



## International Workshop

# Photonics of **Functional Nanomaterials**

6 – 9 May 2013

*City University of Hong Kong*

**Sponsored by**



Croucher Foundation  
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Centre for  
Functional  
Photonics  
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City University  
of Hong Kong



**Department of Chemistry**

RGC Theme-Based Research Scheme on  
Challenges in Organic Photo-Voltaics and Light Emitting Diodes  
- A Concerted Multi-Disciplinary and Multi-Institutional Effort



## International Workshop

# Photonics of **Functional Nanomaterials**

6 – 9 May 2013

*Wei Hing Theatre, City University of Hong Kong*

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Andrey Rogach, *City University of Hong Kong*  
Vivian W.W. Yam, *The University of Hong Kong*  
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### Acknowledgements

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# Nanoscale



## GENERAL INFORMATION

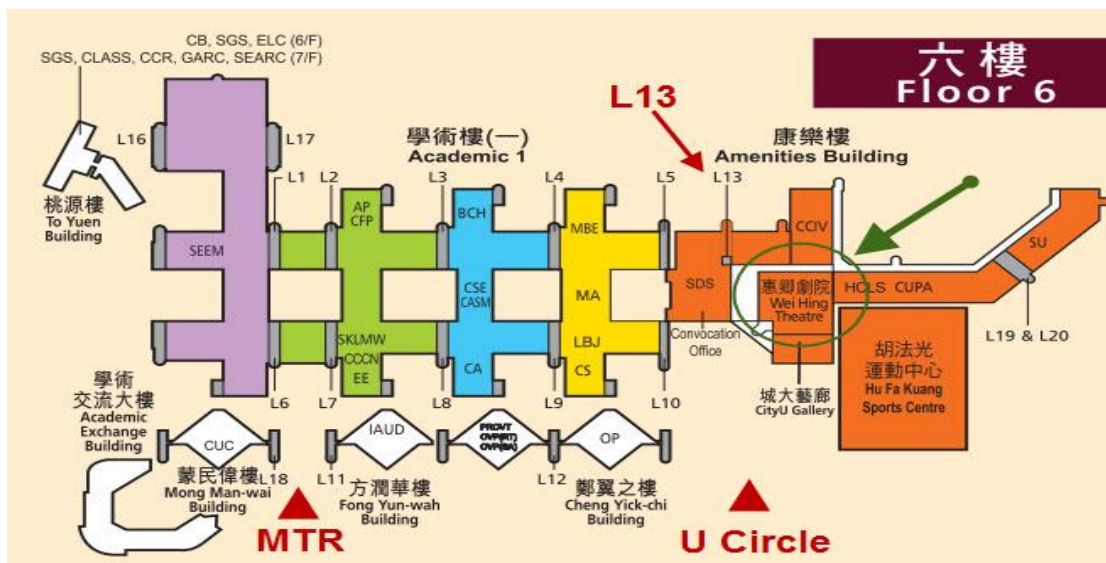
### Registration

Wei Hing Theatre, 6 Floor, Academic Building 1, CityU (Lift 13, see the map below)

08:00 – 16:00 (Monday, 6 May)      08:30 – 11:00 (Tuesday, 7 May)      08:30 – 11:00 (Wednesday, 8 May)

### Conference Venue

Wei Hing Theatre, 6 Floor, Academic Building 1, CityU (Lift 13, see the map below)



### Lunches

8 Floor City Chinese Restaurant

12:40 – 14:00 on 6, 7, 9 May.

- Lunches are covered by the registration fee and are provided for invited speakers
- Lunch tickets will be issued at the registration desk

### Internet

Access to the WLAN internet will be available at City University campus. You will receive the login account and password at the registration desk.

### Boat Trip

Starts at 13:00 on Wednesday, 8 May; includes buffet

Bus pick up at 12:45 from the University Circle (U Circle, see the map above)

### Disclaimer

**The Organizers do not hold any liabilities on damages, losses, health issues, etc. All participants are advised to take care about their travel and health insurances related to this Workshop.**



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## WELCOMING MESSAGE

It is our pleasure to welcome you to International Workshop “Photonics of Functional Nanomaterials”, which will be hosted by the Centre for Functional Photonics of City University of Hong Kong.

Recent progress in nanoscience and nanotechnology allows us to explore photonic functions of artificially fabricated nano-structures, expanding fundamental studies of light-matter interactions and their potential applications in photonics, plasmonics, and biomedicine to the nanoscale. The Workshop will provide a forum for interdisciplinary research in the field of optically active nanostructures. The topics include light harvesting and emission with molecular complexes, conjugated polymers, upconversion nanoparticles, semiconductor nanocrystals and their hybrid structures; plasmonics with metal nanostructures; and metamaterials.

We would like to take this opportunity to acknowledge the Croucher Foundation of Hong Kong for the financial support of this Workshop, and to thank all invited speakers as well as all participants presenting contributed talks and posters. In particular, we thank Kennex Wong and Andrei Sussha for their excellent job devoted to organization of this Workshop.

Please enjoy the science at the Workshop, the communication with colleagues, and please enjoy Hong Kong!

Andrey Rogach

*City University of Hong Kong*

Vivian W. W. Yam

*University of Hong Kong*

Jianfang Wang

*Chinese University of Hong Kong*



## Program of International Workshop Photonic of Functional Nanomaterials

	Monday 06.05.2013	Tuesday 07.05.2013	Wednesday 08.05.2013	Thursday 09.05.2013
8:40	Opening Remarks Andrey Rogach			
9:00	Invited Yury Rakovich	Invited Oliver Schmidt	Invited D.D. Sarma	Invited Zee Hwan Kim
9:30	Hilmi Volkan Demir	Yang Yang Li	Bingsuo Zou	Sun Handong
9:50	Yan-Cheng Lin	Zhiyong Fan	Robert Pansu	Hongbing Fu
10:10	Rui Chen	Amitava Patra	Haizheng Zhong	Ni Zhao
10:30	Coffee Break	Coffee Break	Coffee Break	Coffee Break
11:00	Invited Din Ping Tsai	Invited Prashant Kamat	Invited Lian-Mao Peng	Invited Vasudevanpillai Biju
11:30	Invited Ben Zhong Tang	Invited Kok Wai Cheah	Shengyi Yang	Deng Renren
12:00	Qihua Xiong	Taro Toyoda	Timothy T.Y. Tan	S. Carregal-Romero
12:20	Kai Wang	Xueqing Xu	Kin Hung Fung	Stephen Kershaw
12:40	Lunch	Lunch	Group Photo	Lunch
			Boat Trip	
14:00	Invited John Pendry	Invited Naomi Halas		Invited Xiaogang Liu
14:30	Lin Jiang	Eric Wei-Guang Diau		Sur Chattopadhyay
14:50	Yu Luo	Qing Shen		Xie Xiaoji
15:10	Weihai Ni	K.W. Sun		Dorleta Jimenez de Aberasturi
15:30	Coffee Break	Coffee Break		Coffee Break
16:00	Invited Peter Norldlander	Poster Session		Invited Jochen Feldmann
16:30	Invited Alexander Govorov			Tze Chien Sum
17:00	Qiang Zhang			Closing Remarks Andrey Rogach
17:20	Xiao Ming Zhang			
17:40	Duan Bo			
18:00				



**Monday 06.05.2013**

- 8:40-9:00 **Andrey Rogach** (*City University of Hong Kong, Hong Kong*)  
Opening Remarks
- 9:00-9:30 **Yury Rakovich** (*CFM San Sebastian, Spain*)  
Quantum Dots for Bioenergetics: Exploration of Energy Transfer from Semiconductor Nanocrystals to Photosynthetic Biological Complexes.
- 9:30-9:50 **Hilmi Volkan Demir** (*Bilkent University, Turkey / NTU Singapore*)  
Exciton Transfer Dynamics in Hybrid Organic Nanocomposites of Colloidal Quantum Dots.
- 9:50-10:10 **Yan-Cheng Lin** (*National Chiao Tung University, Taiwan*)  
Photoluminescence and Time-resolved Carrier Dynamics in Thiol-capped CdTe Nanocrystals under High Pressure.
- 10:10-10:30 **Rui Chen** (*Nanyang Technological University, Singapore*)  
Energy Transfer as an Effective Tool to Achieve Functional Nanomaterials.
- 10:30-11:00 **Coffee Break**
- 11:00-11:30 **Din Ping Tsai** (*National Taiwan University, Taiwan*)  
Fabrication of Plasmonic Functional Metamaterials and its Applications.
- 11:30-12:00 **Zhong Ben Tang** (*Hong Kong University of Science & Technology, Hong Kong*)  
Luminogenic Polymeric Materials Constructed from Tetraphenylethene Building Blocks: Aggregation-induced Emission, Two-Photon Absorption, Optical Limiting and Light Refraction.
- 12:00-12:20 **Qihua Xiong** (*Nanyang Technological University, Singapore*)  
Laser Cooling of a Semiconductor by 40 K.
- 12:20-12:40 **Kai Wang** (*Huazhong University of Science and Technology, China*) Laterally Emitted Surface Second Harmonic Generation in a Single ZnTe Nanowire.
- 12:40-14:00 **Lunch**
- 14:00-14:30 **John Pendry** (*Imperial College, UK*)  
Understanding Singular Plasmonic Structures.
- 14:30-14:50 **Lin Jiang** (*Soochow University, China*)  
Advance Plasmonic Properties Based on Multiplexed One-dimensional Arrays of Au Nanoparticles.
- 14:50-15:10 **Yu Luo** (*Imperial College London, UK*)  
Plasmonic Light Harvesting Structures: the Nonlocal and Quantum Tunnelling Effects.
- 15:10-15:30 **Weihai Ni** (*Suzhou Institute of Nano Tech and Nano Bionics, China*)  
Colloidal Chemistry in an Optical Trap.
- 15:30-16:00 **Coffee Break**
- 16:00-16:30 **Peter Nordlander** (*Rice University, USA*)  
Plasmonics: From Fano Interference to Quantum Effects and Light Harvesting.
- 16:30-17:00 **Alexander Govorov** (*University of Ohio, USA*)  
Optically-active Hybrid Nanostructures: Exciton-Plasmon Interaction, Fano Effect, and Plasmonic Chirality.
- 17:00-17:20 **Qiang Zhang** (*Harbin Institute of Technology, China*)  
Plasmonic Nanostructures with Fano Resonances and their Unusual Optical Force Effect.
- 17:20-17:40 **Xiao Ming Zhang** (*Harbin Institute of Technology, China*)  
Tractor Beams to Pull Plasmonic Nanoparticles of Arbitrary Shape: A Numerical Study Based on DDA.
- 17:40-18:00 **Duan Bo** (*Nanyang Technological University, Singapore*)  
SERS-Active Nanoparticles for Sensitive and Selective Detection of Heavy Metal Ions.

**Tuesday 07.05.2013**

- 9:00-9:30 **Oliver Schmidt** (*IFW Dresden, Germany*)  
Photonics with Deformable Nanomembranes.
- 9:30-9:50 **Yang Yang Li** (*City University of Hong Kong, Hong Kong*)  
Metallic Rugate Structures for Near-perfect Absorbers in Visible and Near-infrared Regions.
- 9:50-10:10 **Zhiyong Fan** (*Hong Kong University of Science and Technology, Hong Kong*)  
Three-dimensional Nanostructures for Cost-effective Solar Energy Harvesting.
- 10:10-10:30 **Amitava Patra** (*Indian Association for the Cultivation of Science, India*)  
Luminescent Nano Materials for Photonic Applications.
- 10:30-11:00 **Coffee Break**
- 11:00-11:30 **Prashant Kamat** (*University of Notre Dame, USA*)  
Quantum Dot Solar Cells. Emerging Strategies and Challenges.
- 11:30-11:50 **Kok Wai Cheah** (*Hong Kong Baptist University, Hong Kong*)  
Novel Plasmonic Materials and Devices.
- 12:00-12:20 **Taro Toyoda** (*The University of Electro-Communications, Japan*)  
Photovoltaic Characteristics of CdS/CdSe Quantum Dot-sensitized Solar Cells Coupled to Inverse Opal TiO<sub>2</sub> Electrodes together with Photoexcited Carrier Dynamics.
- 12:20-12:40 **Xueqing Xu** (*Guangzhou Institute of Energy Conversion, China*)  
Characterization of CuInS<sub>2</sub> Sensitized Nanocrystalline TiO<sub>2</sub> Films Fabricated via SILAR.
- 12:40-14:00 **Lunch**
- 14:00-14:30 **Naomi Halas** (*Rice University, USA*)  
Frontiers of Plasmonics: New Materials, Interactions, and Applications.
- 14:30-14:50 **Eric Wei-Guang Diao** (*National Chiao Tung University, Taiwan*)  
Formation of Novel TiO<sub>2</sub> Nanostructures for Highly Efficient Dye-sensitized Solar Cells.
- 14:50-15:10 **Qing Shen** (*The University of Electro-Communications, Japan*)  
Improvement of Charge Separation and Suppression of Charge Recombination in ZnO/P3HT Hybrid Solar Cells by Locating Dye at ZnO/P3HT Interfaces.
- 15:30-15:30 **K.W. Sun** (*National Chiao Tung University, Taiwan*)  
Enhancing the Performance of Si Solar Cells Using Nanophosphors with Metal-enhanced Fluorescence.
- 15:30-16:00 **Coffee Break**
- 16:00-19:00 **Poster Session**

**Wednesday 08.05.2013**

- 9:00-9:30 **D.D. Sarma** (*IISC Bangalore, India*)  
Photoluminescence from Semiconductor Nanocrystals.
- 9:30-9:50 **Bingsuo Zou** (*Beijing Institute of Technology, China*)  
Optical Properties of Mn(II) Ions Doped II-VI Semiconductor Nanostructures.
- 9:50-10:10 **Robert Pansu** (*CEA Grenoble, France*)  
The Poisson Distribution of Quenchers in the Fluorescent Dynamics of Nanoparticles.
- 10:10-10:30 **Haizheng Zhong** (*Beijing Institute of Technology, China*)  
Colloidal I–III–VI Semiconductor Nanocrystals for Light-emitting Applications.
- 10:30-11:00 **Coffee Break**
- 11:00-11:30 **Lian-Mao Peng** (*Peking University, China*)  
Light Emission and Detection with Carbon Nanotubes.
- 11:30-11:50 **Shengyi Yang** (*Beijing Institute of Technology, China*)  
Polymer Solar Cells Based on Carbon Nanotubes Decorated with Colloidal Quantum Dots.
- 11:50-12:10 **Timothy T.Y. Tan** (*Nanyang Technological University, Singapore*)  
Lanthanide-based Nanomaterials in Nanomedicine.
- 12:10-12:30 **Kin Hung Fung** (*The Hong Kong Polytechnic University, Hong Kong*)  
Effects of Broken Time-reversal Symmetry on Periodic Resonator Arrays.
- 12:30-12:45 **Group Photo**
- 13:00 **Boat Trip**

**Thursday 09.05.2013**

- 9:00-9:30 **Zee Hwan Kim** (*Korea University, Korea*)  
Nano-Plasmonics for Single-Molecule Photochemistry and Chemical Microscopy.
- 9:30-9:50 **Sun Handong** (*Nanyang Technological University, Singapore*)  
Micro-Resonators: WGM Lasing and Sensing Applications.
- 9:50-10:10 **Hongbing Fu** (*Chinese Academy of Sciences, China*)  
Slab-nanocrystals of H-aggregation Organic Semiconductors for Low-threshold Nanolasers.
- 10:10-10:30 **Ni Zhao** (*Chinese University of Hong Kong, Hong Kong*)  
Fast, Air-Stable Infrared Photoconductors Based on Water-soluble HgTe Quantum Dots.
- 10:30-11:00 **Coffee Break**
- 11:00-11:30 **Vasudevanpillai Biju** (*AIST, Japan*)  
Multifunctional Engineered Nanomaterials: Bioimaging Applications Vs Toxicity.
- 11:30-11:50 **Deng Renren** (*National University of Singapore, Singapore*)  
Upconversion Nanoparticles Based Energy Transfer for Sensitive Bio-detection.
- 11:50-12:10 **S. Carregal-Romero** (*Institute of Physics and WZMW, Germany*)  
Light-Addressable and Degradable Silica Capsules for Cytosolic Release.
- 12:10-12:40 **Stephen Kershaw** (*City University of Hong Kong, Hong Kong*)  
Emerging Quantum Dot Mid-IR Emitter and Detector Technologies.
- 12:40-14:00  
**Lunch**
- 14:00-14:30 **Xiaogang Liu** (*National University of Singapore, Singapore*)  
Rare-earth Nanocrystals: A New Class of Luminescent Bioprobes.
- 14:30-14:50 **Sur Chattopadhyay** (*National Yang Ming University, Taiwan*)  
Bio-inspired Artificial Photonics Nanostructures for Efficient Antireflective Surfaces and Surface Enhanced Raman Scattering Platform.
- 14:50-15:10 **Xie Xiaoji** (*National University of Singapore, Singapore*)  
Gold Nanoparticle-based Colorimetric Assays.
- 15:10-15:30 **Dorleta Jimenez de Aberasturi** (*Universität Marburg, Germany*)  
How Nano- and Microparticles Can Improve the Properties of Ion-selective Ligands.
- 15:30-16:00 **Coffee Break**
- 16:00-16:30 **Jochen Feldmann** (*Ludwig-Maximilians-Universität München, Germany*)  
Photocatalysis with Semiconductor Nanocrystals
- 16:30-16:50 **Tze Chien Sum** (*Nanyang Technological University, Singapore*)  
Ultralow Two-Photon Pumped Lasing Threshold from Seeded CdSe/CdS Nanorod Heterostructures.
- 16:50-17:10 **Andrey Rogach** (*City University of Hong Kong, Hong Kong*)  
Closing Remarks



**ABSTRACTS**  
**ORAL PRESENTATIONS**

# Quantum Dots for Bioenergetics: Exploration of Energy Transfer from Semiconductor Nanocrystals to Photosynthetic Biological Complexes

Yury Rakovich

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## Abstract

I will review our recent results on development of hybrid material build from semiconductor nanocrystals and photoactive bio-complexes: - membrane protein bacteriorhodopsin and photosynthetic reaction centers purified from bacteria *Rhodobacter spheroides*. We have demonstrated that nanocrystals specifically immobilized on the surface of the photo-active bio-systems are able to play the role of a built-in light energy convertor by harvesting light which would not be absorbed efficiently by the bio-system alone. Semiconductor nanocrystals were further demonstrated to be able to transfer the harvested energy via highly efficient FRET to this complex biological system. We have also demonstrated a first proof-of-the-principle evidence that the bacteriorhodopsin is able to utilize the transferred by nanocrystals additional energy to improve the efficiency of its biological function.

## Exciton Transfer Dynamics in Hybrid Organic Nanocomposites of Colloidal Quantum Dots

Burak Guzelturk<sup>1</sup>, Pedro Ludwig Hernandez Martinez<sup>1,2</sup>, Donus Tuncel<sup>1</sup>, Hilmi Volkan Demir<sup>1,2</sup>

<sup>1</sup> *Department of Electrical and Electronics Engineering, Department of Physics, Department of Chemistry and UNAM – Institute of materials science and nanotechnology, Bilkent University, TR-06800, Ankara, Turkey*

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### Abstract

Colloidal quantum dots (CQDs) make a promising class of materials for optoelectronics owing to their favourable optical properties. However, CQDs are limited in some of their properties including charge transport and film formation. On the other hand, conjugated polymers (CPs) are known to exhibit better charge transport capabilities along with the versatile mechanical film properties as compared to the CQDs. Hence, CQD:CP hybrid systems hold great promise to enable new functional nanomaterials. In this work, we have developed a hybrid material system of CdSe/CdS/ZnS core/graded-shell CQDs and carboxyl-group functionalized polyfluorene derivative CPs. The nanostructure showed highly suppressed phase segregation even at high CQD loadings owing to the specific functionalization of the polymer. Suppressed phase segregation allowed us to study exciton transfer dynamics at high CQD loading cases (up to 45 w%). Here, nonradiative resonance energy transfer (NRET) from the functionalized CPs to the CQDs was studied using temperature dependent time-resolved fluorescence spectroscopy and theoretical modelling of the experimental results.

Unlike the common belief in the literature, where exciton diffusion in the CP was found to be the vital process for NRET to occur [2], in this study it is found that the exciton diffusion does not strongly assist NRET at high CQD loading cases. In the case of low CQD loadings (<~3w%) the CQDs are separated on the average much larger than the Förster radius such that exciton diffusion assistance is essential for NRET to happen. However, at high CQD loadings, the exciton diffusion assistance to NRET is not critical, since the CQDs are separated by a distance that is comparable or smaller than the Förster radius. Modelling of the experimental data revealed that the exciton diffusion is even suppressed at high CQD loadings. This suppression was found to be due to both increased NRET rates and morphological changes. Shortening of the exciton lifetime due to increased exciton transfer rates restricts the diffusion of the excitons. Moreover, morphological changes including isolation of the polymer chains at high CQD loadings leads to dominance of intra-chain exciton diffusion, which has been shown to be intrinsically slower than inter-chain exciton diffusion process. [2]

To summarize, here the cooperative and competitive nature of the exciton diffusion assistance was demonstrated for exciton transfer in the CQD:CP hybrids for high CQD loadings in comparison to low loadings. The findings indicate that exciton diffusion is strongly suppressed in the case of high CQD loadings.

### References

- [1] T. Stöferle, *et al.* Nano Lett. **2009**, 9, 453-456.
- [2] D. Beljonne, *et al.* PNAS, **2002**, 99, 10982-10987.

# Photoluminescence and Time-resolved Carrier Dynamics in Thiol-capped CdTe Nanocrystals under High Pressure

Yan-Cheng Lin,\*<sup>a</sup> Wu-Ching Chou,<sup>a</sup> Andrei S. Susha,<sup>b</sup> Stephen V. Kershaw,<sup>b</sup> and Andrey L. Rogach<sup>b</sup>

<sup>a</sup>*Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan*

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## Abstract

The application of static high pressure provides a method for precisely controlling and investigating many fundamental and unique properties of semiconductor nanocrystals (NCs). This study systematically investigates the high-pressure photoluminescence (PL) and time-resolved carrier dynamics of thiol-capped CdTe NCs of different sizes, at different concentrations, and in various stress environments. The zincblende-to-rocksalt phase transition in thiol-capped CdTe NCs is observed at a pressure far in excess of the bulk phase transition pressure. Additionally, the process of transformation depends strongly on NC size, and the phase transition pressure increases with NC size. These peculiar phenomena are attributed to the distinctive bonding of thiols to the NC surface. In a nonhydrostatic environment, considerable flattening of the PL energy of CdTe NCs powder is observed above 3.0 GPa. Furthermore, asymmetric and double-peak PL emissions are obtained from a concentrated solution of CdTe NCs under hydrostatic pressure, implying the feasibility of pressure-induced interparticle coupling.

## Energy Transfer as an Effective Tool to Achieve Functional Nanomaterials

Rui Chen,<sup>\*</sup> and Handong Sun

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### Abstract

Energy transfer is an optical process characterized by transferring the energy from excited donors to acceptors through interaction. For donor and acceptor with spectral overlap, the energy transfer can be realized by either nonradiative energy transfer (Förster resonance energy transfer: FRET) or radiative energy transfer (radiative recombination in the donor first and then reabsorption by the acceptor). Energy transfer can be a very useful tool to modify the optical property of nanomaterials. Example here includes the interaction between upconversion nanoparticles with dye to realize multicolor emission and improve the performance as luminescence temperature sensor <sup>[1]</sup>; the incorporation of graphene with upconversion nanoparticles to significantly modify the nonlinear optical property and achieve superior optical limiting behavior <sup>[2]</sup>; the surface coating of rare-earth oxide layer on ZnO nanowires to enable the efficient red emission <sup>[3]</sup>. Research along these lines may help to advance functional material applications by combining the advantage with donor and acceptor.

