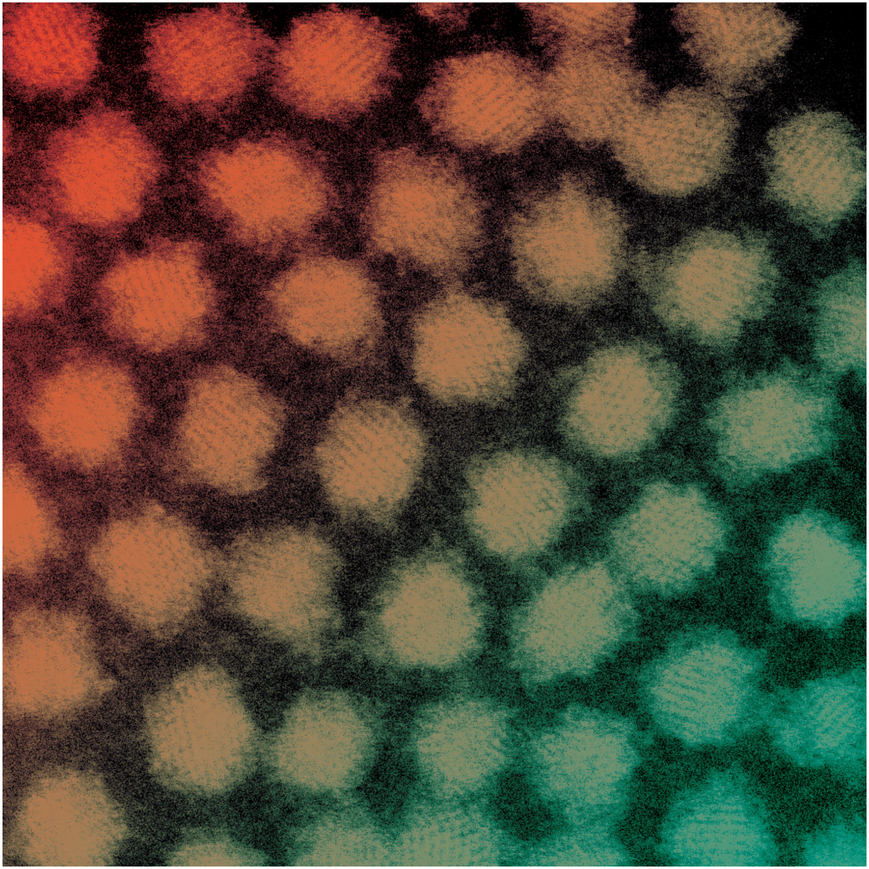
Programme and abstracts



# Colloidal Quantum Dots and Nanocrystals

**14–15 July 2014**
**Chancellors Hotel and Conference Centre,**
**Manchester, UK**

**http://cqdn2014.iopconfs.org**

Organised by IOP Quantum Electronics and Photonics Group

IOP Institute of Physics

# FORTHCOMING INSTITUTE CONFERENCES
# AUGUST 2014 – AUGUST 2016

## 2014

**26–28 August**
**IPTA 2014: Inverse Problems from Theory to Application**
At-Bristol, Bristol, UK
*Organised by IOP Publishing*

**1–4 September**
**Photon14**
Imperial College London, London, UK
*Organised by the IOP Computational Physics, Instrument Science and Technology, Optical, Quantum Electronics and Photonics and Quantum Information, Quantum Optics and Quantum Control Groups*

**3–5 September**
**Physics meets Biology**
University of Oxford, Oxford, UK
*Organised by the IOP Biological Physics Group*

**4–5 September**
**International Conference on the History of Physics**
University of Cambridge, Cambridge, UK
*Organised by the IOP History of Physics Group*

**15–19 September**
**Quantum, Atomic, Molecular and Plasma Physics (QuAMP) Summer School**
Durham/Newcastle University, UK
*Organised by the IOP Atomic and Molecular Interactions, Molecular Physics, Plasma Physics, Quantum Electronics, and Photonics and Quantum Optics, Quantum Information and Quantum Control Groups*

**16–18 December**
**Topical Research Meeting on Hybrid Quantum Systems**
National College for Teaching and Leadership, Nottingham, UK
*Organised by the IOP Quantum Optics, Quantum Information and Quantum Control Group*

## 2015

**29 March – 2 April**
**Microscopy of Semiconducting Materials (MSM-XIX)**
Murray Edwards College, Cambridge, UK
*Organised by the IOP EMAG Group*

**30 March – 2 April**
**Interdisciplinary Surface Science Conference (ISSC-20)**
University of Birmingham, Birmingham, UK
*Organised by IOP Thin Films and Surfaces Group*

**12–15 April**
**2015 Joint UK-Japan Workshop on Physics and Applications of Superconductivity**
King's College, Cambridge, UK
*Organised by the IOP Superconductivity Group*

**12–16 April**
**Electrostatics 2015**
Southampton Solent University, Southampton, UK
*Organised by the IOP Electrostatics Group*

**18–22 May**
**Nuclear Physics in Astrophysics VII: 28th EPS Nuclear Physics Divisional Conference**
The Royal York Hotel & Events Centre, York, UK
*Organised by the IOP Nuclear Physics Group*

**9–10 July**
**Physics of Emergent Behaviour 2015**
Science Museum, London, UK
*Organised by the IOP Biological Physics Group*

**6–9 September**
**Sensors & their Applications XVIII**
Kingston University, Surrey, UK
*Organised by the IOP Instrument Science and Technology Group*

**8–10 September**
**Physical Aspects of Polymer Science**
University of Manchester, Manchester, UK
*Organised by the IOP Polymer Physics Group*

## 2016

**13–15 January**
**15th Anglo-French Physical Acoustics Conference**
Selsdon Park Hotel, Surrey, UK
*Organised by the IOP Physical Acoustics Group*

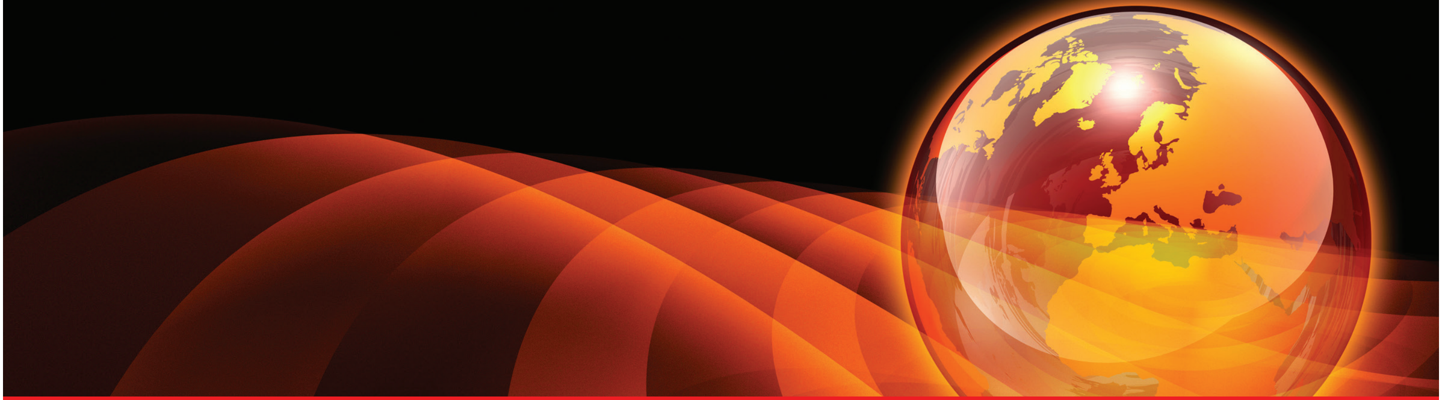
**3–9 July**
**The XXVII International Conference on Neutrino Physics and Astrophysics**
Royal Geographical Society, London, UK
*Organised by the Institute of Physics*

**22–26 August**
**Joint European Magnetic Symposia (JEMS)**
SECC: Scottish Exhibition and Conference Centre, Glasgow, UK
*Organised by IOP Magnetism Group*

See **www.iop.org/conferences** for a full list of IOP one-day meetings.

The conferences department provides a professional event-management service to IOP's subject groups and supports bids to bring international physics events to the UK.

Institute of Physics,
76 Portland Place, London W1B 1NT, UK
Tel +44 (0)20 7470 4800
E-mail **conferences@iop.org**
Web **www.iop.org/conferences**



**IOP** Institute of Physics

Colloidal Quantum Dots
and Nanocrystals

# Welcome

On behalf of the Quantum Electronics and Photonics Group of the Institute of Physics, we welcome you to ‘Colloidal Quantum Dots and Nanocrystals’.

The aim of this meeting is to bring together a diverse community in the UK and further afield: the chemists, material scientists, and physicists who synthesize, characterise and model these materials, and who seek to exploit their properties in applications such as solar cells, displays and lasers. We are in an exciting period at the moment, with devices based on colloidal dots making important advances in efficiency, making this meeting particularly timely and, we hope, lively. We have chosen to co-locate the accommodation and the conference venue in Chancellor’s Hotel and to give the conference a ‘lunchtime-to-lunchtime’ format to encourage as much interaction between the attendees as possible. As we all know, at the most successful conferences the informal discussions in between sessions or over an evening meal can be just as useful as the formal programme, and can be the seed from which successful future collaborations grow.

Finally, we would like thank all our session chairs and contributors, particularly the invited speakers and those who have travelled from overseas, for making for what promises to be an excellent programme. We would also like thank the Institute of Physics for organising the conference and for their financial contribution.

