials CM results in multi-excitons that however decay via Auger recombination before they can dissociate into free charges. In contrast, above a mobility of \(\sim 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}\) multi-excitons dissociate rapidly and are quantitatively converted to free charges before Auger recombination can take place.

In addition we show that the threshold energy for CM is reduced to twice the band gap of the quantum dots in these photoconductive films. This surprising observation could be related to the existence of trap states that participate in the CM process.

Wednesday 10th September 8.30 - 9.00
Multi-pulse Transient Absorption Study of Exciton Dynamics in PbSe Nanocrystals
Itay Gdor\textsuperscript{a}, Chunfan Yang\textsuperscript{a}, Diana Yanover\textsuperscript{b}, Efrat Lifshitz\textsuperscript{b}, Sanford Ruhman\textsuperscript{a}
\textsuperscript{a} Hebrew University of Jerusalem, Institute of Chemistry, Hebrew University, Jerusalem, 91904, IL
\textsuperscript{b} Department of Chemistry and Solid State Institute, Technion, Haifa 32000, , IL

After failing to detect MEG in samples of InAs core shells, and in PbSe quantum dots, using pump-probe methods, we regress to fully characterize exciton cooling dynamics in PbSe quantum dots. Spectral analysis of transient absorption using femtosecond hyperspectral near IR probing has revealed kinetically and spectrally distinct features which are incompatible with prevailing models for nanocrystal absorption and its dependence on excess energy. They appear to be at odds with the expected degeneracies of the low-lying discrete optical transitions and exhibit kinetic correlations which defy associated energy level assignments. Transient spectra of single and double hot exciton states decay with similar dynamics, arguing against the involvement of Auger cooling in the rapid exciton relaxation in PbSe QDs. In order to identify the mechanisms underlying the distinct spectral bands which accompany exciton cooling, double pump-hyperspectral probe experiments have been conducted. Preliminary results demonstrate that the sub-band gap absorption induced by excitation with high energy photons is not correlated with the 1S1S bleach, and that the assumed linearity of this bleach with the number of band edge excitons does not hold. Possible revisions of accepted models for exciton cooling in this material, which are called for by these findings, will be discussed.

Wednesday 10th September 9.00 - 9.30
Optics of 2D-excitons in Colloidal CdSe Nanoplatelets
Ulrike Woggon\textsuperscript{a}, Alexander Achtstein\textsuperscript{a}, Mikhail Artemyev\textsuperscript{b}
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Colloidal CdSe nanoplatelets of zincblende-type crystalline structure represent a novel material system of two-dimensional colloidal nanocrystals, i.e. colloidal quantum wells. In contrast to MBE grown quantum wells, those platelets show a much higher quantum yield and have thus a high potential for usage in photonic devices, like quantum well lasers or sensors. We study excitonic properties, electroabsorption, optical nonlinearities and exciton-phonon coupling in colloidal 2D semiconductor nanocrystals, i.e. CdSe nanoplatelets. Single-particle spectroscopy, temperature-dependent emission and ultrafast recombination dynamics have been measured along with numerical simulations of energy states to understand the influence of 2D quantization and lateral size variation on linear optical properties and exciton-phonon interaction. Single particle spectroscopy is applied to overcome inhomogeneous broadening in ensembles and reveals an excitonic substructure in the photoluminescence emission spectra (PL). Temperature-dependent measurements of the PL spectra show a small exciton-LO-phonon coupling strength in confined ZB systems and therefore a small phonon broadening in the single CdSe platelet emission. We present numerical calculations of the 2D-nanoplatelets quantum well exciton energies including Coulomb interaction and compare the obtained energies with experiments. Due to a large surface to volume ratio, the exciton energies show a strong impact of dielectric confinement. Coulomb interaction corrected numerical simulations reproduce this effect. The thickness quantization to integer monolayers leads to an only lateral size distribution, resulting in narrow PL emission.

**Wednesday 10th September 9.30 - 10.00**

On the Nature of the Surface of Semiconductor Nanocrystals

Patanjali Kambhampati  
*McGill University, 801 Sherbrooke St. West 0 Montreal, CA*

**Wednesday 10th September 10.00 - 10.30**

(Aero-)Gels of semiconductor and metal nanocrystals

Alexander Eychmüller  
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I will touch upon a recent direction of research in our group, namely that of gels and aerogels manufactured from a variety of nanoparticles. This has recently proven to provide an opportunity to marry the nanoscale world with that of materials of macro dimensions which can be easily manipulated and processed, whilst maintaining most of the nanoscale properties. The materials carry an enormous potential for applications. This is largely related to their extremely low density and high porosity providing access to the capacious inner surface of the interconnected nanoobjects they consist of. I will report on a) enzyme encapsulated QD hydrogels as a multi-functional platform in the development of optical biosensors, b) the electrocatalytical activity towards the oxidation of ethanol of a freestanding palladium nanoparticle aerogel with extremely high electrocatalytic current density and good durability, and c) colloidal nanocrystals embedded in macrocrystals and their application in a colour conversion LED with good robustness, photostability, and color purity.

**Wednesday 10th September 11.00 - 11.30**

When Nanocrystals Work as a Team: Collective Properties of Nanocrystal Solids

Dmitri Talapin  
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Development of synthetic methods for well-defined nanostructures has introduced new approaches for engineering functional materials. Single- and multicomponent nanocrystal arrays provide a powerful general platform for designing “programmable” solids with tailored electronic, magnetic, optical and catalytic properties.

We have designed different approaches to engineer nanocrystal structure and surface chemistry for various applications. We particularly focus on the role of surface engineering for electronic properties of nanocrystal arrays. Efficient charge transport is critical for many nanocrystal-based electronic and optoelectronic devices. We developed inorganic chalcogenidometalate surface ligands that enabled record electron mobility in nanocrystal arrays. New all-inorganic colloidal nanocrystals have been used
to make solution processed field-effect transistors with electron mobility over 300 cm²/Vs, thermoelectric materials with ZT>1.2 and solar cells with the power conversion efficiency 12%. Nanoheterostructures with electronic structure of quantum wells show prospects for solution-processed lasers, significantly outperforming quantum dots in the amplified spontaneous emission threshold and modal gain. All these examples demonstrate utility of colloidal nanostructures for real-world technologies and applications.

