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Semiconductor Nanocrystals for New-generation Lightening and Light Harvesting Applications

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Los Alamos, New Mexico

February 27, 2015

LA-UR-

Outline

Motivation and introduction

- Semiconductor nanocrystal quantum dots
- QDs applications; blinking and its suppression

Research works

I. QDs: CdSe/ZnSe and ZnSe/CdS; Synthetic complexities and mitigations

II. Photovoltaics: PLD graphite counter electrode; PbS, PbSe sensitization on TiO_2; NW sensitized solar cell

III. Photocatalysis: ZnSe/CdS/Pt & ZnTe/CdS/Pt

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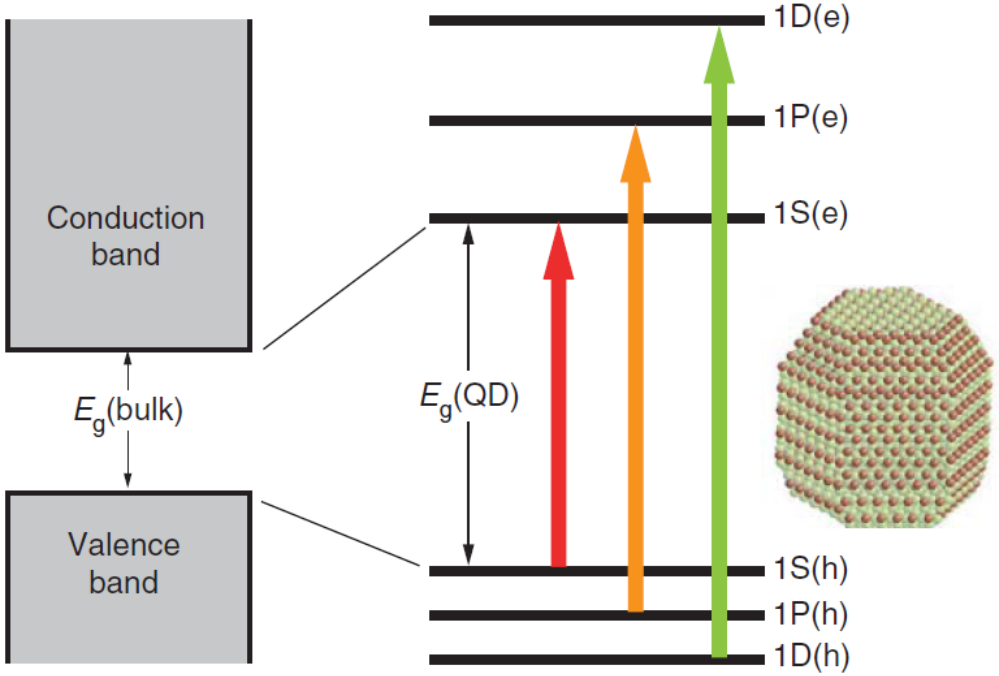
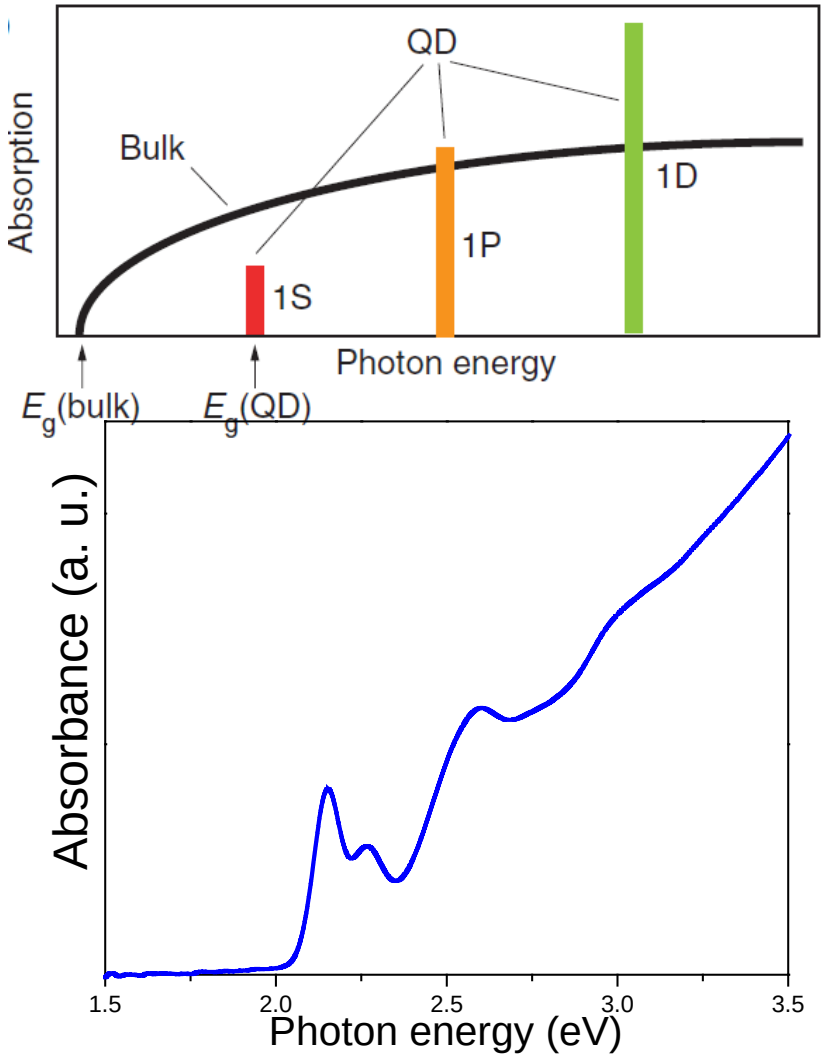
Part I
Semiconductor Quantum Dots



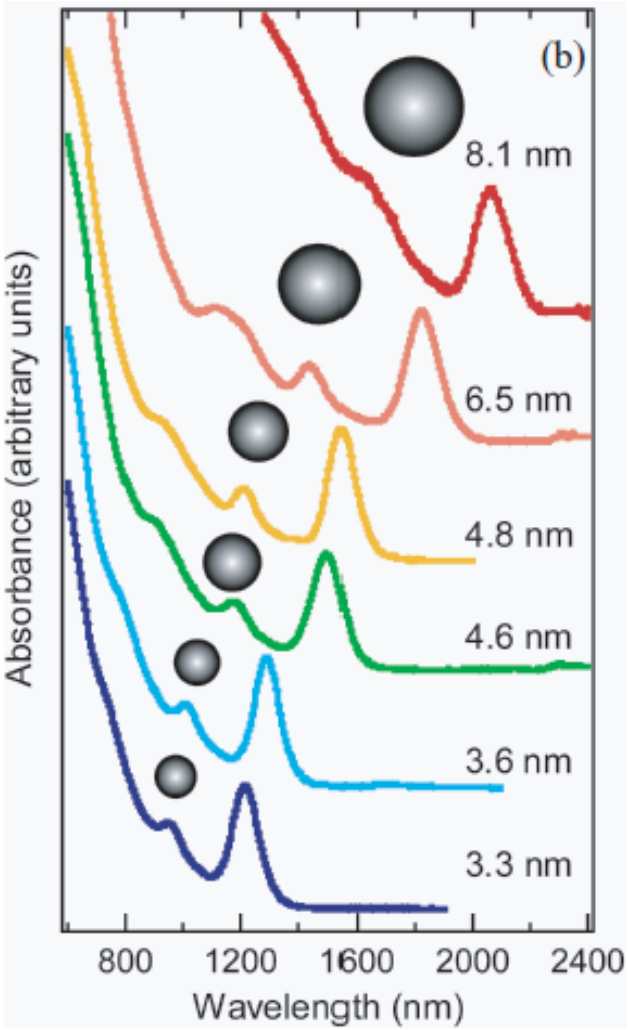


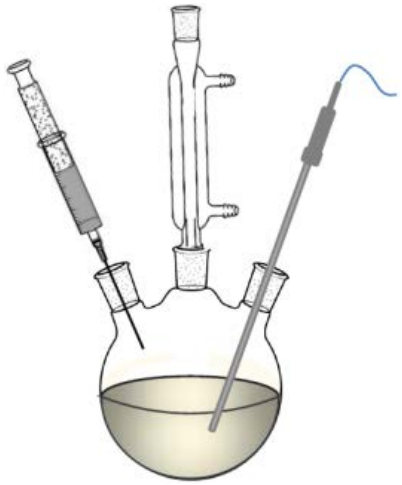
$$E_g(\mathrm{QD}) \approx E_{g0} + \frac{\hbar^2 \pi^2}{2 m_{eh} R^2}$$

$$m_{eh} = \frac{m_e m_h}{m_e + m_h}$$

Victor I. Klimov, Nanocrystal Quantum dots, *Los Alamos Science,* 28, 2003.

Synthesis of Colloidal QDs





Precursors

⇩

Monomers

⇩

Nucleus

⇩

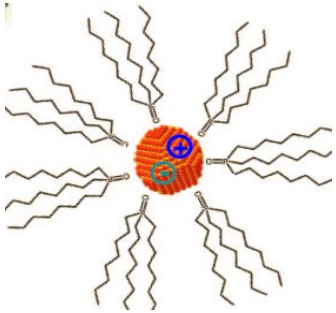
Larger QD

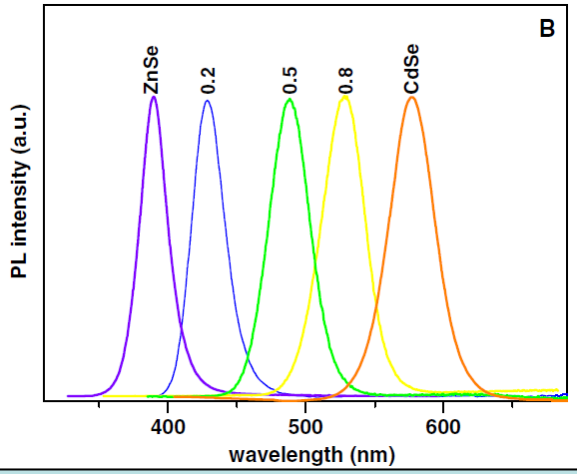
Coordinating ligands/non-coordinating solvents

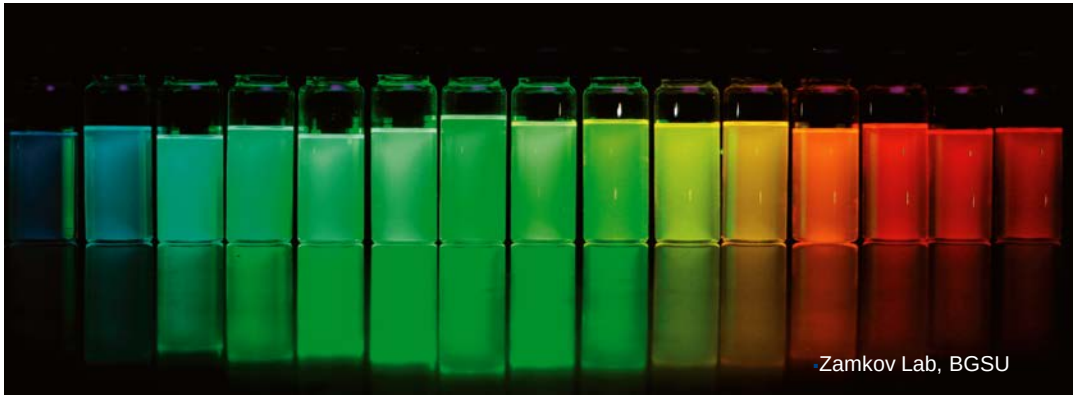
- **Hot injection of precursors**
- **Heating the precursor mixture**
- **Flow cell**
- **Seeded growth**
- **SILAR, continuous injection**

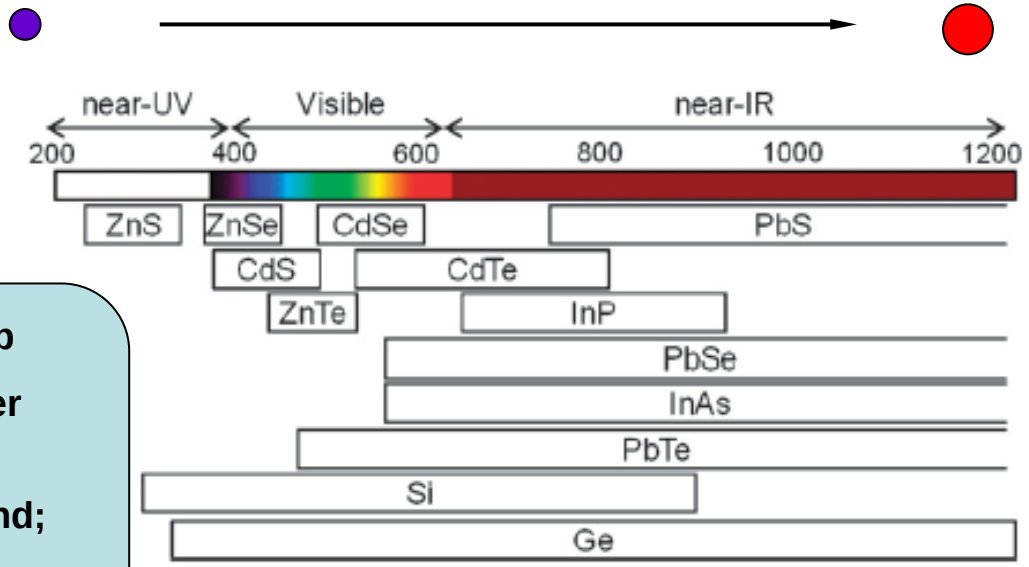
Beard et al., Laser & Photon. Rev., 2008, 2, **377**

Colloidal Semiconductor QDs





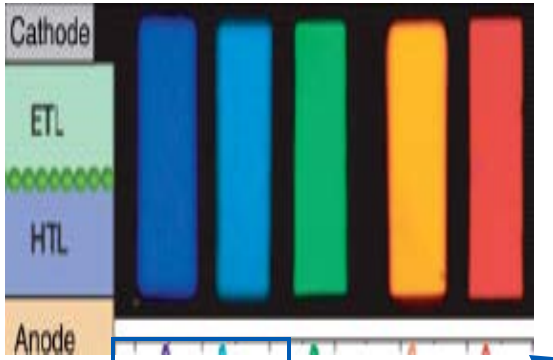




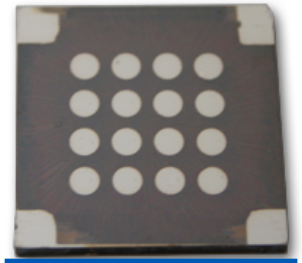
- **Size and composition dependent band gap**
- **Broad absorption, narrow emission, higher PLQY**
- **Tuned by reaction time, temperature, ligand; precursor concentration, synthesized in a simple experimental setup.**
- **Can be processed in solution at low cost**

Zhong, et al., *Nanotechnology* , **2007**, 18, 385606.; N. Shirahata, *Phys. Chem. Chem. Phys*. **2011**, 13, 7284

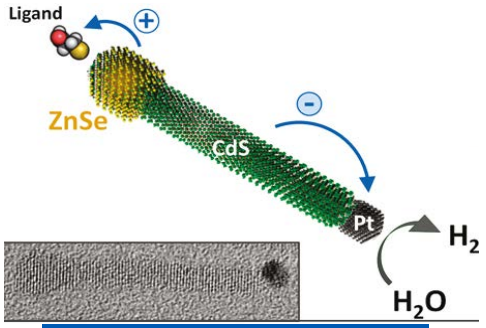
Applications of Colloidal Semiconductor QDs