**Conference Chairs:**

Dr David Binks (University of Manchester)

Dr Jason Smith (University of Oxford)

# Colloidal Quantum Dots and Nanocrystals

## Programme

### Monday 14 July

12:00 Arrival and registration

12:30 Lunch

13:25 **Welcome**
D J Binks, University of Manchester, UK / J Smith, University of Oxford, UK

#### Session 1 - Synthesis

Chair: Dr Mark Green, King's College London, UK

13:30 **(invited) Material design at the nanoscale: how to control optical properties through nanocrystal size, shape and interface engineering**
I Moreels, Istituto Italiano di Tecnologia (IIT), Italy

14:00 **Zinc nitride nanocrystals - synthesis and characterisation**
P N Taylor, Sharp Labs of Europe, UK

14:15 **Synthesis and surface engineering of group IV semiconducting nanocrystals for photovoltaic applications**
D Mariotti, NIBEC - University of Ulster, UK

14:30 **Synthesis of III-V nanocrystals and passivation with $InCl_3$**
C Lydon, University of Manchester, UK

14:45 **Flow synthesis of silver nanowires for transparent conducting electrodes**
T W Phillips, Imperial College London, UK

15:00 **Growth mechanis of InP/ZnS nanocrystals from single molecular ZnS precursors at the moderate low temperature**
L Xi, Forschungszentrum Juelich, Germany

15:15 Refreshment break

#### Session 2 - Characterization

Chair: Dr Sarah Haigh, University of Manchester, UK

15:45 **(invited) Coherent exciton dynamics in quantum dots**
W Langbein, Cardiff University, UK

16:15 **Ultrafast charge dynamics in monodisperse Au nanoparticles on colloidal $TiO_2$ spheres**
M A Leontiadou, University of Manchester, UK

16:30 **Chlorine-passivated colloidal quantum dots - using depth-profiling synchrotron radiation x-ray photoelectron spectroscopy to study the shell structure**
H Radtke, University of Manchester, UK

| | |
|---|---|
| 16:45 | Break |
| 17:30 | **Poster session** |
| 18:30 | Break |
| 19:30 | **Dinner** |

## Tuesday 15 July

| | |
|---|---|
| 09:00 | **(plenary) Dark and photo-conductivity in ordered array of nanocrystals**<br>A L Efros, Naval Research Laboratory (NRL), USA |

### Session 3 - Modelling

Chair: Professor Stanko Tomic, University of Salford, UK

| | |
|---|---|
| 09:30 | **(invited) From semiconductor nanocrystals to artificial graphene and topological insulator**<br>C Delerue, IEMN, France |
| 10:00 | **(invited) Photoinduced carrier trapping in semiconductor nanocrystals**<br>M Califano, University of Leeds, UK |
| 10:30 | **Theoretical studies of biexciton binding energy in CdSe/CdTe core/shell type II quantum dots**<br>J M Miloszewski, University of Salford, UK |
| 10:45 | **Phonon-enhanced coherent scattering in a driven quantum dot**<br>A Nazir, University of Manchester, UK |
| 11:00 | Refreshment break |
| 11:30 | **Geometry effects on electronic and optical properties of PbSe/PbS quantum dots**<br>T Walsh, University of Salford, UK |
| 11:45 | **Phonon effects in cavity quantum dot systems**<br>J Iles-Smith, Imperial College London, UK |

### Session 4 - Devices and Applications

Chair: Dr Jason Smith, University of Oxford, UK

| | |
|---|---|
| 12:00 | **(invited) Single mode single exciton lasing from colloidal nanorods**<br>P Lagoudakis, University of Southampton, UK |
| 12:30 | **Nanocrystal lasing dynamics probed with tuneable optical microcavities**<br>R Patel, University of Oxford, UK |
| 12:45 | **Alloyed-core CdSeS/ZnS colloidal quantum dots for solution-processed lasers**<br>L McLellan, University of Strathclyde, UK |
| 13:00 | Lunch and depart |

## Poster Programme

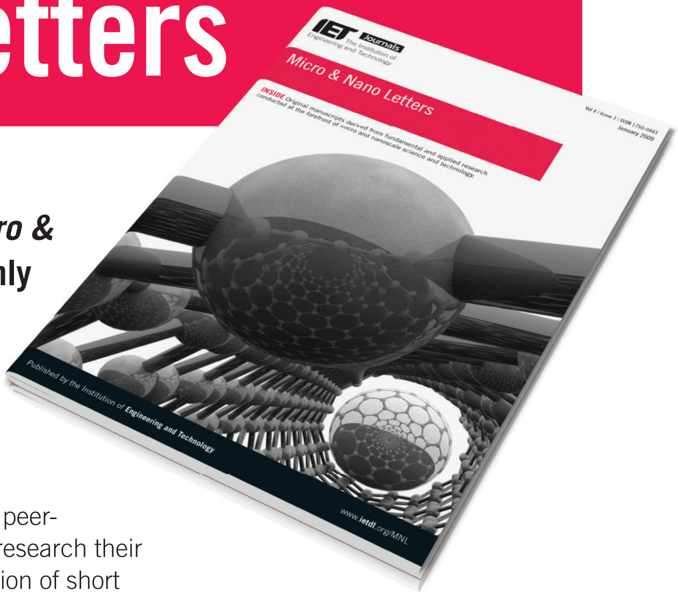
| | |
|---|---|
| P.01 | **Ultrafast charge dynamics of chloride-passivated CdTe colloidal quantum dots**<br>C Smith, University of Manchester, UK |
| P.02 | **Mild cadmium chloride treatment of CdTe quantum dots producing near unity quantum yields**<br>C Lydon, University of Manchester, UK |
| P.03 | **Depth profiling study of colloidal type II quantum dots by synchrotron-radiation-excited x-ray photoelectron spectroscopy**<br>A Pengpad, University of Manchester, UK |
| P.04 | **Type II colloidal quantum dots - using depth-profiling synchrotron radiation x-ray photoelectron spectroscopy to study the effects of oxidation on the shell structure**<br>A Williamson, University of Manchester, UK |
| P.05 | **Hydrophobin phase-Transfer of quantum dots**<br>L Sandiford, King's College London, UK |
| P.06 | **Synthesis of ternary lead chalcogenide quantum dots and related structures**<br>P D McNaughter, University of Manchester, UK |
| P.07 | **Atomistic study of InSb quantum dots**<br>A M Sills, University of Leeds, UK |

**Journals**
The Institution of
Engineering and Technology

OPEN ACCESS
OPTIONS
AVAILABLE

# Access world-leading Nano research with

# Micro & Nano Letters



**Discover a wealth of online nano research with *Micro & Nano Letters*, the internationally renowned online-only express publication journal from the Institution of Engineering & Technology (IET).**

## Top quality research in the Nano field

Available online via the prestigious IET Digital Library, this rigorously peer-reviewed journal offers the researcher the perfect way to publish or research their latest work. ***Micro & Nano Letters*** focuses on express online publication of short research papers containing the latest advances in micro- and nano-scale science, engineering and technology, with at least one dimension ranging from micrometres to nanometres.

Addressing issues spanning fundamental understanding to experimental demonstrations in the disciplines of engineering, physical, chemical, biological and material science, ***Micro & Nano Letters*** places particular emphasis on cross-disciplinary activities and applications.

Typical topics include:

- MEMS and NEMS
- Micro- and nano-structures and devices
- Modelling, simulation and realisation of micro- and nano-scale structures, devices and systems
- Synthesis and processing
- Micro- and nano-photonics
- Molecular machines, circuits and self-assembly
- Organic and inorganic micro- and nano-structures
- Micro- and nano-fluidics

## Publish your research

With an international editorial board, e-first publishing, key database indexing, and now the option of open access publishing your next research paper deserves to be published by the very best in this field.

For more information on the scope and editorial expertise attached to this journal, or to submit your paper, email us, **journals@theiet.org** or visit,

www.**theiet**.org/MNL

www.**theiet**.org/MNL

# Colloidal Quantum Dots and Nanocrystals

## Abstracts

## Monday 14 July

### Session 1 - Synthesis

### (invited) Material design at the nanoscale: how to control optical properties through nanocrystal size, shape and interface engineering

J Q Grim, S Christodoulou, A Polovitsyn, L Manna and I Moreels

Istituto Italiano di Tecnologia (IIT), Italy

Nanocrystals have gained considerable attention over the last two decades because of their excellent fluorescence properties. They have a broadband absorption and narrow emission, enhanced stability compared to organic dyes, and the fluorescence is essentially tunable from the UV, over the visible, to the near-infrared spectral range (300 nm – 3000 nm) by nanocrystal size and material composition. With core/shell heterostructures we can engineer the effective Stokes shift, for example in CdSe/CdS giant-shell nanocrystals, where a large-band gap shell provides the dominant absorption pathway while the emission originates from the smaller-gap core.[1] This permits them to emit in a nearly transparent spectral region when the shell volume largely exceeds the core volume. Control over the fluorescence lifetime has also been demonstrated already, most successfully in CdSe/CdS quasi-type II core/shell nanocrystals through selective electron delocalization. However, this approach typically leads to a reduced recombination rate, from about 20 ns in CdSe/ZnS type-I materials to more than 500 ns in CdSe/CdS systems.[1]

Current challenges therefore lie in the direction of developing new synthesis pathways that yield nanocrystals with engineered emission rate, as well as a full, independent control over the absorption and emission properties. As a first example, we have synthesized flat CdTe quantum disks[2] and CdSe colloidal quantum wells. Their peculiar shape leads to a faster decay by a reduced dielectric screening of the incident and emitted light, as well as a larger oscillator strength of the band-edge transition through in-plane exciton wave function delocalization and thus a larger exciton coherence volume. In the case of CdSe, we could reduce the fluorescence lifetime down to 400 ps, i.e. about 50 times faster than spherical quantum dots. At the other end of the decay rate spectrum, microsecond lifetimes can be achieved in highly fluorescent nanocrystals by turning to CdSe/CdS giant-shell heterostructures synthesized with a hexagonal crystal structure of the core. In contrast to cubic CdSe, we can introduce a piezo-electric field arising from strain and lattice distortions at the CdSe/CdS interface. This additional potential further reduces the electron-hole overlap.