### References

- [1] Chen, R., Ta, V. D., Xiao, F., Zhang, Q. Y., & Sun, H. D. Multicolor Hybrid Upconversion Nanoparticles and Their Improved Performance as Luminescence Temperature Sensors Due to Energy Transfer. *Small* (DOI: 10.1002/sml.201202287)
- [2] He, T., Wei, W., Ma, L., Chen, R., Wu, S., Zhang, H., Yang, Y., Ma, J., Huang, L., Gurzadyan, G. G. & Sun, H. Mechanism Studies on the Superior Optical Limiting Observed in Graphene Oxide Covalently Functionalized with Upconversion NaYF<sub>4</sub>:Yb<sup>3+</sup>/Er<sup>3+</sup> Nanoparticles. *Small* **8**, 2163, (2012).
- [3] Chen, R., Shen, Y. Q., Xiao, F., Liu, B., Gurzadyan, G. G., Dong, Z. L., Sun, X. W. & Sun, H. D. Surface Eu-Treated ZnO Nanowires with Efficient Red Emission. *J. Phys. Chem. C* **114**, 18081, (2010).

## Fabrication of Plasmonic Functional Metamaterials and its Applications

W. T. Chen<sup>1,2</sup>, Y.-W. Huang<sup>1</sup>, K.-Y. Yang<sup>1,3</sup>, M. L. Tseng<sup>1,2</sup>, P. C. Wu<sup>1,2</sup>, C. M. Chang<sup>2,3,4</sup>, S. Sun<sup>2,5</sup>, B. H. Cheng<sup>3,6</sup>, Y. J. Liu<sup>2,3</sup>, C. Y. Liao<sup>2</sup>, H.-K. Tsai<sup>2</sup>, K. S. Chung<sup>2</sup>, Y. L. Chen<sup>2</sup>, H. Y. Chung<sup>3</sup>, Y.-C. Lan<sup>6</sup>, D.-W. Huang<sup>4</sup>, A. Q. Liu<sup>7</sup>, G.-Y. Guo<sup>2</sup>, L. Zhou<sup>8</sup>, N. I. Zheludev<sup>9</sup>, D. P. Tsai<sup>1,2,3,\*</sup>

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### Abstract

We design, fabricate and integrate both of multilayer and three dimensional plasmonic metamaterials [1, 2] for realization on coupling interactions between plasmonic metamaterials and its practical applications, such as electromagnetically induced transparency (EIT) through magnetic interaction, toroidal metamaterials and light manipulation via nanostructures [3, 4]. Figures 1(a) and (b) show the SEM images of 3D split ring resonator (SRR) structures which are fabricated by b-beam lithography with alignment technique and stress-driven assembly method, respectively. High throughput of multilayer structures by laser-induced forward transfer (LIFT) technology will be discussed. LIFT technique is a useful method for fabricating electronic and photonic nanostructures. Using the femtosecond LIFT technique, the multilayer structures such as stacked split ring resonators and plasmonic cavities can be made with high efficiency [5], as shown in Fig. 1(c). These results provide a pathway for fabricating and analyzing the plasmonic metamaterials both in two- and three-dimensional.

### References

1. W. T. Chen, et al., "Optical magnetic response in three-dimensional metamaterial of upright plasmonic meta-molecules" *Opt. Express*, 19, 12837-12842 (2011).
2. M. L. Tseng, et al., "Fabrication of multilayer metamaterials by femtosecond laser-induced forward-transfer technique" *Laser Photonics Rev.*, 6, 702-707 (2012).
3. P. C. Wu, et al., "Magnetic plasmon induced transparency in three-dimensional metamolecules" *Nanophotonics*, 2, 131-138 (2012).
4. Y.-W. Huang, et al., "Toroidal lasing spaser" *Scientific reports*, in press (2013).
5. W. T. Chen, et al., "Fabrication of three-dimensional plasmonic cavity by femtosecond laser-induced forward transfer" *Opt. Express*, 21, 618-625 (2013).

# Luminogenic Polymeric Materials Constructed from Tetraphenylethene Building Blocks: Aggregation-induced Emission, Two-Photon Absorption, Optical Limiting and Light Refraction

Ben Zhong Tang

*Department of Chemistry, Institute of Advanced Study, State Key Laboratory of Molecular Neuroscience, Institute of Molecular Functional Materials and Division of Biomedical Engineering, The Hong Kong University of Science & Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong, China.*

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## Abstract

Development of luminescent materials with functional properties is of great importance for academic research and industrial applications. We observe a novel phenomenon of aggregation-induced emission (AIE): a series of non-luminescent (in solution state) molecules is induced to emit efficiently by aggregate formation due to the restriction of intramolecular rotation<sup>[1]</sup>. Such phenomenon has now been extended to polymeric materials<sup>[2]</sup>. Coupled with our strength in acetylenic polymer chemistry, we have designed and synthesized a group of new high molecular weight polymers with varied functionalities and explored their potential applications in optics and electronics.

A series of linear and hyper-branched conjugated polymers constructed from tetraphenylethene (TPE, an archetypal AIE luminogen) have been synthesized via acetylenic polymerizations with high molecular weight in high yields<sup>[3]</sup>. These polymers possess good processability and high thermal stability. They exhibit AIE characteristics, which are exactly opposite to traditional ACQ (aggregation cause quenching) polymers, making them good solid emitters. Optical properties of these AIE conjugated polymers, such as two-photon absorption, optical limiting and light refraction, have been detailed investigated. All these functional properties, coupling with their AIE features, as well as good processability and high thermal stability, make them promising candidates for potential high-tech applications.

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## Laser Cooling of a Semiconductor by 40 K

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### Abstract

Optical irradiation accompanied by spontaneous anti-Stokes emission can lead to cooling of matter, a phenomenon known as laser cooling or optical refrigeration proposed in 1929 by Peter Pringsheim. In solid state materials, the cooling is achieved by annihilation of lattice vibrations (i.e., phonons). Since the first experimental demonstration in rare-earth doped glasses, considerable progress has been made particularly in ytterbium-doped glasses or crystals with a recent record of ~110 K cooling from ambient, surpassing the thermoelectric Peltier cooler. On the other hand, it would be more tantalizing to realize laser cooling in direct band-gap semiconductors. Semiconductors exhibit more efficient pump light absorption, much lower achievable cooling temperature and direct integrability into electronic and photonic devices. However, so far no net-cooling in semiconductors has been achieved despite of many experimental and theoretical efforts in the past few decades, mainly on III-V group gallium arsenide quantum wells. Here we demonstrate the first net laser cooling in semiconductors using cadmium sulfide (CdS) nanobelt facilitated by multiple longitudinal optical phonon assisted upconversion due to strong and enhanced Fröhlich interactions. Under a low power excitation, we have achieved a ~40 K and ~20 K net cooling in CdS nanobelts starting from 290 K pumped by 514 nm and 532 nm lasers, respectively. The cooling effect is critically dependent on the pumping wavelength, the blue shifting parameters and the absorption, the latter of which can be evaluated from photoconductivity measurement on individual nanowire level. Detailed spectroscopy analysis suggests that cooling to even lower temperature is possible in CdS nanobelt if thermal management is optimized. Our findings suggest alternative II-VI semiconductors for laser cooling compared to III-V GaAs-based heterostructures and may find promising applications in the field of cryogenics with the advantage of compactness, vibration- and cryogen-free, high reliability and direct integrability into nanoscale electronic and photonic devices. A concept of all-solid-state cryocooler based on semiconductor nanobelt will also be presented.

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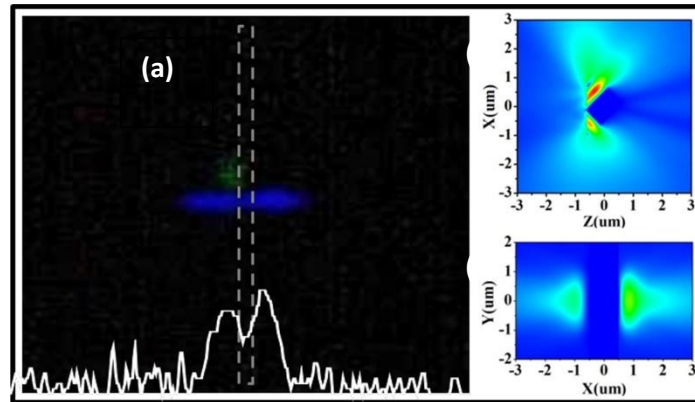
# Laterally Emitted Surface Second Harmonic Generation in a Single ZnTe Nanowire

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## Abstract

We report a direct observation on the unique laterally emitted surface second harmonic generation (SHG) in a single ZnTe nanowire. The highly directional surface SHG signal that polarizes along the direction vertical to the nanowire growth axis, is significantly larger than the bulk SHG contribution, indicating a high efficiency of surface SHG. Two strong SHG peaks are observed on both sides of the nanowire surfaces in the far-field scanning images, which is further supported by FDTD simulations, demonstrating that the unique laterally emitted signal is ascribed to surface SHG in the ZnTe nanowire. The surface SHG in a single ZnTe nanowire with unique lateral emission and high conversion efficiency shows great potential applications in short-wavelength nanolasers, nonlinear microscopy and polarization dependent photonic integrating.



(a) Dark field image of laterally emitted the surface SHG in the ZnTe nanowire pumped with the 800 nm femtosecond laser.

(b) and (c) FDTD simulations of the field distribution of pumping laser in nanowire with a rectangular cross section.

# Understanding Singular Plamonic Structures

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## **Abstract**

Singular metal structures, such as two touching gold spheres, or a rough silver surface, are well know concentrators of radiation responsible for such remarkable effects as surface enhanced Raman signals (SERS). They also play a role in dispersion forces between surfaces, in near field heat transfer, and in quantum friction, though the latter has yet to see experimental verification. Although commercial computer codes allow us to investigate these systems, much greater understanding can be had through analytic treatments enabled by the new technique of transformation optics.

I shall discuss recent progress in the treatment of two spheres in very close proximity where computation techniques are challenged and where our description of the optical response of metals requires refinement.

# Advance Plasmonic Properties Based on Multiplexed One-dimensional Arrays of Au Nanoparticles

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## Abstract

The emergence of plasmonics has raised interest to examine the properties of the collective electronic excitations in metal nanostructure, which shows various promising applications including plasmonic chips, light generation, biosensing, and subwavelength and nonlinear optics. The plasmonic properties are sensitive to changes in the local dielectric environment, which is directly related to the size, shape, and spacing of metal nanostructures. Among various configurations, one-dimensional (1D) nanoparticle arrays are of particular interest because they are a promising approach for deep-subwavelength light confinement and transport. Herein, we demonstrated a synergetic combination of template geometry and electrostatic interaction between nanoparticles and substrate to produce spatially modulated electrostatic potential, which is used to construct 1D multiplexed nanoparticle arrays on one chip. Multiplexed 1D nanoparticle arrays with tunable inter-particle distance and/or multiplexed 1D nanoparticle arrays with different particle size on the same substrate were demonstrated. As a result, the surface plasmon absorption bands on the chip can be tuned depending on the inter-particle distance or the particle size of multiplex 1D arrays, which could enhance the Raman scattering cross section of the adsorbed molecules and result in multiplex surface-enhanced Raman scattering (SERS) response on the chip. This strategy provides a general approach for using colloidal nanoparticle to produce high quality encoded nanostructure with multiplex 1D periodic nanoparticle arrays in desired locations on one chip, which have potential applications in multiplexed response of surface vibrational spectroscopy, biological and chemical diagnostics, and so on. Furthermore, we fabricated 1D complex nanostructures composed of Au nanoparticles and conductive polymer (polypyrrole), where pyrrole can in-situ polymerize on the achieved 1D Au nanoparticle surface. The conductivity of such 1D complex nanostructure was increased upon the light illumination. The advanced optoelectronic device can be achieved based on the nanoantenna effect of 1D plasmonic nanostructures.

## Plasmonic Light Harvesting Structures: the Nonlocal and Quantum Tunnelling Effects

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### Abstract

Metallic nanoparticles that support localized surface plasmon resonances can harvest light into a deep-subwavelength volume, thereby achieving very large field enhancement. Many emerging nanophotonic technologies rely on the careful control of this field enhancement, including cancer therapy, improved photovoltaic devices, and optical antennas for enhanced light-matter interactions. However, at deep subwavelength scales, classical continuum electrodynamics fails to describe the optical responses of nanoparticles owing to nonlocal screening and the spill-out of electrons. Electron correlations that are driven by these effects require a new model of nonlocal transport, which is crucial in nanoscale optoelectronics. In this contribution, I will present a systematic strategy, based on transformation optics, to study the plasmonic interaction at subnanometer scales. Our approach incorporates radiative, nonlocal, and quantum tunnelling effects, and thus can be applied to design realistically sized plasmonic systems. As an example, I will use this method to elucidate the optimum shape of a nanoparticle that maximizes its absorption and field enhancement capabilities.

## Colloidal Chemistry in an Optical Trap

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### Abstract

To date, colloidal chemistry is mostly focused on ensemble solution samples, which is suffered from many limitations. In-depth understanding of the mechanism asks for systematic studies to be done on the basis of single particles. The concept of “Lab on a chip” is advanced recently and featured by many important characteristics including nanoscale manipulation, selectivity of targets, in-situ measurement, and multifunctionality. In order to realize this concept, we propose to develop an approach to colloidal chemistry study using the optical trap.[1] Metal nanostructures, when trapped, is located at the center of the Gaussian beam with high power densities, which not only favors the study of the light-induced chemical reactions, but dramatically accelerates chemistry processes near the surface of the nanoparticle being trapped by elevating the temperature of the nanoparticle through exciting their localized surface plasmon modes. The elevated temperature will also come up with many new phenomena that worth further investigating. This work mainly focuses on the modification and acceleration of surface-chemistry of individual, optically trapped gold nanorods by plasmonic overheating. Depending on the optical trapping power, gold nanorods can exhibit red shifts of their plasmon resonance (i.e., increasing aspect ratio) under oxidative conditions. In contrast, in bulk exclusively blue shifts (decreasing aspect ratios) are observed. Supported by calculations, we explain this finding by local temperatures in the trap exceeding the boiling point of the solvent that cannot be achieved in bulk. Knowledge gained in the study will be of great significance not only in the synthesis of nanostructures but also in the development of functional materials and devices.

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# Plasmonics: From Fano Interference to Quantum Effects and Light Harvesting

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## Abstract

The “plasmon hybridization” concept,[1] shows that the plasmon resonances in complex metallic nanostructures interact and hybridize in an analogous manner as atomic wavefunctions in molecules. The insight gained from this concept provides an important conceptual foundation for the development of new plasmonic structures that can serve as substrates for surface enhanced spectroscopies, chemical and biosensing, and subwavelength plasmonic waveguiding and other applications. The talk is comprised of general overview material interspersed with a few more specialized “hot topics” such as plasmonic Fano resonances,[2] quantum plasmonics,[3] quantum plexcitonics,[4] and active plasmonic nanoantennas for enhanced light harvesting,[5] and plasmon induced chemical reactions.[6]

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# Optically-active Hybrid Nanostructures: Exciton-Plasmon Interaction, Fano Effect, and Plasmonic Chirality

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## Abstract

Excitons and plasmons in nanocrystals strongly interact via Coulomb and electromagnetic fields and this interaction leads to characteristic interference effects which can be observed in optical spectra [1-6]. An interaction between a discrete state of exciton and a continuum of plasmonic states gives rise to Fano-like asymmetric resonances and anti-resonances [2,4]. These interference effects can strongly enhance a visibility of relatively weak exciton signals and can be used for spectroscopy of single nanoparticles and molecules. If a system includes chiral elements (chiral molecules or nanocrystals), the exciton-plasmon interaction is able to alter and enhance circular dichroism (CD) of chiral components [5-8]. In particular, the exciton-plasmon interaction may create new chiral plasmonic lines in CD spectra of a biomolecule-nanocrystal complex [5,7]. Strong CD signals may also appear in purely plasmonic systems with a chiral geometry and a strong particle-particle interaction [6,8]. Recent experiments on molecule-nanocrystal and multi-nanocrystal complexes showed the appearance of strong plasmonic signals in CD spectra [7,8]. Potential applications of dynamic hybrid nanostructures include sensors and new optical and plasmonic materials.

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# Plasmonic Nanostructures with Fano Resonances and their Unusual Optical Force Effect

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## Abstract

Photonic nanostructures that sustain Fano resonances are of both fundamental and application interests. Recently, plasmonic nanosystems featuring multiple Fano spectra are shown to have flexible spectral positioning and line shaping functionalities. In view that optical resonances in plasmonic structure dramatically affect their optical force properties, we study the optical forces induce by Fano resonance in a gold nanorod heterodimer and a ring-disk resonator. For the gold nanorod heterodimer, the numerical results show that there is a binding force reversal between the two nanorods which is due to the out of phase oscillation of the current across the dimer gap. We find that the force reversal may be ubiquitous in the plasmonic structures that sustain Fano resonances and investigated the optical force properties in a ring-disk resonator supporting multiple Fano resonance to confirm that. Our results provide an opto-mechanical way to bridge the plasmonic cluster geometry and spectrum characteristics.



# Tractor Beams to Pull Plasmonic Nanoparticles of Arbitrary Shape: A Numerical Study Based on DDA

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## Abstract

It is well known that light can push an object forward. A focused light beam can also trap particles as small particles will migrate to the intensity maxima as in the case of optical tweezers when the gradient force due to intensity inhomogeneity overcomes the forward scattering force of the photons. Recently, there are a few theoretical reports showing that it is possible to realize a backward scattering force using “tractor beams” (TB) which pull a particle all the way towards the source without an equilibrium point. However, the particles under such studies are all of spherical shape which must not be the case in real situation [1-4]. Here, we develop and implement two methods to calculate the optical forces on three-dimensional arbitrarily-shaped nanoparticles under the illumination of TB. The methods are based on the discrete dipole approximation (DDA) which is a flexible and powerful technique for computing scattering and absorption by targets of arbitrary geometry. We applied two different schemes to calculate the optical forces: (1) DDA plus Lorentz force (DDA-LF) and (2) DDA plus the Maxwell stress tensor integration (DDA-MST). Using both methods, we are able to study both dielectric and metallic particles and examine in detail their scattering force in a TB. In particular, we numerically exploit the possibility of tractor beam for plasmonic nanoparticles of nonspherical shape. The results may be helpful in remote sample collection.

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## SERS-Active Nanoparticles for Sensitive and Selective Detection of Heavy Metal Ions

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### Abstract

Toxic heavy metal ions such as  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  have many detrimental effects on both human health and the environment. Detection of heavy metals in low concentration is of special concern in light of heavy metals' potential for bioaccumulation and biomagnification. Commonly used methods for heavy metal detection (e.g. electrochemical analysis, atomic absorption spectrophotometry, and inductively coupled plasma mass spectrometry, etc.) suffer the disadvantages of being time-consuming, expensive, and cumbersome as well as labour intensive. With the advances in nanotechnology, surface enhanced Raman scattering (SERS) technique, which utilizes interparticle plasmonic coupling for greatly enhanced Raman signals, has been gaining increasing attention in trace detection of various chemicals.

We designed a new class of SERS sensors for the sensitive and selective detection of cadmium ion ( $\text{Cd}^{2+}$ ) by taking advantage of the interparticle plasmonic coupling generated in the process of  $\text{Cd}^{2+}$ -selective nanoparticle self-aggregation. Gold nanoparticles which are encoded with Raman dye and Cd-chelating polymer brush are found to remain stable in solution without Cd ions. In the presence of Cd ions, nanoparticles aggregate and form hot spots, generating greatly enhanced Raman signals. Our SERS probe shows great selectivity among various common metal ions, and exhibits great potential for application in heavily colored samples.

# Photonics with Deformable Nanomembranes

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## Abstract

Nanomembranes are thin, flexible, transferrable and can be shaped into many different 3D geometries. For instance, we transfer single crystalline GaAs nanomembrane devices incorporating epitaxial quantum dots onto piezoelectric substrates.

By applying a bias to the piezo-substrate large amounts of strain are imposed onto the nanomembrane device, which allows us to tune the electronic structure of a single quantum dot with unprecedented control. For instance, it is possible to tune biexciton and exciton recombination lines into perfect resonance [1] or to reduce the fine structure splitting to zero for practically any quantum dot [2]. Differentially strained nanomembranes can roll-up into tubular structures once they are released from their mother substrate. Among others, such tubes can serve as vertical ring resonators which can be employed as optofluidic components [3] to sense single cells [4] and submonolayer condensates [5]. Novel photonic phenomena and unconventional new on-chip technologies will be discussed.

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## **Metallicrugate Structures for Near-perfect Absorbers in Visible and Near-infrared Regions**

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### **Abstract**

Metallic rugate structures are theoretically investigated for achieving near-perfect absorption in the visible and near-infrared regions. Our model builds on nanoporous metal films whose porosity (volume fraction of voids) follows a sine-wave along the film thickness. By setting the initial phase of porosity at the top surface as 0, near-perfect absorption is obtained. The impacts of various structural parameters on the characteristic absorption behaviors are studied. Furthermore, multiple peaks or bands with high-absorption can be achieved by integrating several periodicities in one structure. The rugate absorbers show near-perfect absorption for TE and TM polarizations and large incident angles.

## **Three-dimensional Nanostructures for Cost-effective Solar Energy Harvesting.**

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### **Abstract**

Materials made of nano/micro-structures have unique physical properties, such as fast carrier transport, high surface-to-volume ratio, mechanical flexibility, sub-wavelength optical waveguiding, *etc.* These intriguing properties can be harnessed for a variety of applications in electronics and photonics. In the past, we have developed a series approaches to fabricate three-dimensional (3-D) nanostructures. These 3-D structures have demonstrated geometry dependent photon management property thus have promising potential for solar energy harvesting applications. In particular, we have fabricated 3-D nanopillar arrays, nanowell arrays and more complex structures. Optical absorption properties of these nano-engineered structures have been investigated with experimental methods as well as theoretical simulations. To explore their applications for efficient light harvesting, they have been fabricated into photovoltaic and water splitting devices; preliminary results have shown that they can demonstrate improved performance as compared to their planar counterparts, indicating their potency for cost-effective solar energy harvesting.

## Luminescent Nano Materials for Photonic Applications

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### Abstract

The study of nanoscale matter-radiation interactions offers numerous opportunities for both fundamental research and technological applications in photonics and biophotonics [1-10]. As these potential applications are still very much in the design-phase, the fundamental understanding the luminescence properties of rare-earth ions in oxide nano environments remains a challenge. From the fundamental point of view, the physical understanding of emission (up and down conversion) of rare-earth ions in oxide/semiconducting nanoparticles and the way it changes with size, crystal phase and concentration is very important. Analysis suggests that modifications of radiative and nonradiative relaxation mechanisms are due to local symmetry structure of the host lattice and crystal size, respectively. We also demonstrate the influence of shape of CdS QD on the carrier relaxation dynamics of photo-excited CdS nanocrystals (NCs) using time resolved spectroscopy. A stochastic model of carrier relaxation dynamics of CdS NCs has been proposed to estimate the values of the radiative recombination rate, the average number of surface trap states, the luminescence quenching rate due to surface trap states and the rate due to nonradiative recombination from trap state to ground state.