**Wednesday 10th September 11.30 - 12.00**

**Si Nanocrystals for Spectral Conversion in Future Photovoltaics**

Tom Gregorkiewicz

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The most important limitation for efficiency of photovoltaic energy conversion appears due to the mismatch between the broad-band character of the solar radiation and the discrete operation mode of solar devices, as determined by the specific bandgap energy of the active medium. One remedy for that would be the spectral transformation of the solar radiation before it enters a photovoltaic device. Specifically, such a “solar shaper” should split the large energy photons into smaller ones, whose conversion efficiency is optimal. On the low-energy side, the shaper could “paste” together IR photons thus bringing them into the operational range of the device.

In my presentation, I will discuss how shaping of the solar spectrum can be achieved using layers of Si nanocrystals with and without Er doping. In such systems efficient photon transformation can be realized by quantum cutting and/or emission from Er³⁺ ions sensitized by Si nanocrystals. Also the recently identified ultra-efficient colloidal Si nanocrystals can be used for the purpose. I will present evaluation of external quantum efficiency of emission from thin layers of Si nanocrystals in SiO₂ and its evolution upon introduction of Er³⁺ ions. Using differentially prepared materials I will evaluate how this can be maximized. I will also discuss energy efficiency of solar shapers based on Si nanocrystals and Er³⁺ ions. In a separate part, I will discuss also strategies how Si nanocrystals can be employed for quantum “pasting” by which low-energy photons could be used in photovoltaic conversion by a standard Si solar cell.

**Wednesday 10th September 12.00 - 12.15**

**Synthesis and Shape Control of Colloidal CuInGa(SSe)₂ Semiconductor Nanocrystals**

Claudia Coughlan¹, Shalini Singh², Ajay Singh², Kevin M. Ryan³

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Colloidal semiconductor nanocrystals play a key role in the quest for novel functional materials with enhanced optical, electrical and physical properties. In particular, copper based ternary and quaternary chalcogenides such as CuInS₂ (CIS), CuInGaS₂ (CIGS) and Cu₂ZnSnS₄ (CZTS) are attracting increasing interest as next generation photon absorbing layers due to their high energy conversion efficiencies, high optical absorption coefficients, compositionally tunable band gaps and relatively low toxicity. In comparison to the well-understood binary II-VI systems, where precise size and shape control over the synthesis has become routine, the difficulty in balancing the reactivity of three, four or even five different precursors, to synthesize ternary, quaternary and quinary materials respectively, severely limits comparable control. To date, only one report exists on the formation of CuInGa(SSe)₂ (CIGSSe) nanocrystals by a colloidal based approach, in which 0D nanocrystals have been achieved in the tetragonal phase.

Herein, we conduct a comprehensive study on the synthesis of CIGSSe nanocrystals and achieve compositional, structural and crystal phase control of CIGSSe nanocrystals through optimization of the ligand chemistry. We achieve, for the first time, the formation of 2D nanoplates in the metastable hexagonal wurtzite phase, with the ample chemical and structural freedom in this system permitting band gap tuning through variation of the chalcogen ratio along with no drastic changes in the nanoplate morphology. Interestingly, we also observe the formation of an unusual ‘walnut’ shaped morphology which is the first of its kind in copper chalcogenide based systems. The study was also extended to investigate a series of injection temperatures, precursors, nature of solvents and ultimately understand
how seemingly minute changes in the reaction can significantly alter the nucleation and growth kinetics. The structure, shape and composition of these nanomaterials were subsequently investigated with transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX) and UV-vis-NIR techniques.

**Wednesday 10th September 12.15 - 12.30**
Tuning Electron Transfer Rates in QD-bridge-oxide Systems
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We quantify the rate and efficiency of picosecond electron transfer (ET) between quantum dots (QDs) and oxides as a function of QD-oxide coupling strength in QD–molecular linker–oxide systems. The electronic coupling is controlled through the nature and length of the molecular linker anchoring the QD donor to the oxide acceptor; optical pump-Terahertz probe spectroscopy is used to follow ET. Electron transfer rates are surveyed for two types of bridges based on n-methylene and n-phenylene moieties respectively. For both linkers, temperature independent-ET rates are found to decrease exponentially with molecular length, indicating that ET through the linker occurs as a tunnelling process characterized by decay factors \( ~0.85 \text{ Å}^{-1} \) and \( ~0.29 \text{ Å}^{-1} \), for aliphatic and aromatic bridges, respectively. These numbers imply larger barrier potentials for ET through aliphatic than aromatic linkers, and are in quantitative agreement with previous reports based on conductance measurements through single molecule junctions.

**Wednesday 10th September 12.30 - 12.45**
Seeded Growth in Continuous Flow: Novel Synthetic Route towards Tailor-made CdSe/CdS Nanorods for Optoelectronic Devices
Tobias Jochum, Christoph Gimmler, Daniel Ness, Jan Niehaus, Horst Weller
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Colloidal zero-dimensional semiconducting nanocrystals (NCs) have finally hit the market in large scale for display applications with the first quantum dots (QD)-enhanced TV having been placed in the market early 2013. The material for the next generation of optoelectronic devices will most likely be based on mixed dimensionality nanocrystals like CdSe/CdS dot-in-rod (DRs) nanoheterostructures. These nanoparticles consist of a spherical CdSe core and an elongated CdS shell resulting in a giant extinction coefficient below 450 nm. Additionally, these DRs obtain a high photoluminescence quantum yield achieving values up to 80 %, show thermal- and photooxidation stability, as well as polarized emission of light.

In order to produce these systems in a reliable and robust way, we have developed a continuous seeded growth reactor as synthesis approach to manufacture tailor-made CdSe/CdS NCs for optoelectronic applications and for satisfying industrial demand regarding quality and quantity. This technique is based upon a two step synthesis and guarantees automation, reproducibility and a high degree of control over each step of nanoparticles' growth. After purification of the obtained CdSe cores, these NCs are reintroduced into the reactor set-up. For the following shell synthesis, two different sections of the set-up are essential to mimic the classical hot-injection methodology guaranteeing high quality nanocrystals. On the one hand, a microfluidic mixing chamber which is heated individually to temperatures where nucleation takes place and on the other hand the growth oven, in which size and aspect ratio can be tailored by parameters like flow speed, precursor- and core-concentration.