Finally, the fast decay rate typical for CdSe cores can be maintained in CdSe/CdS giant-shell nanocrystals when first growing a thin barrier layer of CdxZn(1-x)S around the CdSe core. We obtained lifetime values of 20 – 30 ns, an order of magnitude faster than in comparable nanocrystals without a barrier layer. This opens up the possibility to exploit the giant-shell absorption and for instance the associated reduced stimulated emission threshold[3] or enhanced two-photon absorption,[4] while avoiding electron delocalization and concomitant reduced oscillator strength of the band-edge transition.

In conclusion, the engineering of the nanocrystal size, shape and core/shell interface with strain and alloying finally brings about a detailed control over all aspects of the nanocrystal optical properties, from the absorbance and fluorescence spectrum to the emission lifetime. These results will allow targeting a wide range of applications, for examples as color-converting phosphors, gain media for lasing, or bright and fast quantum emitters.

[1] Christodoulou et al., Synthesis of highly luminescent wurtzite CdSe/CdS giant-shell nanocrystals using a fast continuous injection route, *J. Mater. Chem. C* 2014, 2, 3439-3447

[2] Li et al., Synthesis of Uniform Disk-Shaped Copper Telluride Nanocrystals and Cation Exchange to Cadmium Telluride Quantum Disks with Stable Red Emission, *J. Am. Chem. Soc.* 2013, 135, 12270–12278

[3] Moreels et al., Nearly Temperature-Independent Threshold for Amplified Spontaneous Emission in Colloidal CdSe/CdS Quantum Dot-in-Rods, *Adv. Mater.* 2012, 24, OP231–OP235

[4] Allione et al., Two-Photon-Induced Blue Shift of Core and Shell Optical Transitions in Colloidal CdSe/CdS Quasi-Type II Quantum Rods, *ACS Nano* 2013, 7, 2443–2452

## Zinc nitride nanocrystals - synthesis and characterisation

P N Taylor, M A Schreuder, T M Smeeton, A J D Grundy, J A R Dimmock, S E Hooper, J Heffernan and M Kauer

Sharp Labs of Europe, UK

We have recently prepared highly emissive $Zn_3N_2$ nanocrystals, for the first time, from cheap and readily available starting materials.[1] Our synthetic method involves the portion-wise addition of diethylzinc to a heated (225 °C) mixture of 1-octadecene and oleylamine which is saturated with ammonia gas. After each zinc addition the nanocrystals grow over the course of several minutes as evidenced by a visible bathochromic shift in the absorption of the reaction. Subsequent additions of diethylzinc cause further growth of the nanocrystals. Photoluminescence across the entire visible spectrum is observed when samples removed from such a reaction are illuminated with a UV lamp.

This synthesis method has been used to prepare $Zn_3N_2$ nanocrystals with emission wavelengths extending from below 500 nm to above 1100 nm with photoluminescence quantum yields over 50%. We have analysed the materials with X-ray diffraction which confirms the formation of $Zn_3N_2$ nanocrystals with an anti-bixbyite crystal structure while elemental analysis gave a Zn:N atomic ratio of 3.0:2.1 which is in good agreement with that expected for $Zn_3N_2$.

Transmission electron microscopy has been used to further study the structure of the nanocrystals (Fig 1). This confirms that the bathochromic shift observed in the optical spectra is indeed due to the growth of nanocrystals in the strong quantum confinement regime. We have observed samples containing nanocrystals with average diameters ranging from 2-8 nm. High resolution images have also been obtained and detailed analysis of single crystals in these samples further supports the formation of $Zn_3N_2$ nanocrystals with an anti-bixbyite crystal structure.

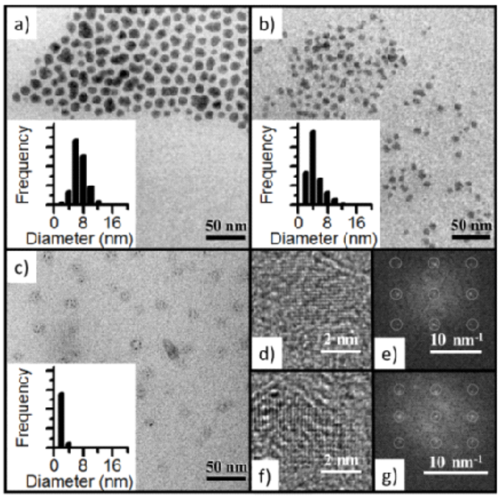


Fig. 1 – TEM images of the $Zn_3N_2$ nanocrystals with peak emission in solution at 1073 nm (a), 752 nm (b) and 585 nm (c); High resolution images observed along the [211] (d) and [110] (f) zone axes and corresponding FFT (e and g). The circles show the expected positions of the spots in the FFT patterns

This work opens up a new class of exciting nanomaterials based on zinc nitride with wide ranging applications due to their high performance and low cost, in addition to being completely free of toxic and scarce elements. Not only is this the first report of zinc nitride nanocrystals it is also the first report of tunable highly emissive nanocrystals made of any nitride based semiconductor, it is our expectation that this work will kick-start a new and fruitful area of research on both zinc nitride and other related materials.

[1] P. N. Taylor, M. A. Schreuder, T. M. Smeeton, A. J. D. Grundy, J. A. R. Dimmock, S. E. Hooper, J. Heffernan and M. Kauer, *J. Mater. Chem. C*, DOI:10.1039/C4TC00 403E

## Synthesis and surface engineering of group IV semiconducting nanocrystals for photovoltaic applications

D Mariotti[1], V Švrček[2], S Askari[1], S Mitra[1], M Macias-Montero[1] and P Maguire[1]

[1]Nanotechnology & Integrated Bio-Engineering Centre (NIBEC), University of Ulster, UK, [2]Research Center for Photovoltaics, National Institute of Advanced Industrial Science and Technology, Japan

Quantum confinement effects in nanoscale structures have attracted intense interest from the scientific community producing considerable progress. This is particularly true for direct semiconducting materials such as II–VI and III–V materials whereby the synthetic capabilities have also achieved excellent results. The indirect nature of silicon has however complicated this ideal scenario because different effects can be observed for direct and indirect transitions. The experimental observables originating from different phenomena can easily overlap providing a complex picture which is further aggravated by still limited synthetic capabilities. Above all, silicon nanocrystals (NCs) present highly reactive surfaces and it can probably be argued that the surface effects in Si NCs have a stronger impact on the overall properties if compared with NCs made of other materials [1].

Here we present a range of synthesis and surface engineering approaches for group IV NCs based on atmospheric pressure gas-phase plasmas and highly novel plasma-induced liquid chemistries [1-5]. In particular we will discuss a range of synthesis methods that rely on atmospheric pressure plasmas for producing quantum confined silicon NCs [4], silicon-carbide NCs [6] as well as alloyed silicon-tin NCs [7]. We will then discuss novel strategies for surface engineering providing unprecedented opportunities for tuning the opto-electronic properties and integration in nano-composites [8-10]. We will then discuss results of silicon-based NCs used in photovoltaic devices, demonstrating their contribution as down-converters and/or as part of the active layer [11, 12]. Finally, the applicability of atmospheric pressure plasmas in different aspects of photovoltaic device fabrication will be discussed presenting opportunities and challenges for large scale NCs manufacturing.

This work was partially supported by a NEDO project, the Royal Society International Exchange Scheme (IE120884), the Leverhulme International Network (IN-2012-136) and EPSRC (EP/K022237/1).

[1] *Nanoscale* 5 (2013) 1385
[2] *J. Phys. D Appl. Phys.* 43 (2010) 323001
[3] *Adv. Funct. Mater.* 22 (2012) 954
[4] *Appl. Phys. Lett.* 104 (2014) 163103
[5] *Plasma Process. Polym.* 9 (2012) 1074
[6] *Eur. Phys. J. Appl. Phys.* 56 (2011) 24020
[7] *Nanoscale* 5 (2013) 6725
[8] *Chem. Phys. Lett.* 478 (2009) 224
[9] *Adv. Funct. Mater.* 23 (2013) 6051
[10] *J. Phys. Chem. C* 117 (2013) 23198
[11] *Jpn. J. Appl. Phys.* 51 (2012) 10NE25
[12] *Appl. Phys. Lett.* 100 (2012) 223904

## Synthesis of III-V nanocrystals and passivation with $InCl_3$

C Lydon, P O'Brien and D J Binks

University of Manchester, UK

Preparation of III-V nanocrystals has proven to be relatively difficult in comparison to their II-VI counterparts, producing lower quality products, with lower quantum yields. This is generally considered to be at least partly due to their more covalent nature and the result of this is that less work is carried out on III-V systems. However, III-V systems are promising due their large exciton diameters, reduced toxicity compared to II-VI systems and less ionic lattices.[1] Recently, there have been reports in the literature in which chlorine and metal halides have been used as passivating agents for II-VI and IV-VI compounds, but this has not so far been extended to III-V compounds.[2,3]

The treatment with chlorine allows protection from oxidation and increases the stability of these nanoparticles, whilst also reducing the number of trap states on the surface to increase photoluminescence.