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## Quantum Dot Solar Cells. Emerging Strategies and Challenges

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### **Abstract**

Semiconductor quantum dots offer new opportunities to develop next generation solar cells. The bench top design of these solar cells offer the convenience of developing transformative photovoltaic technology. Of particular interest are the metal chalcogenides (CdS, CdSe, PbS and PbSe) which offer significant advantage in achieving charge separation when coupled together with TiO<sub>2</sub> in a band energy matching (type II) fashion or integrated with a hole conductor. Manipulation of photoinduced charge separation in semiconductor quantum dots and their transport across the interface dictates the performance of QDSC. Several new approaches such as multiple electron generation, plasmonic effect, sensitization with infrared dyes and use of ternary compound semiconductors, have emerged to boost the efficiency of QDSC in recent years. These new approaches will not only provide ways to increase the photoconversion efficiency, but they will also pave the way towards a fundamental understanding of new phenomena related to excited state dynamics at various interfaces of hybrid assemblies. These new advances including the development of tandem layer quantum dots and coupling of energy and electron transfer processes in QDSC will be discussed.

## Novel Plasmonic Materials and Devices

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### Abstract

Negative Refractive-Index Materials (NIM) were first proposed by Veselago [1] in 1968 when he pointed out theoretically that if a material possesses both negative electrical permeability,  $\epsilon$ , and magnetic permittivity,  $\mu$ , then the refractive index will be negative too, and the reaction of the material to electromagnetic (EM) wave will be contrary to our intuitive expectation. Among materials that possess NIM are metals with strong plasmonic property such as Ag and Au. It was pointed out by Pendry that the novel optical property of the plasmonic materials arise from EM waves crossing the interface between negative and positive refractive index material [2].

In this report, we will present our recent works in studying the plasmonic materials and devices; we have shown that resonant superlens offer the best S/N ratio in superlens design[3], efficient third harmonic generation (THG) from Au grating[4], flexible plasmonic device[5] and plasmonic sensor [6]. Fig. 1 shows generation of THG from near-IR excitations and Fig. 2 shows plasmonic device on a flexible substrate; the device was fabricated using using chip transfer technique[7].

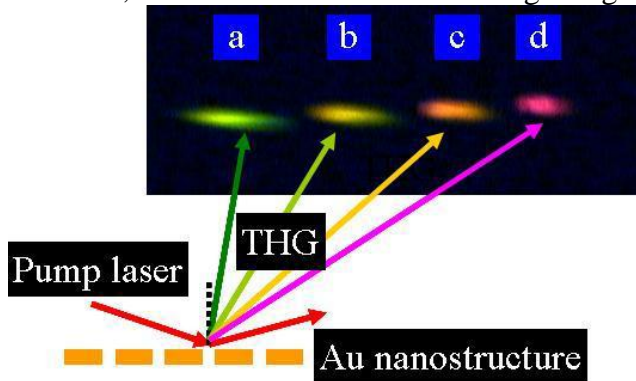


Fig. 1 THG generation with excitation wavelengths (a) 1660nm, (b) 1700nm, (c) 1740nm, (d) 1800nm

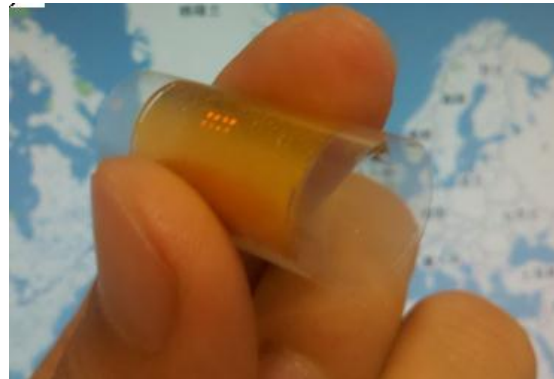


Fig. 2 Flexible plasmonic device was fabricated using chip transfer process

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# Photovoltaic Characteristics of CdS/CdSe Quantum Dot-sensitized Solar Cells Coupled to Inverse Opal TiO<sub>2</sub> Electrodes together with Photoexcited Carrier Dynamics

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## Abstract

Recently, semiconductor quantum dot-sensitized solar cells (QDSCs) have attracted much attention as a candidate of low cost and high efficiency solar cells. The morphology of TiO<sub>2</sub> electrodes and a choice of the sensitizers are important factors for the photovoltaic performance in QDSCs [1]. We have demonstrated that inverse opal (IO) TiO<sub>2</sub> electrode is useful and has fruitful perspective for QDSCs [2]. The improvement in photocurrent has been reported for multilayered CdS/CdSe-QDSCs [3,4]. In this study, we applied multilayered CdS/CdSe QDs as a sensitizer and they were adsorbed on IO TiO<sub>2</sub> electrodes. Optical absorption, photocurrent, photovoltaic performances and ultrafast carrier dynamics of CdS/CdSe-QDSCs have been investigated to make improvements in QDSCs. From photocurrent-voltage characterization, improvements in photocurrent (9.2 mA/cm<sup>2</sup>) and photovoltaic conversion efficiency (~ 3.8%) were realized compared to singlelayered CdSe-QDSCs. The ultrafast carrier dynamic responses of CdS/CdSe-QDSCs measured by transient grating (TG) technique [5] show fast and slow decay processes with relaxation time of a few ps and a few tens to hundreds ps, respectively. The relaxation times of those two processes become faster in the multilayered CdS/CdSe-QDSCs than singlelayered CdSe-QDSCs, indicating that recombination centers, interface state, and inverse transfer rate of photoexcited carriers are decreased by the adsorption of multilayered CdS/CdSe.

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## Characterization of CuInS<sub>2</sub> Sensitized Nanocrystalline TiO<sub>2</sub> Films Fabricated via SILAR

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### Abstract

CuInS<sub>2</sub> has been deposited onto mesoporous TiO<sub>2</sub> films by in sequence growth of In<sub>x</sub>S and Cu<sub>y</sub>S via successive ionic layer absorption and reaction process (SILAR) and post-deposition annealing in sulfur ambiance. The influence of the deposition cycles of the In-S on the microstructure of the CuInS<sub>2</sub> sensitized TiO<sub>2</sub> electrodes and the photovoltaic performance of the solar cells have been investigated. The results show that the CuInS<sub>2</sub> nanoparticles consist of tetragonal CuInS<sub>2</sub> composed of chalcopyrite phase and Cu-Au ordering. When the deposition cycle of Cu-S was fixed at 5, the grain size of tetragonal CuInS<sub>2</sub> increased with the increase of the deposition cycle of In-S at first, and then it tended to be constant at ca. 13 nm after 8 cycles. In the meantime, an ultra thin layer of In<sub>2</sub>S<sub>3</sub> formed between the TiO<sub>2</sub> and CuInS<sub>2</sub>, which can prevent the TiO<sub>2</sub> contamination from copper ions and retard the electron recombination at TiO<sub>2</sub>/CuInS<sub>2</sub> interface. As a result, the  $V_{oc}$  and  $J_{sc}$  of the solar cells increased until the deposition cycle of In-S achieved 10 and a relative high efficiency of ca. 0.92% ( $V_{oc}=0.35V$ ,  $J_{sc}=8.49\text{ mA}\cdot\text{cm}^{-2}$ ,  $FF=0.31$ ) has been obtained based on SILAR process without rapid thermal treatment and KCN treatment for removing redundant copper sulfide phase, which may supply a new route for the fabrication of CIS sensitized photoanodes although the efficiency is still very low. When the deposition cycle of In-S was above 10,  $J_{sc}$  and the fill factor decreased attributed to the over filling of the pores of the TiO<sub>2</sub> films. The pore structure of the TiO<sub>2</sub> films needs to be optimized in the future. It is indicated that the density of the Cu-Au ordering and the defect states in CIS need to be further diminished to improve the photovoltaic performance of the solar cells.

## Frontiers of Plasmonics: New Materials, Interactions, and Applications

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### Abstract

The field of plasmonics is rapidly expanding into new regions of the electromagnetic spectrum, utilizing new materials and structures. In the UV, Al is emerging as a highly promising material for plasmonic nanoantennas,[1] where the harvesting of UV light can be particularly useful for processes such as fluorescence enhancement and chemical transformations. In the IR, the unique electronic properties of graphene not only allow for IR plasmon resonant behavior, but also enable the electrical tuning of plasmon resonances through charge injection in straightforward device structures.[2] Coupled plasmonic systems of noble metal nanoparticles and nanostructures can incorporate new media, giving rise to new mixed-media plexcitonic states, and also transforming coherent plasmon modes into magnetic modes.[3] Advances in nanoassembly have given rise to new 3D plasmonic clusters whose complexity challenges our abilities to interpret plasmonic optical properties in terms of hybridized plasmon modes. Plasmonic nanostructures, when suitably designed, have recently been shown to serve as high-performance media for specific nonlinear optics applications such as four-wave mixing.[4] We have also shown that broadband light-absorbing nanoparticles, when immersed in a fluid such as water, can generate steam at remarkable high efficiency, opening the door for new applications addressing energy and environmental needs.[5]

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## Formation of Novel TiO<sub>2</sub> Nanostructures for Highly Efficient Dye-sensitized Solar Cells

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### Abstract

Nanostructured TiO<sub>2</sub> is of great interest to researchers because the related materials have been utilized in many applications such as photocatalysis, sensors, batteries, photovoltaic, water splitting and so forth. In particular, TiO<sub>2</sub> plays a key role as a mediator of electron transport in working electrodes for dye-sensitized solar cells (DSSC). In the present presentation, I will introduce synthesis and characterization of size-tunable and shape-controlled TiO<sub>2</sub> nanostructures as an active layer (AL) and/or as a scattering layer (SL) for DSSC. For the first part, we propose a sol-gel method comprising three simple steps under low-temperature conditions to synthesize mono-disperse rutile TiO<sub>2</sub> nanospheres with dandelion-like hierarchical morphology (DHRS) as a SL for DSSC. A detailed mechanism is presented to rationalize the formation of nanospheres of uniform size. The DSSC device with a SL made of DHRS (size ~300 nm) performed comparably to that with a SL made of a commercially available TiO<sub>2</sub> paste, making this nano-material a cost-effective alternative for future DSSC commercialization. For the second part, we propose a simple hydrothermal method with titanium tetraisopropoxide (TTIP) as a precursor and triethanolamine (TEOA) as a chelating agent to enable growth, in the presence of a base (diethylamine, DEA), of anatase titania nanocrystals (HD1-HD5) of controlled size. DEA played a key role to expedite this growth, for which a biphasic crystal-growth mechanism is proposed. The nanocrystals of size ~30 nm (HD1) and of size ~300 nm (HD5) served as active layer and scattering layer, respectively, to fabricate N719-sensitized solar cells. These HD devices showed greater  $V_{OC}$  than devices of conventional nanoparticle (NP) type; the overall device performance of HD attained efficiency 10.2 % of power conversion at total film thickness 28  $\mu\text{m}$ , which is superior to that of a NP-based reference device ( $\eta = 9.6 \%$ ) optimized at total film thickness 18–20  $\mu\text{m}$ . According to results obtained from transient photoelectric and charge-extraction measurements, this superior performance of HD devices relative to their NP counterparts is due to the more rapid electron transport and greater TiO<sub>2</sub> potential. The reported novel titania nano-materials have the potential to further promote the device performance of DSSC for future commercialization.

## Improvement of Charge Separation and Suppression of Charge Recombination in ZnO/P3HT Hybrid Solar Cells by Locating Dye at ZnO/P3HT Interfaces

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### Abstract

Organic-inorganic hybrid solar cells (OIHSC) have attracted much interest in recent years as promising candidates for future low-cost photovoltaics. This is because of their unique properties inherited from both types of materials. However, up to now, OIHSCs have not lived up to their potential because of poor interface properties. Thus engineering the electron donor/acceptor interface and controlling the charge separation and recombination at the interfaces of OIHSCs provide new opportunities to optimize device performance and improve the photovoltaic energy conversion efficiency of OIHSCs.

Recently, some of us have fabricated dye-sensitized OIHSCs by one-pot process, using solution processable ZnO precursor as electron acceptor, polythiophene copolymer (P3HT) as donor, and a squaraine dye (SQ36) and energy conversion efficiency of 1% was achieved [1]. In this study, we investigated the chargeseparation and recombination dynamics at the nano-interfaces of the ZnO/SQ36/P3HT hybrid solar cells using a transient absorption (TA) technique. By comparing the TA dynamics of ZnO/P3HT with and without the dye SQ36, we found thatthe ZnO/P3HT interface property can be controlled and charge recombination at the interface can be suppressed greatly by introducing the dye located appropriately at the organic-inorganic interface. Thus, photovoltaic performance of OIHSCs can be expected to be improved greatly by such appropriate interfacial engineering.

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# Enhancing the Performance of Si Solar Cells Using Nanophosphors with Metal-enhanced Fluorescence

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## Abstract

Recently, methods to enhance the short-wavelength ( $\lambda$ ) spectral response and overall conversion efficiency of Si solar cells via luminescence down-shifting (LDS) have been investigated by several groups [1-2]. The LDS nanophosphor layer absorbs photons, typically in the 300 nm - 500 nm range, and re-emits them at a longer wavelength, where the photovoltaic (PV) device exhibits a significantly better response. This work aims to enhance the LDS phenomena on commercially available Si solar cells coated with  $\text{Ba}_2\text{SiO}_4:7\%\text{Eu}^{2+}$  UV nanophosphors using the combination of spin-on Ag nanoparticles and a dielectric spacer.

Schematic of the solar cell device is illustrated in Figure 1. Time-resolved PL measurements show that fluorescence lifetime of the nanophosphors is significantly decreased from 671 ns to 612 ns with the integration of the Ag nanoparticles and a 15 nm thick  $\text{SiO}_2$  dielectric layer. This indicates that the LDS efficiency is greatly enhanced by the metallic particles. The solar cells coated with nanophosphors showed an increase of  $1 \text{ mA/cm}^2$  in short-circuit current density and approximately 0.7% increase in power conversion efficiency when coated with the Ag nanoparticles and a 20 nm  $\text{SiO}_2$  dielectric layer. The enhancement on PL is attributable to the resonant coupling of emission in  $\text{Ba}_2\text{SiO}_4:7\%\text{Eu}^{2+}$  with a surface plasmon (SP) and the electric field of incident light at the metal interfaces. This work provides a facile approach for the fabrication of metal-enhanced fluorescence, which can improve the emission of nanophosphor and reduce the reflection in the visible region of solar cell.

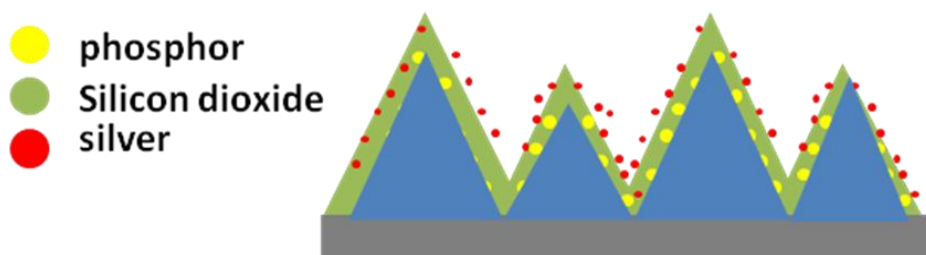


Figure 1. Schematic of textured cell structures covered with  $\text{Ba}_2\text{SiO}_4:7\%\text{Eu}^{2+}$  nanophosphors,  $\text{SiO}_2$  layer, and Ag nanoparticles.

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## Photoluminescence from Semiconductor Nanocrystals

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### Abstract

One of the most spectacular aspect of semiconductor nanocrystals has been their photoluminescence properties, offering wide-ranging tunability of the emitted light and a high degree of quantum efficiency, not usually achievable with corresponding bulk materials; this has led to an intense interest in such materials, both in terms of fundamental science and technological possibilities. There are two distinct classes of light-emitting nanocrystal materials. One class makes use of the band-gap emission, thereby achieving a high degree of tunability as a function of the nanocrystal size via the quantum confinement effect. However, this class of photoluminescence tends to be more easily affected by surface degradation. The other route makes use of deexcitation through atomic-like levels of a dopant ion via energy transfer between the host nanocrystal and the dopant site, thereby achieving a greater stability of the luminescence, but forgoing the tunability with the nanocrystal size. In my presentation, I shall discuss how one may go beyond these expected limitations of each case, making the band-gap emission intrinsically stable and dopant emission tunable, through understanding the fundamental processes involved in each case, that require shifting away from some of the dominant dogmas in the field.

# Optical Properties of Mn(II) Ions Doped II-VI Semiconductor Nanostructures

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## Abstract

We have prepared the Mn ion doped ZnO, CdS and ZnSe nanostructures by using CVD method and their optical properties related to the exciton magnetic polaron (EMP), itinerant or partially itinerant were explored via microphotoluminescence technique. The obtained energy levels agree well with AB initio calculations.

For ZnO:Mn, the EMP can show up very dilute doping (<0.001%) with free exciton. This EMP can form single mode lasing line at fs (femto-second) pulse excitation along with the disappearing of free excitons. With slight increase in Mn doping, the nanowires show EMP lasing mode with background at fs laser pulse excitation. At even higher power, some electron-hole plasma induced lasing modes can be observed due to the carrier effect. The time-delay photoluminescence by ns laser pulse are also studied, only free EMP and localized EMP(d-d transition) are shown in emission spectra, we have clearly assigned all d-d transitions of Mn in ZnO, which have been argued for a long time. It is more interesting that these d-d transitions exhibit clear enhanced coherent relaxation behaviors with increasing excitation power, like that by free excitons, behave a collective spin-dependent coherent radiation. We have also observed the Mn-O-Mn cluster peak in the long wavelength range, which may be related to the ferromagnetic properties.

In CdS:Mn, we have found many peaks above the single Mn ion emission band (575nm) when increasing the Mn concentration. This phenomenon can be well explained by a simple Hydrogen-like cloud theoretical model. In this model, the Mn-S-Mn cluster with variable Mn ion concentration and their ferromagnetic coupling are considered. The SQUID detection proved its ferromagnetic behavior, and MFM result indicates its cluster nature in the nanobelt. Ab initio calculation results also support our cluster assignments.

In ZnSe:Mn, Mn doping often produces many optical domains which can work as optical cavities to produce cavity modes in a wide spectral range. This can be easily observed in the CW laser excitation. If we turn on ns laser, we can detect bandedge emission at low power, but it changes to stimulated emission by EMP at high power excitation. This stimulated emission is usually limited by the magnitude of the optical domain size.

In all our experimental result, the d-d transitions are not absolutely localized, so we call it localized EMP. We have identified the Mn-Mn segregation by the microphotoluminescence technique; this may be used to study more DMS substances. We give clear assignments to emission peaks other than intrinsic d-d transition in the emission spectra; those were often seen as the defect states before. This facilitates us to get better understanding of the DMS magnetism and applications.



## The Poisson Distribution of Quenchers in the Fluorescent Dynamics of Nanoparticles

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### Abstract

In spite of constant improvements in their synthesis,<sup>[1]</sup> the fluorescence decay of CdSe nano crystals is complex and poorly reproducible. We have analysed the fluorescence decay of such QD during dilution experiments. Our QD are stabilized by a layer of surfactants composed of trioctyl phosphine (TOP), oleylamine (OA) and stearic acid (SA). This composition has been optimized for improved fluorescence yield. The mother colloidal suspensions in toluene were further diluted in toluene. The fluorescence yield drops with dilution. The yield is recovered when TOP is added. On the contrary the addition of SA increases the quenching. Such behaviour has already been observed, and the yield drop has been described by a Perrin model where a few defects are produced by the removal of protecting ligand and their replacement by quenchers.<sup>[2]</sup> We have analysed the fluorescence decay during dilution using a “model free” approach.<sup>[3]</sup> We show that indeed  $2.9 \pm 0.1$  quenchers are involved. But the dynamic of the quenching per quencher remains complex with a time dependent rate coefficient. The decay per quencher can be compared with the decay at saturation. It provides a value of  $2.88 \pm 0.02$  for the number of quenchers per QD. The dynamic of the quenching scale as  $\exp(\sqrt{t})$ . This can be the dynamic of mobile quenchers toward fixed excitons or a dipolar energy transfer fixed excitons and fixed quenchers. The time dependent rate coefficient that describes the quenching dynamic added to the presence of binomial distributions of quenchers among QD explains why CdSe decays have never been explained up to now. Temperature dependent studies are included to get further insight in the mechanism of the quenching.

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## Colloidal I–III–VI Semiconductor Nanocrystals for Light-emitting Applications

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### Abstract

Colloidal semiconductor nanocrystals are emerging new generation luminescent materials for light-emitting technologies.<sup>1</sup> In the past 5 years, colloidal I–III–VI nanocrystals such as CuInS<sub>2</sub>, CuInSe<sub>2</sub> have been intensively investigated for the potential to replace commonly available CdSe based nanocrystals in light-emitting applications.<sup>2</sup> Many researchers from different disciplines are working on developing new synthetic protocols, performing spectroscopic studies to understand the luminescence mechanisms, and exploring various applications. To achieve enhanced performance, it is very desirable to obtain high-quality materials with tunable luminescence properties. Recently, we worked on the synthesis to tune the luminescence properties of I–III–VI nanocrystals and explore their applications in light-emitting devices.<sup>3–5</sup> By adapting a combination of size, composition and surface tuning strategies, we are able to synthesize high quality color tunable CuInS<sub>2</sub> based nanocrystals at gram scale. We further fabricated electroluminescence and optical-excited prototype light-emitting diodes.<sup>6,7</sup>

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## Light Emission and Detection with Carbon Nanotubes

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### Abstract

Carbon nanotubes (CNTs) are direct band gap materials that are not only useful for nanoelectronic applications, but also have the potential to make significant impact on the developments of nanoscale optoelectronic devices. In particular CNTs have been investigated for various electronic and optoelectronic device applications, such as light-emitting diodes [1,2], photodetectors and photovoltaic (PV) cells [3,4]. Semiconducting single-wall CNTs (SWCNTs) are direct-gap materials that can efficiently absorb and emit light. The unique band structure of SWCNT suggests that multiple subbands absorptions can contribute to optoelectric properties. By combining sufficient nanotubes with different diameters, it was also demonstrated that it is possible to gain a nearly continuous absorption response within a broad spectral range (from UV to infrared) to match the solar spectrum [5]. In addition, extremely efficient carrier multiplication (CM) effect has been observed [6], which may potentially lead to a higher energy conversion efficiency than that defined by the Shockley-Queisser limit. More recently, efficient photovoltage multiplication was also realized via introducing virtual contacts in CNTs, making the output photovoltage of CNT based solar cells a tunable quantity via choosing the diameter of the tube and the number of virtual contacts introduced in the device [7], making it possible for developing optoelectronic communications between nanoelectronic circuits and high performance infrared photodetectors [8].

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## Polymer Solar Cells Based on Carbon Nanotubes Decorated with Colloidal Quantum Dots

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### Abstract

The need to develop inexpensive renewable energy sources stimulates scientific research for efficient, low-cost photovoltaic devices. The organic, polymer-based photovoltaic elements have interested many attentions due to its potential of obtaining cheap and easy methods to produce energy from light.

In this paper, we fabricated and characterized polymer solar cells based on solution-processed P3HT:PCBM and colloidal quantum dots (QDs). In our experiments, firstly, single-walled carbon nanotubes (SWNTs) was decorated with CdSe/ZnS QDs and the as-synthesized CdSe/ZnS-SWNT nanoarchitecture is further incorporated into bulk heterojunction polymer as active layer to make photovoltaic devices. As compared with the pristine device in which only P3HT:PCBM as active layer, the addition of CdSe/ZnS-SWNT resulted in an improvement in both the short-circuit current density and open-circuit voltage. The device takes advantage of the high electron transport capability of SWNTs and the increasing absorption resulting from the CdSe/ZnS QD in range of the visible light. These results indicate that the addition of CdSe/ZnS-SWNT can greatly enhance the performance of polymer photovoltaic cells.