Herein, we will present high quality DRs with various aspect ratios, the respective spectroscopic data and the set-up which is applied to synthesizing this material, as well as a model optoelectronic device showing their performance.

**Wednesday 10th September 12.45 - 13.00**
Automated Precision Synthesis of Nanocrystals
Johan Paul, Guido Huyberechts, Pieter Castelein, Jeroen Clarebout
A bottle neck that hinders valorisation studies of nanoparticles in functional materials is very often the limited capacity of research groups to synthesize sufficient amounts of nanoparticles that allow preliminary formulation or coating tests. Typical lab scale synthesis yields milligrams to grams of nanoparticle product. However, for first ‘tests’ in coating formulations, usually up to 10 to 100 g of material is required.

Additionally, material industries are struggling with a continuous need to reduce the time to market for new or improved products. High-throughput technologies can be applied for the accelerated discovery of new compounds, the optimization of synthesis conditions up to the extraction of synthesis knowhow.

Flamac has responded to these needs with the development of a unique automated parallel batch mode synthesis platform for nanocrystals. Additionally, automated purification of the nanocrystals, integrated into the platform, is readily developed. Batch synthesis with a capacity up to 10 g/day can be reached. The advantage of using a parallel reactor over simply increasing the reaction volume is that drastic changes of intrinsic synthesis parameters (such as heating up speed, stirring...) which are crucial for the final product, can be avoided. Furthermore, this strategy does not require significant changes of the available synthesis protocols. This is a significant advantage compared to continuous flow synthesis procedures.

Via this setup it is now possible to synthesize ‘tailor made’ nanoparticles at a reasonable scale to allow a first set of experiments to assess the potential of the nanoparticles in functional coatings.

The unique feature of the setup is that it both allows to focus on both high-throughput screening and volume synthesis objectives with the same equipment. It also generates information on reproducibility and repeatability. The variability analysis, together with the knowledge base on reaction chemistry-property relations, and the use and analysis of scalable reactor designs concepts assists in creating materials, data and information relevant for a subsequent upscaling process to industrial pilot scale levels.

This presentation will highlight the successful development and use of this unique platform in areas such as nanocrystals for printed photovoltaic applications. Additionally, the platform acts as an enabler for industrial research in various areas of nanomaterial synthesis and applications beyond photovoltaics.

### Wednesday 10th September 13.00 - 13.15

**Near Infrared LEDs Based on Core-shell PbS/CdS Quantum Dots with Inverted Device Structure**

Rafa S. Sanchez\(^a\), Enrico Binetti\(^b\), Jose A. de la Torre\(^a\), Germà García-Belmonte\(^a\), Marinella Striccoli\(^c\), Ivan Mora-Sero\(^a\)

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\(\text{b, Institute for Composite and Biomedical Materials, National Research Council, Via Sommarive, 14 - 38123 Trento, IT} \)

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Colloidal Semiconductors are extraordinarily appealing for the development of light emitting devices (LEDs) due to tunable and pure color emission, brightness and solution processability. This last advantage of the QD-LEDs is even more evident in the field of infrared emission where the devices currently used are prepared by high cost epitaxial techniques. We will show the fabrication of low cost NIR QD-LEDs based on high quantum yield core/shell PbS/CdS QDs and a novel inverted device structure. Devices are produced on glass substrates using SnO\(_2\):F (FTO) as conductive transparent contact, nanostructured TiO\(_2\) as electron transport layer (ETL) and poly(3-hexylthiophene) P3HT as hole transport layer (HTL). Despite the roughness of this ETL, the obtained external quantum efficiencies (EQE) are similar to previously reported values, obtained with regular configuration and more expensive ITO substrates. A turn-on voltage as low as the QD band gap (1.47 eV) is achieved for a large area (1.54 cm\(^2\)) and relatively stable QD-LEDs.

### Posters session

**Calculation of the Molar Extinction Coefficient of Spherical and Anisotropic CdSe/CdS Nanocrystals**

Ilaria Angeloni, Anatolii Polovitsyn, Rosaria Brescia, Giovanni Bertoni, Liberato Manna, Remo Proietti Zaccaria, Iwan Moreels
In this work we combine inductively coupled plasma optical emission spectroscopy (ICP-OES) with UV-VIS-NIR absorption spectroscopy and transmission electron microscopy to calculate the molar extinction coefficient of colloidal CdSe/CdS nanocrystals. These heterostructures allow the engineering of the band alignment, thus achieving a high photoluminescence quantum efficiency in combination with a controllable photoluminescence spectrum and lifetime, making them high-potential materials for diverse photonic applications.

Since these materials have a configuration in which the hole wave function is localized in the core, while a small conduction band offset allows the electron wave function to be delocalized into the shell region, they have a peculiar dependence of the molar extinction coefficient on size, composition and aspect ratio. We therefore characterized CdSe/CdS core/shell quantum dots and rods with various core/shell compositions and dimensions. From the molar extinction coefficient we obtained the absorption strength per nanocrystal, both at high energy as well as the band gap, and the concentration of nanocrystals in solution. We investigated the effect of shape on the (internal) electric field profile and compared experimental data with the values calculated in the framework of Maxwell-Garnett theory, to model the molar extinction coefficient dependency on aspect ratio and electron delocalization and obtain general calibration curves.