In this work, InP nanocrystals were treated with an $InCl_3$ solution, and the photoluminescence intensity and quantum yields measured. On treatment with $InCl_3$ the intensity of the photoluminescence exhibited a marked increase compared to the untreated samples. The variables of the reaction have been studied, with a view to optimising the process. This includes the concentration and source of chloride ions, temperature and duration of reaction, size of nanocrystal and work up. This work will be extended to other III-V systems in due course.

[1] M. Green and P. O'Brien, J. Mater. Chem., 2004, 14, 629-636
[2] W. K. Bae, J. Joo, L. A. Padilha, J. Won, D. C. Lee, Q. Lin, W.-k. Koh, H. Luo, V. I. Klimov and J. M. Pietryga, Journal of the American Chemical Society, 2012, 134, 20160-20168
[3] D. N. Dirin, S. Dreyfuss, M. I. Bodnarchuk, G. Nedelcu, P. Papagiorgis, G. Itskos and M. V. Kovalenko, J. Am. Chem. Soc., 2014, Article ASAP

### Flow synthesis of silver nanowires for transparent conducting electrodes

T W Phillips, M Heeney and J C de Mello

Imperial College London, UK

The technological and commercial success of printed electronic devices on plastic substrates depends on the development of inexpensive, flexible and solutionprocessable transparent electrodes. To date the most promising candidate is silver nanowires, which offer a good balance of high optoelectronic performance, environmental stability and processability.

Conventional batch production techniques scale poorly (due to the difficulty of achieving a sufficiently uniform reaction environment) resulting in an undesirable trade off between product quality and production rate, and poor overall yield. This makes them prohibitively expensive.

Here we report the synthesis of silver nanowires in a droplet-based flow reactor, demonstrating significantly shorter reaction times and a level of control and reproducibility unattainable in batch. The sub-microliter volume of the droplets ensures rapid equilibration of temperature and composition, providing a highly uniform environment for nucleation and growth. Most importantly, by running many identical channels in parallel, greatly increased production rates can be achieved without diminishing the quality of the product, thus avoiding the principal limitation of batch reactors.

### Growth mechanis of InP/ZnS nanocrystals from single molecular ZnS precursors at the moderate low temperature

L Xi[1], D-Y Cho[2], M Duchamp[1], Y M Lam[3], B Kardynal[4], C B Boothroyd[1], J Y Lek[1], A Besmehn[1] and R Waser[1]

[1]Forschungszentrum Juelich, Germany, [2]Chonbuk National University, Republic of Korea, [3]Nanyang Technological University, Singapore, [4]Semiconductor Nanoelectronics (PGI-9), Germany

A simple approach for synthesis of high quality InP/ZnS nanocrystals (NCs) using air and moisture stable single molecular precursor (SMP) was reported. The role of different end groups of SMP, complex formation time, the amount of SMP and reaction temperature has been fully studied. Based on the XPS, XAS, XRD, TEM and optical results, Ionic diffusion mechanism was proposed for the growth of InP/ZnS NCs. Ionic diffusion or exchange has been reported to synthesis nanodots, nanorods and nanowires in the solution as an alternative to conventional ''hot-injection'' method. The ionic diffusion is thermodynamically favorable due to the thermodynamic instability of NCs. In the synthesis of InP/ZnS NCs, due to the similar ionic radius between $In^{3+}$ or $P^{3-}$ and $Zn^{2+}$ or $S^{2-}$, $Zn^{2+}$ released from SMP firstly attached to InP core which may contain a mixed oxide layer and replaced $In^{3+}$ to form In-P-Zn NCs. When the temperature reaches to around 80°C, $H_2S$ was gradually released from SMP-oleylamine (OLA) complexes. $H_2S$ or $S^{2-}$ slowly attaches the In-P-Zn NCs. The $P^{3-}$ on the Zn-P-In surface was gradually replaced with $S^{2-}$ and thus forms ZnS shell layer. During this processes, InP cores gradually transformed to InP/ZnS structure. Such transformation is consistent with a diffusion controlled pathway. The in-situ generated $H_2S$ acidic gas from the reaction of SMP and OLA may also help the anion exchange process and the size reduction. A previous work showed that the etching/dissolution of II-VI NCs was possible under the elevated temperature and the presence of amine or acid.

## Session 2 - Characterization

### (invited) Coherent exciton dynamics in quantum dots

W Langbein

Cardiff University, UK

Coherent quantum dynamics of excitons in semiconductor quantum dots (QDs) are of key interest, besides fundamental physics, for many applications ranging from quantum computing to advanced photonic devices. Significant achievements have been reported in this area, however investigating almost exclusively epitaxially-grown QDs which are embedded in a matched defect-free crystalline environment. With the advances in colloidal synthesis, high-quality semiconductor nanocrystals have become more available, with the advantage of being less expensive to fabricate and easier to engineer with a large variety of sizes, shapes and compositions. Despite its importance, measuring the exciton dephasing time in colloidal nanocrystals is technically challenging.

Using a sensitive three-beam transient resonant four-wave mixing technique in heterodyne detection not affected by spectral diffusion, we have measured the ground-state exciton dephasing dynamics in CdSe/ZnS wurtzite colloidal QDs, CdSe/CdS spherical zincblende and rod-shape wurtzite QDs with variable core diameter and shell thickness / rod length, CdSe nanoplatelets, and in PbS colloidal QDs.

In these structures, the importance of phonon-assisted transitions, and the zero-phonon line (ZPL) dephasing by phonon-mediated spin-relaxation and radiative decay are vastly varying. In PbS QDs, the peculiar band structure allows coupling with phonons at the zone edge (X-point), resulting in dominating phonon assisted transitions [1] even at low temperatures with sub-picosecond dephasing and a ZPL weight of less than 7%. In CdSe QDs [2,3] and dots in rods of similar size, the ZPL weight instead is above 50% since only zone-center phonons can couple, and the ZPL dephasing is limited by spin-relaxation into dark states on a 10-1000ps time scale, faster than the radiative lifetime of about 10ns. In CdSe nano-platelets, the quasi two-dimensional confinement leads to quantum-well type behaviour, with a large exciton coherence area, such that the exciton dephasing is dominated by a fast radiative decay in the picosecond range [4].

[1] F. Masia et. al., Phys. Rev. B 83, 201309(R) (2011) DOI:10.1103/PhysRevB.83.201309
[2] F. Masia et al. Phys. Rev. Lett. 108, 087401 (2012) DOI:10.1103/PhysRevLett.108.087401
[3] N. Accanto et al., ACS Nano 6, 5227-5233 (2012) DOI:10.1021/nn300992a
[4] A. Naeem et al., arXiv:1403.7798 (2014) http://arxiv.org/abs/1403.7798v1

### Ultrafast charge dynamics in monodisperse Au nanoparticles on colloidal $TiO_2$ spheres

Ali Al-Otaify[1], M A Leontiadou[1], F V E dos Reis[2], T C Damato[2], P H C Camargo[2] and D J Binks[1]

[1]University of Manchester, UK, [2]Instituto de Química, Universidade de São Paulo, Brazil

$TiO_2$ has been widely investigated as a photocatalyst for water splitting and degradation of organic pollutants, and in the development of dye sensitized solar cells [1-3]. On its own, its performance is limited by a relatively large band gap and a high recombination rate for photo-generated charges. However, this can be improved significantly by the deposition of noble metal nanoparticles onto the $TiO_2$ surface. These can act as electron traps, aiding charge separation, and also enhance photogeneration in the visible part of the spectrum via a localized surface plasmon resonance[4]. However, the synthesis of samples containing $TiO_2$ decorated with metal NPs of well-controlled sizes remains challenging, restricting the systematic investigation of their properties.

Here, we present a study of sub-nanosecond charge dynamics in monodisperse Au nanoparticles (NPs) on $TiO_2$ colloidal spheres as a function of NP diameter using ultrafast transient absorption spectroscopy. The transmittance changes observed in the region of the plasmon resonance of the Au NPs following photo-excitation of the $TiO_2$ spheres are well-described by a bi-exponential function consisting of a fast component of 2ps duration associated with electron-phonon scattering, followed by a slow component associated with phonon-phonon scattering. The decay constant characterising the latter component was found to be dependent on the size of the Au NPs, increasing from 49±3 to 128±6 ps as the diameter of the Au NPs rose from 12.2±2.2 nm to 24.5±2.8 nm.