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## **Lanthanide-based Nanomaterials in Nanomedicine**

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### **Abstract**

Lanthanide-based nanomaterials have demonstrated strong potentials in nanomedicine due to its upconversion and strong magnetic properties, and low toxicity. The current talk will focus on the synthesis of various lanthanide nanostructures and their application in bioimaging, drug delivery and targeted cancer cells ablation. In particular, it will discuss various strategies in lanthanide nanostructure engineering to achieve strong and simultaneous  $T_1$  and  $T_2$  MRI contrasts without compromising on upconversion emission. The tuning of ultrasensitive sub-10 micron lanthanide-based nanocrystals for pure red or near-infrared chromatic upconversion fluorescence in the presence of  $Mn^{2+}$  dopant will also be presented. Finally, a new lanthanide-based nanostructure capable of generating radicals through an upconversion mechanism, and its demonstration in triggered drug delivery and cancer cells killing will be featured.

## Effects of Broken Time-reversal Symmetry on Periodic Resonator Arrays

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### Abstract

We discuss the effects associated with the broken time-reversal symmetry on periodic resonator arrays. These effects include the decoupling between resonators by static magnetic field and the splitting of leaky modes by absorption. To show the first effect, we consider the wave propagation in periodic arrays of gyromagnetic resonators. When the external static magnetic field is off, electromagnetic waves can propagate in the array with a finite group velocity. When the external static magnetic field is on, even nearly touching resonators can be decoupled so that almost no wave propagation is allowed. The wave is thus localized within one single resonator. This interesting effect is explained by the splitting of photon angular momentum states by external static magnetic field [1]. For the second effect, we consider a linear array of plasmonic resonators [2,3]. When there is no absorption, the degeneracy of two leaky modes is protected by time reversal symmetry. When absorption exists, two modes split and thus lead to two different exponential decays together with an additional long-range power-law decay [2]. These two effects are of different origins although both are associated with broken time-reversal symmetry. The first one has a broken reciprocity while the second one does not. We will also have some discussions on distinguishing different types of broken symmetries in Green's functions that are associated broken time-reversal symmetry.

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## **Nano-Plasmonics for Single-Molecule Photochemistry and Chemical Microscopy**

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### **Abstract**

I will present my research group's recent investigation on how the localized plasmon of a nanoparticle interacts with another plasmon, and with nearby molecules. The talk will cover three different yet related topics. First, I will demonstrate the use of scattering-type scanning near-field microscopy (s-SNOM) to directly visualize the capacitive / conductive coupling in dimeric nanoparticles and heterometallic nanorods. Second, I will talk about the use of gap-plasmons to locally induce photochemical reactions, and to follow chemical kinetics of individual organic molecules using the surface-enhanced Raman scattering (SERS). As a last topic, I will talk about the use of near-field coupling between a scanning probe and graphenes to visualize / identify the stacking domains (e. g., ABA versus ABC-type stacking in triple layer) hidden in multilayer graphenes.

## Micro-Resonators: WGM Lasing and Sensing Applications

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### Abstract

Microresonators have drawn a lot of attention due to their importance of practical applications as well as of fundamental physics interest in light-matter interaction. The optical confinement provided by a microcavity greatly enhances the coupling between optical spatial mode and the light emitting materials. Conventional fabrication of micro-cavities adopting semiconductor processing technology through either top-down or bottom-up approaches still faces some challenges. Here we demonstrate the feasibility of constructing solid state microcavities with various configurations like spheres, hemispheres and fibres in a flexible way. We realize optically pumped lasing from these structures after loading some gain materials. The lasing characteristics have been systematically examined in terms of size dependence, temperature dependence and polarization. The optical modes are well defined by WGM lasing. We have demonstrated single-frequency operation in both spheres and fibres with reduced sizes. We are also able to tune the lasing by deforming the shape of micro-spheres, which represents the convenient manipulation of light matter interaction. Finally refractive index sensing with high sensitivity can be readily realized from these structures enabled by the existence of evanescent waves.

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# Slab-nanocrystals of H-aggregation Organic Semiconductors for Low-threshold Nanolasers

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## Abstract

Organic semiconductors are of current interest in photonic applications,<sup>[1]</sup> because of their chemically tuneable optoelectronic properties and their ability to self-assembly for bottom-up fabrication. Optically pumped organic lasers had been demonstrated in a variety of resonator geometries, such as microcavity, micro-ring, distributed feedback (DFB), and photonic bandgap structures.<sup>[2]</sup> In these cases, stimulated emission takes place from the lowest electronic excited state  $|10\rangle$  to the first vibronic replica  $|01\rangle$  of the ground state, exhibiting a lasing threshold that depends on both amplification and loss processes. The unoccupied  $|01\rangle$  state in thermal equilibrium facilitates the population inversion. However, the concomitant radiative loss of the exciton reservoir to  $|00\rangle$  state increases the required population inversion density threshold; meanwhile, the intrinsic ground state self-absorption represents a major channel of optical losses. As a matter of fact, electrically driven organic lasers remain a grand challenge, partially due to the high lasing-threshold observed so far. Therefore, development of organic gain materials with optimized energy levels that help decrease the lasing threshold is of crucial importance.

Nanowire lasers are promising for applications ranging from on-chip optical communication to high throughput sensing.<sup>[3]</sup> Recently, crystalline nanowires of organic semiconductors had shown capabilities in both photon waveguiding and charge transporting properties. Still, even though these nanowires are ultra-small in two-dimensions, the axial cavity defined between the two wire-end-faces has to be ca. 10  $\mu\text{m}$  to build up enough gain for lasing. Here, we prepared rectangular slab-nanocrystals (SNCs) of 1,4-dimethoxy-2,5-di[4'-(methylthio)styryl]benzene (TDSB), in which H-aggregation is advocated by tight co-facial molecular packing. Due to the exciton-vibration coupling, the optically allowed  $|10\rangle \rightarrow |0n\rangle$  ( $n \geq 1$ ) transitions make H-aggregate SNCs of TDSB highly emissive with a solid-state quantum yield of 0.81; meanwhile, the optically forbidden  $|10\rangle \leftrightarrow |0n\rangle$  transitions not only reduces the self-absorption effect but also minimizes the direct radiative loss of the excitation reservoir to  $|00\rangle$  state. The two lateral-faces of SNCs constitute a high quality ( $Q \approx 1000$ ) built-in Fabry-Pérot (FP) cavity at wavelength scale, in which a lasing threshold as low as  $100\text{ nJ cm}^{-2}$  was achieved. Moreover, the laser light generated in the ultra-small radial cavity of SNCs can propagate along its length up to hundreds of micrometers, making them attractive building blocks for miniaturized photonic circuits.

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## Fast, Air-stable Infrared Photoconductors Based on Water-soluble HgTe Quantum Dots

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### Abstract

The ability to detect near-infrared and mid-infrared radiation has spawned great interest in colloidal HgTe quantum dots (QDs). Photodetectors based on HgTe QDs with spectral sensitivity up to 5  $\mu\text{m}$  have been reported. On the other hand, the temporal response time, another important figure of merit for HgTe QD photodetectors, is rarely studied. In this work, we report a simple HgTe QD photoconductor structure fabricated through a spray-coating process performed in air. The devices exhibit up to 1 MHz 3dB bandwidth. The origin of this remarkably fast time response is investigated with optical and electrical characterization techniques, including light intensity-dependent and temperature-dependent transient photocurrent measurements, FET measurements and time-resolved photoluminescence spectroscopy. The results suggest that under high light intensity electron-hole recombination occurs through a fast bimolecular recombination process, leading to the fast response in the expense of low gain. Interestingly, we found that the time response, or more fundamentally the position of the trap states and recombination centers, can be tuned by controlling the QD size and surface chemistry. This allows us to balance between the responsivity and bandwidth to optimize the device performance. It is worth mentioning that the use of water-soluble QDs, which are capped with very short ligands and stabilized in water via electrostatic interaction, obviates the need for post-deposition ligand exchange and therefore allows a less laborious and higher throughput manufacturing process. In addition, all the devices are fabricated in ambient condition and show good stability after long time testing.

# Multifunctional Engineered Nanomaterials: Bioimaging Applications Vs Toxicity

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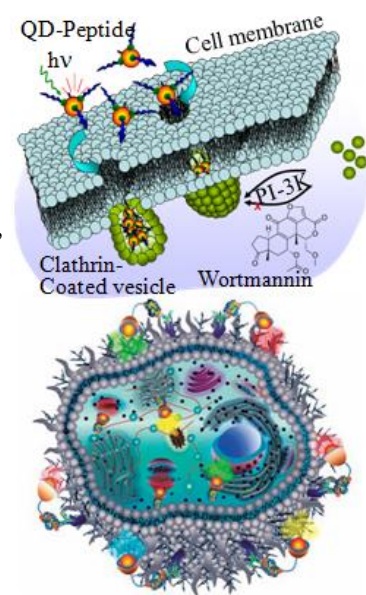
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## Abstract

Size-dependent tunable electronic property of materials, which was unlocked in the past two decades, is the most exciting innovation that reinforces the present status of nanoscience and nanotechnology.<sup>1</sup> As a result of this innovation, engineered nanomaterials have not only infiltrated into various disciplines of science and technology but also reformed or lives as key elements of electronic displays, cosmetics, nanomedicine, bioimaging probes and food. One of the most exciting aspects of our ongoing research is the ever accelerating progress of engineered nanomaterials towards practical applications in biology.<sup>2</sup> Among various nanomaterials, semiconductor nanoparticles, also called quantum dots, are of particular interest owing to their exceptionally bright and highly stable photoluminescence in the visible spectral range. We mostly focus on improvement of the photoluminescence properties of quantum dots<sup>3,4</sup> by modifying their surface using organic/inorganic coatings, and subsequently formulate quantum dots bioconjugates for looking at how such bioengineered quantum dots literally light up biomolecules and cells (Figure).<sup>5,6</sup> Conversion of quantum dots into their bioconjugates is a prerequisite for labeling of biomolecules, cells and tissues. The biomolecules recruited to the surface of quantum dots depends on a particular application aimed for, such as single-molecule detection, extracellular labeling, gene delivery, intracellular labeling, or *in vivo* imaging. Cells can be labeled using quantum dots in a nonspecific or targeted manner. Targeted labeling of cells has been extensively investigated in the recent past for finding a bridge between quantum dots and biomedical imaging using various antibodies, proteins, peptides, amino acids, liposomes, aptamers, DNA, RNA, or certain simple biomolecules.<sup>2</sup> In addition to showing the specific labeling of certain proteins in selected cell lines, we also highlight on the intracellular delivery of bioconjugated quantum dots and other nanomaterials. Despite all the above advantages and potential applications of quantum dots, their environmental



Scheme of intracellular delivery of bioconjugated quantum dots (top), and a cell labeled with quantum dots (bottom)

transformations and the toxicity of transformed materials are of more general concern, summary of which is also touched in this presentation.

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## Upconversion Nanoparticles Based Energy Transfer for Sensitive Bio-detection

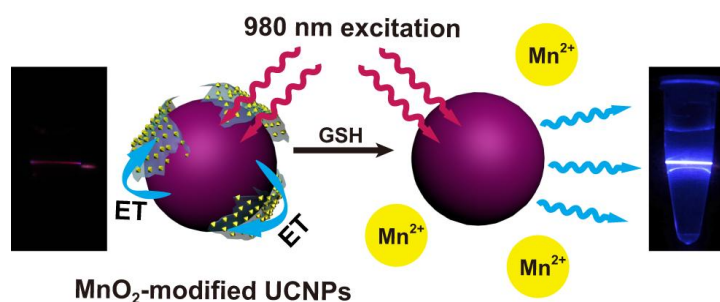
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### Abstract

We report a novel design, based on a combination of lanthanide-doped upconversion nanoparticles and manganese dioxide nanosheets, for rapid, selective detection of glutathione in aqueous solutions and living cells. In this approach, manganese dioxide ( $\text{MnO}_2$ ) nanosheets formed on the surface of nanoparticles serve as an efficient quencher for upconverted luminescence. The luminescence can be turned on by introducing glutathione that reduces  $\text{MnO}_2$  into  $\text{Mn}^{2+}$ . The ability to monitor the glutathione concentration intracellularly may enable rational design of a convenient platform for targeted drug and gene delivery.



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## Light-Addressable and Degradable Silica Capsules for Cytosolic Release

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### Abstract

Plasmonic nanoparticles can be used to destroy cancer cells and tumors by applying light. Cancer cells are more sensitive to slight increases of temperature and therefore the relaxation of the electrons that had absorbed light into heat can be used to produce hyperthermia and tumor destruction. <sup>[1, 2]</sup> Applying lower power density of light, similar plasmonic structures can optically trigger the delivery of certain drugs and biofunctional molecules from their surface or from microscopic structures acting as carrier systems. <sup>[3, 4]</sup> Light-responsive polyelectrolyte capsules have been used as efficient carrier systems to deliver into the cytosol different kinds of proteins and molecules such mRNA by keeping intact their biological activity. <sup>[4]</sup> In this work, we describe the synthesis of silica capsules that depending on the composition can deliver functional molecules through degradation or light-triggered release. The two different release mechanisms of cargo molecules *in vitro* will be discussed and compared with the aforementioned polyelectrolyte capsules.

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## Emerging Quantum Dot Mid-IR Emitter and Detector Technologies

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### Abstract

Metal chalcogenide quantum dots such as mercury, lead, cadmium and silver tellurides and selenides have low or even inverted bandgaps as bulk semiconductors (semi-metals) and are well known electro-optic materials for mid-IR device applications. In nanocrystal form, as quantum dots, nanorods and other heterostructures, and as alloyed nanoparticles, we can manipulate not only the bandgap energy,  $E_g$  but also other useful optical and electronic properties of these materials to tailor them to particular applications, for example; as mid-IR light emitters; as photodetectors; or as extended IR coverage absorbers in solar cell applications. In many cases, the nanoparticle form of these materials may offer distinct advantages in the device fabrication process compared with the bulk forms of the same materials – e.g. devices do not need to be made on a particular lattice matched substrate that may be expensive or mechanically fragile and difficult (and low yield) to work with from the manufacturing point of view. Indeed films of the QD materials may be highly suitable for integration with other quite different electro-optic technologies as hybrid device structures.

We will describe our work with several colloidal QD materials with bandgap energies ranging down to 0.35eV and discuss how these are finding applications in the gas sensing, biological through-tissue imaging and IR photodetector fields.

## Rare-earth Nanocrystals: A New Class of Luminescent Bioprobes

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### Abstract

Lanthanide-doped inorganic nanocrystals typically comprise an insulating host material and lanthanide dopant ions embedded in the host lattice. The luminescence of lanthanide-doped nanocrystals primarily originates from intra-configurational 4f electron transitions within the localized dopant ions. In stark contrast to quantum dots, quantum confinement effects are typically not expected in lanthanide-doped nanocrystals due to small Bohr radius of the exciton in the host, as well as weak interaction between the 4f electrons of the dopant ions and the host material. As a result, the luminescence properties of lanthanide-doped nanocrystals closely resemble those of the bulk counterparts. The emission profiles of lanthanide-doped nanocrystals are usually manipulated by varying dopant compositions and concentrations in the host lattice. In this talk, I will present a doping principle that is capable of altering nanocrystal growth processes with simultaneous control over crystallographic phase and size of the nanocrystals. I will also discuss our recent efforts in developing novel photon upconversion schemes based on energy migration processes and utilizing upconversion nanocrystals as novel luminescent labels for biological applications.



# Bio-inspired Artificial Photonics Nanostructures for Efficient Antireflective Surfaces and Surface Enhanced Raman Scattering Platform

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## Abstract

Natural photonic structures continue to provide inspiration for technological applications, initiating an active field of “optical biomimetics”. In particular, nature makes use of superficial photonics nanostructures in many ways in order to achieve unique optical effects, such as colorfulness in butterflies and anti-reflectivity in moth eyes.

In this work, we try to mimic the moth eye type antireflective surfaces (ARS), and propose a general design rule based on gradient index of refraction using finite-difference time-domain (FDTD) simulation. The nanotip shape of ARS is considered equivalent to a film-stack with gradually increasing refractive index (from the apex to the base), and FDTD calculations elucidate that the nanotips perform as better antireflectors over the visible and near IR wavelength zone and over a wider angle of incidence.

Further, we also present a high-quality surface enhanced Raman scattering (SERS) active template prepared by self assembly of silver nanoparticles on these silicon nanotip arrays. The surface morphologies and optical properties were characterized using SEM, Raman and FDTD simulation, respectively. Malachite green (MG), used in pisciculture, was chosen as toxic analyte for detection by SERS. SERS spectra of MG adsorbed on Ag coated nanotips were investigated. The results reveal that these Ag coated nanotips are promising for SERS applications in trace measurement and analysis of biological molecules.

Biomimetic photonic nanostructures were probed for better antireflection designs and SERS sensor platform. We are of the opinion that biological photonic surfaces hide virtually endless potential for development of new applications in optical and optoelectronic fields.

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## Gold Nanoparticle-based Colorimetric Assays

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### Abstract

The discovery of the DNA-mediated assembly of gold nanoparticles was a great moment in the history of science; this understanding and chemical control enabled the rational design of functional nanomaterials as novel probes in biodetection. In contrast with conventional probes such as organic dyes, gold nanoparticles exhibit high photostability and unique size-dependent optical properties. Because of their high extinction coefficients and strong distance-dependent optical properties, these nanoparticles have emerged over the past decade as a promising platform for rapid, highly sensitive colorimetric assays that allow for the visual detection of low concentrations of metal ions, small molecules, and biomacromolecules. These discoveries have deepened our knowledge of biological phenomena and facilitated the development of many new diagnostic and therapeutic tools.

Herein, I will describe the gold nanoparticle-based colorimetric assays for DNA, enzyme and small molecules developed by our group. These colorimetric systems offer convenient, low cost and fast assay methods for biosensing and small molecule screening.

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## How Nano- and Micoparticles Can Improve the Properties of Ion-selective Ligands

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### Abstract

Functionalized colloidal nanoparticles can introduce new properties and functionalities to existing materials and thus are a valuable building block for the construction of novel materials [1]. Combining ion selective ligands with particles new functionalities are provided to them [2]. Ion selective ligands can specifically bind ions of one type. Moreover when ligands are attached to the surface of fluorescent nanoparticles, specific binding of ions close to the nanoparticle surface can be managed, and changes in the fluorescence of the nanoparticle can be achieved. Thus specific fluorescence-based ion sensors can be constructed [3,4]. Second, in the case ligands are bound to the surface of general nanoparticles, the binded ions can provide contrast and thus the particles can be imaged. This is related for example to Gd-ions, which provide contrast for magnetic resonance imaging (MRI) [5,6], and In-ions, which in case a radioactive In-isotope is used, provide contrast for imaging of radioactivity. Thus the chelators with their complexed ions provide contrast to particles. In addition, ion-specific ligands can be also attached to the surface of magnetic nanoparticles or inside of magnetic microparticles [7]. In this case ions bound to the ligands can be extracted with magnetic field gradients and magnetic separation becomes possible [8-10]. In this case, magnetic particles provide the ligands a handle with which they can be extracted from solution.

These examples demonstrate that attaching ion-specific ligands to particles we could improve their properties and use them for different applications such as sensing, imaging and separation.

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## Photocatalysis with Semiconductor Nanocrystals

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### Abstract

Photocatalytic water splitting and carbon dioxide reduction under visible light illumination have gained considerable scientific interest during the last years. Efficient conversion of optical into chemical energy would be one strategy to deal with the storage problem of renewable solar energy systems.

I will review our work on light induced water splitting utilizing Pt-decorated CdS nanorods. We have investigated the efficiency of hydrogen production as a function of Pt-cluster size and concentration and have chosen different hole scavenger molecules leading to very different efficiencies and degradation effects of the nanorods.

In order to realize an efficient and stable photocatalytic system, both the energies for water reduction/oxidation and for reduction/oxidation of the active semiconductor material have to be taken into account.

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[2] Hole scavenger redox potentials determine quantum efficiency and stability of Pt-decorated CdS nanorods for photocatalytic hydrogen generation; M.J. Berr, P. Wagner, S. Fischbach, A. Vaneski, J. Schneider, A.S. Susha, A.L. Rogach, F. Jäckel, J. Feldmann, *Appl. Phys. Lett.* 100, 223903 (2012).

[3] Colloidal CdS nanorods decorated with sub-nanometer sized Pt clusters for photocatalytic hydrogen generation; M. Berr, A. Vaneski, A. S. Susha, J. Rodríguez-Fernández, M. Döblinger, F. Jäckel, A. L. Rogach, J. Feldmann, *Appl. Phys. Lett.* 97, 093108 (2010).

# Ultralow Two-Photon Pumped Lasing Threshold from Seeded CdSe/CdS Nanorod Heterostructures

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## Abstract

Over the last two decades, multi-photon absorption (MPA) in colloidal semiconductor quantum dots (QDs) has been intensively investigated for potential applications in bio-imaging, two-photon pumped lasing, three dimensional data storage and optical limiting [1]. These applications leverage on the unique characteristics of QDs: size-dependent optoelectronic properties, large MPA cross-sections, relatively high quantum yields, good photostability and flexible surface chemistry. Recently, the MPA cross-sections of QDs have been found to increase with size, and this general trend is attributed to a corresponding increase in the density of states [2]. Increasing the MPA cross-sections of QDs without significantly degrading its quantum yield or altering its emission wavelength can be highly desirable for example, in multi-photon fluorescence imaging where greater signal may be achieved using less average incident power, thus minimizing sample damage. While the pronounced size-dependence of the emission of fluorescent QDs in the strong confinement regime presents a convenient way to achieve desired emission wavelengths by simply changing the dot size, it also simultaneously imposes severe restrictions on the ability to vary the absorption cross-section while maintaining the emission at a required wavelength. Thus from the stand point of wavelength-specific applications, increasing the MPA cross-section of a QD without significantly modifying its size-dependent emission is an important and yet non-trivial challenge to overcome.

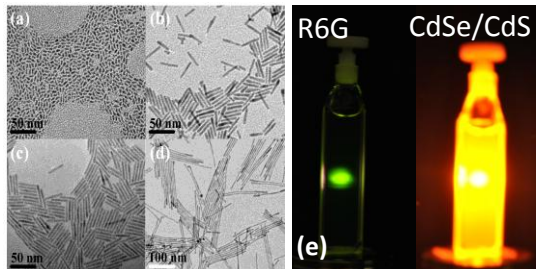


Figure 1: (a) TEM images of the CdSe/CdS nanodot/nanorod heterostructures with (a) 8.5 nm, (b) 34 nm, (c) 39 nm and (d) 180 nm average lengths. (e) Images of R6G and 39 nm CdSe/CdS heterostructures of the same concentration under the same intensity 800 nm laser pulse excitation. These photographs were taken with the same camera exposure time and settings.

Herein we present a method that permits the independent tuning of the MPA cross-section and its corresponding luminescence properties using a representative CdSe/CdS nanodot/nanorod system [3-5]. The elongated CdS shell is used as a photon-capturing “antenna”, which can greatly enhance the overall MPA cross-section of the QD. Photoexcitation of the CdS shell leads to ultrafast carrier transfer to the CdSe core where radiative recombination subsequently occurs. Ultralow threshold two-photon pumped amplified spontaneous emission (2ASE) and lasing in seeded CdSe/CdS nanodot/nanorod heterostructures is also demonstrated for the first time. With an enhanced  $\sigma_2$ , 2ASE in these heterostructures is achieved with an ultralow threshold fluence of  $\sim 1.5 \text{ mJ/cm}^2$  – which is as much as 1-2 orders less than that required for spherical semiconductor NCs. The origins of their ultralow threshold stems from: (i) the enlarged  $\sigma_2$ ; and (ii) a suppression of the Auger processes in these heterostructures,

even though the population inversion could also be strongly affected by the competition to the CdS surface states. The new insights into the carrier dynamics in these heterostructures are highly relevant for the development of seeded nano heterostructures as a gain medium for nanoscale lasers.