Posters session
Growth of Gold onto Semiconductor Ternary and Quaternary Nanorods to Form Metal-Semiconductor Hybrids

Louise Barry, Jianjun Wang, Shalini Singh, Pai Liu, Claudia Coughlan, Kevin M. Ryan
Department of Chemical and Environmental Sciences, Material and Surface Science Institute, University of Limerick, Castletroy, Limerick, 0, IE

In this study we have achieved gold growth on ternary and quaternary copper chalcogenide nanorods (Cu₂ZnSnS₄, CuInₓGaₓS₂ and Cu₂SnS₃) and on ternary alloyed cadmium chalcogenide NRs (CdSeₓS₁₋ₓ NRs). Nanorods (NRs) benefit from length dependent properties such as stronger dipole moments, linearly polarized emission along the c-axis, and enhanced light absorption. Also, compositional tunability in ternary and quaternary semiconductors allows modulation of the band gap as a function of the cation or anion ratios. The growth of a metal onto semiconductor NRs is an important integration step for device applications including nanoelectronics, photocatalysis, photovoltaics and biosensing. Two methods were employed to grow gold onto the NRs. The first method involved the reduction of a metal onto the nanorods directly in the organic phase using surfactants. The second method involved phase transferring the metal ions from the aqueous phase to the organic phase where they were reduced onto the dispersed NRs. We studied the effect of various growth conditions including valency of gold in the precursors, gold concentration, organic solvents and growth time and temperatures. In this study we have successfully yielded multiple gold tip growth on the NRs using both gold growth methods. Transmission electron microscopy was used to determine the shape of the as synthesized NRs and the size and position of the gold tips. X-Ray diffraction was used to determine the structure of the NRs.

Posters session
Surface Dependent Optical Properties of Silicon Carbide Quantum Dots

David Beke¹,², Zsolt Szekrényes³, Tibor, Z. Jánosi³, János Erostyák³, Katalin Kamaras³, Adam Gali¹,²
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Visual analysis of biomolecules is an integral avenue of basic and applied biological research. Quantum dots (QDs) are semiconductor inorganic nanoparticles that are emerging as alternative or complementary tools to the organic fluorescent dyes currently used in bioimaging. Although these QDs have great potential as probes for bioimaging, certain limitations may restrict their applications. Cytotoxicity strongly influencing is one of the major limiting factors for the application of II-VI QDs in efficient in vivo imaging. We propose silicon carbide (SiC) QDs for bioimaging in order to eliminate
numerous disadvantages of traditional QDs. SiC is a stable, chemically inert wide band gap indirect semiconductor. Biocompatibility of bulk SiC and SiC QDs has been proven by several research teams. We developed a two-step experimental routine based on SHS synthesis and wet chemical etching for producing luminescence SiC QDs with high quantum yield. These SiC QDs are less than 3 nm in diameter and make stable colloid sol in polar solvents like water without the need of any surfactant or capping layer thanks to the surface termination that was studied by infrared spectroscopy. We demonstrate that the optical properties of SiC QDs are highly influenced by the chemical surface groups. Luminescence of SiC QDs was studied with time resolved luminescence spectroscopy on different surface terminated SiC QDs to understand the physics behind the complex luminescence process. The synthesis method and further chemical modification of the surface allow us to tune the optical properties and the sensitivity of the QDs making narrow luminescent peak or change the chemical environment sensitivity of the optical properties. Reduced surfaces show less pH sensitivity while carboxyl terminated SiC QDs have effective optical responses to pH change making them applicable for intracellular pH measurement or in harsh environment.

Posters session
Electronic Coupling between Dye Molecules and CdSe-Core and CdSe/Core-Shell Nanocrystals
Anne Bottin\textsuperscript{a}, Lars Dworak\textsuperscript{b}, Zhihong Liu\textsuperscript{c}, Klaus Müllen\textsuperscript{b}, Josef Wachtveitl\textsuperscript{b}, Thomas Basché\textsuperscript{a}
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CdSe and CdSe/CdSe/ZnS core shell quantum dots were prepared and coupled to a rylene-diimide dye (DYE) furnished with a di-carboxylate anchor. The resulting complexes with different DYE-to-QD ratios were investigated using steady-state and time-resolved absorption and fluorescence spectroscopy.

In the case of CdSe/CdS/ZnS-QDs, energy transfer from QD to DYE occurred when QDs were excited. From femtosecond transient absorption (TA) spectroscopy, the energy transfer rate could be determined and used to calculate the absolute and relative DYE-to-QD ratios in various samples.

Remarkably, in contrast to the DYE-CdSe/CdS/ZnS system, in the DYE-CdSe system the TA measurements indicated that after energy transfer from excited CdSe to DYE electron transfer occurred from the CdSe ground state to the excited state of DYE. This finding was corroborated by measuring the fluorescence decay time of the selectively excited DYE in the complexes by time-correlated single photon counting. The experiments showed that an additional component appeared in the fluorescence decay whose time constant decreased with increasing DYE amount.

Posters session
Efficient Light Absorption Modulation in Germanium Nanostructures
Salvatore Cosentino\textsuperscript{a}, Rosario Raciti\textsuperscript{a}, Eric Barbagiovanni\textsuperscript{a}, Emel S. Ozen\textsuperscript{b}, Isodiana Crupi\textsuperscript{a}, Maria Miritello\textsuperscript{a}, Giuseppe Nicotra\textsuperscript{a}, Salvatore Mirabella\textsuperscript{a}, Corrado Spinella\textsuperscript{a}, Atilla Aydinli\textsuperscript{b}, Domenico Pacifici\textsuperscript{a}, Antonio Terrasi\textsuperscript{a}
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Ge nanostructures (NS) are gaining a renewed interest because of their lower synthesis temperature, larger optical absorption and stronger quantum confinement effect (QCE) compared to Si NS. Ge NS are now valuable candidate for applications in optoelectronics and photovoltaics. In this work we report on the fundamental mechanisms of light absorption in Ge NS and how to efficiently control the light harvesting by acting on the fabrication process.

In particular, structural and optical characterizations are presented for single amorphous Ge quantum well (QW) grown at room temperature by magnetron sputtering deposition. We used transmission electron microscopy (TEM) and rutherford backscattering spectrometry (RBS) to measure the QW thickness (2-30 nm) and atomic density. The optical absorption of single amorphous Ge QW evidences a marked blue-shift (from 0.8 to 2.1 eV) and an enhanced oscillator strength with reducing
the QW thickness. The experimental values of the bandgap and oscillator strength have been modelled in agreement with the effective mass approximation (EMA) model, demonstrating a strong QCE of excitons occurring at room temperature for amorphous Ge QWs.