[1] P. V. Kamat, *The Journal of Physical Chemistry C*, 2007, 111, 2834-2860
[2] P. V. Kamat, and D. Meisel, *Current Opinion in Colloid & Interface Science*, 2002, 7, 282-287; *Comptes Rendus Chimie*, 2003, 6, 999-1007
[3] L. M. Peter, *The Journal of Physical Chemistry Letters*, 2011, 2, 1861-1867
[4] P. L. Stiles, J. A. Dieringer, N. C. Shah, and R. R. Van Duyne, in Annual Review of Analytical Chemistry, 2008, vol. 1, pp. 601-626

## Chlorine-passivated colloidal quantum dots - using depth-profiling synchrotron radiation x-ray photoelectron spectroscopy to study the shell structure

H Radkte[1], A Pengpad[1], R C Page[1], D J H Cant[1], K Schulte[2], J Osiecki[2] , F Bondino[3], E Magnano[3], I Pis[3], D J Binks[1] and W R Flavell[1]

[1]University of Manchester, UK, [2]Lund Universitet, Sweden, [3]IOM CNR, Laboratorio Nazionale TASC, Italy

A common problem in using nanoparticles produced by colloidal routes for applications such as solar cells is their instability. Recently a new approach to passivate the surface of PbSe quantum dots (QDs) by replacing selenium atoms with chlorine atoms has shown an increase in stability and enhanced the optical properties of these nanoparticles.[1]

The tunable photon energy of a synchrotron radiation source can be used to change the kinetic energy of the emitted electrons and therefore the sampling depth in materials studied via X-ray photoelectron spectroscopy. This has been shown to be a powerful technique to study the surface chemistry of nanoparticles (e.g. PbS [2]) and can be used to determine the layer thicknesses in core-shell QDs (e.g. ZnTe/ZnSe [3]).

Here, the structure of colloidal CdTe(core-only) QDs which have been chlorine passivated is investigated, with a special emphasis on the determination of the thickness of the Cl passivation layer. Furthermore the results of the analysis of chlorine-passivated CdTe(core)/CdSe(shell) QDs are presented. These QDs have a so-called 'Type II' structure, where the band offsets are engineered to separate the photoexcited charges, lengthening the recombination lifetime. We demonstrate the presence of a Cl 'capping layer' on the outside of the dots, which does not completely displace the initial organic ligands present during synthesis. This is consistent with the model suggested for PbSe [1]. Also the core-shell structure of the QDs is investigated.

[1] Wan Ki Bae, Jin Joo, Lazaro A. Padilha, Jonghan Won, Doh C. Lee, Qianglu Lin, Weon-kyu Koh, Hongmei Luo, Victor I. Klimov, and Jeffrey M. Pietryga, *J. Am. Chem. Soc. 134* (49), 20160-20168 (2012)
[2] Samantha J. O. Hardman, Darren M. Graham, Stuart K. Stubbs, Ben F. Spencer, Elaine A. Seddon, Ho-Ting Fung, Sandra Gardonio, Fausto Sirotti, Mathieu G. Silly, Javeed Akhtar, Paul O'Brien, David J. Binks, and Wendy R. Flavell, *Phys. Chem. Chem. Phys.13*, 20275-20283 (2012)
[3] Simon M. Fairclough, Edward J. Tyrrell, Darren M. Graham, Patrick J. B. Lunt, Samantha J. O. Hardman, Annette Pietzsch, Franz Hennies, Jonathan Moghal, Wendy R. Flavell, Andrew A. R. Watt, and Jason M. Smith, *J. Phys. Chem. C 116* (51), 26898-26907 (2012)

## Tuesday 15 July

### (plenary) Dark and photo-conductivity in ordered array of nanocrystals

A L Efros

Naval Research Laboratory (NRL), USA

A theory of photo- and dark-band conductivities in semiconductor supercrystals consisting of nanocrystals is developed by assuming scattering by structural defects in the supercrystals[1]. A new proposed mechanism of photoexcitation, which is triggered by an efficient Auger ionization of charged nanocrystals, provides explanation for the measured photocurrent being 2−3 orders of magnitude larger than the dark current. For dark conductivity, the metal−insulator transitions and temperature dependence of mobility in the metal phase are considered.

[1] A. Shabaev, Al. L. Efros, and A. L. Efros, Nano Lett. 13, 5454 (2013)

## Session 3 - Modelling

### (invited) From semiconductor nanocrystals to artificial graphene and topological insulator

E Kalesaki[1,2], C Delerue[1], C Morais Smith[3], W Beugeling[3], G Allan[1] and D Vanmaekelbergh[3]

[1]IEMN, France, [2]University of Luxembourg, Luxembourg, [3]University of Utrecht, Netherlands

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

[1] W. H. Evers, B. Goris, S. Bals, M. Casavola, J. de Graaf, R. van Roij, M. Dijkstra, and D. Vanmaekelbergh, Nano Lett. 13, 2317 (2013)

[2] E. Kalesaki, C. Delerue, C. Morais Smith, W. Beugeling, G. Allan, D. Vanmaekelbergh, Phys. Rev. X 4, 011010 (2014)

### (invited) Photoinduced carrier trapping in semiconductor nanocrystals

M Califano

University of Leeds, UK

In recent years, quantum confined semiconductor nanomaterials, such as quantum dots (QDs), nanorods and carbon nanotubes, have emerged as a new class of light harvesting materials for solar energy conversion. For these applications, one of the most fundamental and crucial steps is the dissociation of excitons (bound electron-hole pairs) through interfacial charge (electron or hole) transfer to acceptor materials. Due to the strong electron-nuclear interaction in molecules, inter- and intra- molecular electron transfer (ET) is accompanied by large rearrangement of the nuclear configuration, which are described by the Marcus ET theory, exhibiting the well-known dependence of

the ET rates on the driving force in the Marcus normal, barrier-less, and inverted regimes. In many bulk semiconductor materials (such as CdSe), the week electron-nuclear and electron-electron interaction justify the treatment of electrons and holes as quasi-free and independent particles, in which photoinduced electron transfer requires negligible change in nuclear configurations or the motion of the accompanying holes. In excitonic nanomaterials, such as QDs, both the electron-hole interaction and electron-phonon interactions fall between those of the bulk semiconductor materials and molecular chromophores and the appropriate model for describing photoinduced charge transfer (or exciton dissociation) remains unclear. In this talk I will discuss a novel mechanism that can describe both electron and hole transfer to acceptor states on the surface of QDs of different materials, and explain otherwise puzzling features observed in these processes, which are inconsistent with Marcus ET theory.

## Theoretical studies of biexciton binding energy in CdSe/CdTe core/shell type II quantum dots

J M Miloszewski and S Tomić

University of Salford, UK

Theoretical predictions indicate that multiple exciton generation (MEG) has the potential to enhance the efficiency of a single gap cell from 33% to 42% [1]. Full realization of this potential requires that the energy threshold for MEG be minimized. An attractive interaction between excitons reduces the threshold by the biexciton binding energy, Bxx, but this has been found to be small (-10meV) for type I QDs [2]. Previous calculations of Bxx in type II CdSe/CdTe QDs have found a large repulsion between excitons. Here, we show that, by taking into account CI, combinations of core diameter and shell thickness can be found for a CdSe/CdTe core/shell QD that result in large negative values of Bxx.

In our theoretical model, we use a 14-band **k.p** Hamiltonian, with the correct atomistic symmetry, C2v, of the zinc-blend structure, which incorporates the effects of band mixing between the p-bonding, s-anti-bonding and p-anti-bonding states, spin-orbit interaction, crystal-field splitting, strain between core and shell and piezoelectric potentials [3]. We also take into account large variations in dielectric constant (polarization and self-polarization effects). Kane parameters and dielectric constants of CdSe and CdTe at the transition energies are predicted using *ab initio* time-dependent density functional theory[4].

We discover that inclusion of the correlation interaction is essential in predicting negative biexciton binding energies, thus they can only be predicted with a full CI Hamiltonian. Another crucial element is the polarization effect which, if ignored, makes it impossible to predict negative biexciton binding for structures with shell thickness > 0.75 nm. When both correlation and polarization effects are correctly accounted for, our biexciton energies are negative and agree very well with experimentally obtained values. We use the Aufbau principle and Hund rule to explain large Bxx binding energies in the core/shell QDs.

[1] V. I. Klimov, Appl Phys Lett 89, 123118 (2006)
[2] R. D. Schaller, J. M. Pietryga, & V. I. Klimov, Nano letters, 7, 3469 (2007)
[3] S. Tomic and N Vukmirovic J. Appl Phys 110, 053710 (2011)
[4] L. Bernasconi, S. Tomic et al, Phys Rev B 83, 195325 (2011)

## Phonon-enhanced coherent scattering in a driven quantum dot

A Nazir[1] and D P S McCutcheon[2]

[1]University of Manchester, UK, [2]Technical University of Denmark, Denmark

The recent experimental characterisation of exciton-phonon interactions in a coherently-driven semiconductor quantum dot (QD), and their interpretation in terms of a two-level system in contact with a bosonic environment, have demonstrated that QDs offer a natural platform in which to explore dissipative dynamics in the solid-state. In particular, the interplay between laser-driven coherent excitonic oscillations and incoherent phonon-induced processes leads to a rich dynamical behaviour, which can also have a profound effect on the dot photon emission characteristics.

Here [1], I shall explore the crucial role played by the solid state environment in determining the photon emission properties of a driven QD. I shall show that such environmental interactions can lead to QD emission characteristics that deviate fundamentally from the well established quantum optical behaviour of driven atoms.

Specifically, for resonant driving, the theory outlined here predicts a phonon enhancement of the coherently emitted radiation field with increasing driving strength, in stark contrast to the conventional expectation of a rapidly decreasing fraction of coherent emission with stronger driving. This surprising behaviour results from thermalisation of the dot with respect to the phonon bath and leads to a nonstandard regime of resonance fluorescence in which significant coherent scattering and the Mollow triplet coexist.