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- [4] G. C. Xing, S. Chakraborty, S. W. Ngiam, Y. Chan and T. C. Sum\*, *Journal of Physical Chemistry C*, **115**, 17711-17716 (2011)
- [5] G. C. Xing, Y. Liao, X. Wu, S. Chakraborty, X. Liu, E. K. L. Yeow, Y. Chan\* and T. C. Sum\*, “Ultralow Threshold Two-Photon Pumped Amplified Spontaneous Emission and Lasing from Seeded CdSe/CdS Nanorod Heterostructures”, accepted by *ACS Nano* (2012) - DOI: 10.1021/nn304200a

**ABSTRACTS**

**POSTER PRESENTATIONS**

**Tuesday 7 May 2013**

**16:00 – 19:00**

# 1

## Near-infrared Emitting Cadmium Mercury Chalcogenide Alloy Quantum Dots and Nanorods Wavelength Tuned by Cation Exchange

Shuchi Gupta,<sup>1</sup> Olga Zhovtiuk,<sup>1</sup> Aleksandar Vaneski,<sup>1</sup> Yan-Cheng Lin,<sup>2</sup> Wu-Ching Chou,<sup>2</sup> Stephen V. Kershaw,<sup>1</sup> Andrei S. Susha,<sup>1</sup> Tai Lun Wong,<sup>3</sup> Koichi Higashimine,<sup>3</sup> Shinya Maenosono,<sup>3</sup> Andrey L. Rogach<sup>1</sup>

<sup>1</sup>City University of Hong Kong, Hong Kong SAR

<sup>2</sup>National Chiao Tung University, Hsinchu, Taiwan (R.O.C.)

<sup>3</sup>Japan Advanced Institute of Science and Technology, Ishikawa, Japan

### Abstract

In addition to the well known size confinement sensitivity of the bandgap energy in colloidal quantum dots, ternary composition semiconductor nanoparticles bring the additional flexibility that their electronic structure may also be manipulated via the composition. Mixed metal cation alloys with metal lattices ranging from a core shell to a near homogeneous distribution of the metal ions can be formed by using (partial) cation exchange starting with one of the component binary semiconductors. In the limiting case near complete exchange of the metals can often be achieved resulting in the alternate binary semiconductor. In cases where the lattice types of the two extremes of the ternary composition differ (e.g. cubic vs. hexagonal lattices), exchange may be only partial and limited by the energy required to effect a lattice rearrangement.

Here we describe two of these ion exchange cases:

In 2.3nm diameter  $Cd_xHg_{1-x}Te$  quantum dots, exchange ranged from  $x=1$  to  $x=0.1$ , and the lattice remained zincblende throughout. The CdTe and HgTe lattices have near identical lattice parameters ( $a=6.482 \text{ \AA}$  and  $6.462 \text{ \AA}$  respectively). Apparent bowing curve, compositionally dependent Stokes shift and kinetic data support an exchange process model which in the intermediate stages is not uniform in metal distribution, but on longer timescales (days) becomes more evenly spread.

With  $15 \pm 2 \text{ nm} \times 3 \text{ nm}$  CdSe nanorods, attempts to exchange Cd for Hg led to only partial exchange (with  $x$  from 1 to 0.9). Detailed microscopy (HAADF-STEM) and EDS studies revealed that the exchanged Hg was not uniformly distributed within the nanorods, but located around localized lattice distortions along the rods. Again the kinetics of the exchange process was relatively slow (mins to hours) allowing the effect on optical properties (absorption and PL) to be followed.

We present extensive optical data for these materials across their respective compositional ranges including quantum efficiencies, PL life times, intrinsic absorption coefficients, and absorption and PL spectral evolution over time.



**Polyhedral Oligomeric Silsesquioxane as a Ligand for Light-Emitting CdSe Quantum Dots**

Y. Wang,<sup>1</sup> A. Vaneski,<sup>1</sup> H. Yang,<sup>1</sup> S. Gupta,<sup>1</sup> F. Hetsch,<sup>1</sup> S. V. Kershaw,<sup>1</sup> W. Y. Teoh,<sup>2</sup> H. Li,<sup>3</sup> A. L. Rogach<sup>1</sup>

<sup>1</sup>*Department of Physics and Materials Science and Centre for Functional Photonics (CFP), City University of Hong Kong, Hong Kong*

<sup>2</sup>*School of Energy and Environment, City University of Hong Kong, Hong Kong*

<sup>3</sup>*School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin, China*

**Abstract**

Polyhedral oligomeric silsesquioxane (POSS) has attracted a great deal of interest owing to its unique cage-like molecular structure containing an inorganic siloxane core surrounded by eight organic corner groups. These organic groups can serve as reaction sites for further functionalization, while the rigid inorganic silica-like structure of the core makes POSS an ideal building block for constructing novel functional materials with enhanced thermomechanical properties, thermal stability, as well as oxygen and corrosion resistance. We developed [1] the synthesis of CdSe quantum dots (QDs) using a mercapto-substituted polyhedral oligomeric silsesquioxane (SH-POSS). The bulky siloxane cage-like core of the ligand makes this an ideal steric stabilizer, and comparison with conventional branched alkyl phosphonic acid capped CdSe QDs shows SH-POSS capped QDs to have superior optical properties including photoluminescence quantum efficiencies and fluorescence lifetimes. The POSS shell allows for the access of small electrolyte ions and electron transport from the surface of the QDs, evidenced by better performance as a photosensitizer in conjunction with a titania nanotube array electron acceptor in comparison to the conventionally stabilized QDs. The POSS-CdSe QDs introduced here may therefore be promising for a wide range of applications ranging from QD-based solar cells to memory devices. Owing to the availability of siloxane cages on the QD surface, these nanocrystals could also find use as building blocks for semiconductor chalcogenide aerogels.

## Reference

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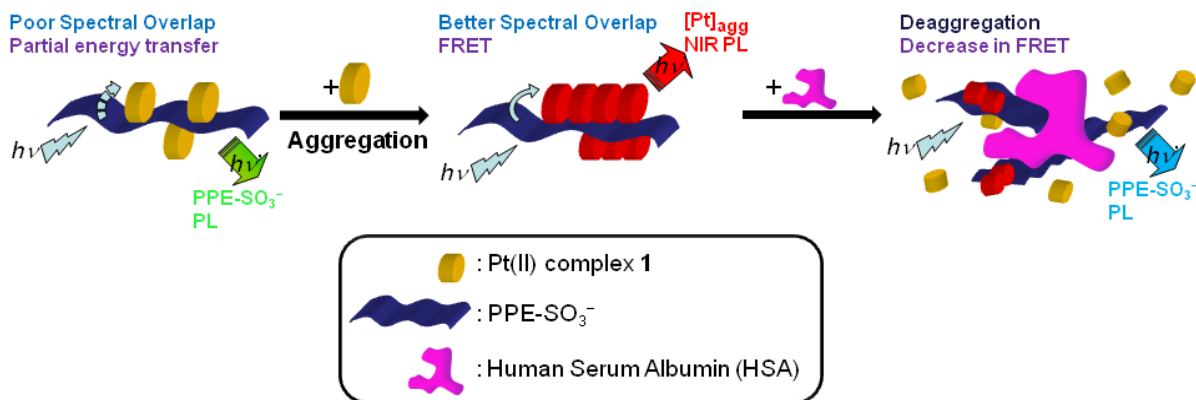
**Induced Self-Assembly and Förster Resonance Energy Transfer Studies of Alkynylplatinum(II) Terpyridine Complex Through Interaction With Water-soluble Poly(phenylene ethynylene sulfonate) and the Proof-of-Principle Demonstration of this Two-component Ensemble for Selective Label-free Detection of Human Serum Albumin (HSA)**

Clive Yik-Sham Chung and Vivian Wing-Wah Yam\*

*Institute of Molecular Functional Materials (Areas of Excellence Scheme, University Grants Committee, Hong Kong) and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong,*

**Abstract**

The interaction of conjugated polyelectrolyte, PPE-SO<sub>3</sub><sup>-</sup>, with platinum(II) complexes, [Pt(tpy)(C≡CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>3</sub>-4)](OTf)<sub>2</sub> (**1**) and [Pt(tpy)(C≡C-CH<sub>2</sub>NMe<sub>3</sub>)](OTf)<sub>2</sub> (**2**), has been studied by UV-vis, and steady-state and time-resolved emission spectroscopy. A unique FRET from PPE-SO<sub>3</sub><sup>-</sup> to the aggregated complex **1** on the polymer chain with Pt··Pt interaction has been demonstrated, resulting in the growth of triplet metal-metal-to-ligand charge transfer (<sup>3</sup>MMLCT) emission in the near-infrared (NIR) region. This two-component ensemble has been employed in a “proof-of-principle” concept for the sensitive and selective label-free detection of HSA by the emission spectral changes in the visible and NIR region, which have been ascribed to the disassembly of the polymer-metal complex aggregates upon the binding of PPE-SO<sub>3</sub><sup>-</sup> to HSA, leading to the decrease in FRET. The ensemble is found to have high selectivity towards HSA over a number of polyelectrolytes, proteins and small amino acids. This has been suggested to be a result of the extra stabilization gained from the Pt··Pt and π-π interactions in addition to the electrostatic and hydrophobic interactions found in the polymer-metal complex aggregates. [1]



Reference

[1] C. Y. S. Chung and V. W. W. Yam, *J. Am. Chem. Soc.*, **2011**, *133*, 18775-18784.

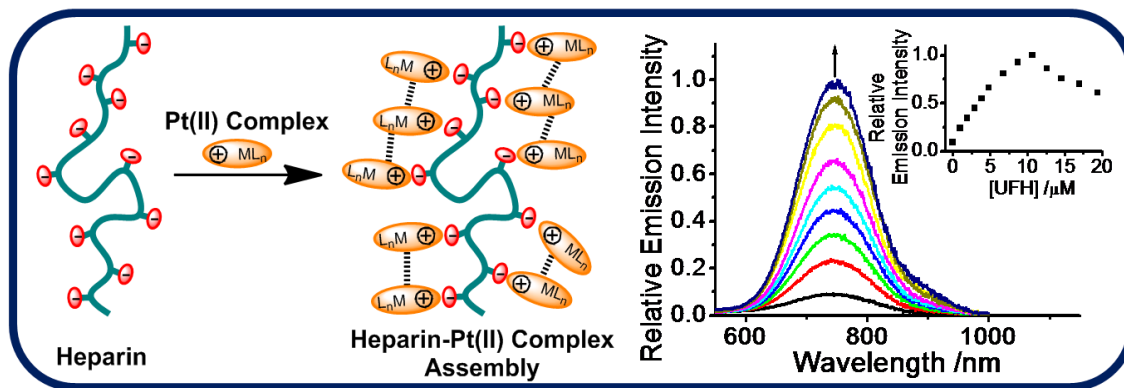
## NIR-emissive Alkynylplatinum(II) Terpyridyl Complex as a Turn-On Selective Probe for Heparin Quantification by Induced Helical Self-Assembly Behaviour

Margaret Ching-Lam Yeung and Vivian Wing-Wah Yam\*

*Institute of Molecular Functional Materials (Areas of Excellence Scheme, University Grants Committee, Hong Kong) and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China.*

### Abstract

The extent of self-assembly *via* metal–metal and  $\pi$ – $\pi$  stacking interactions, induced by the polyanionic biopolymers, enables the class of alkynylplatinum(II) terpyridyl complexes to be applicable for the sensing of important biomacromolecules through the monitoring of spectral changes. Strong demand arises for the design of selective and practical detection techniques for the quantification of heparin, a highly negative-charged polysaccharide that can function as anticoagulant, due to the prevention of hemorrhagic complications upon overdose usage. A convenient sensing protocol for the detection of UFH and LMWH, two common forms of heparins in clinical use, in buffer and biological medium has been demonstrated with the spectral changes associated with the induced self-assembly of a NIR-emissive platinum(II) complex. The detection range has been demonstrated to cover clinical dosage levels and the structurally similar analogues can be effectively differentiated based on their anionic charge density and the formation of supramolecular helical assembly of the platinum(II) complex with them.



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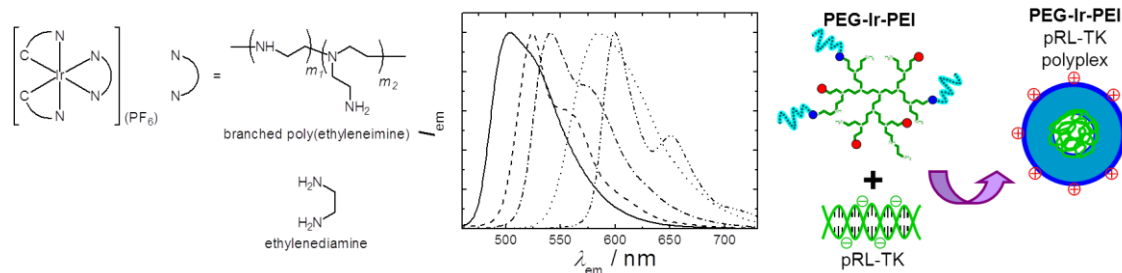
## Cyclometalated Iridium(III) Polyamine Complexes with Intense and Long-lived Multicolor Phosphorescence: Synthesis, Crystal Structure, Photophysical Properties, Cellular Uptake, and Transfection Properties

Steve Po-Yam Li, Tommy Siu-Ming Tang, Ken Shek-Man Yiu, and Kenneth Kam-Wing Lo\*

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China

### Abstract

We have synthesized and characterized a new class of luminescent cyclometalated iridium(III) polyamine complexes  $[\{\text{Ir}(\text{N}^{\wedge}\text{C})_2\}_n(\text{bPEI})](\text{PF}_6)_n$  (bPEI = branched poly(ethyleneimine), average  $M_w \approx 25$  kDa) and  $[\text{Ir}(\text{N}^{\wedge}\text{C})_2(\text{en})](\text{PF}_6)$  (en = ethylenediamine) and investigated their electrochemical and photophysical properties and lipophilicity. The cytotoxicity towards HeLa and HEK293T cell lines has been evaluated by the MTT assay. The cellular uptake and intracellular localization of the complexes by HeLa cells have been examined by ICP-MS and laser-scanning confocal microscopy, respectively. The DNA-binding properties of the bPEI complexes have been investigated by gel retardation assays, particle size estimation, and zeta potential measurements. Furthermore, one of the bPEI complexes has been grafted with poly(ethylene glycol) (PEG, average  $M_w \approx 2$  kDa) to different extents, yielding the copolymers **PEG<sub>12.3-g-5a</sub>**, **PEG<sub>25.4-g-5a</sub>**, and **PEG<sub>62.1-g-5a</sub>**. These PEGylated conjugates showed enhanced transfection activity as revealed by *in vitro* transfection experiments using tissue culture-based luciferase assays.



We thank the Hong Kong Research Grants Council (Project No. CityU102410) and City University of Hong Kong (Project No. 7002575) for financial support.

### Reference

Li, S. P.-Y.; Liu, H.-W.; Zhang, Y.; Lo, K. K.-W. *Chem. Eur. J.* **2010**, *16*, 8329 – 8339.

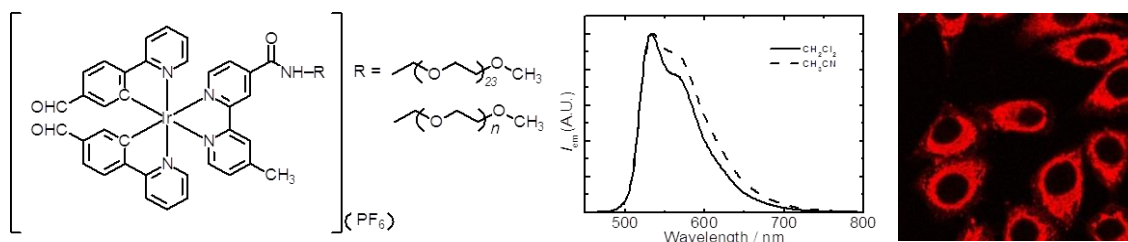
## PEGylation Reagents Derived from Luminescent Iridium(III) Polypyridine Complexes

Hua-Wei Liu, Steve Po-Yam Li, Kenneth Yin Zhang, and Kenneth Kam-Wing Lo\*

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China

### Abstract

We report the synthesis, characterization, and photophysical properties of a class of luminescent cyclometalated iridium(III) polypyridine poly(ethylene glycol) (PEG) complexes. We have investigated the cytotoxicity and cellular uptake of these complexes by the MTT assay, ICP-MS, laser-scanning confocal microscopy, and flow cytometry. The results illustrated that the PEG complexes can act as biological imaging reagents with extremely low cytotoxicity. Since the aldehyde groups of the complexes are reactive toward primary amines, they have been conjugated to bovine serum albumin (BSA) and poly(ethyleneimine) (PEI), and the resulting conjugates have been isolated, purified, and their photophysical properties studied.



We thank The Hong Kong Research Grants Council (Project Nos. CityU 102109 and 102410) for financial support.

### References

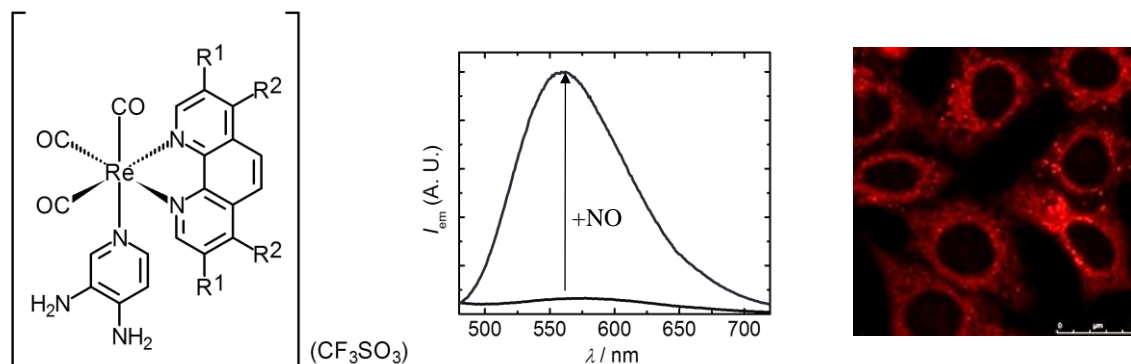
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## Rhenium(I) Polypyridine Complexes Functionalized with a Diaminoaromatic Moiety as Phosphorescent Sensors for Nitric Oxide

Alex Wing-Tat Choi, Che-Shan Poon, Hua-Wei Liu, Heung-Kiu Cheng, and Kenneth Kam-Wing Lo\*  
 Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China

### Abstract

A series of rhenium(I) polypyridine complexes appended with a diaminoaromatic moiety has been developed as phosphorescent sensors for nitric oxide (NO). These complexes were only weakly emissive due to the diaminoaromatic moiety that quenches the  $^3\text{MLCT}$  ( $d\pi(\text{Re}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$ ) emission by photoinduced electron transfer. However, in the presence of NO, these diamine complexes were converted to the triazole derivatives, which revealed intense emission upon excitation. The cytotoxicity and cellular uptake properties of these complexes were studied by the MTT assay and ICP-MS, respectively. The potential application of these complexes as intracellular NO sensors was also investigated.



We thank the Hong Kong University Grants Committee (Areas of Excellence Scheme AoE/P-03/08) and the Hong Kong Research Grants Councils (Project No. CityU 102311) for financial support.

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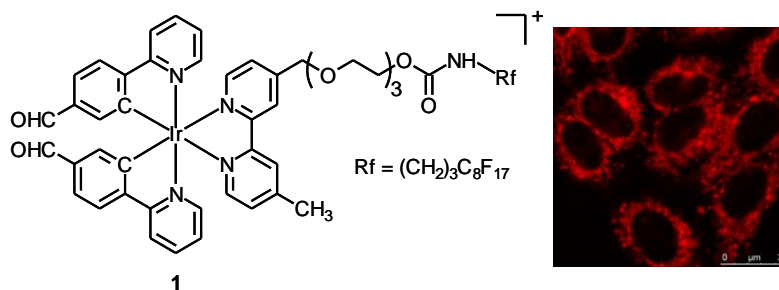
## Luminescent Cyclometalated Iridium(III) Polypyridine Fluorous Complexes: Photophysics, Bioconjugation, Cytotoxicity, and Cellular Uptake Properties

Li-Juan Hua, Siu-Kit Leung, Man-Wai Louie, Hua-Wei Liu, and Kenneth Kam-Wing Lo\*

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China

### Abstract

We present the synthesis, characterization, and photophysical properties of a series of luminescent cyclometalated iridium(III) polypyridine complexes containing a fluorous moiety [Ir(pba)<sub>2</sub>(bpy-TEG-OCONHRf)](PF<sub>6</sub>) (**1**), [Ir(ppy-C4)<sub>2</sub>(bpy-TEG-OCONHRf)](PF<sub>6</sub>) (**2**), [Ir(pba)<sub>2</sub>(bpy-HEG-OCONHRf)](PF<sub>6</sub>) (**3**) and their fluorous-free counterparts [Ir(pba)<sub>2</sub>(bpy-TEG-OMe)](PF<sub>6</sub>) (**1a**), [Ir(ppy-C4)<sub>2</sub>(bpy-TEG-OMe)](PF<sub>6</sub>) (**2a**). The pba complexes have been used to label bovine serum albumin (BSA). The photophysical properties of resultant bioconjugates have been studied. The cytotoxicity of all the complexes toward HeLa cells has been investigated by the 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyltetrazolium bromide (MTT) assay. The cellular uptake properties of the complexes have also been examined by ICP-MS and laser-scanning confocal microscopy.



We thank the Hong Kong Research Grants Council (Project Nos. CityU 102109 and CityU 101908) for financial support.

### References:

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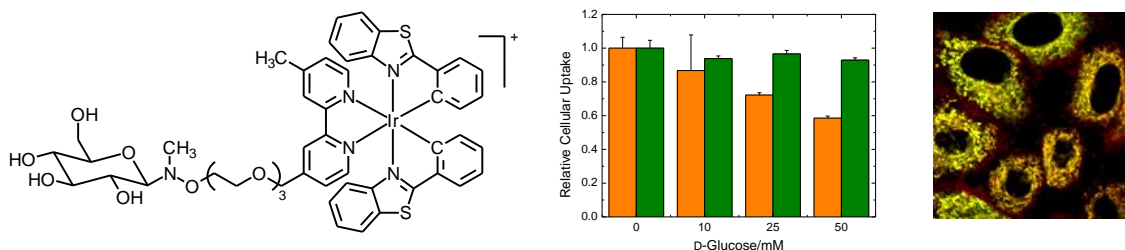
## Phosphorescent Cyclometalated Iridium(III) Bipyridine Complexes Appended with a Carbohydrate Unit as Novel Cellular Uptake Indicators

Wendell Ho-Tin Law, Man-Wai Louie, Hua-Wei Liu, Tim Wai-Hung Ang, and Kenneth Kam-Wing Lo\*

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China

### Abstract

A series of luminescent cyclometalated iridium(III) bipyridine complexes appended with a carbohydrate unit has been synthesized, characterized, and their photophysical properties investigated. Upon photoexcitation, all the complexes exhibited green to yellow luminescence in fluid solutions at 298 K and in low-temperature glass. The lipophilicity and cytotoxicity of these complexes have been studied. Also, the cellular uptake efficiencies of one of the glucose complexes in the presence of different biological molecules such as glucose, insulin, and other chemicals have been examined. Furthermore, the intracellular distribution and photostability of this complex have been investigated by laser-scanning confocal microscopy.



We thank the Hong Kong Research Grants Council (Project No. CityU 102109) and City University of Hong Kong (Project No. 7002575) for financial support.