Though size-dependent bandgap is typically advocated for tuning the light absorption in NS, it is essential to disentangle the role of size from other effects related to the hosting matrix or synthesis techniques. For this reason, we performed a detailed investigation on Ge quantum dots (QDs) synthesized by annealing of Ge-rich SiO$_2$ or Si$_3$N$_4$ thin films produced by magnetron sputtering and plasma enhanced chemical vapor deposition. Si$_3$N$_4$ matrix hosts QDs at higher density and lower size than SiO$_2$, with Raman spectroscopy revealing a higher threshold for the amorphous-to-crystalline transition. Light absorption spectroscopy shows a clear size-dependent shift in the optical bandgap, between 1.4 – 2.5 eV, that was modeled using EMA or a spatially dependent effective mass (SPDEM) approximation. The reported QCE was exploited to enhance the light harvesting efficiency of Ge QDs-based devices. We demonstrate a tunable, and high photoconductive gain (up to 15x) in metal-insulating-semiconductor photodetectors based on a preferential trapping of photo-generated holes by QDs that enhance the charge carrier collection. These results demonstrate the potentiality of Ge QDs as active material for the development of efficient light harvester and solar cells.

**Posters session**

Shape Controlled Colloidal Synthesis of Polytypic Cu$_2$ZnSn($SSe$)$_4$ Semiconductor Nanocrystals

Shalini Singh, Claudia Coughlan, Kevin M. Ryan

*University of Limerick, Ireland, Materials & Surface Science Institute, University of Limerick, Limerick, IE*

Occurrence of polytypism in II–VI and III–V semiconductors has been broadly observed due to the stacking faults between lattice planes. Zinc Blende and wurtzite are the two very commonly observed polymorphs. Due to low energy difference between these polymorphs, switching between them can be possible either kinetically or by selective ligand attachment. This allows the tuning and fabrication of complex shaped nanocrystals. Since the modification in crystal structures induces changes in optical, electronic, and other properties, these polytypic nanocrystals, having engineered structural faults, are expected to provide new possibilities for photovoltaic and optoelectronic devices. In colloidal based approaches, binary chalcogenide nanocrystals such as CdSe and CdTe are well known examples of linear and branched polytypic II–VI semiconductors. However, ternary and quaternary copper-based chalcogenides are more complex systems for phase control due to their intense atomic organization, involvement of various ligands in synthesis and wide range of composition variation. Recently, linear polytypism in CZTSSe$_2$ and branched polytypism in CTS$_2$ and CCTSe$_3$ has been reported, giving a new direction to the shape and phase controlled multicomponent copper chalcogenide nanocrystals.

Here, we have explored various possibilities of formation of different shaped linear and branched polytypic Cu$_2$ZnSn($SSe$)$_4$ nanocrystals via colloidal synthesis. In our studies, we designed synthetic routes to form novel morphological structures of polytypic Cu$_2$ZnSn($SSe$)$_4$ nanocrystals by different approaches such as ligand variation, phase transformation and different metal precursors- (i) Cu$_2$ZnSn($SSe$)$_4$ monopods having a pyramidal shaped zinc blend core with a wurtzite arm emerging from one of the faces, (ii) Cu$_2$ZnSn($SSe$)$_4$ rugby shaped nanocrystals two zinc blend-derived ends and one wurtzite-derived centre part, (iii) Cu$_2$ZnSn($SSe$)$_4$ bullet shaped polytypic nanocrystals via phase transformation of wurtzite Cu$_2$ZnSn($SSe$)$_4$. The synthesis of these different polytypics has been tried on various Se/S compositions. The effect of different reaction parameters has been extensively studied and focus has been given on the formation mechanism of polytypes. The nanocrystals have been characterized by TEM, STEM, EDX, SEM, XRD, UV-vis NIR techniques. These polytypic nanostructures are being expected to open up new avenues to band-gap alignment and engineering.

**Posters session**

A In Silico Method of Designing Compounds with Aimed for Functionality as Semi-conductors in Targeted Contexts

Catherine Kari Derow

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A program to design the best semi-conductor materials meeting various performance standards relating to functionality in target contexts, could be designed. This program could use empirical and
projected data, relating to conductivity, temperature and pressure-related properties in order to design semi-conductors as required. The program would be based on decision tree form algorithm. Thus with the required performance data loaded, the program could work in a combinatorial manner to find the best semi-conductor compound meeting questions asked in a decision tree manner, e.g., a soft metal halide or transition metal oxide, in terms of conductivity in terms of load and velocity, temperature and pressure-related properties and other properties such as how brittle or flexible, as well as longevity given the projected workload. The level of importance of each criterion could be ranked, e.g., temperature might the most important and thus compounds suitable with respect to this criterion selected and then ranking in terms of the other properties would follow. A final list could deliver compounds ranked with respect to these requirements. Thus, for example, the program might first considering temperature related features and considering compounds in a combinatorial fashion, find a range that meet that criteria, then for example flexibility could be considered and the compounds found to be suitable in terms of temperature could be ranked in terms of required flexibility of the material and so on in the order of priority in terms of required properties. Triangulation would allow the optimum semi-conducting material to be chosen, given the relative importance of the various criteria and the semi-conductor’s properties as ranked with respect to various aspects under consideration. In this way, circuitry could be designed for all types of computational devices, from super-computers, laptops and tablets, to computational hardware relating to such devices as mobile telephones, portable mp3 players as well as home entertainment systems. After in silico design of a semi-conducting material, empirical studies could be used to confirm and indeed optimize the choice of material for the target device and context.