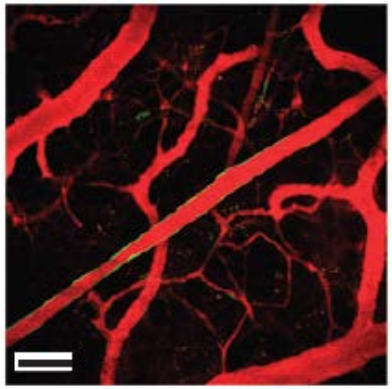
LEDs



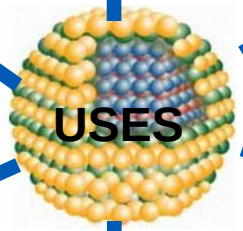
Solar cells

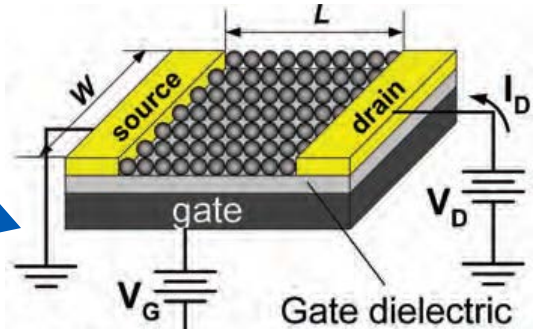


Photocatalysis



Biolabeling



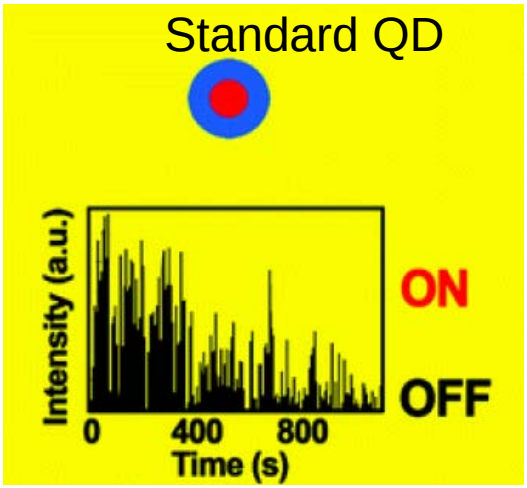


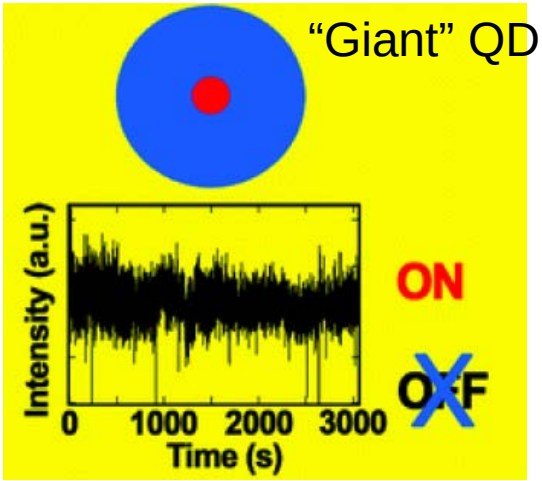
Transistors

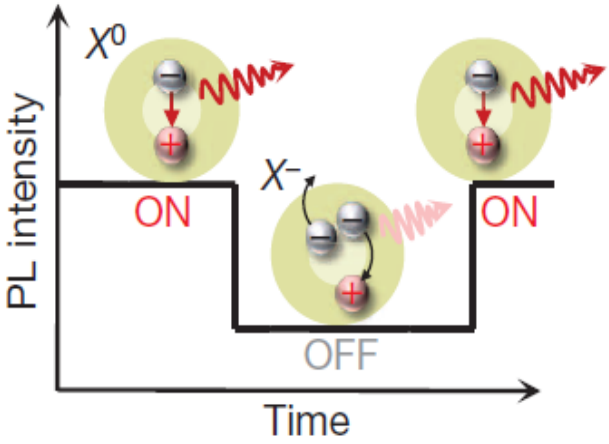
Photodetectors & memory elements

K. P. Acharya, et al. Nano Lett. 2011, 11, 2919; V. Wood and V. Bulovic, Nano Reviews, 2010, 1, 5202; O. Chen et al., Nature Materials, 12, 445, 2013 D. V. Talapin et al., *Chem. Rev. 2010, 110, 389–458,* U. ot Toronto Engg. News, July 30, 2012

QD Blinking, Conventional Mechanism, and the Role of Thick shell in Blinking Suppression









Blinking dots movie



Non-blinking dots movie

Role of thick shell

- **Limits extent of charging**
- **Auger Recombination suppression**
  - **Large-volume effect**
  - **Interfacial alloying**
  - **Electronic structure**

Chen et al. *J. Am. Chem. Soc*. **2008**, 130, 5026; Mahler et al., *Nat. Mater.* **2008**, 7, 659, Galland et al., *Nature*, 2011, 479, 203.Y Y. Ghosh et al., *J. Am. Chem. Soc*. **2012**, 134, 9634; Dennis et. Al., Nano Lett. **2012**, 12, 5545

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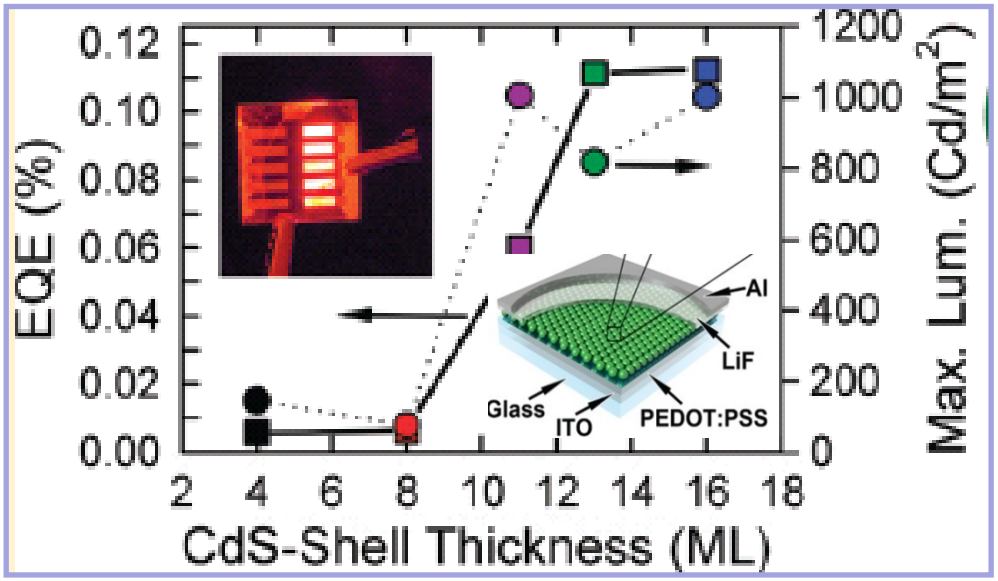
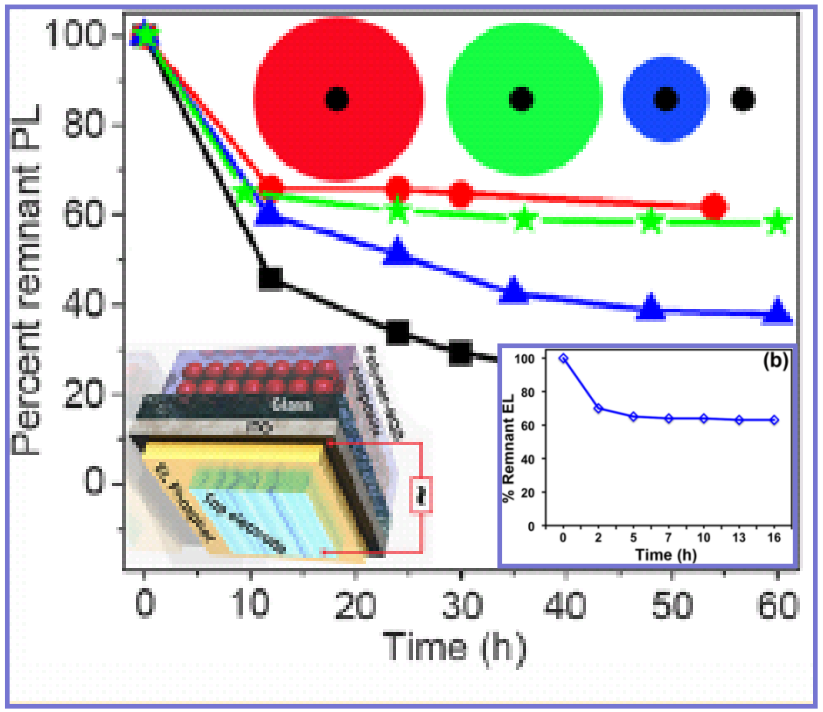
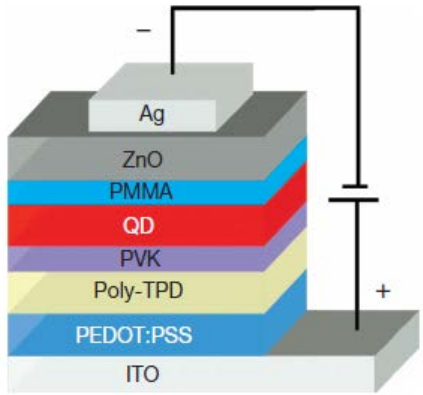
Thick- & Thin-shell QD Devices Performance

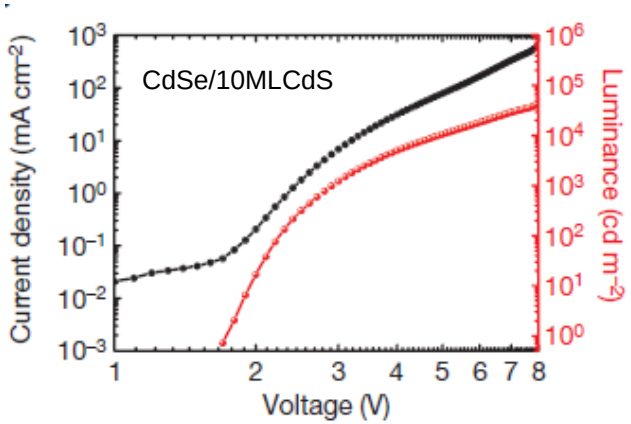
QD-LED



QD phosphors







Pal et al., *Nano Lett*. 2012, 12, 331
Kundu et al.*Nano Lett.* 2012, 12, 3031
Dai et al., *Nature*, 2014, 515, 96.

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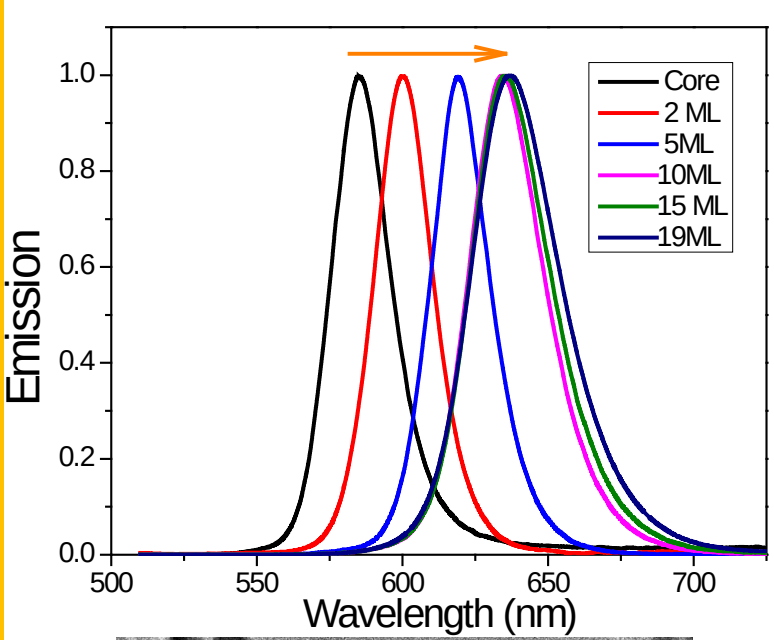
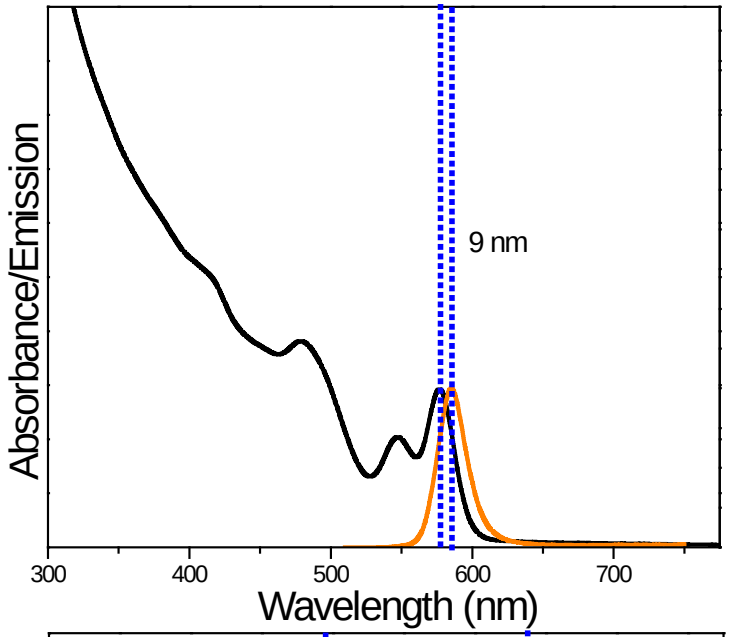
CdSe/CdS Core/Thick-shell QDs: An Example





~PLQY

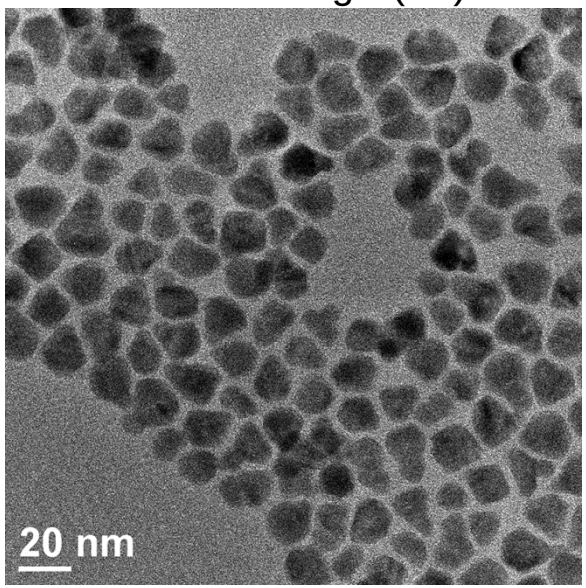
Core: 11%

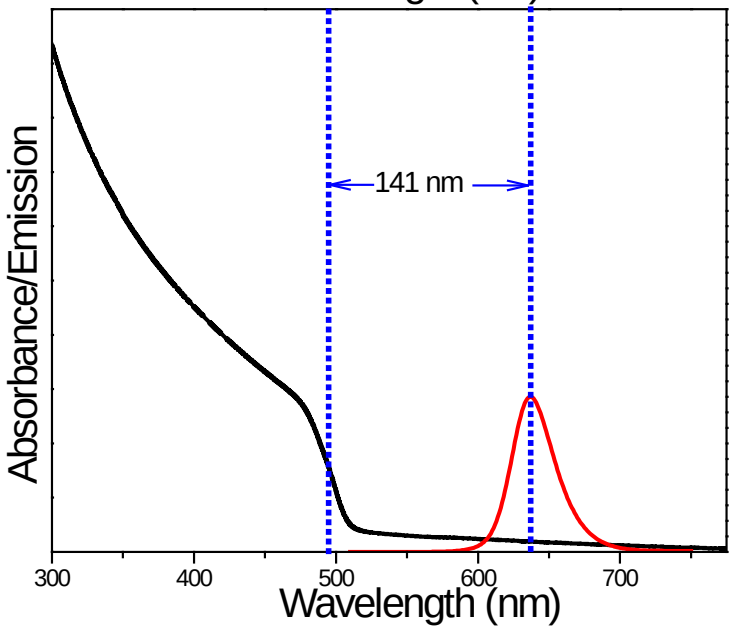
5ML: 93%

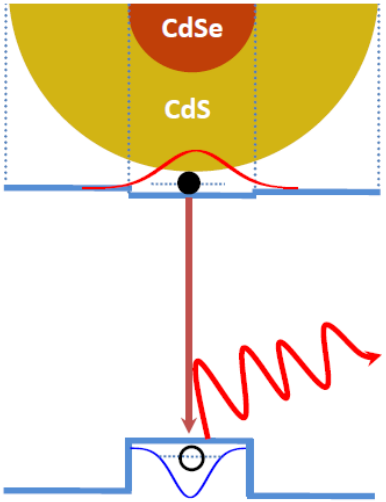
10 ML: 80%

15 ML: 55%

19ML: 34%







Unpublished

CdSe/15 ML CdS

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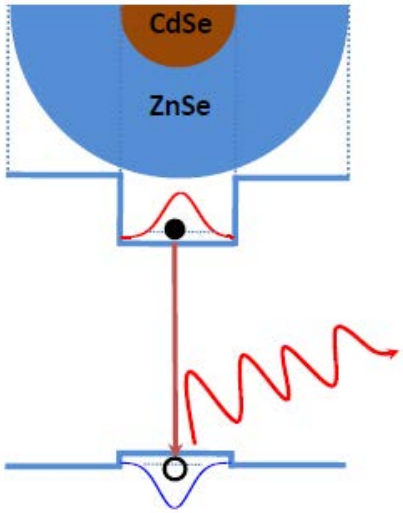
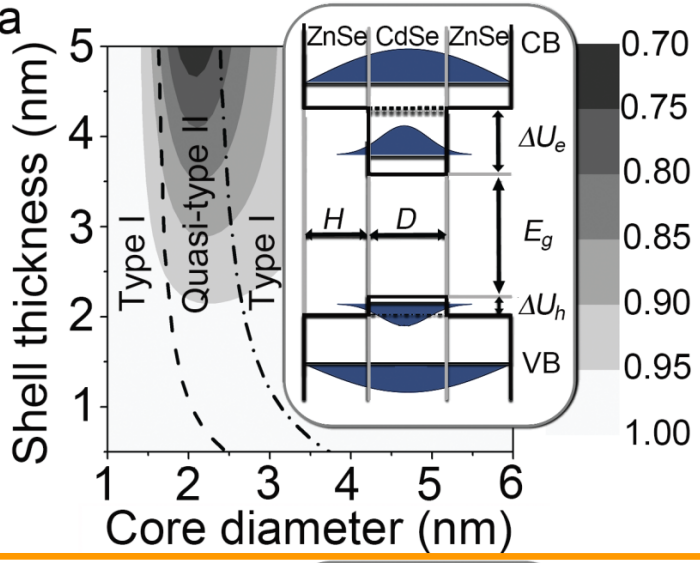
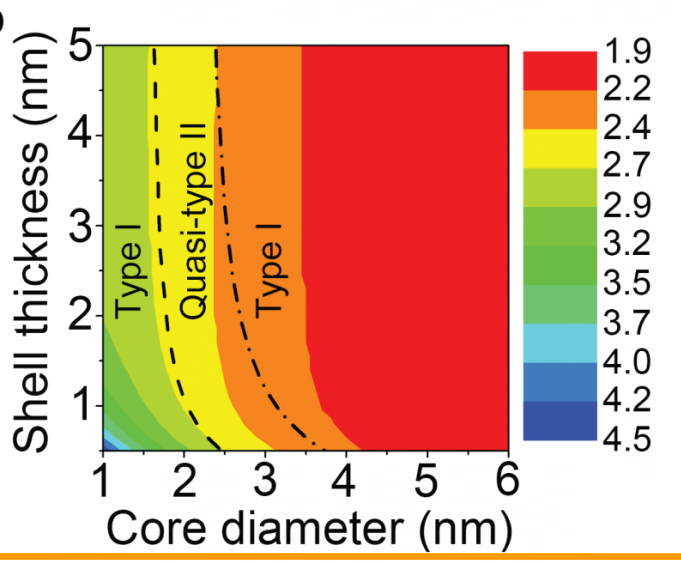
CdSe/ZnSe and ZnSe/CdS Core/thick-shell QDs