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3. Louie, M.-W.; Liu, H.-W.; Lam, M. H.-C.; Lam, Y.-W.; Lo, K. K.-W. *Chem. Eur. J.* **2011**, *17*, 8304–8308.
4. Lee, P.-K.; Law, W. H.-T.; Liu, H.-W.; Lo, K. K.-W. *Inorg. Chem.* **2011**, *50*, 8570–8579.



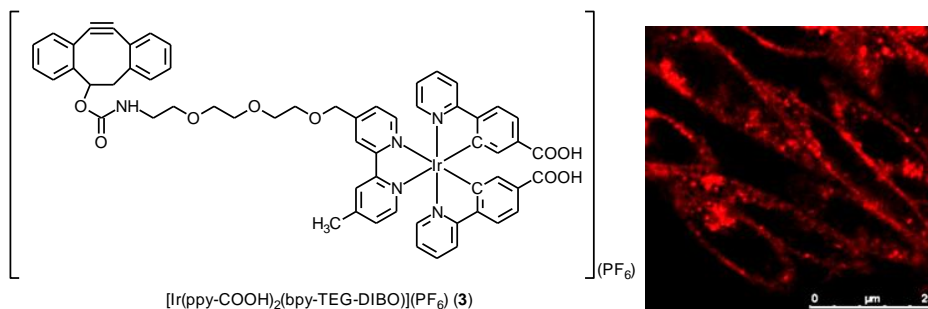
## Cyclometalated Iridium(III) Polypyridine Dibenzocyclooctyne Complexes as the First Phosphorescent Bioorthogonal Probes

Tommy Siu-Ming Tang, Bruce Ting-Ngok Chan, Hua-Wei Liu, Kenneth Yin Zhang, Steve Po-Yam Li, and Kenneth Kam-Wing Lo\*

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China

### Abstract

Two phosphorescent cyclometalated iridium(III) polypyridine complexes appended with a dibenzocyclooctyne (DIBO) moiety [Ir(ppy)<sub>2</sub>(bpy-C<sub>6</sub>-DIBO)](PF<sub>6</sub>) (**1**) and [Ir(pq)<sub>2</sub>(bpy-C<sub>6</sub>-DIBO)](PF<sub>6</sub>) (**2**) were initially designed to probe azide-tagged sialic acid located on the cell surface of the Ac<sub>4</sub>ManNAz-pretreated CHO cells through the strain-promoted alkyne-azide cycloaddition (SPAAC). However, the high lipophilicity of these complexes led to facile cellular uptake and very inefficient tagging of azide-labeled membrane glycans. Thus, another iridium(III)-DIBO complex [Ir(ppy-COOH)<sub>2</sub>(bpy-TEG-DIBO)](PF<sub>6</sub>) (**3**) containing two polar carboxylic acid groups and a hydrophilic triethylene glycol linker was synthesized. Confocal microscopy images revealed intense staining of the membrane of Ac<sub>4</sub>ManNAz-pretreated CHO cells incubated with the complex, with negligible luminescence in intracellular compartments, highlighting the bioorthogonal nature of the labeling. Additionally, the lipophilicity, reaction kinetics, cytotoxicity, and cellular uptake properties of all the complexes were investigated.



We thank The Hong Kong Research Council (Project Nos. CityU 102212 and CityU 102410) for financial support.

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Lo, K. K.-W.; Chan, B. T.-N.; Liu, H.-W.; Zhang, K. Y.; Li, S. P.-Y.; Tang, T. S.-M. *Chem. Commun.* **2013**, DOI:10.1039/C2CC36907A.

## Synthesis and Characterization of Folate-receptor Targeting CdTe/CdS Quantum Dots Fluorescent Probe

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### Abstract

**Objective** To develop a CdTe/CdS quantum dots fluorescent probe (FA-PEG- CdTe/CdS) with ability of folate receptor targeting.

**Methods** CdTe/CdS QDs were synthesized in aqueous phase using thioglycolic acid (TGA) as stabilizer and linker. The spectral properties were investigated via fluorescence spectrophotometer and UV spectrophotometry. Crystal composition was determined via X-radial Diffractometer. Morphology of the prepared QDs was determined on a transmission electron microscopy (TEM). CdTe/CdS QDs was coupled with FA-PEG-NH<sub>2</sub> to prepare folate receptor targeting quantum dots fluorescent probe FA-PEG- CdTe/CdS. The Coupling effect was evaluated by agarose gel electrophoresis and spectral analysis. The cellular uptake in FR-positive human nasopharyngeal carcinoma cells (HNE-1 cells) and FR-negative human nasopharyngeal carcinoma cells (CNE-2 cell) for FA-PEG- CdTe/CdS was found by means of Inverted Fluorescence Microscopy.

**Results** In the condition of pH=10, n(Te<sup>2+</sup>):n(Cd<sup>2-</sup>):n(MSA)=1:10:10.5, the diameters of TGA-stabilized CdTe QDs is increasing and adsorption spectra and emission spectrum is constantly red shifting with reaction time but the PL QY of CdTe QDs is decreasing. The XRD patterns of TGA-stabilized CdTe had proved the corresponding (111), (220), (311) lattice faces of cubic crystal CdTe. The picture of TEM show the CdTe particle size distribution is uniform and the average particle diameter is 3nm. The agarose gel electrophoresis and spectral analysis proved that CdTe/CdS-PEG-FA is stable. From the result of Inverted Fluorescence Microscopy, we can see FR-positive HNE-1, Hep-2 can be specifically marked by FA-PEG- CdTe/CdS.

**Conclusion** CdTe quantum dots can be used as a new fluorescent marking material. FA-PEG- CdTe/CdS QDs have a good stability and targeting. The value of the folate receptor targeting QDs applying in diagnosis and therapy of cancers in which the FA receptor (FR) is over expressed is brilliant.

**Multifunctional Upconversion Nanoprobe for Bio-imaging and Drug Delivery**

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**Abstract**

Lanthanide-doped upconversion nanoparticles, which can convert NIR long-wavelength excitation radiation into shorter visible wavelengths, are promising luminescent nanomaterials in biological applications.<sup>[1,2]</sup> Herein, we propose a new type of nanoscale integration (NaYF<sub>4</sub>@SiO<sub>2</sub>-Au) of lanthanide-doped upconversion materials with plasmonic Au nanoparticles. Typically, small Au nanodots are chosen to selectively quench UV and visible emissions of upconversion, with only the single band near infrared (NIR) emission (800 nm) left. The resulting multifunctional nanoprobe create a new imaging mode, which has a deep penetration in biological tissues with NIR emission as an imaging probe and reduces the damage caused by UV and visible emission. Furthermore, good biocompatibility and easy functionalization of Au and SiO<sub>2</sub> on the particle surface make NaYF<sub>4</sub>@SiO<sub>2</sub>-Au heterostructure an ideal candidate for the biosystem. In addition, we utilized the NaYF<sub>4</sub>@SiO<sub>2</sub>-Au hybrid nanostructure as a nanoplatform to assemble multiple copies of hairpin DNA (hpDNA). With precisely controllable density and covalent conjugation, the binding of hpDNA onto the surface of NaYF<sub>4</sub>@SiO<sub>2</sub>-Au nanoparticles greatly increases their stability in physiological environments. Based on these features, we attempt to explore an ideal platform for bio-imaging and light-controlled drug delivery in cancer therapy using the hpDNA NaYF<sub>4</sub>@SiO<sub>2</sub>-Au nanoconjugate as a smart drug carrier and bio-imaging probe.

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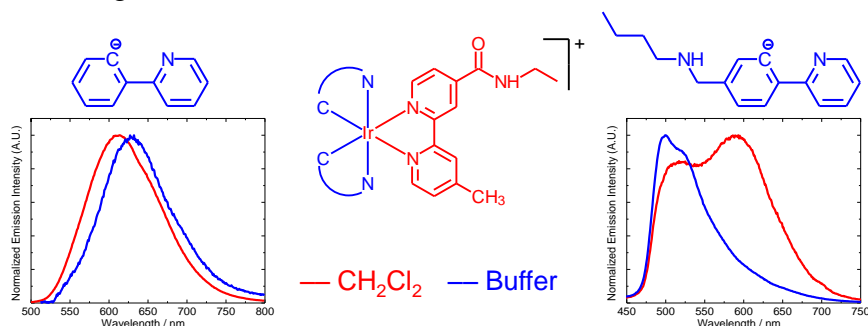
## Effects of Ligand Design on the Photophysical and Cellular Uptake Properties of Dual-emissive Cyclometalated Iridium(III) Polypyridine Complexes

Kenneth Yin Zhang, Hua-Wei Liu, Alex Wing-Tat Choi, Man-Chung Tang, Xi-Guang Wei, Nianyong Zhu, Kai-Chung Lau,\* and Kenneth Kam-Wing Lo\*

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### Abstract

A series of bis-butylaminomethyl-substituted cyclometalated iridium(III) complexes has been synthesized and characterized. Upon photoexcitation, they showed interesting dual emission in fluid solutions at room temperature. On the basis of the photophysical data, the high-energy (HE) and low-energy (LE) emission features of the complexes have been assigned to triplet intraligand ( $^3\text{IL}$ ) and triplet charge-transfer ( $^3\text{CT}$ ) excited states, respectively. TD-DFT calculations indicated that the dual emission originated from the interruption of communication between the higher-lying  $^3\text{IL}$  to the lower-lying  $^3\text{CT}$  state due to an additional triplet amine-to-ligand charge-transfer ( $^3\text{NLCT}$ ) state. The cellular uptake and cytotoxicity of the complexes have been studied. Additionally, laser-scanning confocal microscopy revealed that the complexes were localized on cell membrane or mitochondria, depending on the nature of the substituents of the ligands.



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**You Cannot Have Your Cake and Eat It Too: Comparison of the Plasmonic Performance between Lithographically Fabricated and Chemically Grown Gold Nanorods**

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**Abstract**

Gold nanorods have been receiving extensive attention owing to their attractive applications in biomedical technologies, plasmon-enhanced spectroscopies, and optoelectronic devices. In most applications, the plasmonic properties of Au nanorods play a vitally important role. The plasmonic properties, however, are strongly influenced by the fabrication techniques. We have systematically investigated the plasmonic properties of the Au nanorods prepared by two most frequently adopted methods, seed-mediated wet-chemistry growth and electron-beam lithography (EBL) writing, each of which has unique advantages. Dark-field scattering spectroscopy was employed to characterize the plasmonic properties of the colloidal and the lithographically fabricated Au nanorods, including the plasmon resonance wavelength, the resonance bandwidth and the scattering intensity. Compared to their colloidal counterparts at approximately the same sizes, the EBL-fabricated Au nanorods suffer a ~75% reduction in the scattering intensity, and their plasmon resonances exhibit slight red shifts and spectral broadening. Their plasmonic response degradations brought by the adhesion layers and multi-crystalline structures were carefully examined. We further studied the performances of the Au nanorods obtained from the above two strategies in the applications of surface-enhanced Raman scattering and refractive index-based sensing, respectively.

The wet-chemistry method can produce large amounts of single-crystalline Au nanorods at low cost. The powerful EBL method can fabricate periodic Au nanorod arrays with any designed geometries but poorer plasmonic performances. The details on the plasmonic properties of both colloidal and EBL-written Au nanorods will be provided. Our results are expected to greatly facilitate the performance evaluation and therefore the selection of Au nanorods for different plasmonic applications.

## Plasmonic Behaviors of Metal–Semiconductor Hetero-nanorods

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### Abstract

Metal–semiconductor hybrid nanocrystals, in which a metal and its semiconductor counterpart are closely coupled in an effort to produce intriguing behaviors and functionalities far beyond those of their individual counterparts.<sup>[1,2]</sup>

We proposed a method to synthesize Au–AgCdSe hybrid nanorods with controlled morphologies and spatial distributions.<sup>[3]</sup> The synthesis involved deposition of Ag tips at the ends of Au nanorod seeds, followed by selenization of the Ag tips and overgrowth of CdSe on these sites. By manipulating growth rate, a mike-like, dumbbell-like, or toothbrush-like hybrid nanorod could be generated. These three types of Au–AgCdSe hybrid nanorods displayed distinct localized surface plasmon resonance (SPR) and photoluminescence (PL) properties, demonstrating an effective pathway for maneuvering the optical properties of nanocrystals. By the similar method, we also synthesized Au–CdS core–shell hetero-nanorods with controllable shell thickness.<sup>[4]</sup> Exciton–plasmon interactions observed in the Au–CdS nanorods induce shell thickness-tailored and red-shifted longitudinal SPR. The Au–CdS nanorods demonstrate an enhanced two-photon PL.

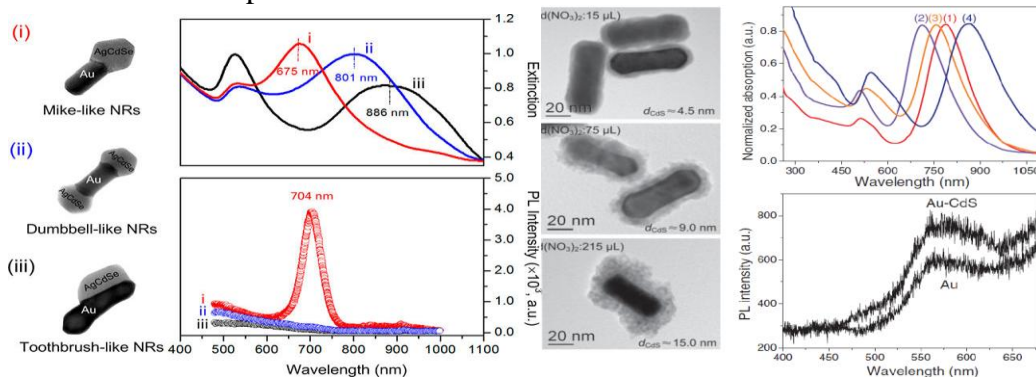


Fig. 1 (Left) TEM images, extinction spectra and PL spectra of mike-like, dumbbell-like, and toothbrush-like Au-AgCdSe hetero-nanorods. (Right) TEM images, extinction spectra and two-photon PL spectra of Au-CdS core-shell hetero-nanorods.

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**Mass-based Photothermal Comparison among Gold Nanocrystals, PbS Nanocrystals, Organic Dyes, and Carbon Black**

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**Abstract**

Gold nanocrystals have intriguing localized surface plasmon resonances (LSPRs), which are the collective oscillations of the conduction band electrons under the electromagnetic wave excitation. The LSPR endows Au nanocrystals with many peculiar properties. Photothermal conversion, a very important one among them, can be used in photothermal therapy and solar energy harvesting. For practical applications, the mass-normalized photothermal conversion performance is often desired to be known for Au nanocrystals with different shapes and sizes and for different nanomaterials. In this regard, we study the photothermal conversion performance of differently shaped and sized Au nanocrystals and compare them with those of PbS nanocrystals, carbon black, and organic dyes at the same mass concentrations under laser and solar radiation. Both the photothermal conversion efficiency and the mass-normalized extinction cross section decrease as the Au nanocrystal size is increased. The photothermal conversion performance of Au nanocrystals therefore decreases with the increase in Au nanocrystal size. Under laser illumination at the plasmon resonance wavelength, small Au nanocrystals show the best photothermal conversion performance among all studied materials. Carbon black has a better photothermal conversion performance than relatively large Au nanocrystals and other materials. Organic dyes are very unstable under laser illumination. Therefore, Au nanocrystals are superior to organic dyes in photothermal conversion performance. Under solar radiation, a Au nanocrystal mixture, which is made of differently sized Au nanocrystals with the overall extinction spectrum matching with the solar spectrum, and carbon black exhibit similar photothermal conversion performances, and PbS nanocrystals show a relatively weak photothermal conversion capability. Our results are useful for the design of Au nanocrystals and the choice of nanomaterials for different photothermal applications.

## **Growth of Highly Monodisperse Gold Nanospheres over a Large Size Range and Their Core/Satellite Nanostructures for Raman Enhancement**

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### **Abstract**

Gold nanocrystals and nanoassemblies have attracted extensive attention for various applications, including photothermal therapy, chemical and biological sensing, and plasmon-enhanced spectroscopies, due to their unique plasmonic properties. It is of great importance to fabricate shape-controlled gold nanocrystals with high monodispersity over a large range of sizes. We herein present the growth of gold nanospheres (NSs) with sizes ranging from 20 nm to sub-micrometer using a simple seed-mediated growth method aided with mild oxidation. As-prepared Au NSs are remarkably uniform and of narrow size distributions (relative standard deviation < 8%). The sizes of the resultant Au NSs can be well controlled by adjusting the seed amount. The prepared Au NSs of different sizes can serve as building blocks for plasmonic nanoassemblies.

We in next step fabricated Au NS core/satellite structures by first depositing NSs of 180-nm diameter on indium tin oxide glass slides/silicon wafers. Small Au NSs at 24-nm diameter were then assembled onto the 180-nm NS cores that were functionalized with 1,8-octanedithiol or *p*-aminothiophenol (pATP). Compared with the NS cores, the core/satellite nanostructures exhibited red shifts in their plasmon resonances recorded by dark-field scattering spectroscopy. The red shifts were found to be consistent with the calculation results given by Mie theory. Finite-difference time-domain simulations revealed the strongly enhanced electric field located at the gaps between the core and satellites. We thus employed the prepared core/satellite structures for surface-enhanced Raman scattering. The pATP assembled core/satellite structures exhibited strongly enhanced Raman signals from pATP, while the Raman bands could not be distinguished for the Au NS cores functionalized only with pATP. Our facile growth and assembly approaches are expected to facilitate the fabrication of novel nanoassemblies with desired plasmonic properties and functions.



**Plasmonic-enhanced Near-infrared Photodetectors Based on Colloidal Quantum Dots**

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**Abstract**

Plasmonic nanostructures, with the special resonance enhancement property and wavelength-tunability, are becoming a promising light manipulating method for photovoltaic or photodetection devices. There have been numerous reports on the efficiency improvement of organic or thin film solar cells by incorporating metal nanoparticles in the device structure. However, the applications of the plasmonic nanoparticles in colloidal quantum dot (QD) based devices, are less explored. In this study, making use of the wet-chemistry-based immobilization of colloidal Au nanorods and spray-coating deposition technique, an aqueous HgTe QDs based infrared photodetector embedded with homogeneously distributed Au nanorods is demonstrated. The light absorption and scattering enhancement in the QDs film are proved both by FDTD simulation and the experimental measurements. The best ratio between the diameter and the length of the nanorods for infrared detection, as well as the optimal volume and density of the nanorods in the material system are numerically investigated. The comparison of the performances of the nanorods and nanobipyramids embedded in the QD layers is also analyzed using both simulation and experiment approaches.

## Improving the Efficiency of Polymer Solar Cells by Incorporating Gold Nanoparticles into All Polymer Layers

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### Abstract

Polymer solar cells (PSCs) have been a highly interesting field in recent years, as they have a strong potential to realize low cost solar cells which are highly portable and deployable due to their flexibility and light weight. Compared with inorganic solar cells, PSCs usually suffer from the insufficient light absorption due to the thin active layer restricted by the short exciton diffusion length and low carrier mobilities.<sup>1–3</sup> To overcome these limits, metallic (e.g., Au, Ag) nanoparticles (NPs) have been incorporated into the polymer layers conveniently in solution processing. Although the power conversion efficiency (PCE) of PSCs has been shown to improve by incorporating metallic NPs in either the buffer layer such as poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) or the active layer,<sup>4</sup> the understanding on the changes is still not quite clear.

In this work, monofunctional poly(ethylene glycol)(PEG)-capped Au NPs of sizes 18 nm and 35 nm are doped in the PEDOT:PSS and poly(3-hexylthiophene) (P3HT):phenyl-C61-butyric acid methyl ester (PCBM) layers, respectively, leading to an improvement of PCE by 22% compared to the optimized control device.<sup>5</sup> Au NPs are found to have distinct mechanisms in improving device performance when incorporated in different polymer layers. Au NPs in poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate) mainly contribute to better hole collection, while Au NPs in active layer contributes to the enhanced optical absorption and more balanced charge-transport. Our theoretical result shows that the absorption enhancement at the active layer is attributed to plasmon resonances with strong near-field distributions penetrated into absorption polymers. We demonstrate that the accumulated benefits of incorporating Au NPs in all organic layers of PSCs can achieve larger improvements in PSC performances. These findings can be applied to design high-efficiency metallic NPs-incorporated PSCs.

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## Rational Geometrical Design of Multi-diameter Nanopillars for Efficient Light Harvesting

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### Abstract

Three-dimensional arrays of nanostructures have drawn increasing attention for solar energy harvesting recent years. In this work, with Ge as the model material, broadband solar spectrum absorption of arrays of multi-diameter nanopillars is explored with emphasis on the geometry dependent light absorption analyzed with finite difference time domain simulations. It is found that light absorption of a nanopillar array is either determined by the material filling ratio or by transverse resonance leaky modes depending on input wavelength. And a properly designed multi-diameter nanopillar array can compete with a nanocone array on broadband light absorption capability. As the single crystalline multi-diameter nanopillars can be grown with a bottom-up approach, the investigation here can serve as important design guidelines for fabrication of efficient nanostructured photovoltaic and other optoelectronic devices.

## Efficient Light Absorption with Integrated Nanopillar/Nanowell Arrays for Three-dimensional Thin-Film Photovoltaic Applications

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### Abstract

Efficient light absorption is crucial for enhancing the performance of thin-film photovoltaic (PV) devices, which requires both broadband antireflection coatings and efficient light trapping techniques. Properly engineered three-dimensional (3-D) photonic nanostructures have demonstrated highly promising capability of harvesting sunlight over a broad range of wavelengths and incident angles. In particular, arrays of a variety of 3-D nanostructures, such as nanowires, nanopillars (NPLs), nanowells (NWLs), nanocones, nanopyramids, nanospheres, and so forth, have been extensively studied for light trapping and solar energy conversion with photonic materials including Si, Ge, CdS, and Cu(In, Ga)Se (CIGS), *etc.* By rational integration of these 3-D nanostructures, photons can be trapped efficiently within the thin-film absorber layer, consequently improving light absorption and thus conversion efficiencies. Additionally, enhanced absorption efficiency leads to utilization of thinner absorber layer, which improves carrier collection, as well as reduces production costs and environmental concern for solar cells made of rare materials, *e. g.* CIGS, and environmentally unfriendly material. *e. g.* CdTe. Our previous work demonstrated that a properly designed 3-D NWL array fabricated by a low-cost and scalable approach can serve as an efficient photon harvester confirmed by both experiments and simulations systematically. In this work, it was found that highly regular NPL arrays can be fabricated with precisely controlled wet chemical etching after obtaining 3-D NWL arrays. In addition, a unique integrated-NPL-NWL (i-NPW) structure has been successfully realized by carefully designing and controlling the wet etching and anodization processes. Furthermore, systematic optical property investigations on the obtained 3-D structures have been performed experimentally assisted with optical simulations. It was found that NWL arrays with cylindrical cavities provide efficient geometric confinement for normal incident incoming photons naturally, while NPL arrays with small diameter tips lead to a broadband suppression of reflectance with superior angular absorption performance. Therefore, a rationally vertical integration of the two types of 3-D nanostructures, *i. e.* i-NPW, leads to much improved photon harvesting property over large wavelength and incident angle range. These results not only shed light on light trapping mechanism in complex 3-D nanophotonic structures, but also provide a facile approach to fabricate the 3-D nanostructures for ultra-thin film photovoltaics.