Posters session
Exploring Exciton Relaxation and Multi Exciton Generation in PbSe Nanocrystals Using Hyperspectral near IR Probing
Itay Gdor, Chunfang Yang, Diana Yanover, Hanan Sachs, Efrat Lifshitz, Sanford Ruhman
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A novel ultrafast transient absorption spectroscopy is employed to detect and quantify multi exciton generation (MEG) in lead selenide (PbSe) nanocrystals. This involves comparing signals obtained in “equivalent” experiments conducted with two different pump photon energies one below and the other well above the theoretical threshold for MEG, at 800 and 400 nm respectively. This “equivalence” involves production a similar distribution of absorbed photons at both photon energies. This can be guaranteed by preparing samples of identical optical density at each pump wavelength and scaling the pump pulse intensities inversely the extinction coefficient. Thus ambiguity due to direct multi-photon excitation, uncertainties of absolute absorption cross sections, and low signal levels are overcome. The results show that a single scaling factor, related to the ratio of the samples absorption cross sections at both excitation wavelengths, brings the spectral and temporal cuts after 400nm and 800nm into perfect overlap. In particular, no excess in bleach is observed at early times after 400 nm excitation, which would be indicative of the presence of extra carrier. The satisfactory match of spectra at all delays through the described scaling demonstrates the absence of carrier multiplication up to a photon energy level of 3.7 times the band gap. Beyond the issue of carrier multiplication, Following the Exciton cooling during the first few picoseconds reveals; 1) at both pump wavelengths, the entire transient spectrum seems at early delays to be dominated by a broad absorptive background extending throughout the probed range. 2) The apparent background is broader when exciting with the more energetic photons. 3) The amplitude of the localized bleaching component at the band edge is nearly conserved during the process of cooling independent of the exciting photon energy.

Posters session
Molecular-level Control of Broadband Optical Absorption and Self-assembly of Colloidal Quantum Dots and its Relevance to Solution-processed Photovoltaics
Carlo Giansante
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Colloidal quantum dots (QDs) are among the most attractive photo-active materials to be exploited for solution-processed optoelectronic applications. To this aim, replacement of the surface-bound bulky electrically-insulating ligands coming from the synthetic procedure is mandatory. Here we demonstrate that tailoring QD surface chemistry with suitable short molecules permits to (i) tune their optical absorption properties and (ii) mediate non-covalent interactions with the surroundings, while preserving good long-term colloidal stability. Indeed, rational design of anchoring and pending moieties which constitute the replacing ligand framework is exploited to (i) enhance broadband solar-light absorption of colloidal QDs and to (ii) dictate the morphology of hybrid composites with conjugated polymers during formation from blend solutions, thus markedly affecting the resulting optoelectronic properties. The relevance of our approach is demonstrated by (i) achieving an optical absorbance increase in the UV-Vis-NIR spectral range larger than 300 % for colloidal PbS QDs and by (ii) fabricating hybrid solar cells based on poly(3-hexylthiophene)/PbS QD nanocomposites which display a power conversion efficiency that reaches 3 %, far beyond any previous report for this blend. Interfacial photo-induced processes, investigated by (quasi)steady-state and time-resolved photo-induced absorption and luminescence spectroscopy, are discussed.

We thus provide straightforward evidence that ligands at the QD surface do not merely confer colloidal stability, while hindering charge separation and transport, but represent a simple yet powerful tool to gain control over the macroscopic optoelectronic properties of colloidal QD and solids thereof. More broadly, organic ligands and inorganic cores are inherently coupled materials which may be considered as a whole system rather than the sum of the components.

**Posters session**

**A Facile Route to Ligand Exchange for Efficient Colloidal Quantum Dot Photovoltaics**

Ahmad Kirmani\(^a\), Graham Carey\(^b\), Maged Abdelsamie\(^a\), Buyi Yan\(^a\), Dongkyu Cha\(^a\), Lisa Rollny\(^b\), Xiaoyu Cui\(^c\), Edward Sargent\(^b\), Aram Amassian\(^\ast\)

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State-of-the-art colloidal quantum dot (CQD) solar cells have been shown to achieve power conversion efficiencies (PCEs) approaching 9%. However, deposition of the CQD absorber layer is tedious requiring a layer-by-layer (LbL) buildup and is a major obstacle to industrial scale-up. Understanding why the LbL process is needed to achieve state-of-the-art devices is crucial to improving manufacturability and to improving solar cells further. In this study we have sought to evaluate the solvent-QD interactions in terms of physical and chemical changes to the CQD absorbing layer in order to identify an alternative and more facile ligand exchange route. We have demonstrated that an extended exposure of CQD films to methanol (MeOH) is harmful for the overall performance. This explains why the standard CQD solar cells made with MeOH require tedious LbL buildup involving nearly a dozen steps.

Understanding of solvent interactions with QD films has led us to develop more efficient processing conditions based on use of acetonitrile (ACN) which allow us to achieve state-of-the-art performance in only three steps. This work could shed light on ways to achieve a single step deposition and solid-state ligand exchange.

**Coupling NIR PbS QDs and Graphene-based Materials for Photovoltaic Applications**

Beatriz Martin-Garcia, Mirko Prato, Liberato Manna, Iwan Moreels

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In quantum dot (QD) solar cells it has already been shown that the incorporation of graphene enhances the photocurrent due to its extraordinary electron transport properties. However, only few experimental studies, mainly carried out with cadmium-based QDs, were focused on the understanding of the electronic interaction between the QDs and graphene sheets in the composite. Therefore, we
developed QD-graphene hybrid inks with highly efficient charge transfer from the QDs to graphene, based on different QD and graphene synthesis procedures and coupling strategies. The key point is to enhance the graphene light absorption by broadening the spectral range with NIR PbS QDs. We have prepared stable hybrid solutions using ligand-modified PbS QDs, and chemically reduced graphene oxide (RGO) or liquid-exfoliated graphene (GLE) (from graphite as carbon source).

When keeping a constant concentration of QDs in solution, we observed that their PL emission properties were quenched when decreasing the degree of reduction of the graphene (which was verified with XPS), and increasing the concentration of the graphene-based materials. The strongest quenching effect has been observed using GO-based materials. This can be ascribed to a greater electron-accepting and interacting capacity of the GO derivatives.

Apart from the optical characterization, the TEM images of the QD-graphene composites show that it is possible to modulate the QD coverage and dispersion on the graphene sheets varying the coupling strategy used to prepare the hybrid ink.

**Posters session**

Anomalous Band Gap of ZnO Crystal Surfaces: Effect on Sensitized Solar Cell

Shaibal Sarkar, Neelam Rathore

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ZnO, with a high band gap and tunable nanostructures, is a well known material for sensitized solar cell. There have been several examples, where ZnO nanorods thin film is used as electron conductor for sensitized solar cell. But it has often been seen that the ZnO nanorod solar cell has never crossed the efficiency produced by TiO2 solar cell inspite of having single crystal nanorod structure and higher surface area. Several reasons have been given for it eg. Non conformal deposition of absorber layer, shunt and series resistance due to hole conductor etc.