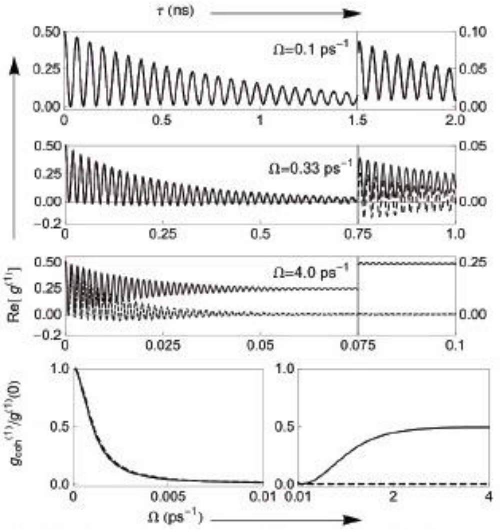


Fig.1 Upper three plots: First order field correlation function of the QD emission for various driving strengths, as indicated, calculated from the full phonon theory (solid curves), and a standard quantum optics treatment (dashed curves). The right-most parts show enlargements of the long-time behaviour. Lower plots: Coherent fraction as a function of driving strength, calculated using the same methods as in the upper plots. The left plot shows the only region where the standard quantum optics treatment gives a non-negligible coherent fraction, close to the origin

[1] D. P. S. McCutcheon and A. Nazir, Phys. Rev. Lett. 110, 217401 (2013)

## Geometry effects on electronic and optical properties of PbSe/PbS quantum dots

T Walsh, J M Miloszewski and S Tomić

University of Salford, UK

The geometry of a quantum structure plays a key role in determining its electronic and optical characteristics.

Factors such as size, shape and composition may be selected in order to produce quantum dots (QDs) with the desired properties. For non-interacting electrons, the electronic structure, dipole matrix elements, absorption cross-sections etc. may be predicted via the standard **k ·p** Hamiltonian expanded in the vicinity of the characteristic *L*-point of the rock-salt crystal structure's first Brillouin zone[1]. The anisotropy between the $x/y$- $(\langle\bar{1}\bar{1}2\rangle/\langle 1\overline{10}\rangle)$ and $z$- $(\langle 111\rangle)$ directions is accounted for within the electron effective masses, $m^*_{\pm,\parallel}$ and $m^*_{\pm,z}$, and within bulk dipole matrix elements $P_{0,\parallel}$ and $P_{0,z}$.

Polarization-dependent optical matrix elements $\left|e\cdot P_{if}\right|^2$ required for the description of radiative transitions are calculated via the *Hellmann-Feynman theorem*. Here, $e$ is the light polarization unit vector, with $P_{if}(k)$ = $(m_0/h)\,\langle i|dH(k)/dK|f\rangle$ being the electron-hole momentum matrix element with initial and final state envelope functions $|i\rangle$ and $|f\rangle$. The inclusion of the radial variation of $P_{0,\parallel/z}$ and $m^*_{\pm,\parallel/z}$, as well as the variation in the VB maximum and CB minimum incorporates the different material parameters of the core, shell, and surrounding colloid. All functionalities here described are implemented in the kppw code[2, 3].

In this work we use the above methodology to examine the effects of QD geometry and anisotropy on electronic and optical properties. Transition energies, optically allowed and forbidden dipole matrix elements, and absorption cross sections are predicted for ellipsoidal PbSe/PbS core/shell structures of varying size, eccentricity, and for different ratios of core-to-shell thickness. For highly elliptical QDs ($x : z$ ratio 2:1), elongated along the $x$ -axis from a spherical QD with core/shell radii 20Å/30Å, we find a reduction of up to 8.5% in the energy of the characteristic $e_0 - h_0$ transition, from 0.72 eV to 0.66 eV. Furthermore, for a spherical QD of core radius 20Å, a ratio of PbS/PbSe=1 (i.e. shell thickness = core radius) reduces $e_0 - h_0$ transition energy by 47%, from 1.14 eV (core only) to 0.60 eV. Due to crystal anisotropy, we present results for QDs elongated in both the $x$ - and $z$ - directions.

[1] I. Kang and F. W. Wise, J.Opt. Soc. Am. B., 1997, 14, 1632-1646
[2] U. Aeberhard, R. Vaxenberg, E. Lifshitz, and S. Tomić, Phys. Chem. Chem. Phys. 14, 16223 (2012)
[3] S. Tomić, A. G. Sunderland and I. J. Bush, J. Mater, Chem., (2006), 16, 1963-1972

## Phonon effects in cavity quantum dot systems

J Iles-Smith[1,2] and A Nazir[2]

[1]Imperial College London, UK, [2]University of Manchester, UK

Semiconductor quantum dots (QDs) in combination with high-Q semi-conductor microcavities are central to many proposals for quantum technologies, examples of which include single photon sources and optical switches, to name a few. Many of these proposals rely both on the two level nature of QDs and their 'atomic like' emission characteristics.

Recently, however, theoretical studies have suggested that in the absence of a cavity, non-trivial phonon interactions can lead to a striking departure from the accepted atomic behaviour, predicting enhanced coherent scattering well beyond saturation, behaviour which can be attributed to competing phonon and photon processes [1].

Here we examine the effect of phonon interactions on the emission spectrum of a quantum dot in a high-Q optical cavity, focussing in particular on a micropillar type setup. By making use of the master equation formalism we show that phonon interactions actively alter the emission properties of the cavity in the Purcell regime, leading to an enhanced asymmetry in Fano lineshapes. Furthermore, we show that a phenomenological pure dephasing model is unable to capture the underlying physical processes responsible for this behaviour, thus requiring us to respect the full eigenstructure of the cavity quantum dot system when deriving the appropriate master equation.

[1] D. P. S. McCutcheon and A. Nazir, "Model of the optical emission of a driven semiconductor quantum dot: Phonon-enhanced coherent scattering and off-resonant sideband narrowing," Phys. Rev. Lett., vol. 110, p. 217401, May 2013.

## Session 4 – Devices and Applications

### (invited) Single mode single exciton lasing from colloidal nanorods

P Lagoudakis

University of Southampton, UK

Abstract not available

### Nanocrystal lasing dynamics probed with tuneable optical microcavities

R Patel[1], M A Leontiadou[2], P Dolan[1], S M Fairclough[1], E Jang[3], A Trichet[1], R A Taylor[1], E Tsang[3], H Jang[3], D J Binks[2] and J M Smith[1]

[1]University of Oxford, UK, [2]University of Manchester, UK, [3]Samsung Advanced Institute of Technology, Samsung Electronics Co, Republic of Korea

We present progress in the use of tuneable, open access optical microcavities containing thin films of semiconductor nanocrystals to develop a detailed understanding of the dynamics of the nanocrystal lasing process. By measuring the dependence of the lasing threshold on the spectral position of the cavity mode we can infer information regarding internal photo-physics of the lasing process such as the balance between absorption and emission processes in the pumped system. We also examine the threshold as a function other parameters such as nanocrystal packing density and film thickness of the quantum dots to provide further insight into the lasing dynamics of the system as a whole. It is hoped that this will inform the development of optimal resonant optical feedback structures and of nanocrystal materials with reduced gain thresholds.

We will report lasing using CdSe/CdS core shell nanocrystals with a measured pump pulse energy threshold of order 250 pJ (at 400 nm), corresponding to an average pumped exciton population per nanocrystal of about 5, and describe these results with an intuitive cascade model of exciton relaxation in which gain is preserved over multiple Auger lifetimes. Ultrafast transient absorption measurements reveal Auger rates of order 100 ps and provide further information about the relaxation process. We will report some preliminary results of the effect of ligand exchange by which we seek to modify the gain properties of the nanocrystals.

### Alloyed-core CdSeS/ZnS colloidal quantum dots for solution-processed lasers

L McLellan, C Foucher, B Guilhabert, N Laurand and M D Dawson

University of Strathclyde, UK

Wavelength versatility and compatibility with solution-processing make CQDs an attractive material technology for lasers. CQDs have already enabled a wide range of optically-pumped lasers, including in mechanically-flexible formats [1-5] .However, CQD lasers are not yet practical sources. The majority of the demonstrations to date are in ultra-fast pulse regimes (*fs* to a few *ps*) that require large pump lasers. Closing the gap to real-world applications is critical and the recent demonstrations of state-of-the-art laser operation in the *ns* regime using red-emitting CdSe/ZnS core/shell CQDs is a first step in that direction [5-6]. Building on these demonstrations, the present work investigates the use of alloyed-core CdSeS/ZnS quantum dots to further improve performance as well as extend the range of operating wavelengths.