## To Improve the Efficiency of Polymer Organic Solar Cells by Blending Covalent Modified Carbon Nanotubes

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### Abstract

Organic solar cells are promising low-cost alternatives to silicon solar cells, but the main handicap is the low power conversion efficiency of these devices. Nowadays, a promising approach to tackle the charge carrier dissociation and transport drawbacks is the addition of one-dimensional nanostructures like carbon nanotubes (CNTs), because of their outstanding properties and versatility, such as the ballistic charge transport along their axis, the high surface area (about  $1600 \text{ m}^2\text{g}^{-1}$ ) and the electron-accepting properties.

In this paper, covalently modified single-walled carbon nanotubes (SWNTs) with polymers have been blended into the P3HT:PCBM photoactive layer, a significantly improvement in power conversion efficiency compared to the pristine device without SWNTs has been achieved. This improvement of device performance is attributed to the extension of excitons dissociation area and faster electron transfer through SWCNTs, as well as a more efficient dispersion of the nanotubes within the photoactive layer.

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## Single-Layer Graphene as Efficient Transparent Cathode for Organic Solar Cells with Al-TiO<sub>2</sub> Composite Interfacial Layer

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### Abstract

While challenges remain in tuning the properties of graphene (surface wettability, workfunction alignment and carrier transport) for realizing efficient graphene cathode in organic solar cells (OSCs), we propose and demonstrate an Al-TiO<sub>2</sub> composite to modify single-layer graphene as efficient cathode for OSCs. To unveil the contributions of the composite in addressing the aforementioned challenges, the evaporated aluminum (Al) nanoclusters in the composite benefit the graphene cathode by simultaneously achieving two roles of improving its surface wettability for subsequent TiO<sub>2</sub> deposition and reducing its work function to offer better energy alignment. To address challenges related to charge transport, solution-processed TiO<sub>2</sub> with excellent electron transport can offer charge extraction enhancement to the graphene cathode, which is essential to efficient devices. However, it is a well-known issue for methods such as spin coating to produce uniform films on the initially hydrophobic graphene, even with the improved wettability. The undesirable morphology of TiO<sub>2</sub> by such methods considerably inhibits its effectiveness in enhancing charge extraction. We propose a self-assembly method to deposit the solution-processed TiO<sub>2</sub> on the Al-covered graphene for forming the Al-TiO<sub>2</sub> composite. Compared with spin-coating, the self-assembly method is found to achieve more uniform coating on the graphene surface, with highly controllable thickness. Consequently, the graphene cathode modified with Al-TiO<sub>2</sub> composite in inverted OSCs gives rise to enhanced power conversion efficiency of 2.58%, which is two-fold of the previously best reported efficiency (1.27%) for graphene cathode OSCs, reaching ~ 75% performance of control devices using indium tin oxide.

## Synthesis and Characterization of Novel Heteroleptic Ruthenium Complexes Containing Benzimidazole Ligands for Dye-Sensitized Solar Cells

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### Abstract

We designed heteroleptic ruthenium complexes (**RD12**–**RD18**) containing fluoro-substituted benzimidazole ligands (**RD12**–**RD15**) with further modification by enhancing the light harvesting ability with thiophene substituting ligands (**RD16**–**RD18**) for dye-sensitized solar cells. The eventual devices of (**RD12**–**RD15**) show a systematic trend of increasing  $V_{OC}$  and decreasing  $J_{SC}$  with fluorine atoms of increasing number substituted on the ligand. The charge-extraction (CE) results show that upward shifts of the  $TiO_2$  potential occurred when the fluoro-substituted dyes were sensitized on  $TiO_2$  with a systematic trend of shift **N719** > **RD15** (with 5 F) > **RD12** (with 2 F) > **RD5** (no F); the intensity-modulated photovoltage spectra (IMVS) indicate that those fluoro-substituents retard charge recombination with the electron lifetimes ( $\tau_R$ ) in the order **RD15** > **RD12** > **RD5** > **N719**, consistent with the variation of  $V_{OC}$  for the systems. Additional substitution of thiophene in the **RD16**–**RD18** systematic enhanced short-circuit current density ( $J_{SC}$ ) and efficiency ( $\eta$ ) of power conversion of the devices had the order **RD18** > **RD17** > **RD16** > **RD12** > **N719**, attributed to the increasing light-harvesting ability and the broadened spectral features with thiophene-based ligands. Measurements of (CE) and (IMVS) indicate that thiophene substitution shifts downward the  $TiO_2$  potential and accelerates charge recombination, but inclusion of a long hexyl chain on the thiophene moiety retards charge recombination to account for the variation of  $V_{OC}$  in the series. Finally we can get the best efficiency **RD18** attaining an efficiency 10.0 % of power conversion, superior to that of **N719** ( $\eta = 9.3$  %) under the same experimental conditions.

## Enhancing the Efficiency of Solar Cells by Luminescent Down-shifting Using Semiconductor Quantum Dots: Simulations

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### Abstract

In recent years, luminescent materials, capable of converting a broad incident solar spectrum into photons of a narrower, longer wavelength band, have been synthesized and used to minimize the overall losses in photovoltaic solar-cell-based energy conversion process via luminescent down-shifting (LDS). This study demonstrates the possibility of using II-VI semiconductor colloidal quantum dot (QD) films to enhance the efficiency of typical commercial photovoltaic (PV) solar cells. QDs in comparison to organic dyes and lanthanide-doped phosphors have attractive optical properties: an absorption that gradually increases toward shorter wavelengths (below the first absorption band) and a narrow emission band; the spectral position of absorption and emission are tunable by particle size due to the quantum confinement effect; the (size-dependent and excitonic) molar absorption coefficients at the first absorption band of QDs are generally large. Photoluminescence quantum yields of properly surface-passivated QDs are in most cases high in the visible, visible-NIR and NIR light ranges.

In this work we present figures of merit values which allow quantitative determination of the optical properties of suitable luminescent materials allowing comparison of the properties of an optimum planar LDS layer combined with amorphous-Si (a-Si), microcrystalline-Si (mc-Si), single crystal-Si (c-Si) or CdTe solar cells. The photoluminescence quantum yield and evaluation of the overlap between QD fluorescence and absorption provide figures of merit for the emission properties of the fluorophore and the emission and absorption spectral matching values that are characteristic of each luminescent material and solar cell pairing.

A simple, universally applicable optical model to analyze the wavelength dependent efficiency of solar modules with a planar LDS layer will be presented. The model requires three inputs: (i) photoluminescence and (ii) absorbance spectra of the LDS layer and (iii) the EQE spectrum of the underlying solar cell. The EQE of the solar module with the LDS layer is fully described by only two parameters: the LDS efficiency and the optical density. Simulations show the viability of CdSe/CdS core/shell QDs and PbS NIR-emitting QDs as efficient down-shifting materials in planar LDS layers on CdTe and c-Si solar cells respectively (fig. 1). In contrast, calculations for LDS layers on a-Si, mc-Si solar cells show no beneficial effects, due to the already high PV spectral responses at short wavelength.



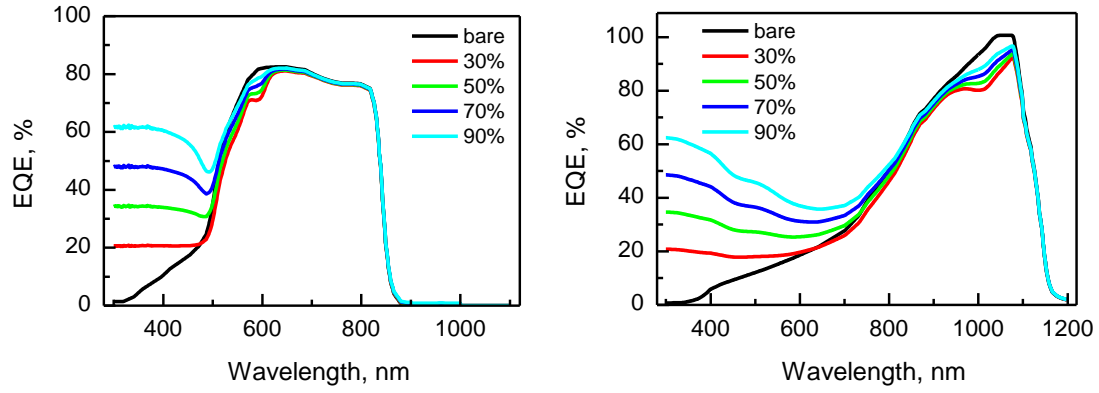


Fig. 1. Calculated EQE spectra of CdTe (a) and c-Si (b) solar cell with CdSe/CdS and PbS QDs LDS layer respectively for different QY values (colored lines) compared to the bare solar cell (solid black line).

## Elucidating the Role of Reduced-Graphene-Oxide and Platinum Nanoparticles Integrated with TiO<sub>2</sub> during Photocatalysis

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### Abstract

The recent years saw overwhelming interests in graphene-based photocatalysis, driven largely by the innate ability of graphene as excellent platform for interfacial photoelectrons transport, large specific surface area and high adsorption capacity.<sup>[1-3]</sup> Despite so, very little is understood pertaining to the exact role of graphene entities in the photocatalytic mineralisation of organic compounds, where depending on their classes, undergo various degradation paths.

Here, up to three-component nanocomposites are designed, consisting of TiO<sub>2</sub> photocatalyst, reduced-graphene-oxide (rGO) as the electron transporter and Pt as the electron sink and co-catalyst. The organic probes used include oxalic acid (OA) as holes scavenger, *tert*-butanol (TBA) as hydroxyl radicals scavenger and 2,4-dichlorophenoxyacetic acid (2,4-D) as the model halogenated aromatic compound.

In all cases, the interfacing of rGO with TiO<sub>2</sub> (rGO/TiO<sub>2</sub>) improved the photocatalytic mineralisation of OA and TBA, with respect to bare TiO<sub>2</sub>. This is attributed to the efficient photoelectrons transport across the TiO<sub>2</sub>-rGO interface, leading to improved net charge separation. In other words, more photoholes or formed hydroxyl radicals are available for the mineralisation of OA and TBA, respectively. However the effect of charge separation of rGO/TiO<sub>2</sub> is not as efficient as that prompted by the Schottky barrier at the Pt-TiO<sub>2</sub> interface. Further bridging of Pt and TiO<sub>2</sub> by rGO (Pt/rGO/TiO<sub>2</sub>) although enhanced the photocatalytic mineralisation of OA and IPA with respect to TiO<sub>2</sub> and rGO/TiO<sub>2</sub>, was less efficient than that by the conventional Pt/TiO<sub>2</sub> composite. This is likely due to the charge recombination on rGO sheet as the photoelectrons diffuse towards Pt cocatalysts.

The photocatalytic mineralisation of 2,4-D over all photocatalysts, i.e., bare TiO<sub>2</sub>, rGO/TiO<sub>2</sub>, Pt/TiO<sub>2</sub> and Pt/rGO/TiO<sub>2</sub> was limited by the aromatic ring-opening step. Among which include the characteristic benzoquinone (BQ)/hydroquinone (HQ) short-circuit equilibrium. The reductive dehalogenation step was however not affected by the limitation of ring-opening step. Here, the presence of electron transport and trap entities, i.e., Pt and rGO, was beneficial to the dehalogenation step. The order of dehalogenation rate follows the order of Pt/TiO<sub>2</sub> > Pt/rGO/TiO<sub>2</sub> > rGO/TiO<sub>2</sub> > TiO<sub>2</sub>, corroborating the observation of charge separation efficiency at the Pt/TiO<sub>2</sub> and rGO/TiO<sub>2</sub> interfaces.

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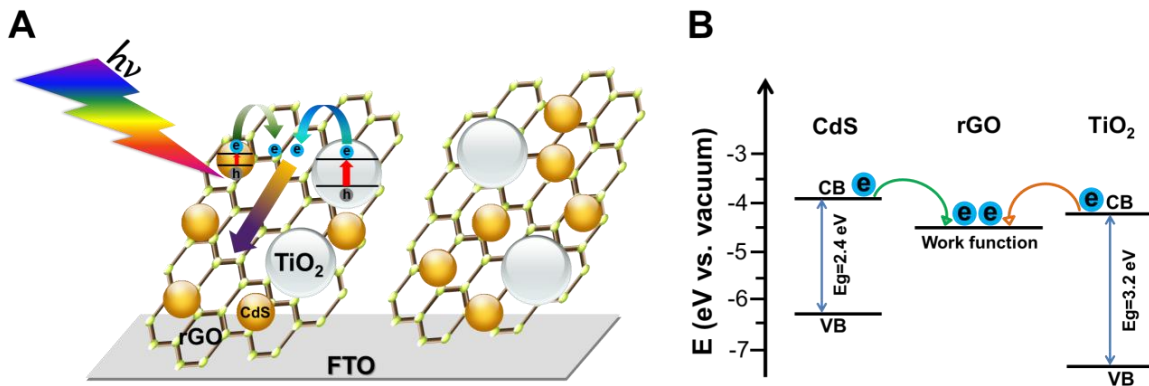
## Photoelectrons Accepting and Storage of Reduced Graphene Oxide within Titanium Dioxide/ Reduced Graphene Oxide/Cadmium Sulfide Nanocomposites

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### Abstract

The electron-accepting ability of graphene within graphene/semiconductor hybrid material shows important implications on the efficiencies of photoelectrochemical solar cell. The poster demonstrates the incorporation of titanium dioxide ( $\text{TiO}_2$ ) and graphene oxide (GO) into solvothermal synthesis of cadmium sulfide (CdS) producing  $\text{TiO}_2$ /reduced graphene oxide (rGO)/CdS nanocomposites which possesses intimate contact between semiconductor nanoparticles ( $\text{TiO}_2$  and CdS) and rGO. During the solvothermal reaction, GO was reduced by thermal reduction as well as the reductant  $\text{H}_2\text{S}$  from dimethyl sulfoxide (DMSO). In particular, compared with pristine  $\text{TiO}_2$  or CdS,  $\text{TiO}_2$ /(rGO)/CdS nanocomposites shows ~5 times higher incident photon to charge carrier generation efficiency (IPCE). Incorporation of rGO results in similar prolonged electrons lifetime for  $\text{TiO}_2$ , CdS, and  $\text{TiO}_2$ /CdS. rGO first acts as supporting scaffold, which ensures highly dispersion of  $\text{TiO}_2$  and CdS. With excellent electron-accepting ability, rGO further exhibits as a conductive platform for electrons collection and transport at the electrode surface, so IPCE and electrons lifetime are mostly related to the photoelectrons accumulated on rGO.



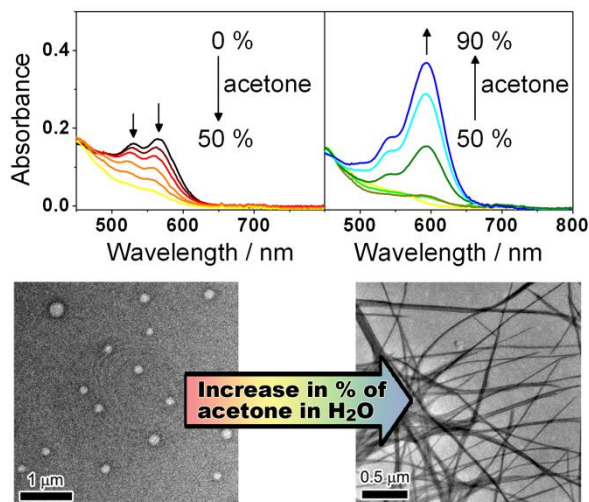
**Scheme.** (A) Charge separation and transfer, and (B) energy level alignment in the  $\text{TiO}_2$ /rGO/CdS nanocomposites.

**Amphiphilic Anionic Pt(II) Complexes – From Spectroscopic to Morphological Changes**

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*Institute of Molecular Functional Materials (Areas of Excellence Scheme, University Grants Committee Hong Kong) and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China.***Abstract**

A new class of amphiphilic anionic platinum(II) bzimpy complexes has been demonstrated to show aggregation in water through Pt··Pt and  $\pi$ - $\pi$  stacking interactions. An interesting aggregation–partial deaggregation–aggregation process and a morphological transformation from vesicles to nanofibers have been demonstrated. These changes can be systematically controlled by the variation of solvent composition and could readily be probed by UV-vis absorption, emission, NMR, transmission electron microscopy and even with our naked eyes.



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**Synthesis of ZnO/CuO Hetero Nanostructures with Improved Photoelectrochemical Properties**

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**Abstract**

As a well-known wide band gap semiconductor with large exciton binding energy, ZnO has been explored extensively as photoanodes in photoelectrochemical cells (PEC) for water splitting and hydrogen generation owing to its unique physical and chemical properties, simple process of manufacture, and strong photocatalytic activity [1]. However, ZnO can only utilize the light in ultraviolet region due to its wide band gap ( $E_g=3.2\text{eV}$ , corresponding to 390nm), which contributes less than 5% of the total energy of the solar spectrum and thus imposes a fundamental limitation on its capacity for water splitting and hydrogen generation [1-2]. CuO, as a p-type semiconductor with a narrow band gap (1.2–1.9eV), can absorb light in the visible spectrum, which is suitable for solar energy harvesting [2]. As a result, the combination of p-type CuO with n-type ZnO to enhance the light absorption by matching with the solar spectrum has been widely employed as a promising way to improve the PEC conversion efficiency. In this work, we present a simple method for direct integration of CuO nanostructures with ZnO nanorods on ITO substrates and then use them as photoanodes in PEC cells for water splitting and hydrogen generation.

ZnO nanorods on ITO substrates are synthesized by the galvanostatic cathodic reduction method based on our previous work [3]. The electrolyte contains 5mmol/L  $\text{Zn}(\text{NO}_3)_2$  and hexamethylenetetraamine aqueous solution. The current density is  $0.25\text{mA}/\text{cm}^2$  and the temperature of electro bath is  $90^\circ\text{C}$ . And then the as-prepared ZnO nanorod arrays are integrated with CuO nanostructures to form the ZnO/CuO hetero nanostructures. Figure 1(a) shows a SEM image of the ZnO/CuO hetero nanostructures, where the inset is a SEM image of the ZnO nanorods on an ITO substrate. It can be seen that the CuO nanostructures can be successfully integrated not only on the top surface of the ZnO nanorods, but also inside the ZnO nanorods arrays resulting in intimate contact between the p-type CuO and n-type ZnO. Figure 1(b) shows the photocurrents generated by using the ZnO/CuO hetero nanostructures as photoanodes in three-electrode photoelectrochemical cells under the illumination of one sun (AM1.5, 100mW). The combination of p-type CuO nanostructures with n-type ZnO nanorods can significantly enhance the PEC properties. The photo-to-hydrogen generation efficiency of the ZnO/CuO hetero nanostructures reaches a maximum value of 0.86% at the bias potential of 0.94 V, which is higher than the reported efficiency (0.71%) of CuO-core/ZnO-shell nanostructures in reference [2].

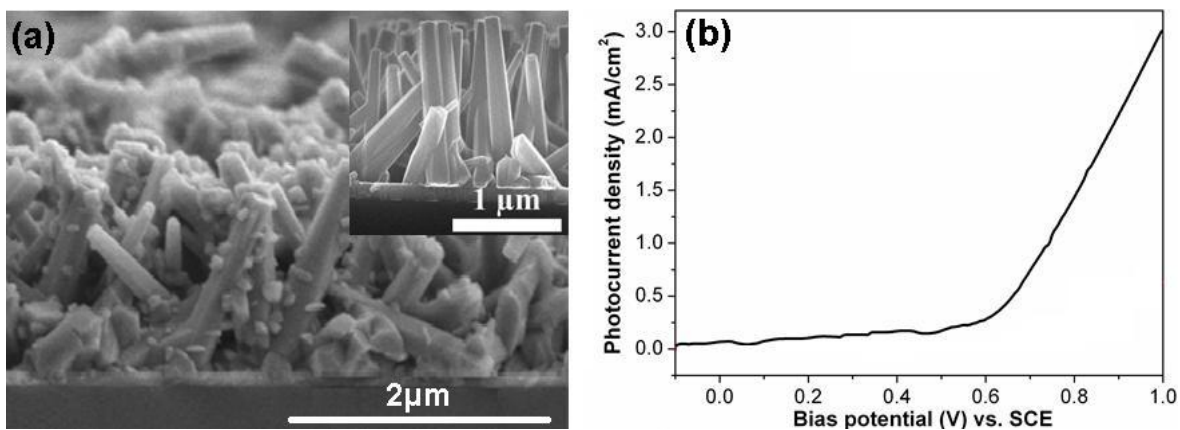


Figure 1(a) SEM image of the ZnO/CuO nanostructures (inset shows the ZnO nanorods) and (b) photocurrent density versus bias potential at white light illumination of 100 mW/cm<sup>2</sup>

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## Efficient Energy Transfer in Hybrid Organic/inorganic Semiconductor Nanostructures

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### Abstract

Highly luminescent semiconductor nanocrystals possess a number of interesting and important properties that are tunable thanks to their size-dependent discrete electronic spectra characteristic of quantum dots (QDs). In this work we studied the optical properties of a novel type of hybrid structures that combine CdTe QDs with organic dye molecules (Pseudocyanine iodide (PIC)) in a J-aggregate state. Due to the excitonic nature of electronic excitations, J-aggregates have the narrowest absorption and luminescence bands among organic materials, large oscillator strengths and giant third-order nonlinear susceptibility. It was found that aggregation of PIC molecules can be efficiently triggered by fast injection of solution of CdTe QDs into concentrated dye solution resulting in formation of hybrid nanostructures.

In developed structures optical energy harvested by the quantum dots as artificial antennas then transferred to J-aggregates to enhance the photostability and efficiency of the carriers recombination. To fabricate CdTe/J-aggregates hybrid nanostructures we have used an approach based on electrostatic interaction between the positively charged dye and CdTe QDs capped with thioglycolic acid and, thus, carrying a negative charge. In order to develop an efficient hybrid material operating in the FRET regime, we carefully selected the PL colors (diameters) of the QD (donors of energy) to be optically coupled with absorption of J-aggregates. Also we took advantage of extremely thin surface ligand shell (~0.5 nm) of CdTe QDs, which insures high efficiency of energy transfer. Formed QD/J-aggregate FRET system shows the broadband absorption in the visible and the ultraviolet part of the spectrum typical of quantum dots, along with the narrow emission linewidths characteristic of J-band emitters (~15 nm full width at half-maximum). We use absorption and photoluminescence spectroscopy and photoluminescence lifetime studies to conclude that efficiency of energy transfer is 95%.

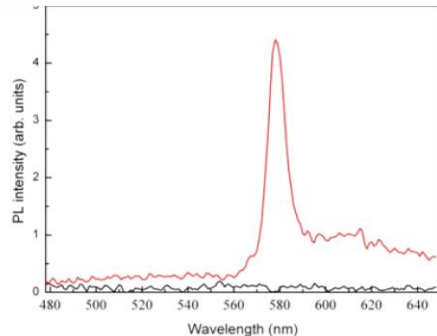


Figure 1. PL spectra recorded using excitation at 400 nm. Black line – without QDs. Red line – after injection of QDs

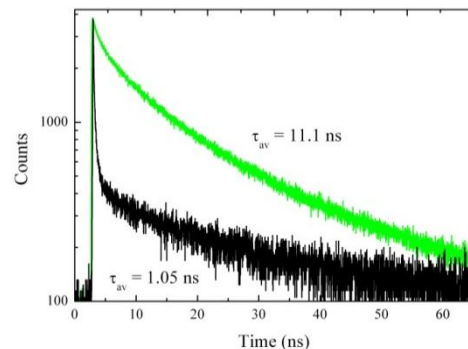


Figure 2. Comparison of PL decays for the QDs (green line) and QDs injected in PIC (black line).