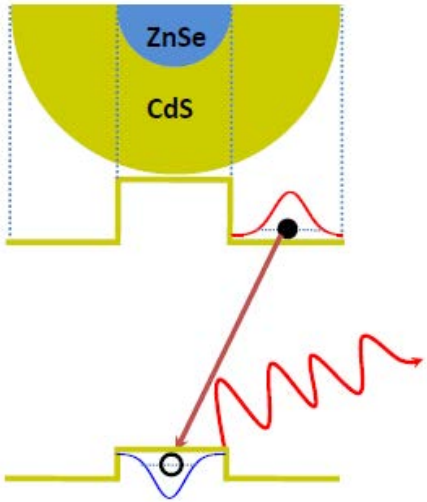


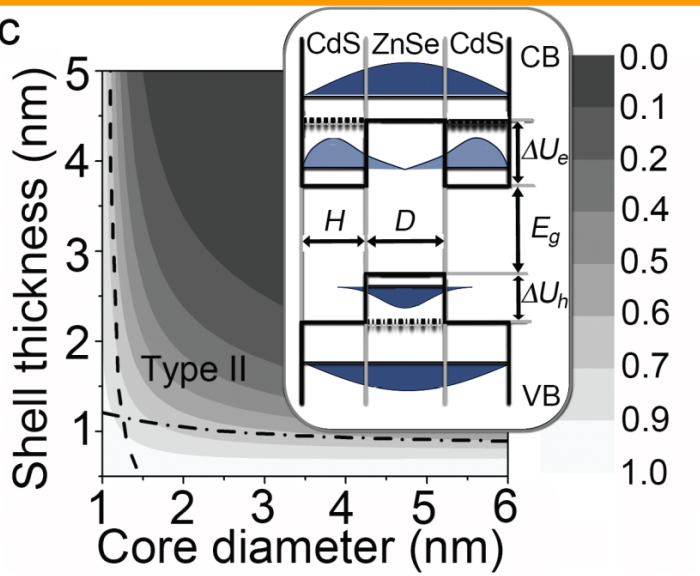
Overlap Integral

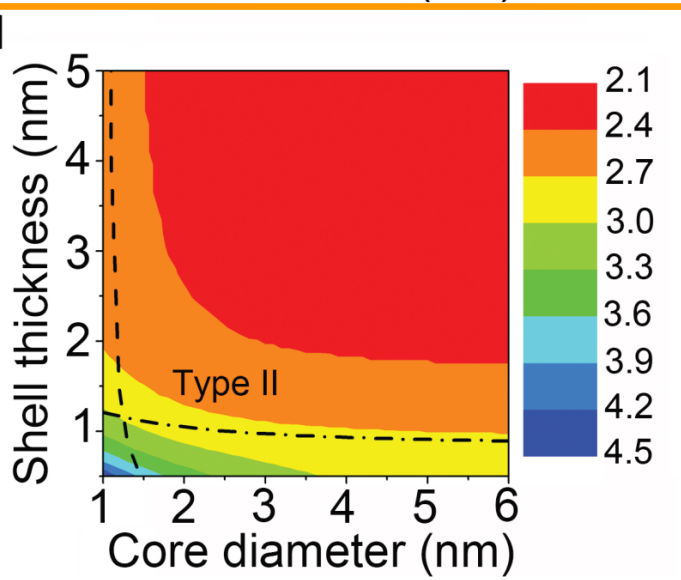


Band gap energy









Acharya, et al., Submitted, 2015

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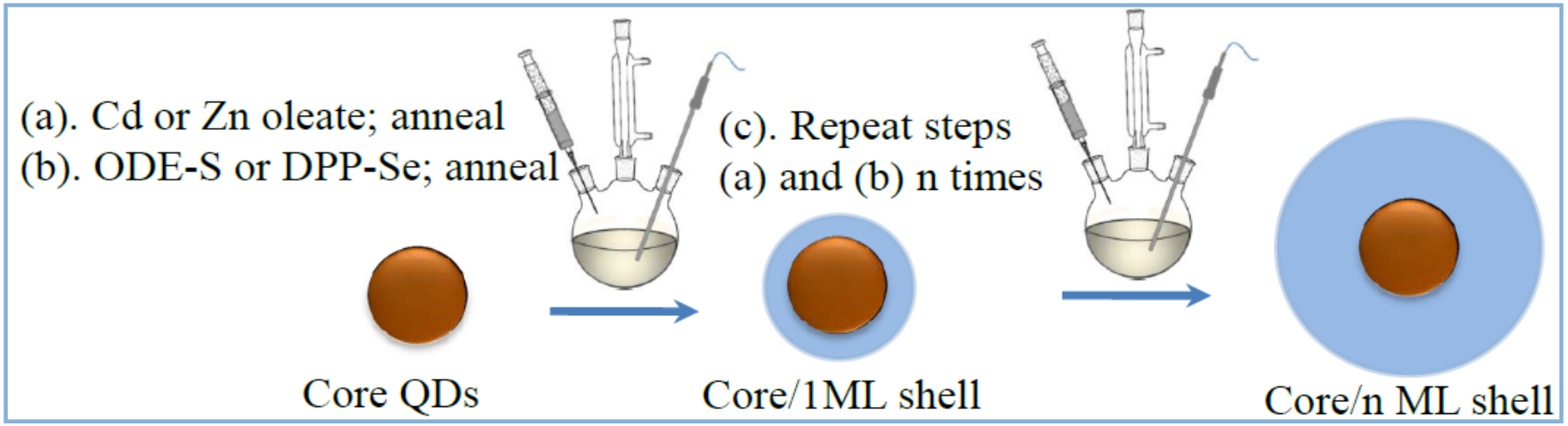
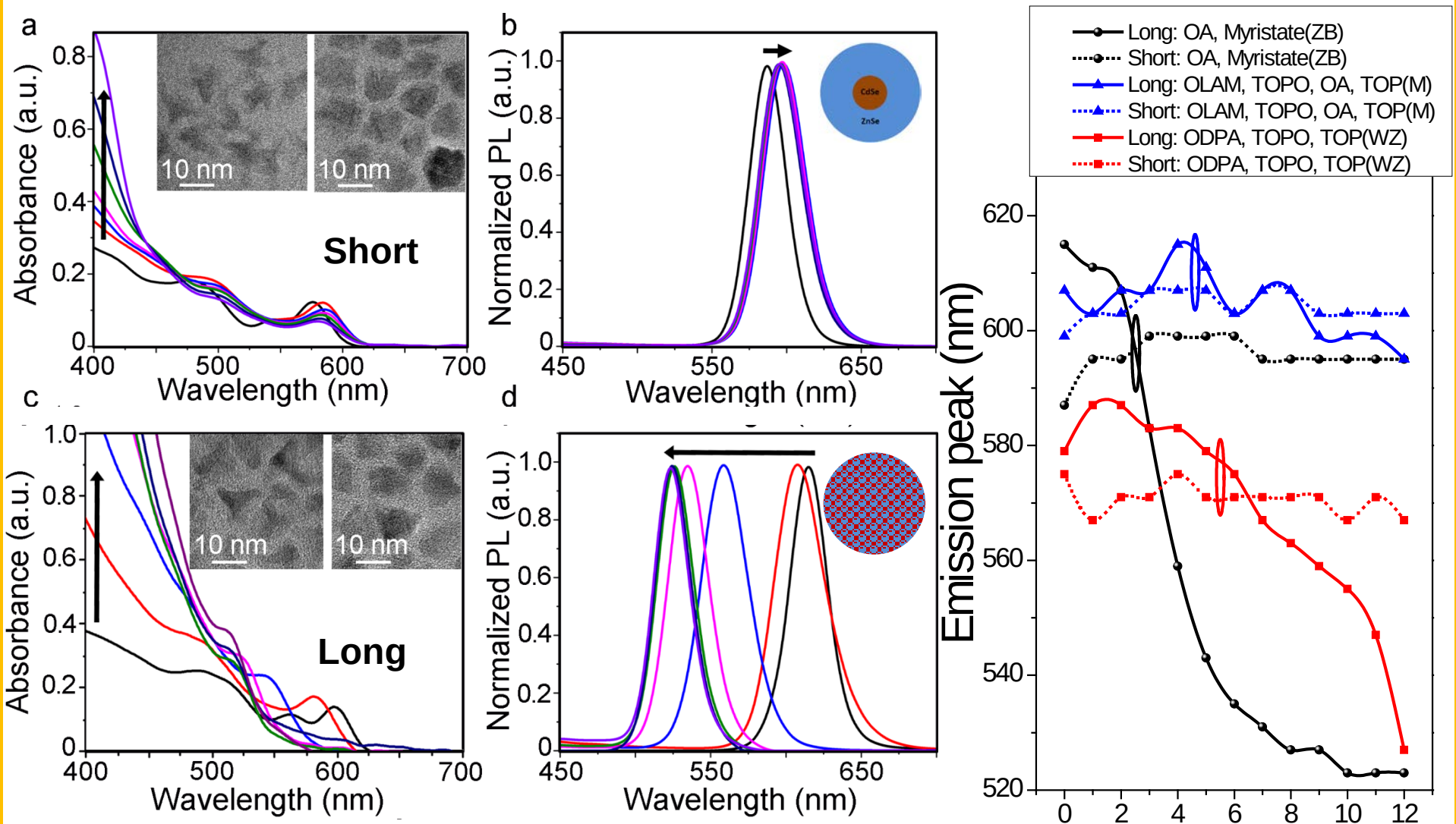
Synthesis of ZnSe/CdS and CdSe/ZnSe Thick-shell QDs

Successive Ionic Layer Adsorption and Reaction (SILAR)



- **CdSe core QD surface ligands/crystal phase**
- **Annealing time: Short (20 minutes); or Long (3 hr)**
- **Temperature**

All CdSe QDs forms CdSe/ZnSe at Short but WZ and ZB Cores form Alloy at Long Anneal time



Acharya, et al., Submitted, 2015

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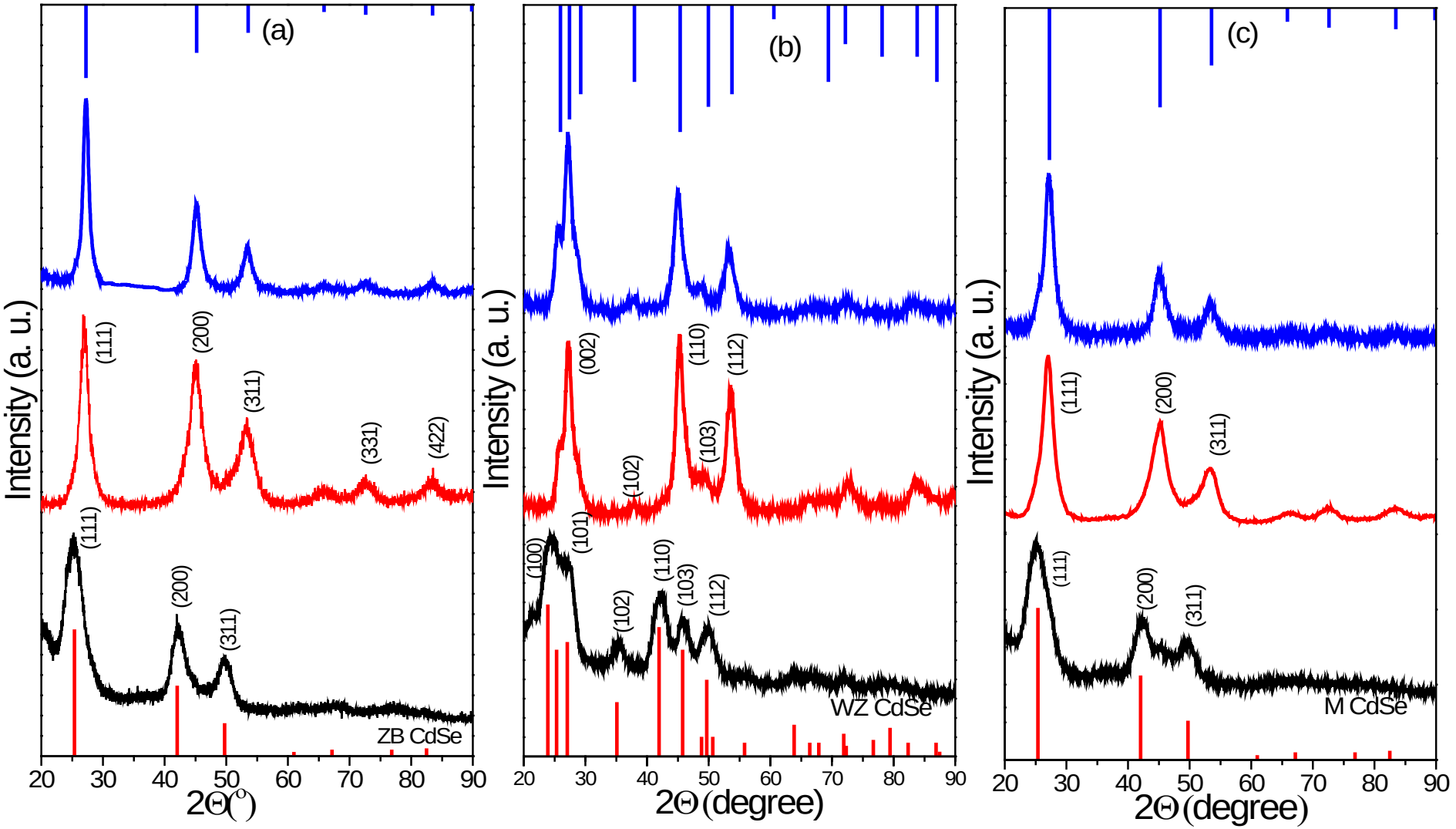
The CdSe/ZnSe Crystal Phase is Same as that of Starting Core



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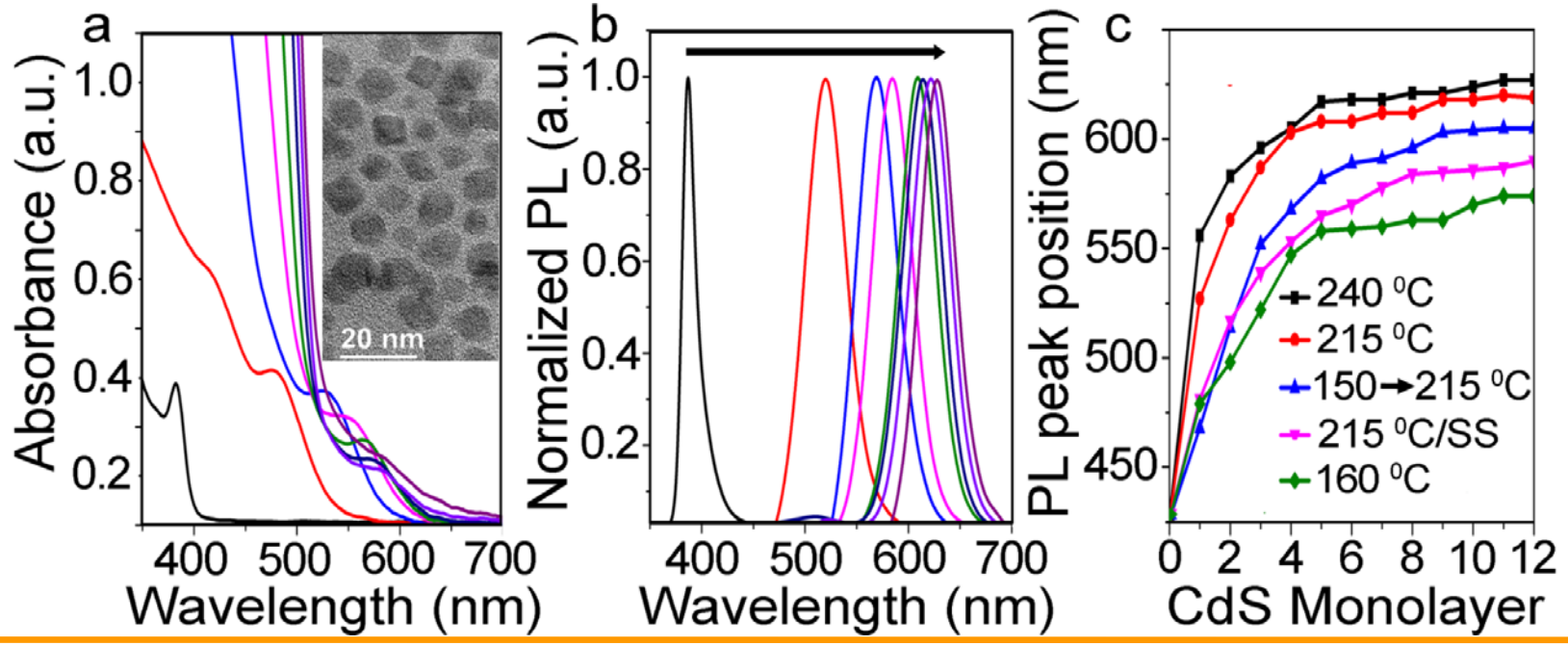
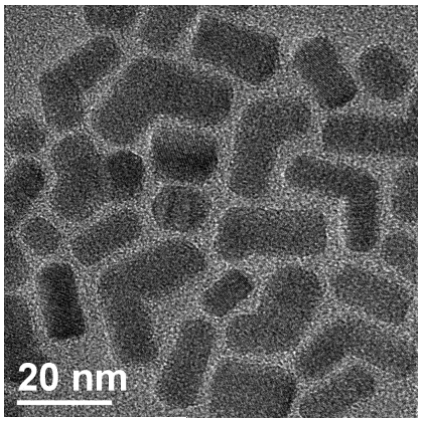
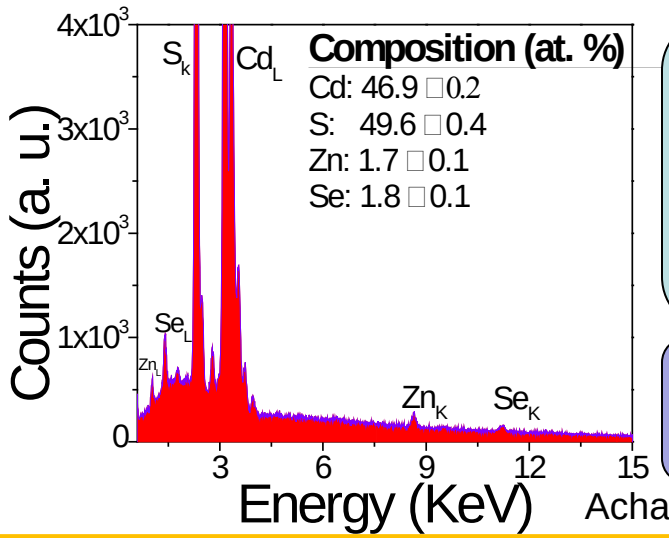
ZnSe/CdS Core/Thick-shell QDs Synthesis