In CQD lasers, Auger recombination can be a limiting factor. This is enhanced in CQDs having a well-defined core/shell interface and is more pronounced in small-size CQDs [7]. CdSeS/ZnS CQDs that have a multishell architecture for a smoother core-shell band gap transition and that permit wavelength tuning for a fixed size through alloying of the core could mitigate this issue. The CdSeS/ZnS CQDs studied in this work have a 6nm mean size. Their peak emission wavelengths in solution range from 490 nm to 664 nm. The

Stokes shift, an important parameter for a laser material, is above 10 nm (Fig. 1a shows the 630nm CQD data). CQD thin films (100 to 200nm thick) are formed onto glass substrates and characterised in terms of amplified spontaneous emission (ASE) by exciting the samples with 355nm pump pulses of 5ns duration (excitation area 1.5mm x 4.4mm). Results for the 630nm samples are summarised in Fig. 1b (ASE threshold below 200 μJ per pulse). ASE is also demonstrated under the same conditions for the 575nm CQD sample at similar pump levels. These results indicate that CdSeS/ZnS CQD could enable visible lasers with similar performance over a >60nm spectral window. More details of the results and the opportunities they create for lasers will be discussed.

a) b)

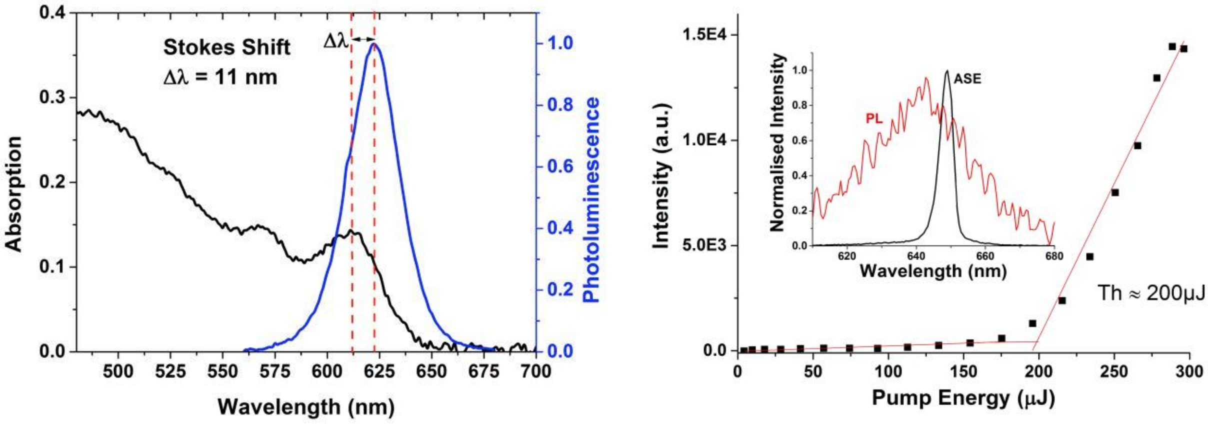


Figure 1a): Absorption and emission spectra of alloyed 630nm CdSeS/ZnS CQDs in toluene at 1 mg.ml$^{-1}$.
b) Representative power transfer function of a film of alloyed CdSeS/ZnS optically-pumped in the ns-regime; Inset: normalised spectra below (PL) and above the ASE threshold (ASE).

[1] A. V. Malko, A. A. Mikhailovsky, M. A. Petruska, J. A. Hollingsworth, H. Htoon, M. G. Bawendi, and V. I. Klimov, Appl. Phys. Lett. 81, 1303 (2002)
[2] S. Hoogland, V. Sukhovatkin, I. Howard, S. Cauchi, L. Levina, and E. H. Sargent, Opt. Express 14, 3273–3281(2006)
[3] V. M. Menon, M. Luberto, N. V. Valappil, and S. Chatterjee, Opt. Express 16, 19535–19540 (2008)
[4] C. Dang, J. Lee, C. Breen, J. S. Steckel, S. Coe-Sullivan and A. Nurmikko, Nature Nanotechnology 7, 335–339(2012)
[5] B. Guilhabert, C. Foucher, A-M. Haughey, E. Mutlugun, , Y. Gao, J. Herrnsdorf,, H. D. Sun, H. V. Demir, M. D Dawson and N. Laurand, Opt. Express 22, 7308-7319 (2014)
[6] C. Foucher, B. Guilhabert, N. Laurand and M. D. Dawson, Appl. Phys. Lett. 104 (14), 141108 (2014)
[7] G. E. Cragg and A. L. Efros, Nano Lett. 10, 313-317 (2010)

## Poster abstracts

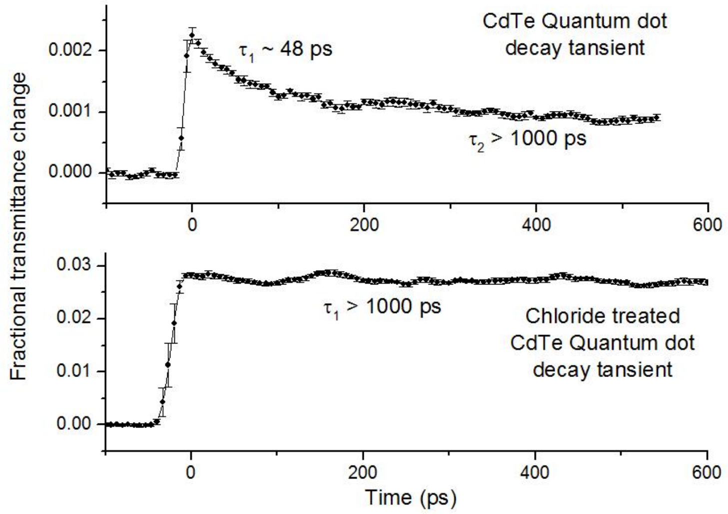
### P.01 **Ultrafast charge dynamics of chloride-passivated CdTe colloidal quantum dots**

C Smith, M Leontiadou, R C Page, P O'Brien and D J Binks

University of Manchester, UK

Colloidal quantum dots (CQD) have a number of potential applications including as the luminophores in light emitting devices and for bio-labelling, and as the light absorbing species in next generation photovoltaic solar cells. However, in CQDs the photoluminescence quantum yield and the extraction efficiency of photo-generated charges can be limited by surface-mediated non-radiative recombination, which can occur on a sub-nanosecond time-scale [1]. Treatment with halide ions has emerged recently as a particularly effective method of surface passivation resulting in significant improvements in device performance, such as the demonstration of record efficiency for a CQD-sensitised solar cell [2].

In this study, we compare for the first time the picosecond-scale charge dynamics of a CQD before and after passivation with chloride ions using ultrafast transient absorption spectroscopy. Electron relaxation to the conduction band edge was found to be 2.3 ps and 4.1 ps for the untreated and treated CdTe CQDs, respectively, indicating that surface-mediated cooling has been reduced or eliminated. The recombination of photo-generated electrons at the conduction band minimum of the untreated CQDs was found to include a significant component with a time-constant of 46 ± 2 ps. In contrast, no recombination was observed for the Cl-treated CQDs over the 1000 ps duration of the experiment, consistent with the elimination of surface-mediated recombination.



Treated vs Untreated CdTe Decay Transients

[1] P. Tyagi, P. Kambhampati, J Chem Phys, 134 (2011)

[2] A.H. Ip, S.M. Thon, S. Hoogland, O. Voznyy, D. Zhitomirsky, R. Debnath, L. Levina, L.R. Rollny, G.H. Carey, A. Fischer, K.W. Kemp, I.J. Kramer, Z. Ning, A.J. Labelle, K.W. Chou, A. Amassian, E.H. Sargent, Nat Nano, 7 (2012) 577-582

### P.02 **Mild cadmium chloride treatment of CdTe quantum dots producing near unity quantum yields**

R C Page[1], D Espinbarro-Velazquez[1], M Leontiadou[1], E Lewis[1], S J Haigh[1], H Radtke[1], A Pengpad[1], F Bondino[2], E Magnano[2], I Pis[2], W R Flavell[1], P O'Brien[1], C Lydon[1], and D J Binks[1]

[1]University of Manchester, UK, [2]IOM CNR, Italy

Colloidal quantum dots (CQDs) have been widely studied for their use in optoelectronic devices due to their solution processibility and tunable band gaps. Their high surface area to volume ratio leads to CQDs being prone to surface defect states, brought about by incomplete passivation of their surface. This leads to the formation of trap states within the band gap of the semiconductor, resulting in the formation of undesired recombination pathways and subsequent reduced carrier lifetimes. It is these non-radiative recombination rates allied with carrier mobility rates that are the key limiting factors CQD photovoltaic (PV) efficiencies today. Recently a metal chloride passivation technique was used to create a CQD PV device with a record certified efficiency of 7.0 % [1].

Here we present the first detailed study of cadmium chloride treated CdTe CQDs. Effective passivation by chloride ions has led to quantum yields (QYs) reaching near unity to be achieved. Typically untreated CdTe samples have QYs about less than 5% which increase to 95% upon chloride treatment. X-ray photoelectron spectroscopy (XPS) show that after treatment, a chloride species resides upon the surface and doesn't penetrate deep into the crystal, with the CQDs retaining their size, shape and crystallinity after treatment. Transient photoluminescence (PL) studies show monoexponential PL decay traces upon treatment as all non-radiative relaxation pathways, typically from surface trap states, are suppressed in the chloride treated samples. These lead to long lived charge carriers which have the potential be extracted into an external circuit, leading to potential increases in CQD PV efficiencies.

[1] Ip, A. H. et al. Hybrid passivated colloidal quantum dot solids. Nat Nano 7, 577–582 (2012)

### P.03 **Depth profiling study of colloidal type II quantum dots by synchrotron-radiation-excited x-ray photoelectron spectroscopy**

A Pengpad[1], H Radkte[1], A Williamson[1], R C Page[1], A Knight-Percival[1], F Sirotti[2], M G Silly[2], K Schulte[3], J Osiecki[3], F Bondino[4], E Magnano[4], D J Binks[1], A G Thomas[1] and W R Flavell[1]

[1]University of Manchester, UK, [2]Synchrotron SOLEIL, France, [3]Lund Universitet, Sweden, [4]IOM CNR, Italy

Type II quantum dots are nanoparticles of semiconductor with a 'core-shell' structure which on photoexcitation results in the separation of the excited charges. This results in an increased recombination time for the carriers, which can be used in many applications such as solar cells. However, colloidal QDs do not necessarily have the target composition, or have complete and atomically-abrupt interfaces between the core and the shell. The shell structure is critical to carrier separation. Moreover, significant surface degradation of colloidal QDs has been observed[1], and this influences charge recombination. The purpose of this study is to investigate the chemical composition of type II quantum dots at various depths for determining the structure and surface oxidation of the dots. Synchrotron-radiation- (SR-) excited X-ray photoelectron spectroscopy (XPS) is suitable for this study[1, 2]. The principle of depth profiling XPS is that the information deep inside the dots can be revealed by increasing the inelastic mean free path length (IMFP) of the photoelectrons. This IMFP parameter depends on the kinetic energy of the photoelectrons that can be varied by tuning the photon energy using a synchrotron source. The results show variations of element compositions with depth and the core-shell structure is revealed.