We propose that the fundamental reason for the lesser efficiency of ZnO nanorod based solar cell is the complete ignorance about the anomalous behavior of different crystal surfaces and the band gap of different crystal surfaces. The band gap of (0002) and (11-20) crystal surfaces is 3.2 eV (same as bulk ZnO), while for (10-10) surfaces is 2.85 eV-1 eV. The (10-10) crystal surface forms more than 80% of the ZnO nanorod crystal surface area. With lower band gap of (10-10) nanorod crystal surface, the conduction band (CB) edge goes down with respect to the absorber (CdS, Sb2S3) CB edge. This may cause a lower transition rate of the carriers (in accord with the Fermi’s golden rule), and thus a lower charge separation. Also the (0002), (000-2) and (10-10) surfaces have different schottky barrier heights for different semiconductor and metal junctions. These surfaces also differ in their mobility, defect density, surface energy and available density of states.

Due to these fundamental differences, we see that the ZnO nanorods have never performed as good as TiO2 mesoporous structures for solar cell applications. On depositing TiO2 on ZnO, we are able to increase the efficiency of solar cell as it forms a cascading conduction band structure, which helps in better charge separation. Also it is seen that, a flat layer of ZnO results in better solar cell as compared to nanorods, because we don’t have to fight with anomalous band gaps, electron mobility etc.

**Posters session**

Independently Blinking Bands in the Spectra of Single CdSe Nanowires

Aina Reicch, Dennis Franz, Zhe Wang, Tobias Kipp, Alf Mews

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CdSe nanowires (NWs) are structures with high absorption cross sections and easy current flow along their long axis – desirable properties for applications, for example in photovoltaics. Additionally, easily affordable methods of chemical synthesis can be used to prepare nanowires with different structural properties. Specifically quantum nanowires (QNWs) – nanowires with radii below the exciton Bohr radius – are of interest, as the wires’ effective band gaps depend on their respective radius.

Photoluminescence spectroscopy of single QNWs can give valuable information about the NWs’ electronic structure and charge carrier dynamics. Confocal microscopy and spectroscopy of single QNWs at temperatures at about 5 K yield additional information. The single broad band which can be observed at room temperature splits into several narrow bands. The definition and narrowness of these bands is
highly dependent on the individual wire samples but can be reproduced within each batch – i.e. synthesis – of wires.

We show for the first time that for QNWs the spectrum consists of two groups of several sharp peaks. The peaks of the high energy group are narrowly spaced. The spectrum's low energy side consists of one or more bands with pronounced LO phonon replicas. Both groups are subject to a spectral shift to higher energies with decreasing wire diameter.

In both spectral groups the bands are highly dynamic in terms of spectral position and intensity. Both groups show apparently independent spectral shifts, as well as particular intensity fluctuations on remarkably different time scales. The low energy bands show discrete On and Off states with the dark states of these bands lasting up to a minute. The high energy bands fluctuate on a much smaller time scale.

Our experimental findings can be explained by model calculations based on the effective mass approximation. By assuming the occurrence of positively and negatively charged defect sites as steep potential traps in the QNW the low energy side of the spectrum can be explained. These phonon-assisted peaks arise from recombinations of charge carriers, each trapped by such a site. This is analogous to the donor–acceptor pair recombinations commonly assigned in bulk CdSe fluorescence spectra. The higher energy bands accordingly result from recombinations of free or nearly free excitons bound to very shallow potential undulations.

**Posters session**

Spectroscopic Study of Hole and Electron Transfer in PbS Quantum Dot Blends and Bilayers

Irene Sanchez-Molina, Andrew M. Telford, Jason Rohr, Jenny Nelson, Saif A. Haque  
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Blends and bilayers of PbS quantum dots (QDs) and different organic materials have been prepared with the aim of systematically studying electron and hole injection into the QDs. A set of polymers (P3HT, PCPDTBT, PBTT) with higher LUMO than the conduction band of the QDs has been chosen as electron donor material. Organic molecules (Spiro-OMe-TAD, C_{60} fullerene, C_{60}-PCBM) with a HOMO deeper than the valence band of the QDs have been employed as electron acceptor materials. A spectroscopic study, including techniques as UV-vis absorption, photoluminescence, and transient absorption spectroscopy, has been carried out on the samples. The results comprise a first set of data that will be employed for the design of QD sensitized hybrid solar cells. Recently, an PCE of 5.50% has been reported in a bilayer solar cell where the active layer contained PbS,Se, QDs and a low band-gap polymer, a result that may be improved with the fabrication of blends that provide a higher interface for exciton dissociation.

**Posters session**

Semiconductor Nanocrystal Doping with Manganese Ions

Andriy Savchuk, Oleksandr Savchuk, Petro Tkachuk, Ihor Stolyarchuk  
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Doping of semiconductors with magnetic impurities has led to formation of new class of materials, diluted magnetic semiconductors (DMSs). The most studied during last few decades are Mn-doped II-VI based DMSs. Dopant-carrier exchange interactions or so-called sp-d spin interactions are responsible for large Zeeman spin splitting of the excitonic or band states and giant magneto-optical Faraday rotation. Implementation of such a kind of magnetic doping for nanostructured materials type of nanocrystals or quantum dots gives rise to new ways of manipulating polarization of the spins of carriers and dopants. However, in this particular case there appeared problems in introducing the impurities into nanocrystals. For instance, it was revealed that the impurity atoms prefer to allocate at the surface of the nanocrystals. Up to now, the mechanism that controls dopant incorporation into nanoparticle is not fully understood. Available theoretical models are mainly applied to chemically synthesized colloidal DMS nanocrystals. No doubt, there is need in extension of such studies for the other nanocrystal synthesis techniques. In this study, we compare optical and magneto-optical properties of Mn-doped semiconductor CdS, CdTe nanocrystals prepared by different physical and chemical methods. As physical techniques we have applied ball milling or mechanical synthesis, melting powder mixtures of
semiconductor and glass components, and laser ablation technique. The aqueous solution precipitation technique has served as chemical method. The Cd$_{1-x}$Mn$_x$Te solid solution nanocrystals with Mn content $x$ in range of (0 – 0.45) were synthesized using all the mentioned physical methods and CdS:Mn nanocrystals were prepared by the aqueous solution precipitation technique. All the samples were characterized by optical absorption, photoluminescence, and Faraday rotation spectroscopy.