Composition (at. %)

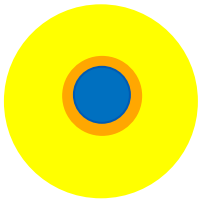
Cd: 46.9 □0.2
S: 49.6 □0.4
Zn: 1.7 □0.1
Se: 1.8 □0.1

Zn:Se ratio (ZnSe core r = 2.3nm)

240°C: 0.60
215 °C: 0.65
150 °C(2ML) 215 °C: 0.70
215 °C, SS precursor: 0.94
160 °C: 0.80

Cation Exchange Reaction:

ZnSe/CdSe/CdS
Cd-Se 310kJ/mol, Zn-Se 136 kJ/mol



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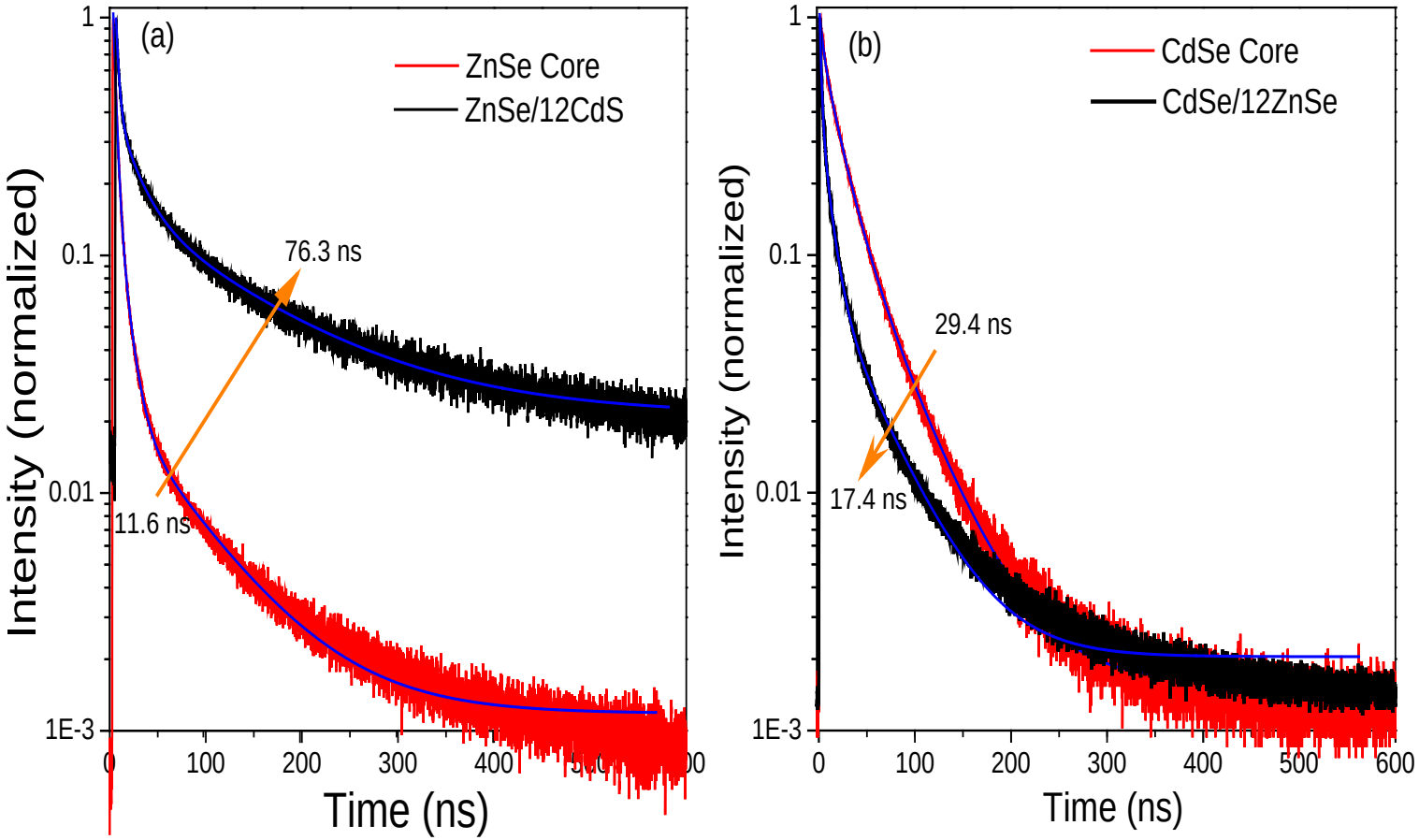
PL Life Time is Increased in ZnSe/CdSe but Decreased in CdSe/ZnSe



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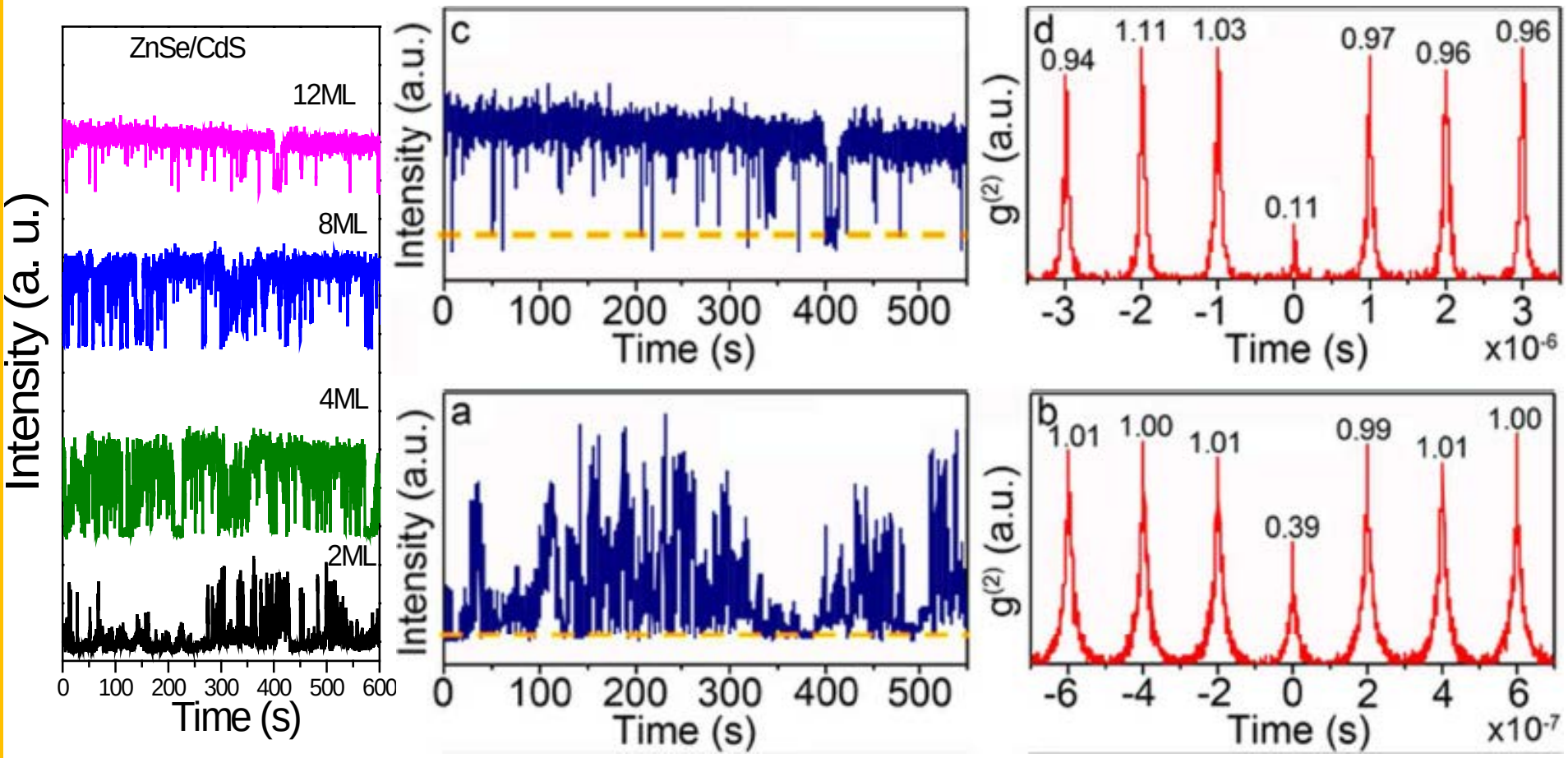
ZnSe/CdSe are Blinking Suppressed, while CdSe/ZnSe have High Biexciton Efficiencies



Acharya et al., Submitted, 2015

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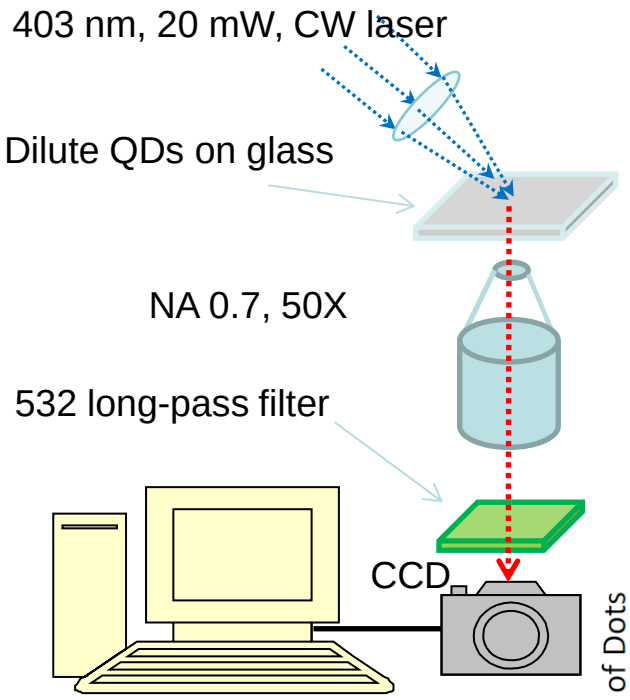
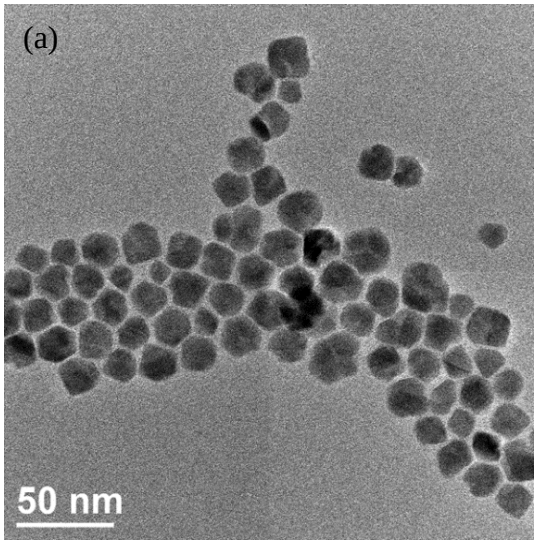
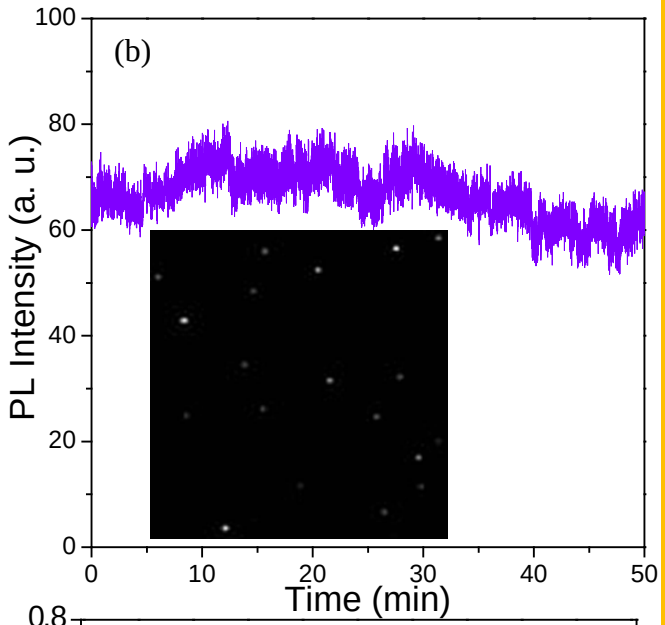
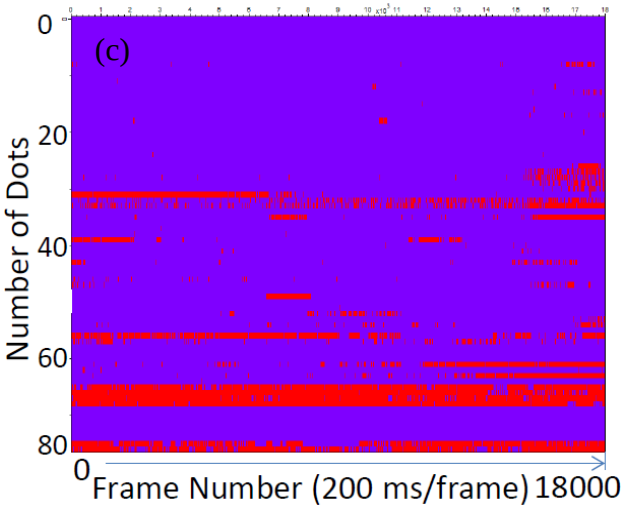
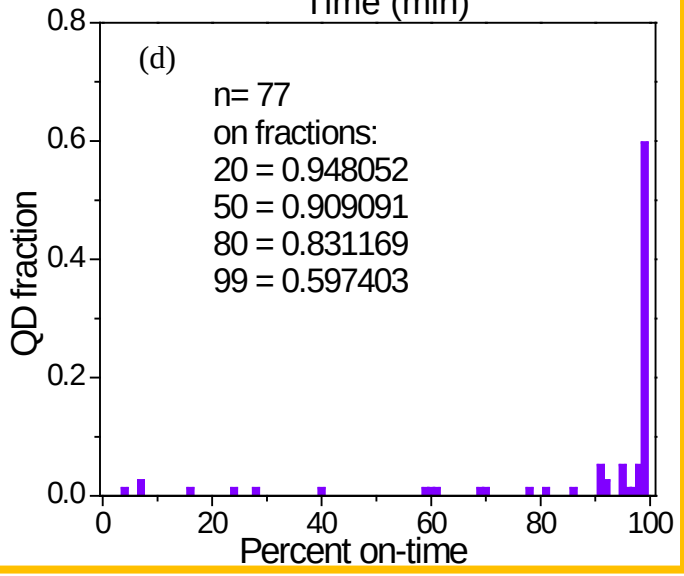
Blinking Statistics:~ 60% of ZnSe/CdS Core/Thick-shell are Non Blinking