**Dynamics of Multiple Exciton Generation in PbS Quantum Dots**Qing Shen,<sup>1,2\*</sup> Kenji Katayama,<sup>3</sup> Tsuguo Sawada,<sup>4</sup> Sojiro Hachiya,<sup>1</sup> and Taro Toyoda<sup>1,2</sup><sup>1</sup>*Faculty of Informatics and Engineering, The University of Electro-Communications, Tokyo 182-8585, Japan*<sup>2</sup>*CREST, Japan Science and Technology Agency (JST), Saitama 332-0012, Japan*<sup>3</sup>*Faculty of Science and Engineering, Chuo University, Tokyo 112-8551, Japan*<sup>4</sup>*Japan Science and Technology Agency (JST), Saitama 332-0012, Japan***Abstract**

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 [1]. 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 [1,2]. However, several recent reports have questioned the experimental results on the quantum yields of MEG in QDs and even its existence [3]. 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 [4,5] 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. 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  $2.7E_g$ . The new peak intensity decreased as the photon energy of the pump light decreased and the peak disappeared for the photon energies smaller than  $2.7E_g$ . In addition, a fast Auger recombination decay with a decay time of about 100 ps was observed when the photon energy is larger than  $2.7E_g$ . 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 semiconductor QDs for the first time.

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## Study of the Third-order Optical Nonlinearities of CdSeS Quantum Dots/Polystyrene Composite

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### Abstract

The off-resonant nonlinear optical properties of the composite film of CdSeS quantum dots (QDs) stabilized in polystyrene (PS) nanosphere were investigated by Z-scan technique with femtosecond laser (800nm, 50fs, 1Khz). It was observed that the signs of the nonlinear absorption coefficients and refractive indices changes from negative to positive with laser intensity increase, which is due to the transition from saturable absorption to two-photon absorption (TPA). With laser intensity of 4.2 GW/cm<sup>2</sup> and 16.8 GW/cm<sup>2</sup>, the two-photon absorption coefficient ( $\beta$ ) were  $1.6 \times 10^{-8}$  cm/W and  $8 \times 10^{-8}$  cm/W respectively, the third-order nonlinear refractive indices ( $n_2$ ) were  $-6.2 \times 10^{-11}$  cm<sup>2</sup>/W and  $2.7 \times 10^{-12}$  cm<sup>2</sup>/W respectively, which shows an increase of about one magnitude for  $\beta$  and one to two magnitude for  $n_2$  compared with previous reports. These results indicate CdSeS QDS doped PS has high potential for all-optical switching devices.

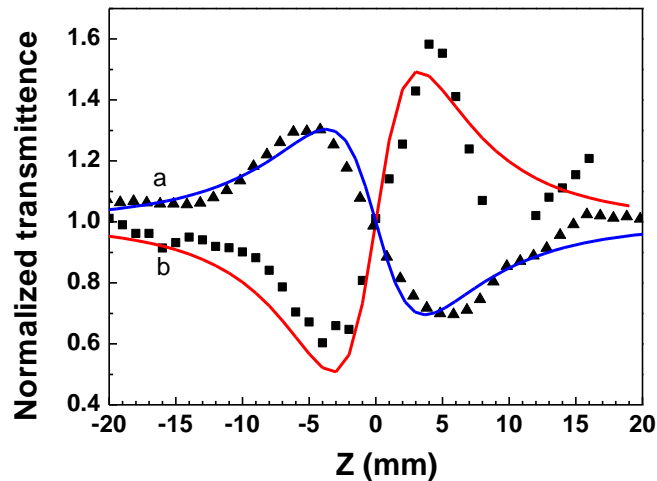


Fig.1 Normalized CA transmittance curves of the composite film at laser intensity of (a) 4.2 GW/cm<sup>2</sup> and (b) 16.8 GW/cm<sup>2</sup>.

## **Optical Interferometric Logic Gates Based on Metal Slot Waveguide Network Realizing Whole Fundamental Logic Operations**

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<sup>3</sup>*Division of Solid State Physics/The Nanometer Structure Consortium, Lund University, Box 118, SE-22100 Lund, Sweden*

### **Abstract**

Optical interferometric logic gates in metal slot waveguide network are designed and investigated by electromagnetic simulations. The designed logic gates can realize all fundamental logic operations. A single Y-shaped junction can work as logic gate for four logic functions: AND, NOT, OR and XOR. By cascading two Y-shaped junctions, NAND, NOR and XNOR can be realized. The working principle is analyzed in detail. In the simulations, these gates show large intensity contrast for the Boolean logic states of the output. These results can be useful for future integrated optical computing.

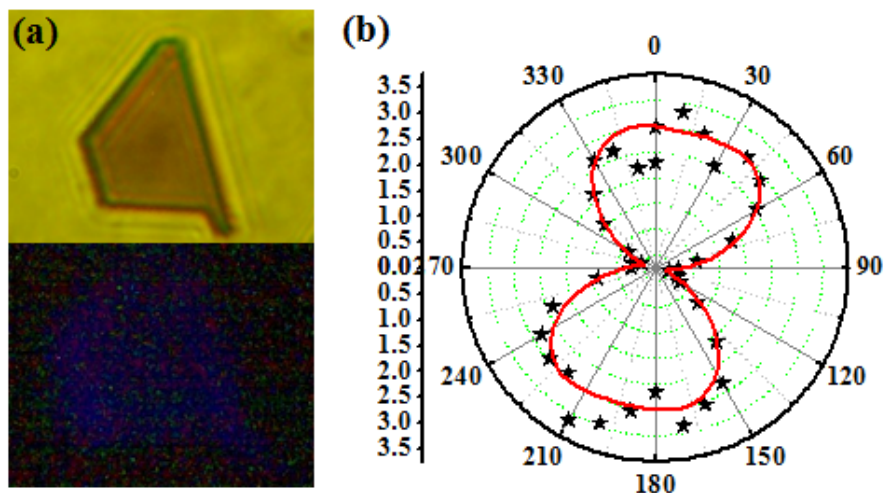
## Whispering Gallery Mode of Second Harmonic Generation in ZnTe Microdisks

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### Abstract

Whispering gallery mode of second harmonic generation (SHG) in ZnTe microdisks of different shapes are studied with 800nm femtosecond laser. The 400nm blue-violet SHG is clearly observed distributing in the edges of the microdisks and emits out in the corners, indicating a feature of whispering gallery mode. Polarization properties of the SHG are investigated and the results show that intensity ratio between TM and TE component is as high as 13, revealing a dominance of the TM component. Whispering gallery mode distributions of the SHG in microdisks of different shapes is in greatly different characters, and result in different mode characteristics, which is instrumental in optimizing the material parameters to achieve higher SHG efficiency. Whispering gallery mode of SHG in microdisks is of great potential in nanolasing, nonlinear optics and polarized photonic integration.



(a) ZnTe microdisk of a trapezoid and the dark field image of SHG.  
 (b) Polarization measurement of the whispering gallery mode SHG signal.

**Porous Metal-based Multilayers for Selective Thermal Emitters**

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*Centre for Functional Photonics, City University of Hong Kong, Kowloon, Hong Kong*

**Abstract**

We report the numerical study of a novel type of selective thermal emitter based on a metallic multilayered structure consisting of a graded antireflection top layer, a middle layer with uniform porosity (i.e., volume fraction of voids) and a non-porous substrate layer. Simulation results show that the proposed emitters feature an emission edge in near-infrared where the emissivity drops from over 0.9 to below 0.1, for both the TE and TM polarizations. Moreover, these desired emission characteristics persist for a wide range of emission angles with the emission edge nearly non-shifted, making the proposed emitters promising for achieving isotropic thermal emission. The designed emitters are particularly attractive for the thermal-photovoltaic applications by suppressing emission below the photovoltaic material bandgap which is normally in near-infrared.

**Effect of the Magnetic Order on the Room-temperature Band-gap of Mn-doped ZnO Thin Films**

Qi Shao,<sup>1,\*</sup> Xiaolei Wang,<sup>1</sup> Antonio Ruotolo,<sup>1</sup> Juan Antonio Zapien,<sup>1,2</sup> Chi Wah Leung,<sup>3</sup> Rolf Lortz<sup>4</sup>

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**Abstract**

The wide band-gap semiconductor zinc oxide (ZnO) is commonly used in optics applications. The observation of ferromagnetism in un-doped ZnO [1] has opened up the possibility to use this compound in magneto-optics and magneto-electronics. Yet, the saturation moment at room temperature in un-doped ZnO is only a few emu/cm<sup>3</sup>, too small to be of practical use. The magnetic moment can be dramatically increased by doping with transition metals. Of particular interest is the compound Manganese (Mn)-ZnO. Mn is an isovalent impurity for Zn and the Mn<sup>2+</sup> ionic radius (0.066 nm) is comparable to that of Zn<sup>2+</sup> (0.060 nm), which assures a theoretical solubility limit of 35% [2] while maintaining the wurtzite structure.

Doping with transition metals can also be used to tune the optical behavior of ZnO. In particular, doping with Mn is expected to widen the band gap and produce a blue-shift in the near band edge emission peak. Interestingly, a red-shift has been reported in weakly doped Mn-ZnO nanorods [3,4] and crystallites [5] showing ferromagnetism at room temperature. It has been therefore suggested that the red-shift is due to the samelong-range exchange interaction which is at the origin of the magnetic order, *i.e.* a correlation exists between optical and magnetic properties.

We investigated the possibility of such correlation in thin films of Mn-ZnO. Films with different concentration of Mn were grown on Al<sub>2</sub>O<sub>3</sub><0001> crystal substrates by using a pulsed KrF excimer laser ( $\lambda = 248$  nm) with a repetition rate of 10 Hz and energy 300 mJ. In order to increase the concentration of charge carriers we grew the films in high vacuum (10<sup>-5</sup> mbar), which results in an increase of double-donor oxygen vacancies.

The structural, electrical, magnetic and optical properties of the films were studied. We observe a red-shift at room temperature in the near-band-edge emission peak in films with 2% Mn doping. Increasing the magnetic moment by increasing the carrier concentration leads to an increase of the red-shift. Instead, increasing the Mn concentration widens the band gap and the expected blue-shift is recovered. The red-shift is due to *sp-d* interaction between free charge carriers in the band of the semiconductor and the localized magnetic moments.

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## Effects of Post-synthesis Chemical Treatment on the Electronic Properties of Water-soluble HgTe Quantum Dots

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### Abstract

HgTe quantum dots (QDs) have attracted considerable interest for a variety of optoelectronic device applications due to their excellent photosensitivity in near-infrared and shortwave infrared wavelength as well as the potential for low-cost fabrication through solution processes. In this study, we fabricated a photoconductor structure based on water-soluble HgTe QDs and showed that the performance of the photoconductor device depended strongly on the post-synthesis treatments on the QDs. In particular, we compared two methods to remove the impurities and excess ligands in the QD solution: (1) precipitating QDs with various polar solvents and (2) selectively removing excess ions or ligands using dialysis through a semi permeable membrane. The stability and electronic properties of HgTe QDs after different treatments were systematically studied using zeta-potential measurement, light scattering measurement, time-resolved photoluminescence spectroscopy and transient photocurrent measurement. Based on the results we can identify the key factors that dominant the spectral responsivity and temporal response of the HgTe QD photoconductors.

## Templating Molecular Orientation of Pentacene Thin Film and in Relation to Mobility on Graphene and Dielectric Substrates

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### Abstract

Pentacene is one of the conducting oligomer materials commonly used in small molecule organic electronic devices, such as organic light-emitting diode (OLED), organic field-effect transistor (OFET), and organic photovoltaic cell (OPV). The pentacene thin films are deposited on gate dielectrics, e.g., SiO<sub>2</sub>, where a substrate induced phase of pentacene molecules is in the appropriate charge transport direction for an OFET. Therefore, the effects of substrate can play a dominant role in orientation and morphology.

In this work, by using chemical vapor deposition (CVD) graphene as a template, we investigate the molecular orientations, crystal phases, and mobility of pentacene thin films with different thickness. The thin films have been characterized by polarized micro-Raman spectroscopy for identifying the molecular orientation dependence on graphene. X-ray diffraction (XRD) is employed to resolve the crystal phases and tilt angle ( $\theta_{\text{tilt}}$ ). From XRD result, the (022) phase indicates a horizontal alignment with the graphene/Cu substrate, compared with the (001) phase oriented vertically on the glass. Raman spectra of pentacene on graphene/Cu substrate show an additional long axis vibration mode that does not appear on the glass substrate.

These results provide a direct evidence that pentacene orients in the perpendicular direction with respect to the glass, whereas it is parallel on graphene/Cu substrate. The effects of strong molecule–substrate interaction such as standing-up and lying-down molecules on different substrates have also been discussed based on the fact that they enable to determine the charge transport and mobility properties, and further influence the performance of OPV devices.





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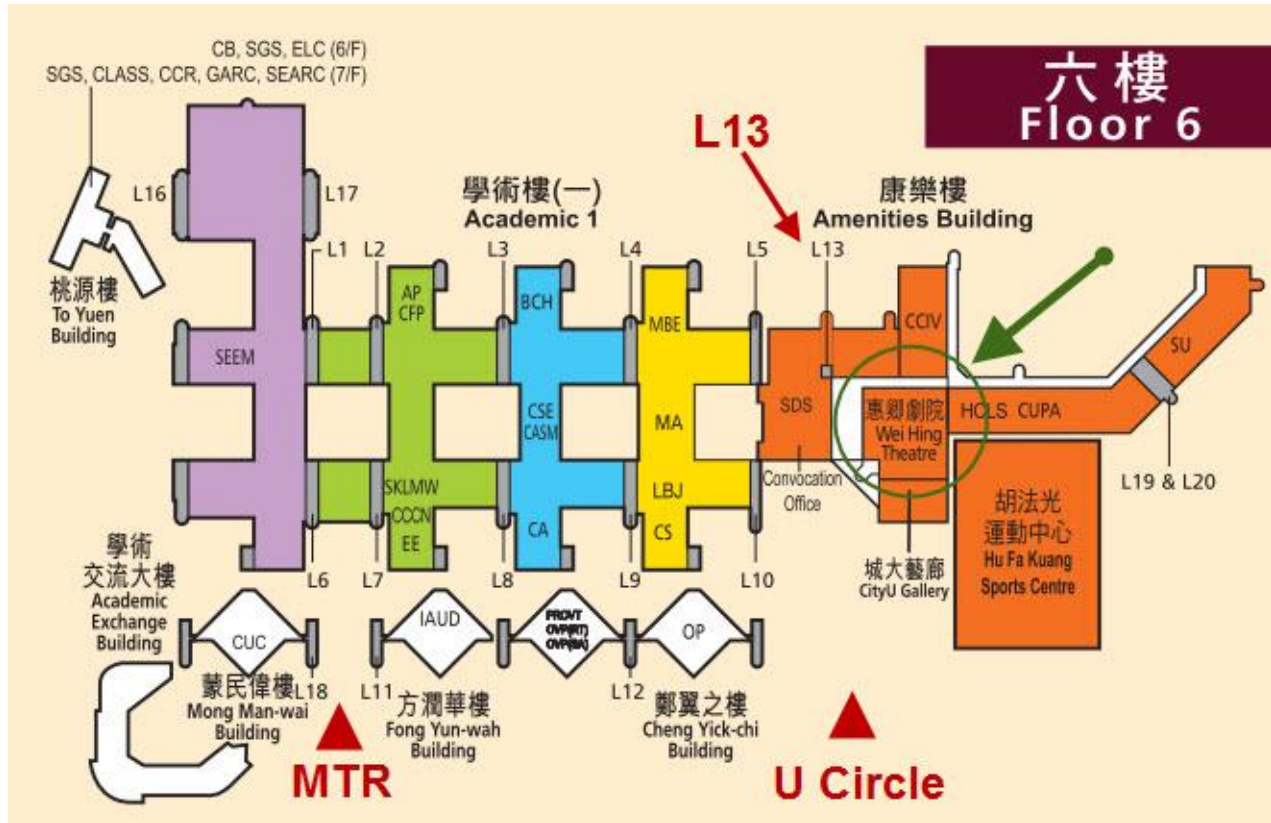
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## WEI HING THEATRE LOCATION PLAN



<b>How to get to Wei Hing Theatre for International Workshop "Photonics of Functional Nanomaterials" 6-9 May 2013</b>	
<p>Arrived at Pedestrian Subway</p> <ol style="list-style-type: none"> <li>1. When you get off the MTR, look for Festival Walk exit.</li> <li>2. In Festival Walk, on Level LG1, there is a Pedestrian Subway which will lead you to CityU campus.</li> <li>3. After walking through the Pedestrian Subway, go down the staircase on your right and follow the directional signs, you will find yourself walking under a covered corridor alongside the garden which will lead you to the University Circle.</li> <li>4. From the University Circle, go along the Covered Walk Way which will lead you to the Amenities Building.</li> <li>5. Take Lift No. 13 opposite to the Security Counter to Floor 6.</li> <li>6. Turn left and you will see Wei Hing Theatre.</li> </ol>	<p>Arrived at University Circle</p> <ol style="list-style-type: none"> <li>1. When you drop off at the University Circle, go along the Covered Walk Way which will lead you to the Amenities Building.</li> <li>2. Take Lift No. 13 opposite to the Security Counter to Floor 6.</li> <li>3. Turn left and you will see Wei Hing Theatre.</li> </ol>



## CATERING FACILITIES

### City Express

Location: 5/F Amenities Building  
Opening Hours: 07:30 – 21:00 (Mon – Sun)  
Type of Service: Self-service  
Menu: Fast food, dim sum, short orders, set meal, health food, daily carving and bakery products

### 8/F City Chinese Restaurant

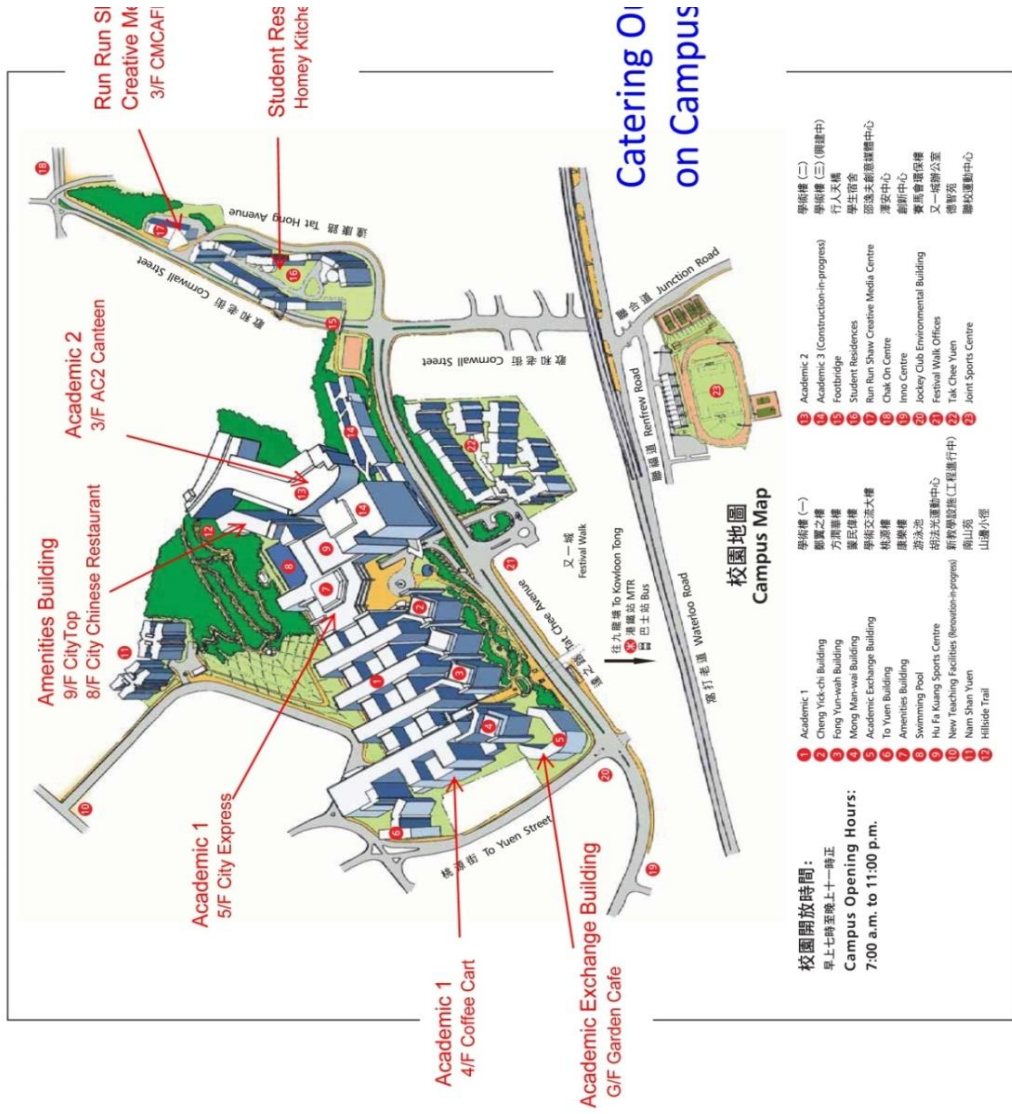
Location: 8/F Amenities Building  
Opening Hours: 11:00 – 22:30 (Mon – Fri)  
09:00 – 22:30 (Sat – Sun)  
Type of Service: Full table service  
Menu: Chinese menu with full selection

### 9/F City Top and Staff Lounge

Location: 9/F Amenities Building  
Opening Hours: 11:00 – 22:30 (Mon – Sun)  
Type of Service: Full table service, tea set, buffet dinner  
Menu: Western menu

### Garden Cafe and Coffee Cart

Location: G/F Academic Exchange Building  
4/F Academic Building 1  
Opening Hours: 08:00 – 21:00 (Mon – Fri)  
08:00 – 18:00 (Sat)  
Type of Service: Self service  
Sandwich, Salad, Daily Hot meal, Japanese Set Meal, Snacks and Drinks



## Notes

## Notes

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**Program of International Workshop**  
**Photonic of Functional Nanomaterials**

	Monday 06.05.2013	Tuesday 07.05.2013	Wednesday 08.05.2013	Thursday 09.05.2013
8:40	Opening Remarks Andrey Rogach			
9:00	Invited Yury Rakovich	Invited Oliver Schmidt	Invited D.D. Sarma	Invited Zee Hwan Kim
9:30	Hilmi Volkan Demir	Yang Yang Li	Bingsuo Zou	Sun Handong
9:50	Yan-Cheng Lin	Zhiyong Fan	Robert Pansu	Hongbing Fu
10:10	Rui Chen	Amitava Patra	Haizheng Zhong	Ni Zhao
10:30	Coffee Break	Coffee Break	Coffee Break	Coffee Break
11:00	Invited Din Ping Tsai	Invited Prashant Kamat	Invited Lian-Mao Peng	Invited Vasudevanpillai Biju
11:30	Invited Ben Zhong Tang	Invited Kok Wai Cheah	Shengyi Yang	Deng Renren
12:00	Qihua Xiong	Taro Toyoda	Timothy T.Y. Tan	S. Carregal-Romero
12:20	Kai Wang	Xueqing Xu	Kin Hung Fung	Stephen Kershaw
12:40	Lunch	Lunch	Group Photo	Lunch
			Boat Trip	
14:00	Invited John Pendry	Invited Naomi Halas		Invited Xiaogang Liu
14:30	Lin Jiang	Eric Wei-Guang Diau		Sur Chattopadhyay
14:50	Yu Luo	Qing Shen		Xie Xiaoji
15:10	Weihai Ni	K.W. Sun		Dorleta Jimenez de Aberasturi
15:30	Coffee Break	Coffee Break		Coffee Break
16:00	Invited Peter Norldlander	Poster Session		Invited Jochen Feldmann
16:30	Invited Alexander Govorov			Tze Chien Sum
17:00	Qiang Zhang			Closing Remarks Andrey Rogach
17:20	Xiao Ming Zhang			
17:40	Duan Bo			
18:00				