Contribution of magnetic ion doping was clearly visible from photoluminescence and Faraday rotation spectra. In photoluminescence spectra of Mn-doped DMS nanocrystals there appeared emission bands due to Mn$^{2+}$ ions and their intensity increased with increasing of Mn$^{2+}$ content. In case of CdS:Mn nanocrystals, the observed spectral dependences of the Faraday rotation confirm small contribution of sp-d exchange interaction and surface character of Mn$^{2+}$ ion distribution.

**Posters session**

Multiple Exciton Generation Dynamics in PbS Quantum Dots Characterized Using A Transient Grating Technique

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In recent years, multiple exciton generation (MEG) in semiconductor quantum dots (QDs) has received much interest, because MEG has a potential to produce an appreciable improvement in a energy conversion efficiency of solar cells through increased photocurrent. MEG in some QDs such as PbSe, PbS, CdSe, PbTe, and Si QDs has been observed at threshold photon energies of 2-3 times the HOMO-LUMO transition energy ($E_g$) using transient absorption spectroscopy and time-resolved photoluminescence. However, several recent reports have questioned the experimental results on the quantum yields of MEG in QDs and even its existence. Further theoretical and experimental studies to better understand the mechanism and occurring conditions of MEG in QDs are necessary and important.

In this study, we apply an improved transient grating (TG) technique to characterize hot carrier cooling and MEG in PbS colloidal QDs.

The improved TG technique is one kind of pump-probe methods and transient refractive index changes in the sample due to photoexcited carriers can be measured. Thus, ultrafast photoexcited carrier dynamics can be monitored by using this technique. In this study, the pump light wavelength was changed from 290 nm to 520 nm. The probe light wavelength was 775 nm.

We have characterized pump light intensity and photon energy dependences of the TG responses in PbS colloidal QDs. We found that besides a peak existing at about 300 fs in the TG responses, a new peak appeared at about 3 ps when the photon energy of the pump light is larger than 2.7$E_g$ as shown in Fig. 1. The new peak intensity decreased as the photon energy of the pump light decreased and the peak disappeared for the photon energies smaller than 2.7$E_g$. In addition, a fast Auger recombination decay with a decay time of about 100 ps was observed when the photon energy is larger than 2.7$E_g$. We think that the first peak at about 300 fs resulted from photoexcited hot carriers and the second peak at about 3 ps resulted from MEG in the PbS QDs. We succeeded in separate detection of hot carrier and MEG in PbS colloidal QDs.

**Posters session**

Hot Exciton Relaxation in PbSe Quantum Dots

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Semiconductor nanocrystals are of great promise to develop highly efficient photovoltaic devices. This is caused in particular by the possibility of exciting two or more electrons over the band gap after absorption of only a single photon, via a process known as Carrier Multiplication (CM). One particularly important aspect of carrier multiplication is the rate of hot carrier cooling, which occurs in competition with CM. So far cooling rates have been investigated for charges with a relatively small excess energy. The cooling rates relevant to CM however are those at high energy above the band edge. In addition, spectroscopic studies into carrier cooling have not distinguished between electron and hole cooling.
Here we present an ultrafast White-Light Transient Absorption study of charge signatures at high excess energy. We distinguish between electron and hole cooling via addition of electron acceptors. The determined cooling rates have direct relevance for the efficiency of CM and lead to more insight into the electronic structure of PbSe quantum dots.

**Posters session**

**Electron Transfer Efficiency in QD-oxide Systems: Atomic vs Molecular Passivation**

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Effective passivation schemes for solution processed quantum dots (QDs) are essential for the successful implementation of QDs in optoelectronic devices. In this contribution, we explore the interplay between electron transfer (ET) efficiency and surface passivation (atomic vs molecular) for QDs grown by the successive ionic layer adsorption and reaction (SILAR) method onto a mesoporous oxide phase. Complete- and half- SILAR cycles provide QDs which are defined by anion and cation rich surfaces, respectively. Atomic and molecular passivation can be achieved by simple post-growth treatments. Optical pump-THz probe (OPTP) spectroscopy reveals that the electron transfer efficiency from PbS QDs to SnO\(_2\) is maximized in QDs with lead-rich surfaces (terminated by half SILAR cycle). This effect is can be explained by the atomic surface passivation of QDs provided by lead cations - in perfect agreement with theoretical calculations. The cation passivation efficiency is found to be QD size dependent, and increases linearly with QD surface area. This surface area-dependence points to a kinetic competition between electron trapping at the QD surface and ET to the oxide. Finally, we demonstrate that the improvement in ET efficiency obtained for atomically passivated QDs is in quantitative agreement with results achieved with thiol-based passivating molecules.

**Posters session**

**Chemically Stable Halogenated PbS Nanoparticles**

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Lead chalcogenide nanoparticles have a large Bohr radius and therefore they attract a lot of scientific attention for fundamental studies of strongly confined quantum systems. However, their limited chemical stability requires encapsulation of the devices under inert conditions, prevents a study of their properties under ambient conditions (without host matrix) and hinders their encapsulation in electro-optical devices. Over years, various post-synthesis passivation techniques were examined. However some of them are complex, safety dangerous and time consuming. Recently synthesis in situ surface passivation approach was proposed. This technique makes it possible to synthesize PbS and PbSe nanoparticles that show stable photoluminescence quantum efficiency in TCE solvent other a month. Here we report spectral and temporally resolved results of chlorine passivated PbS in tetrachloroethylene solution (TCE) and as a film. The films were examined upon exposure to air and to different chemical species that are used in microelectronics fabrication processes. The experimental results show excellent chemical stability and exhibit signatures of energy transfer in film.