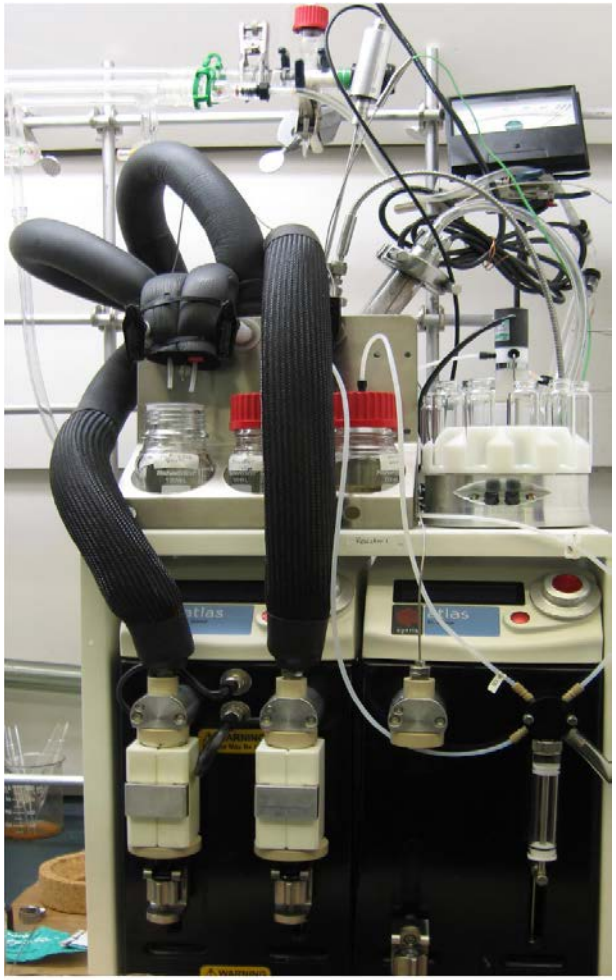






Acharya, et al., Submitted, 2015

Current Work: Core/shell Synthesis using Custom Designed Automated Reactor



- Can be programmed
- Capable to inject three different precursors; two heated lines
- Automated sampling
- Real time turbidity, absorbance and emission monitoring and data collection

Part II

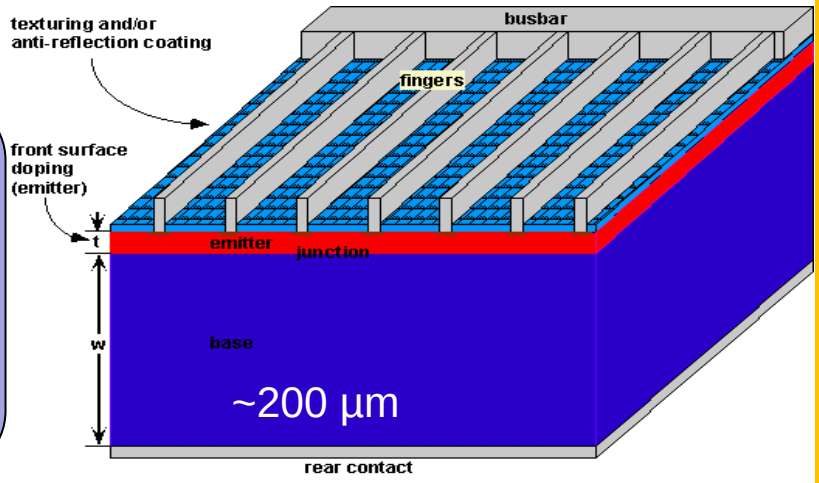
Colloidal Nanocrystals for Photovoltaics

Background and Motivation

- Present global energy consumption: ~15 TW
- 2050 projection: ~30 TW
- Fossil fuel: ~ 86 %, Green house effect
- Photovoltaics: Alternative renewable energy source, which can provide secure, reliable, and clean energy

First Generation Solar Cells

- Single and polycrystalline silicon solar cells
- Longest production history of over 60 years
- Well developed technology
- Accounts for ~86% of solar cell market



η= 25.0%

pveducation.org,

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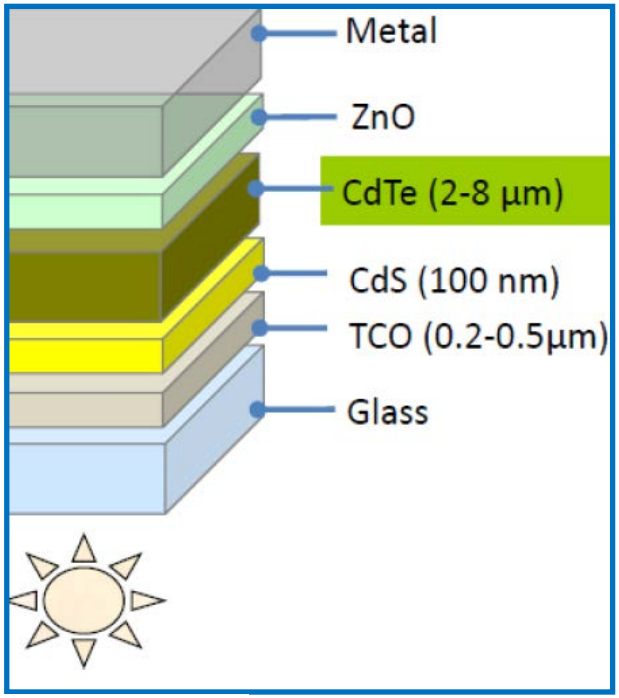
Thin Film and Solution Processed Solar Cells

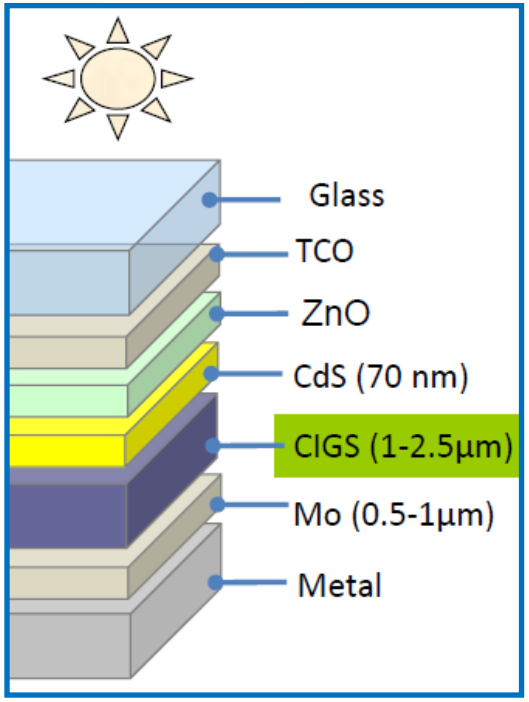
Second Generation

- Thin film solar cells: CIGS, CdTe, a-Si
- Good light absorber
- Lab efficiency ~20%
- Less cost/watt

CdTe



CIGS



New-generation Solar Cell

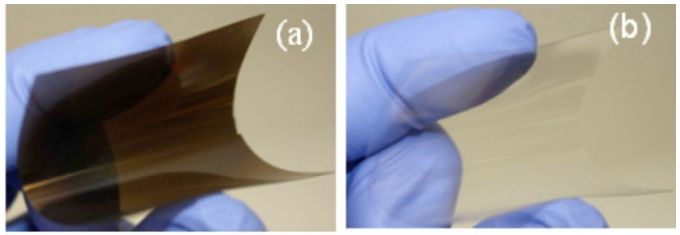
I. Potentially able to overcome Scockley-Queisser Limit

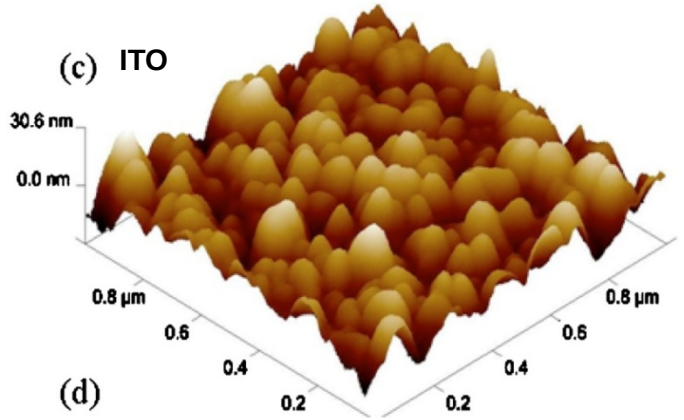
- Hot carrier and multi-junction solar cell

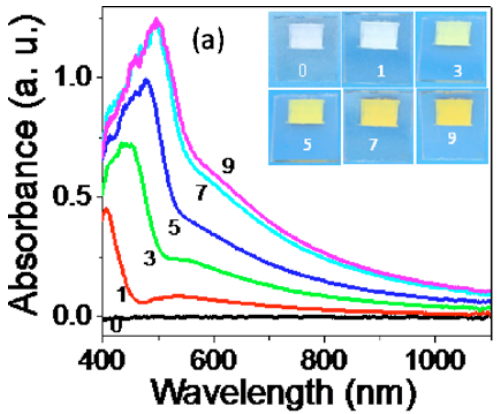
II. Solution processed

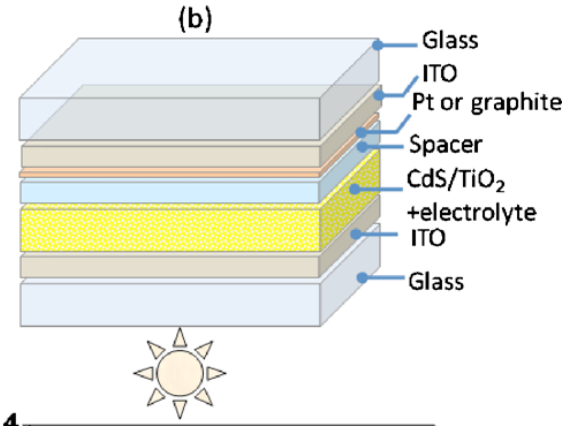
- Dye sensitized, organic, polymer, perovskite, nanocrystal solar cells

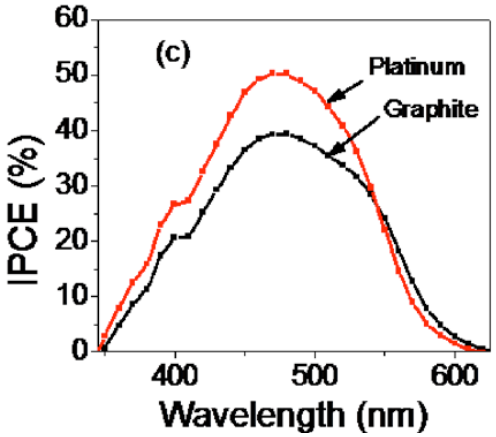
Pulsed-laser Deposition of Graphite Counter Electrodes for Dye-sensitized Solar Cells

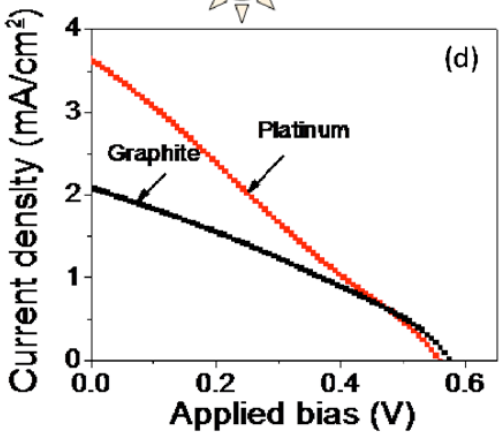












Counter electrode	J_{sc} (mA/cm^2)	V_{oc} (V)	Fill factor (%)	η (%)
Platinum	3.69	0.559	25.62	0.51
Graphite	2.13	0.575	31.16	0.37

Acharya et al; *Appl. Phys. Lett.* 97, 201108, **2010**

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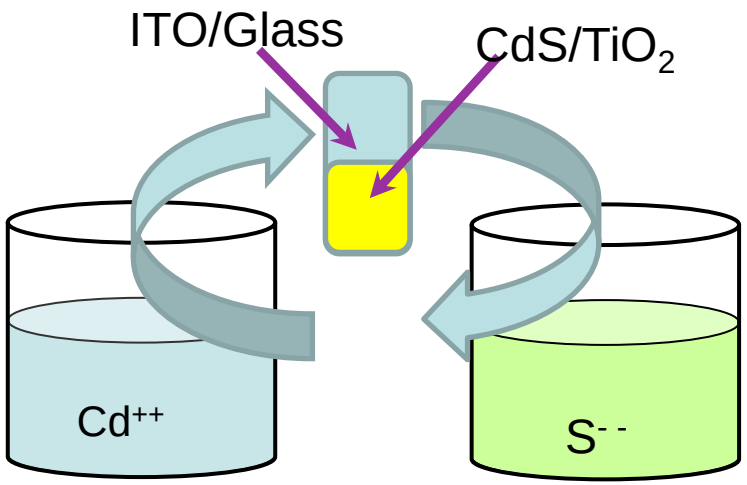
TiO_2 Sensitization Schemes

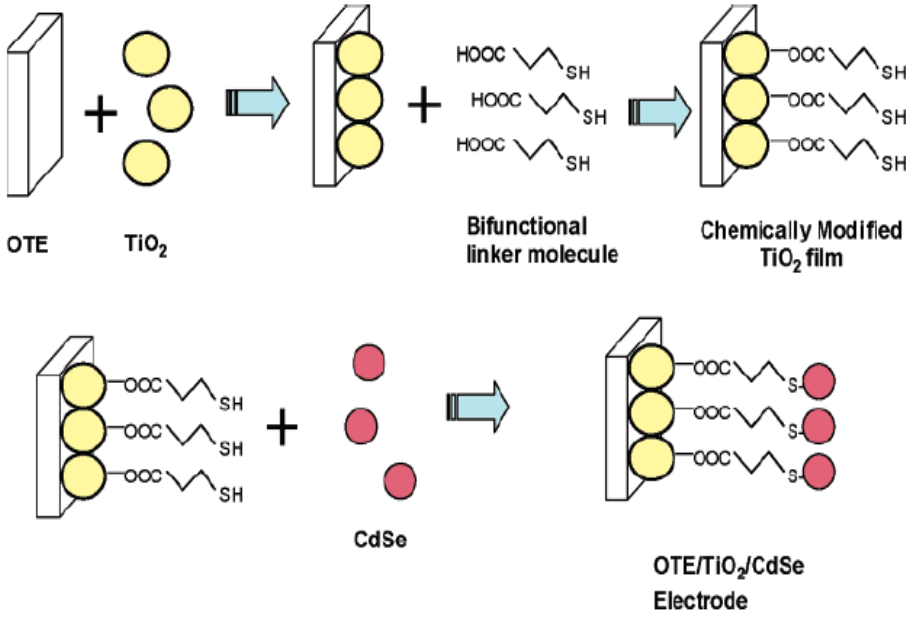
In situ chemical bath deposition



Successive Ionic Layer Adsorption and Reaction (SILAR)