[1] S. J. O. Hardman, D. M. Graham, S. K. Stubbs, B. F. Spencer, E. A. Seddon, H. T. Fung, S. Gardonio, F. Sirotti, M. G. Silly, J. Akhtar, P. O'Brien, D. J. Binks and W. R. Flavell, Phys. Chem. Chem. Phys. 13, 20275 (2011)

[2] S. M. Fairclough, E. J. Tyrrell, D. M. Graham, P. J. B. Lunt, S. J. O. Hardman, A. Pietzsch, F. Hennies, J. Moghal, W. R. Flavell, A. A. R. Watt and J. M. Smith, J. Phys. Chem. C 116, 26898 (2012)

## P.04 Type II colloidal quantum dots - using depth-profiling synchrotron radiation x-ray photoelectron spectroscopy to study the effects of oxidation on the shell structure

A Williamson[1], H Radkte[1], A Pengpad[1], R C Page[1], A Knight-Percival[1], D J H Cant[1], K Schulte[2], J Osiecki[2], D J Binks[1] and W R Flavell[1]

[1]University of Manchester, UK, [2]Lund Universitet, Sweden

Type II colloidal semiconductor quantum dots are nanoparticles with a 'core-shell' structure which on photoexcitation results in spatially separated carriers. This reduces the recombination rate for these carriers, which can be used in many applications such as solar cells. However, colloidal QDs do not necessarily have the target composition, or have complete and atomically-abrupt interfaces between the core and the shell. Moreover, significant surface degradation of colloidal QDs has been observed[1], and this influences carrier recombination as well as the bandgap structure within the QDs. The purpose of this study is to investigate how oxidation affects the structure of type II quantum dots through comparison of QDs that both have and have not been after exposed to ambient conditions.

Synchrotron-radiation- (SR-) excited x-ray photoelectron spectroscopy (XPS) is suitable for this study[1, 2]. The principle of depth profiling XPS is that the information deep inside the dots can be revealed by increasing the inelastic mean free path length (IMFP) of the photoelectrons. This IMFP parameter depends on the kinetic energy of the photoelectrons that can be varied by tuning the photon energy using a synchrotron source. In this work, we performed depth-profiling XPS on CdTe (core)/CdSe (shell)/CdS (shell)/butylamine acid (BA) (ligand) quantum dots.

[1] S. J. O. Hardman, D. M. Graham, S. K. Stubbs, B. F. Spencer, E. A. Seddon, H. T. Fung, S. Gardonio, F. Sirotti, M. G. Silly, J. Akhtar, P. O’Brien, D. J. Binks and W. R. Flavell, Phys. Chem. Chem. Phys. 13, 20275 (2011)

[2] S. M. Fairclough, E. J. Tyrrell, D. M. Graham, P. J. B. Lunt, S. J. O. Hardman, A. Pietzsch, F. Hennies, J. Moghal, W. R. Flavell, A. A. R. Watt and J. M. Smith, J. Phys. Chem. C 116, 26898 (2012)

## P.05 Hydrophobin phase-Transfer of quantum dots

L Sandiford, M Burkitt-Gray, S Taniguchi, E Rosca, R A Khanbeigi, M Thanou, L A Dailey, W Wohlleben, B Von Vacano, R T M de Rosales, P Dobson and M Green

King's College London, UK

There is increasing interest in the use of quantum dots (QDs) for biological applications due to their tuneable emission, long-lasting luminescence and high quantum yields. However, current synthesis routes often result in water insoluble particles that require phase-transfer either by surface ligand exchange or encapsulation. This study focuses on surface encapsulation using the commercially available H star protein B, a class-I hydrophobin with a molecular weight of 18.8 kDa and a diameter of *ca.* 1.2 nm. Hydrophobins are derived from filamentous fungi and are a class of cysteine-rich amphiphilic proteins consisting of approximately 100 amino acid residues. Their biocompatibility and stability against pH and ionic salts arising in biological media makes them favourable for use as a phase-transfer reagent.

A straightforward, quick and effective aqueous phase-transfer method for both III-V and II-VI QDs has been developed, maintaining optical properties and allowing the potential for functionalization. Characterisation using transmission electron microscopy revealed an initial core size of 6 nm with no change once surface encapsulation had occurred. Dynamic light scattering measurements of the hydrophobin-QDs gave a hydrodynamic diameter of 42.35 ± 4.15 nm. Absorption and emission profiles obtained before and after phase-transfer displayed no significant shift in the absorption or emission wavelength of the QDs.

This research so far has demonstrated that these amphiphilic proteins can be used to simply transfer inorganic nanoparticles to water whilst retaining a significant amount of their emissive characteristics. Future work will be aimed at investigating the cell uptake of these hydrophobin stabilized QDs *in vitro* using confocal microscopy.

## P.06 **Synthesis of ternary lead chalcogenide quantum dots and related structures**

P D McNaughter and P O'Brien

University of Manchester, UK

Quantum dots (QDs) are attractive light harvesters for solar cells and have resulted in a variety of QD sensitised solar cells (QDSSCs). The ability to tune the band gap makes QDs attractive in solar cells as this allows harvesting in controlled region of the solar spectrum[1]. The band gap of a QD is typically controlled by adjustment of the size of the QD, i.e. a smaller QD has a larger band gap. Another method to control the band gap and maintain nanocrystal size is to create an alloy of semicondutors.

Lead chalcogenide nanocrystals are of interest for solar cells due to their tunable band gaps within the infra-red part of the solar spectrum. This combined with their large exciton Bohr radii, i.e. PbS with 18 nm and PbSe with 47 nm, allows for wide tunability of the band gap with nanocrystal size. The use of ternary $PbS_xSe_{1-x}$ QDs opens the possibility of creating nanocrystals with properties of both of the binary counterparts. In the case of PbS a larger $V_{OC}$ has been observed at similar band gaps to the PbSe counterparts while PbSe nanocrystals generate larger short circuit photocurrents than PbS devices[2].

Ternary lead chalcogenide QDs have previously been synthesised in our group using duel source methods[3]. In this work the synthesis of high quality $PbS_xSe_{1-x}$ QDs has been achieved using an adapted methodology. This methodology has been extended to synthesise $PbS_xSe_{1-x}$ quantum rods using combinations of surface capping agents.

[1] P. V. Kamat, J. Phys. Chem. Lett., 2013, 4, 908–918, DOI: 10.1021/jz400052e

[2] J. M. Luther, M. Law, M. C. Beard, Q. Song, M. O. Reese, R. J. Ellingson and A. J. Nozik, Nano Lett., 2008, 8, 3488–3492, DOI: 10.1021/nl802476m

[3] J. Akhtar, M. Afzaal, M. Banski, A. Podhorodecki, M. Syperek, J. Misiewicz, U. Bangert, S. J. O. Hardman, D. M. Graham, W. R. Flavell, D. J. Binks, S. Gardonio and P. O'Brien, J. Am. Chem. Soc., 2011, 133, 5602–5609, DOI: 10.1021/ja200750s

## P.07 **Atomistic study of InSb quantum dots**

A M Sills, P Harrison and M Califano

University of Leeds, UK

Quantum dot solar cells present a promising alternative to conventional photovoltaic devices. Unlike in bulk semiconductors, the carriers experience quantum confinement within the boundaries of the crystal. This phenomenon makes way for a new model of excitation known as carrier multiplication, whereby multiple electron hole pairs can be created from the absorption of just a single photon. Currently PbSe is the most widely used material in these devices, however InSb could potentially present an attractive alternative due to its high room-temperature carrier mobility ($78 \times 10^3$ $cm^2/(Vs)$) of any, together with a small band gap (0.17 eV at 300 K) and the largest known value for the exciton Bohr radius ($\sim$60 nm). As a result of these properties, reducing the size of InSb crystals to the sub-10 nm range should lead to extremely strong quantum confinement. Here, we employ Atomistic semi-empirical pseudopotential methods to investigate the optical and electronic properties of nearly spherical colloidal InSb nanocrystals. More specifically, the size dependent absorption spectra are calculated for structures with diameters ranging from around 3nm to 7nm, which correspond to the interband (valence to conduction) exciton energies. The chief motivation behind this is to shed some light on key differences between the currently available theoretical [1] and experimental [2] data on this topic, where 8 band k*p methods appear to overestimate the bandgap by 0.5 eV for structures with diameters of ~3nm. Our calculated optical bandgaps are in agreement with experiment, at small sizes, confirming the accuracy of our atomistic method.

[1] Efros, A., & Rosen, M. (1998 *Physical Review B*, *58*(11), 7120–7135
[2] Liu, W et al. (2012). *Journal of the American Chemical Society*, *134*(50), 20258–61

**Institute of Physics**
76 Portland Place, London W1B 1NT, UK
Telephone: +44 (0)20 7470 4800
Fax: +44 (0)20 7470 4848
**www.iop.org/conferences**

Registered Charity Number: 293851