Size can not be controlled, less stable

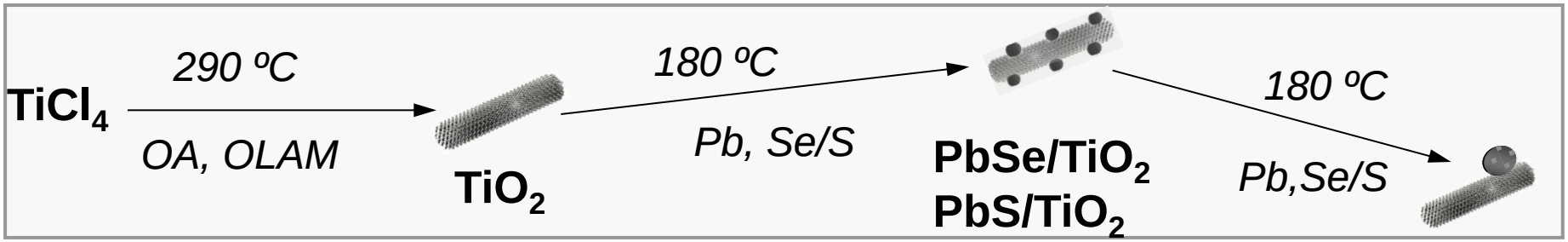
Bi-functional linker

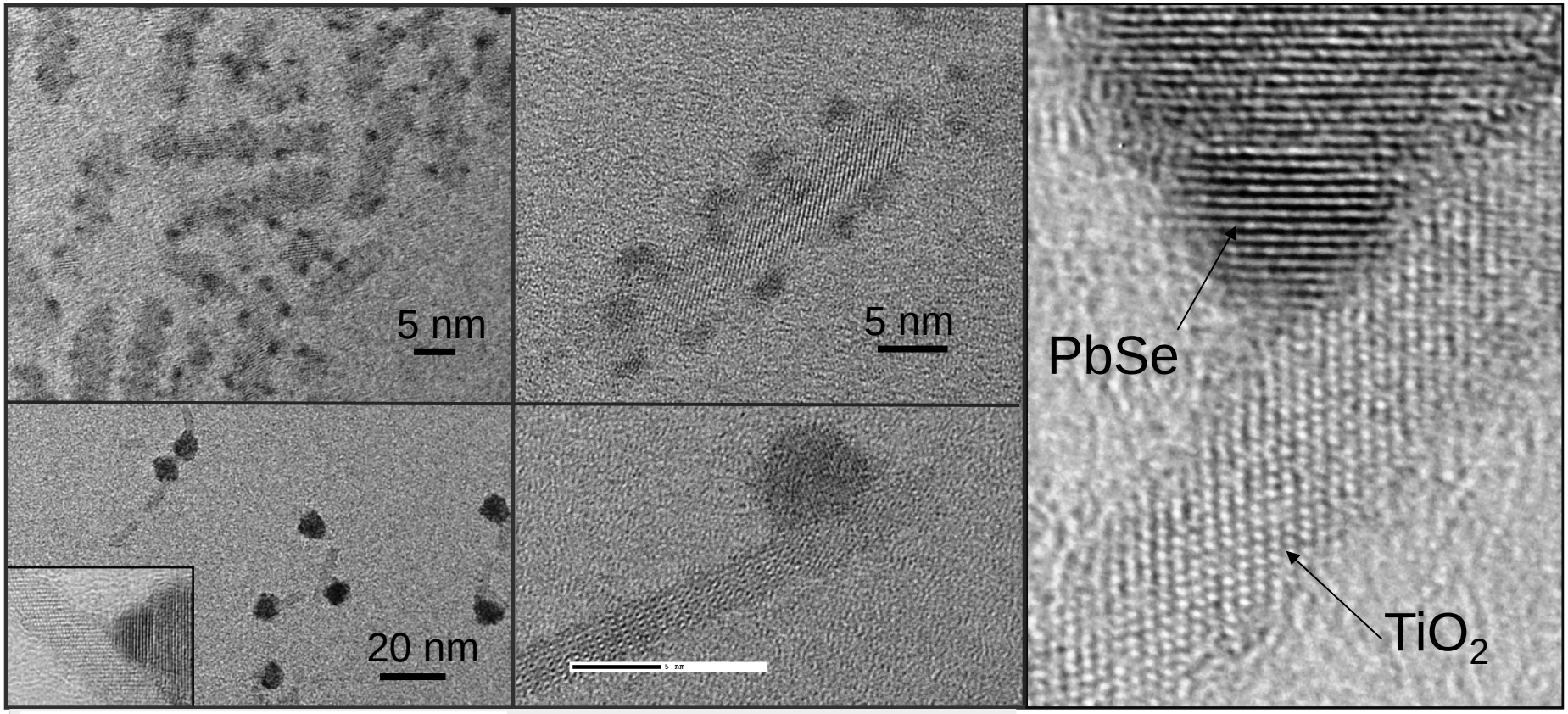


Organic spacer works as a barrier for electron transport

Robel et al., *J. Am. Chem. Soc.* **2006**, 128, 2387

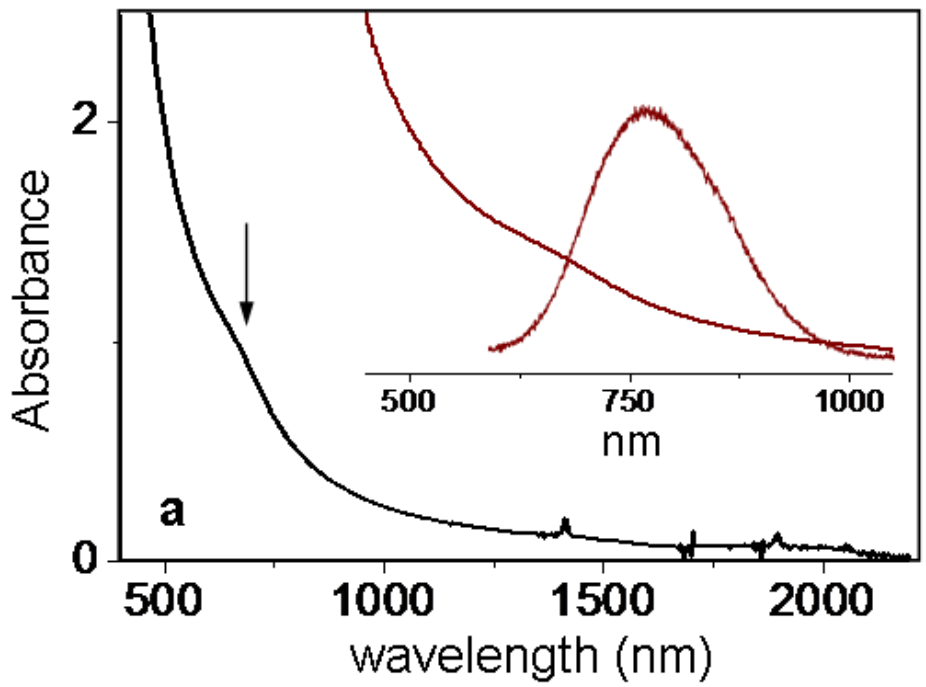
TiO_2 Nanorods Sensitization with PbSe or PbS NCs

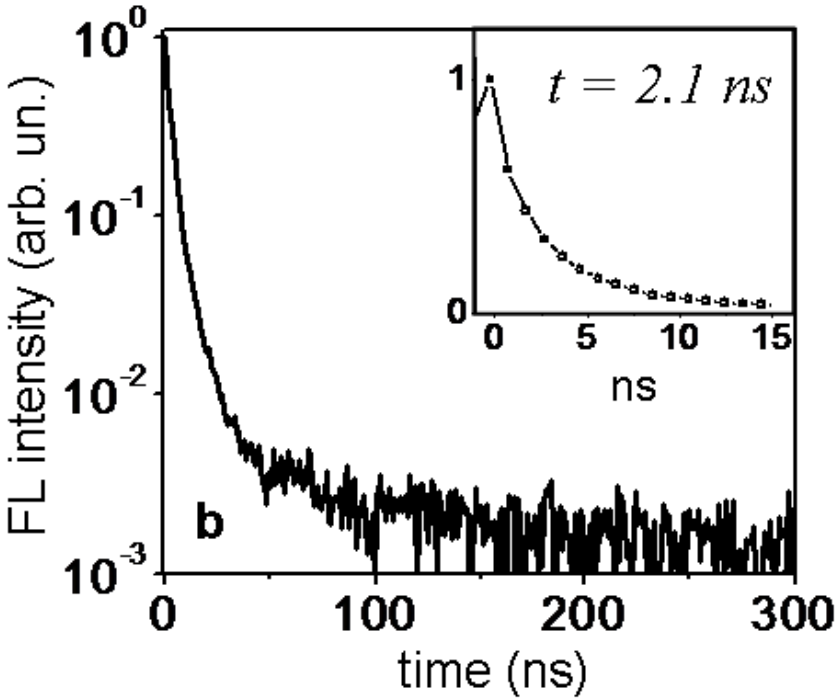


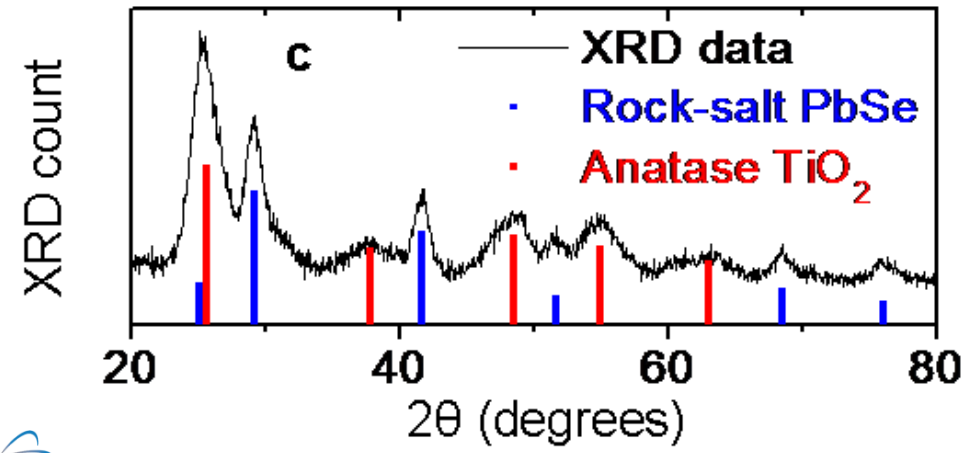


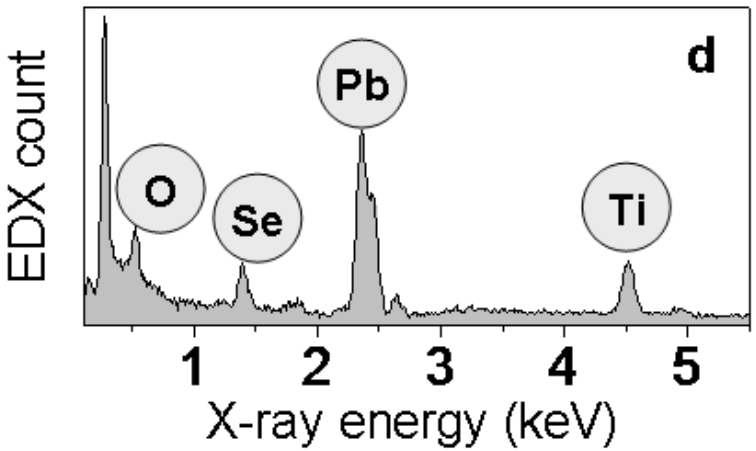
J. Phys. Chem. C 2009, 113, 19531

$PbSe/TiO_2$ Characterization









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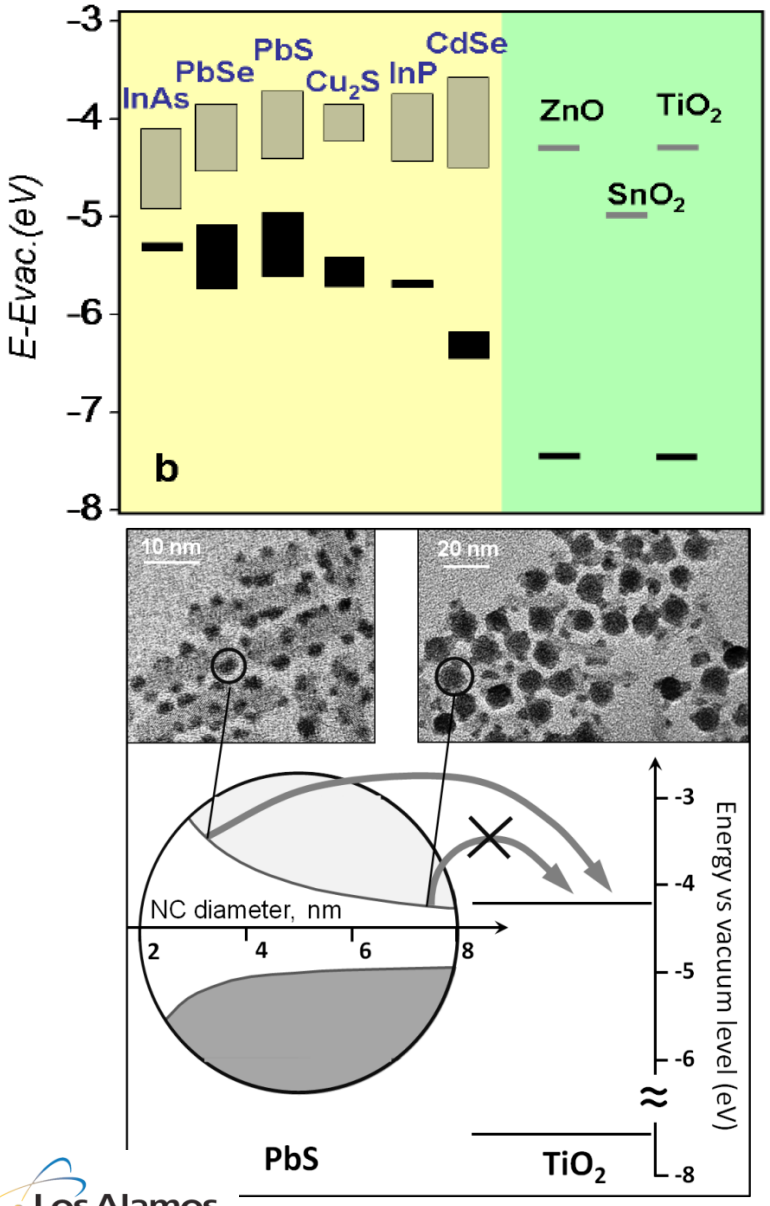
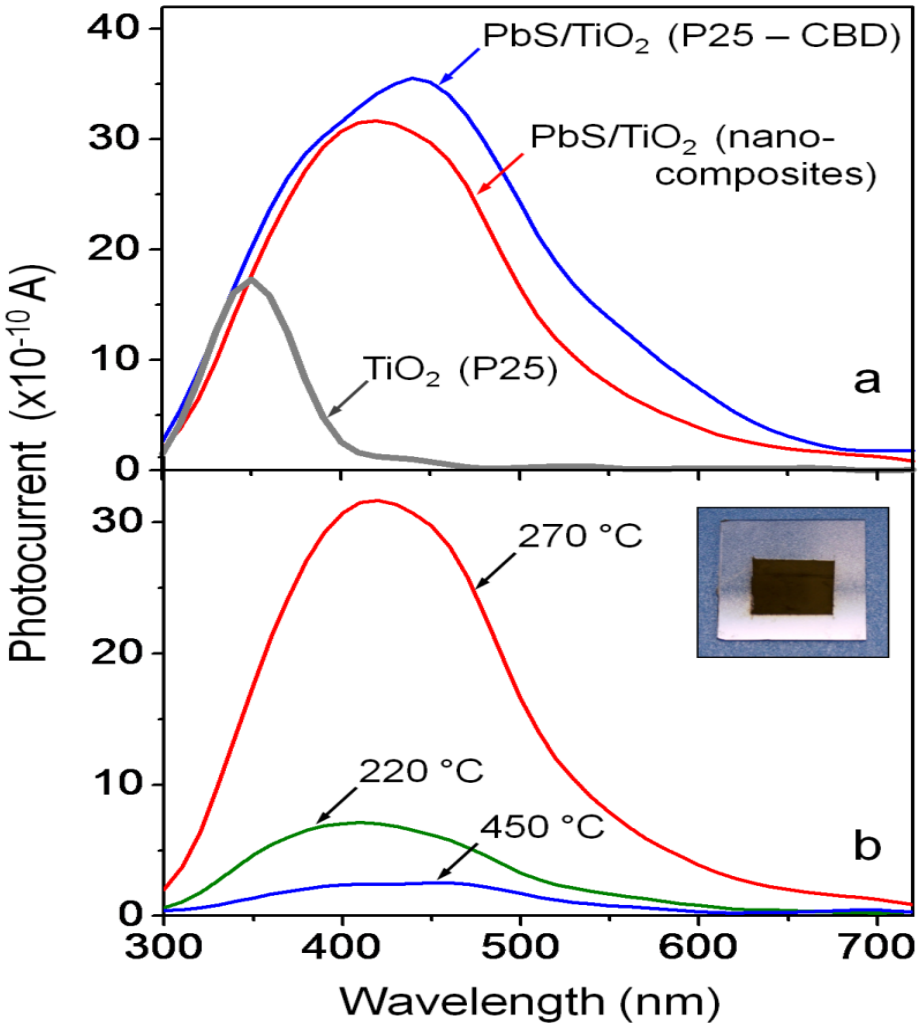
Acharya et al., *J. Phys. Chem. C* 2009, 113, 19531

Energy Levels and PC Spectra of PbS/TiO_2





Limitations

- Film quality
- Electrolyte
- TiO_2 coupling

Acharya, et al. *J. Phys. Chem. C* **2010**, 114, 19531

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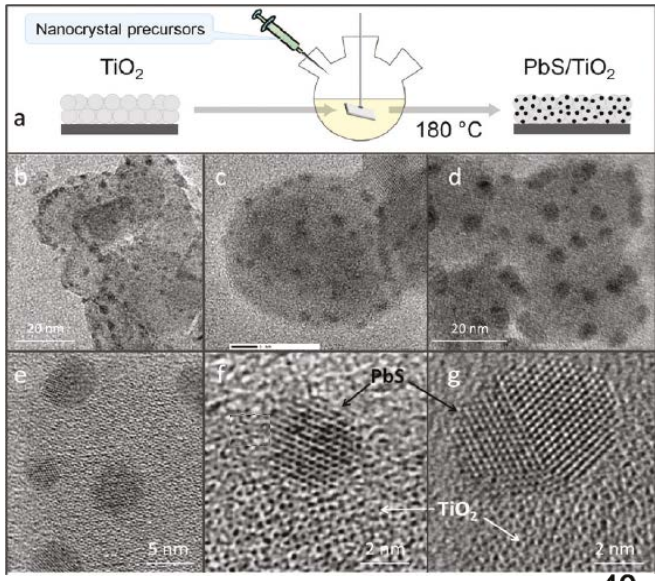
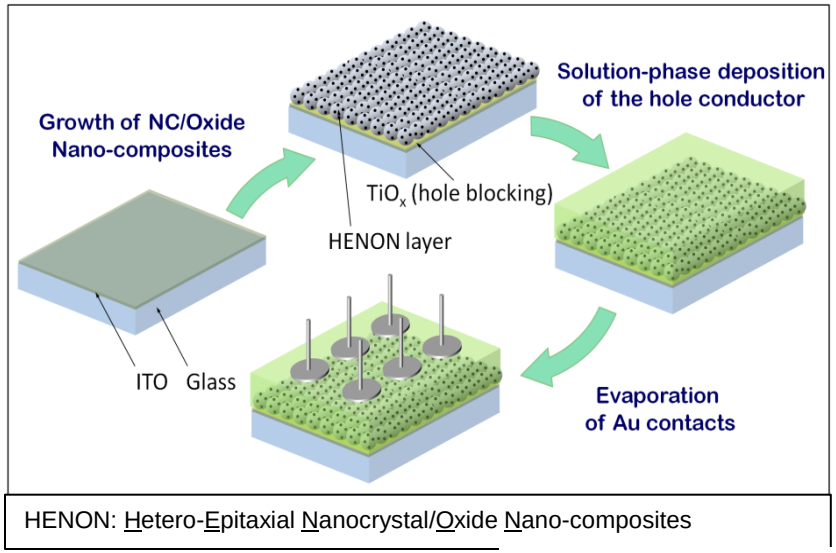
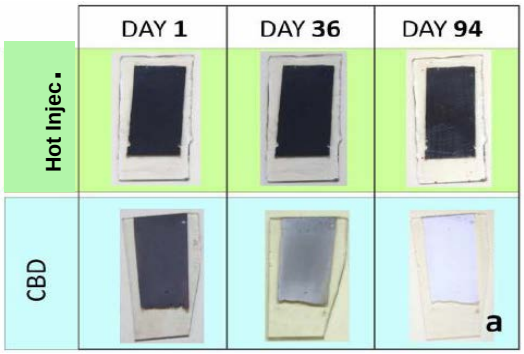
PbS NCs Growth on Sintered TiO_2 Films and its PV Application

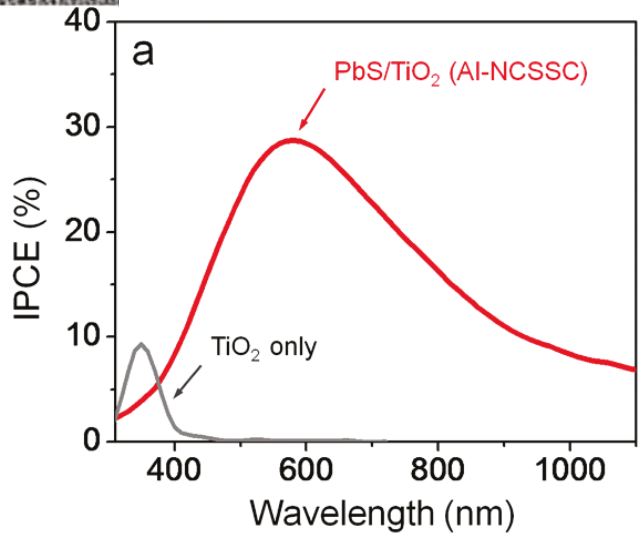


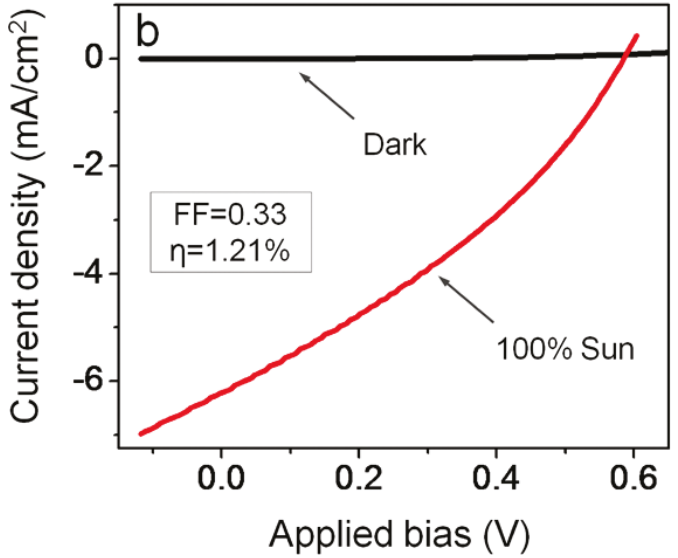


HENON: Hetero-Epitaxial Nanocrystal/Oxide Nano-composites









Acharya, et al. *ACS Nano*. **2011**, 5, 4953

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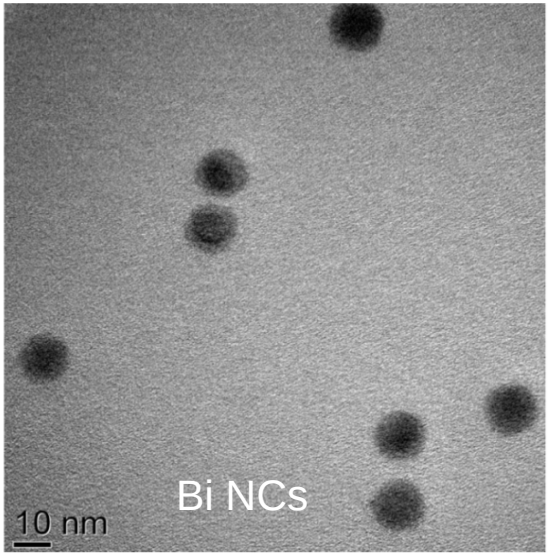
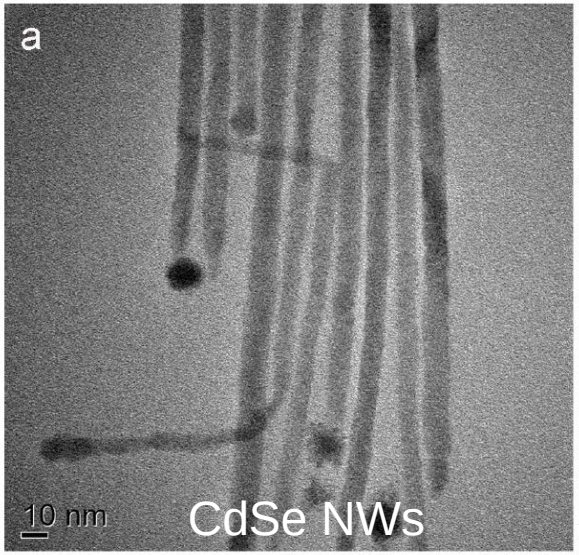
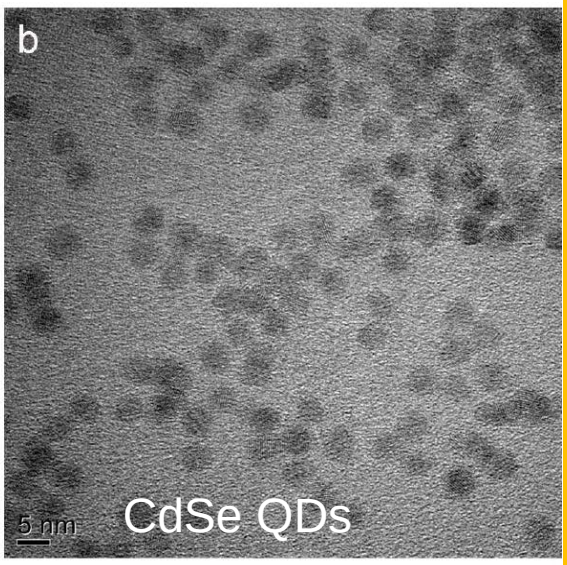
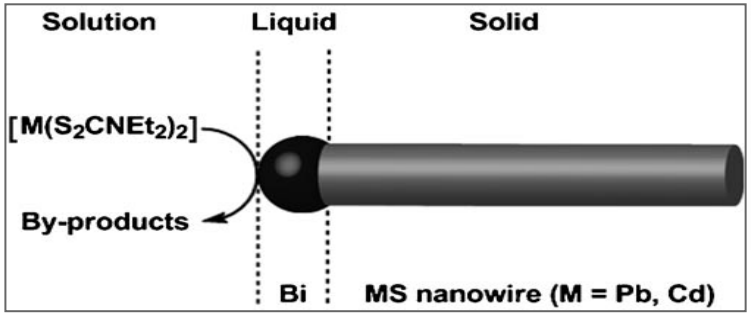
Nanowire Sensitized Solar Cells: Comparison with QD Sensitized Solar Cell

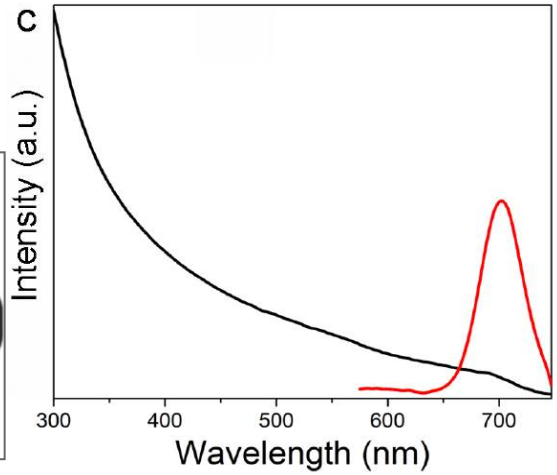


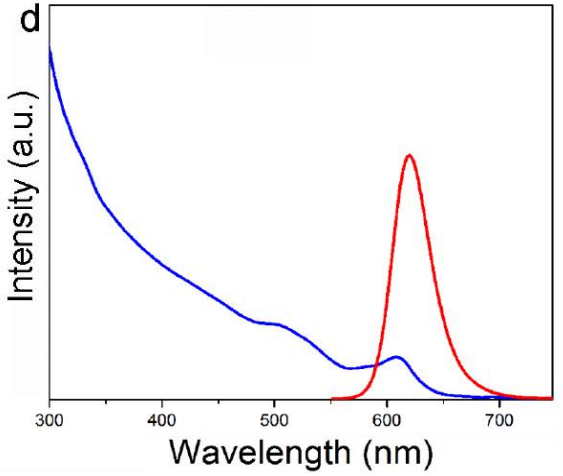




NW Synthesis







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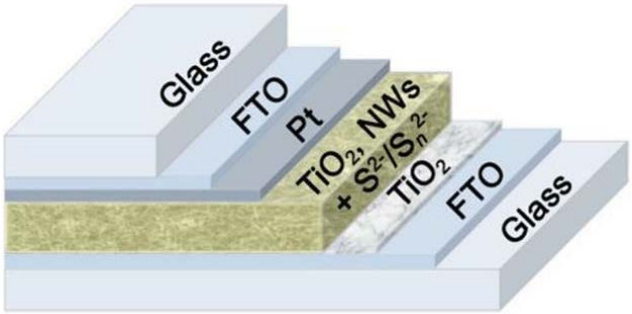
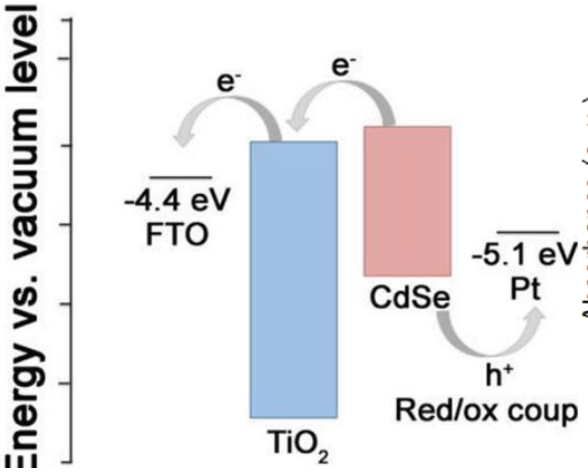
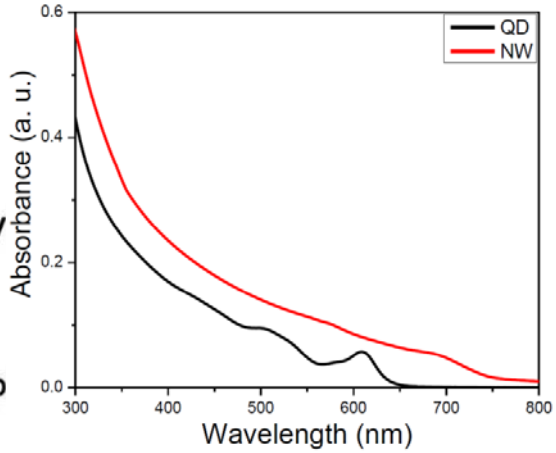
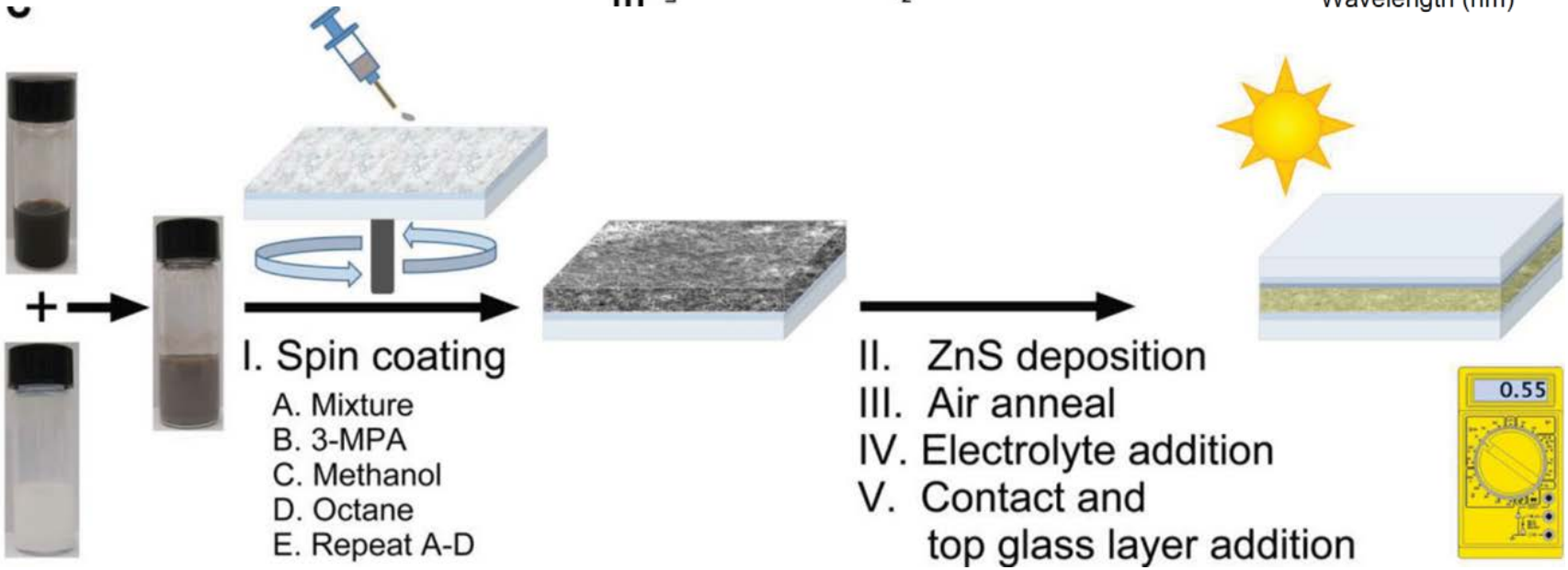
Layer-by-Layer Fabrication of NW sensitized Solar Cell









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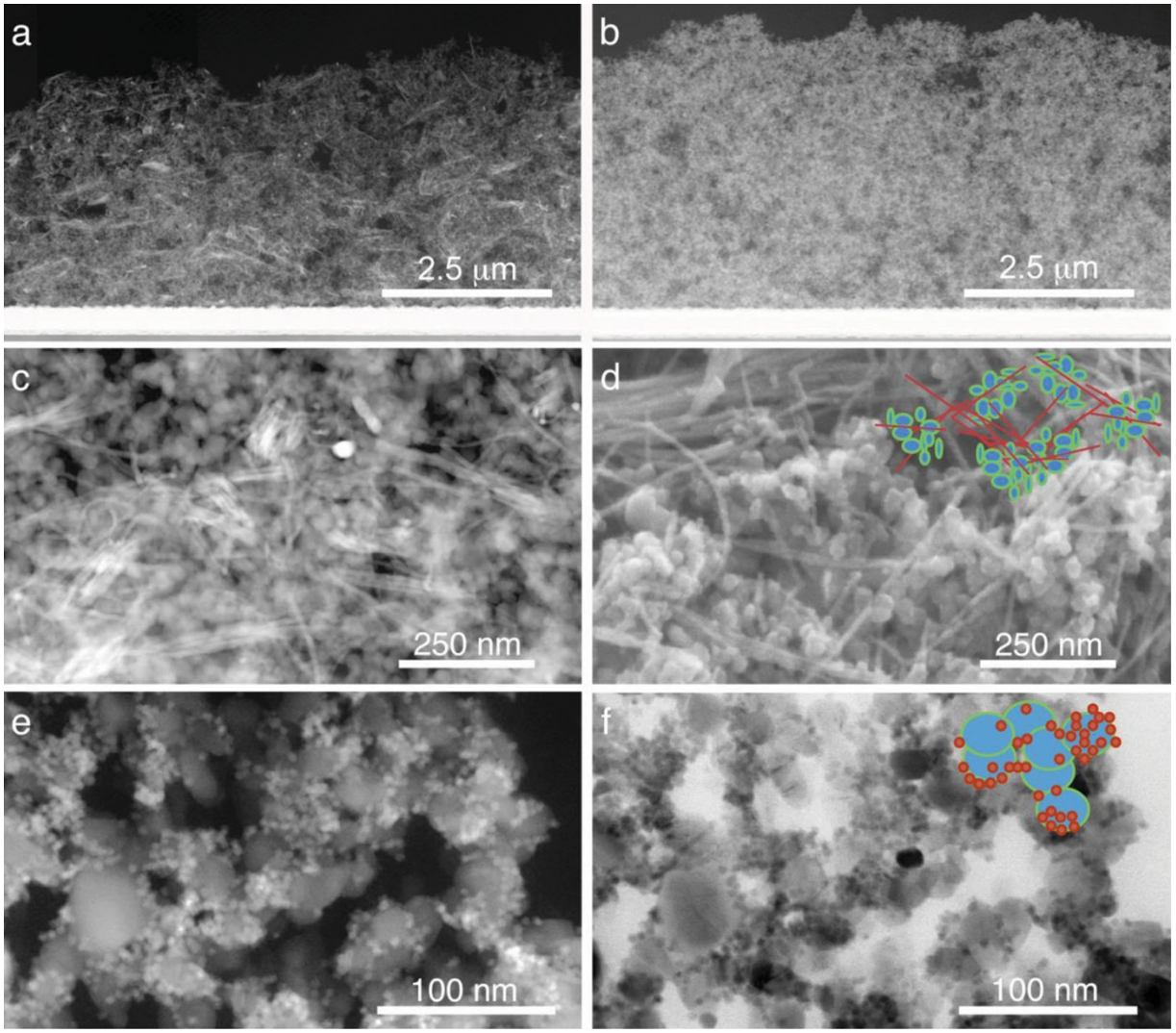
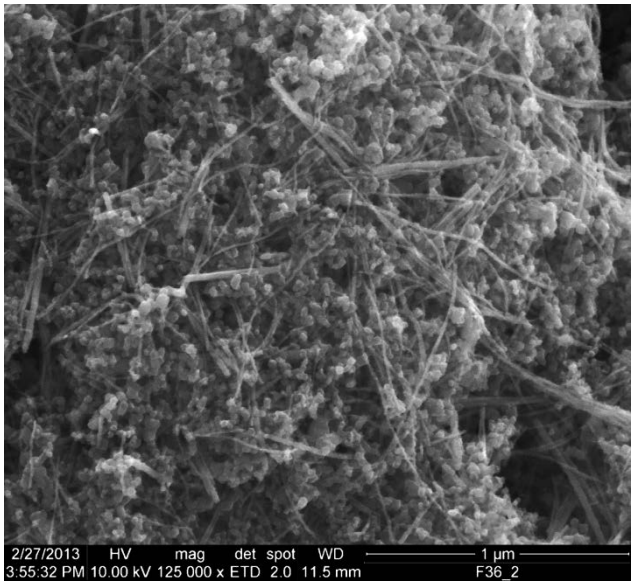
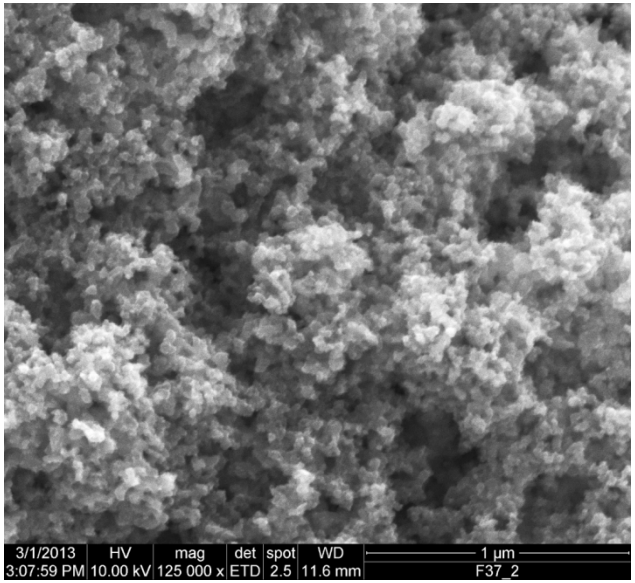
Acharya et al., Adv. Func. Mater. 2014, 24, 6843

NWs and QDs Films Morphology







Low magnification Z contrast STEM of (a) NW and (b) QD cross section (c) Z contrast STEM and (d) SEM of NW film (e) Z contrast and (f) bright field STEM of QD film

Acharya et al., Adv. Func. Mater. 2014, 24, 6843

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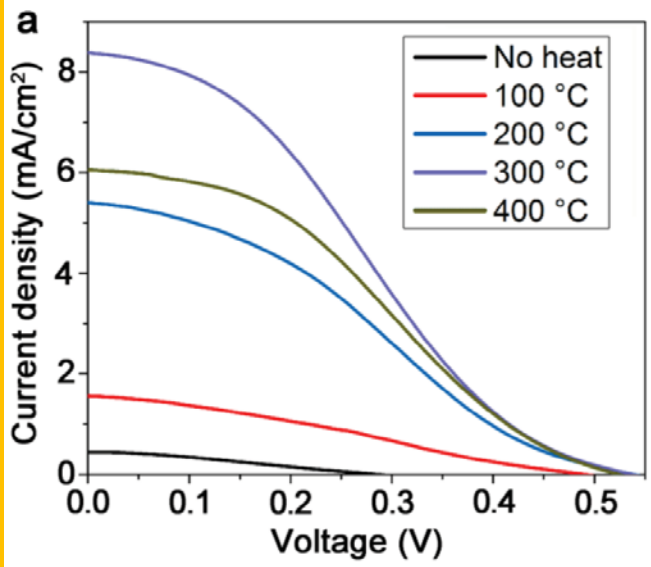
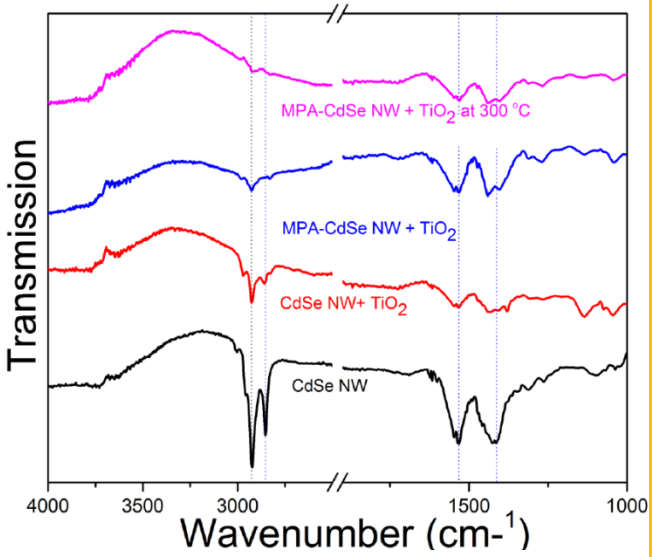
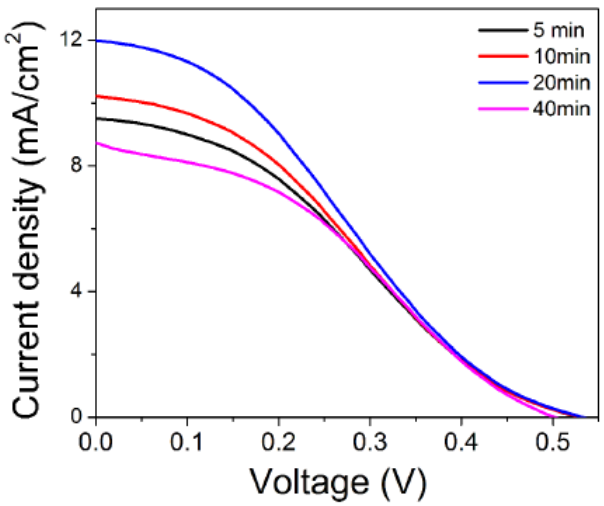
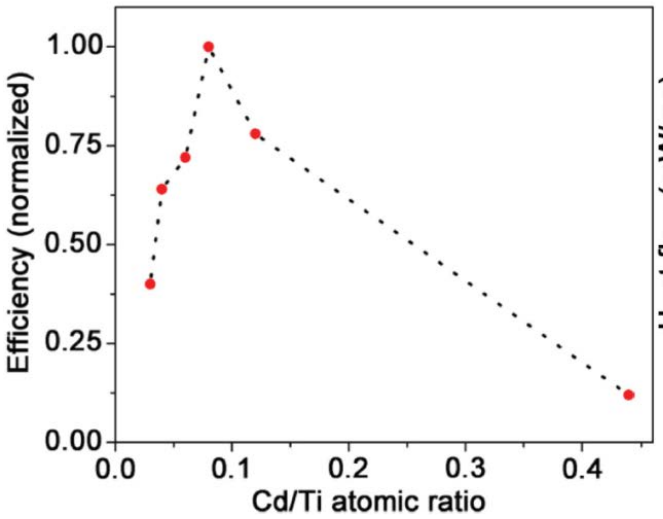
NWSSC Performance Parameters

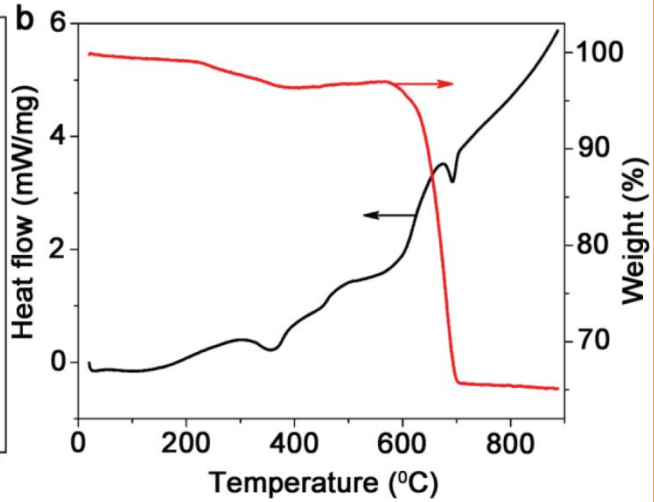


- Annealing temp. (300 ºC)
- Annealing time (20 min)
- Cd/Ti ratio (0.08)









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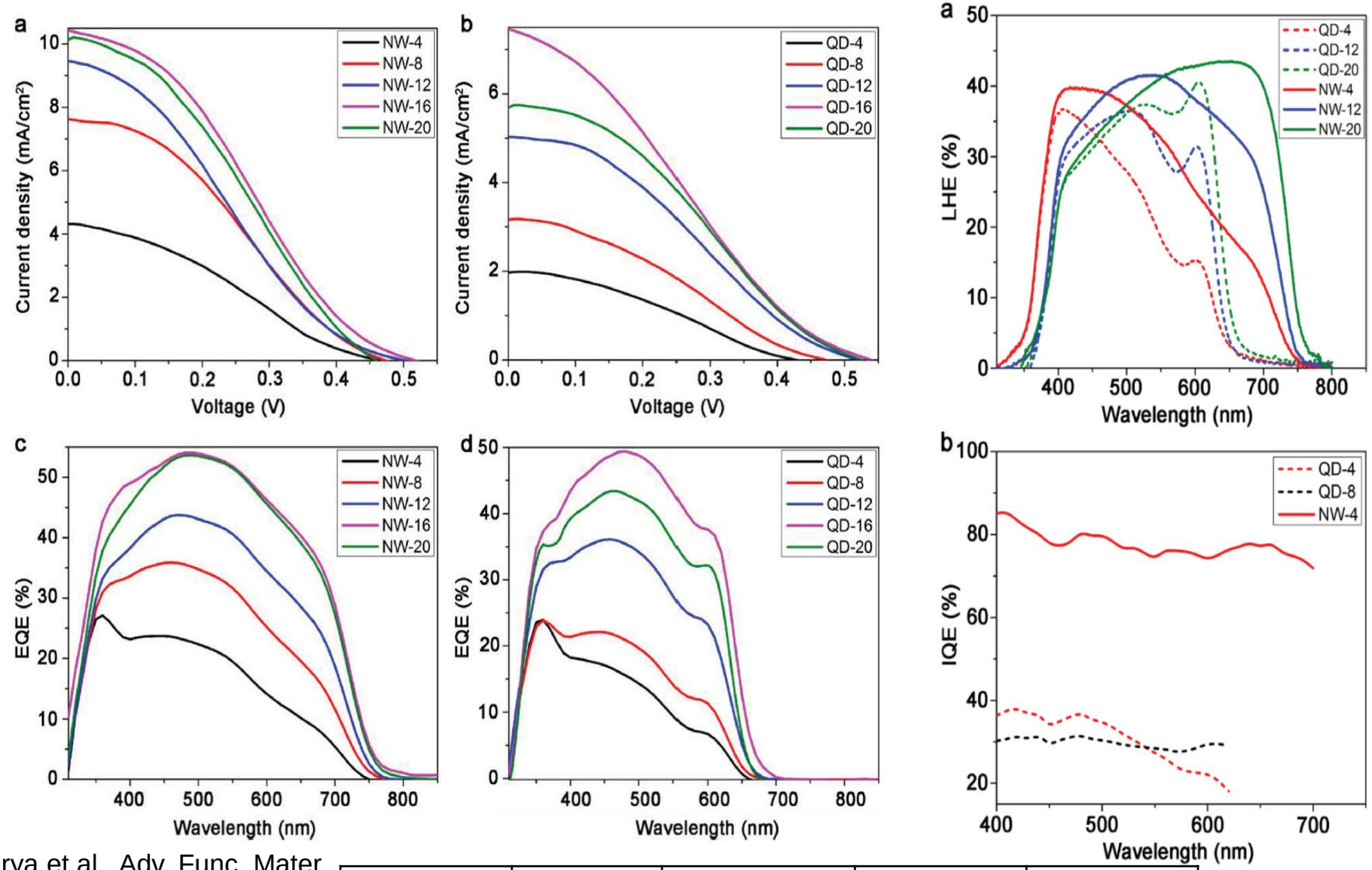
Acharya et al., Adv. Func. Mater. 2014, 24, 6843

Comparison of QD and NW Sensitized Solar Cells



Acharya et al., Adv. Func. Mater. 2014, 24, 6843

Device	V_{oc} (V)	J_{sc} (mA/cm²)	FF (%)	PCE %
NW (16)	0.55	8.67	34.34	1.65*
QD(16)	0.50	6.40	36.39	1.17

*1.83% PCE @ 20 min anneal time

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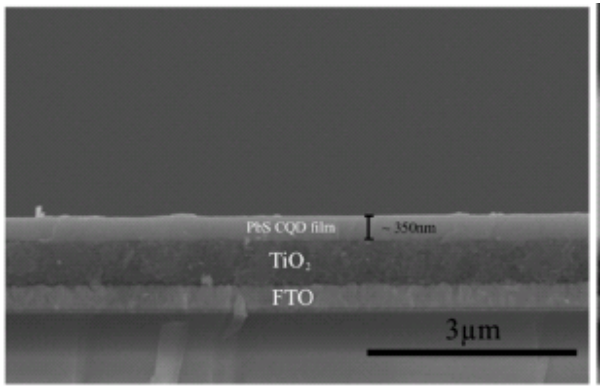
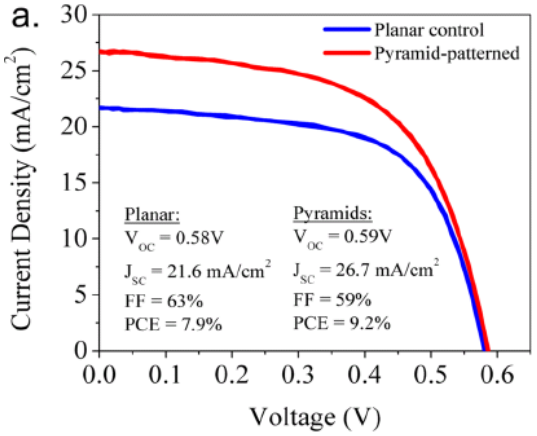
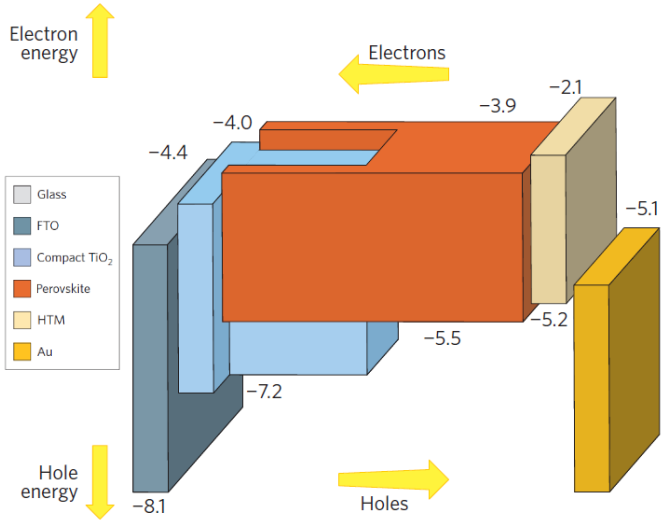
Nanocrystal-based Solar Cell

Depleted Heterojunction



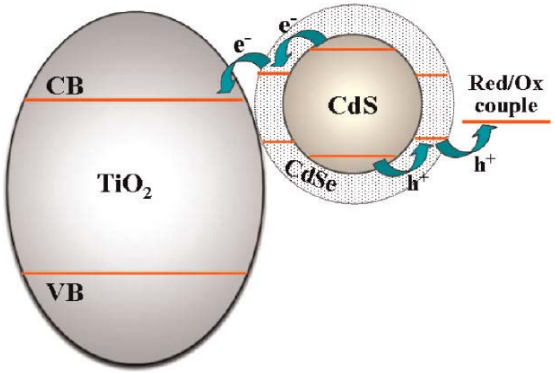


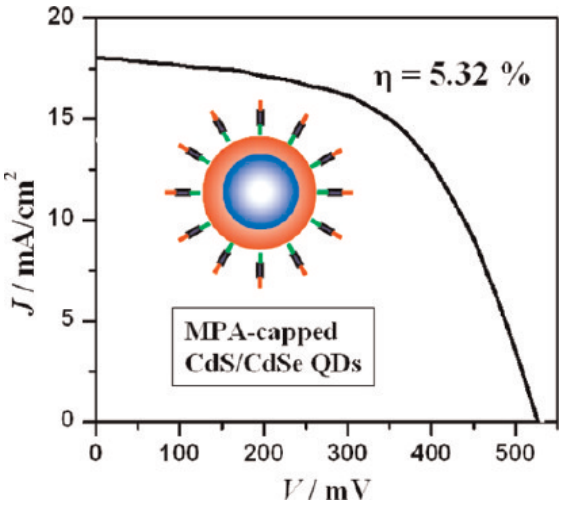


17.9%

Perovskite: $CH_3NH_3PbI_3$

Inverted type-I





Labelle et al., Nano Lett., 2015, 15,1101;Pan et al., ACS Nano, 2012, 6, 3982, Green et al.; Nature Photonics, 2014, 8, 506

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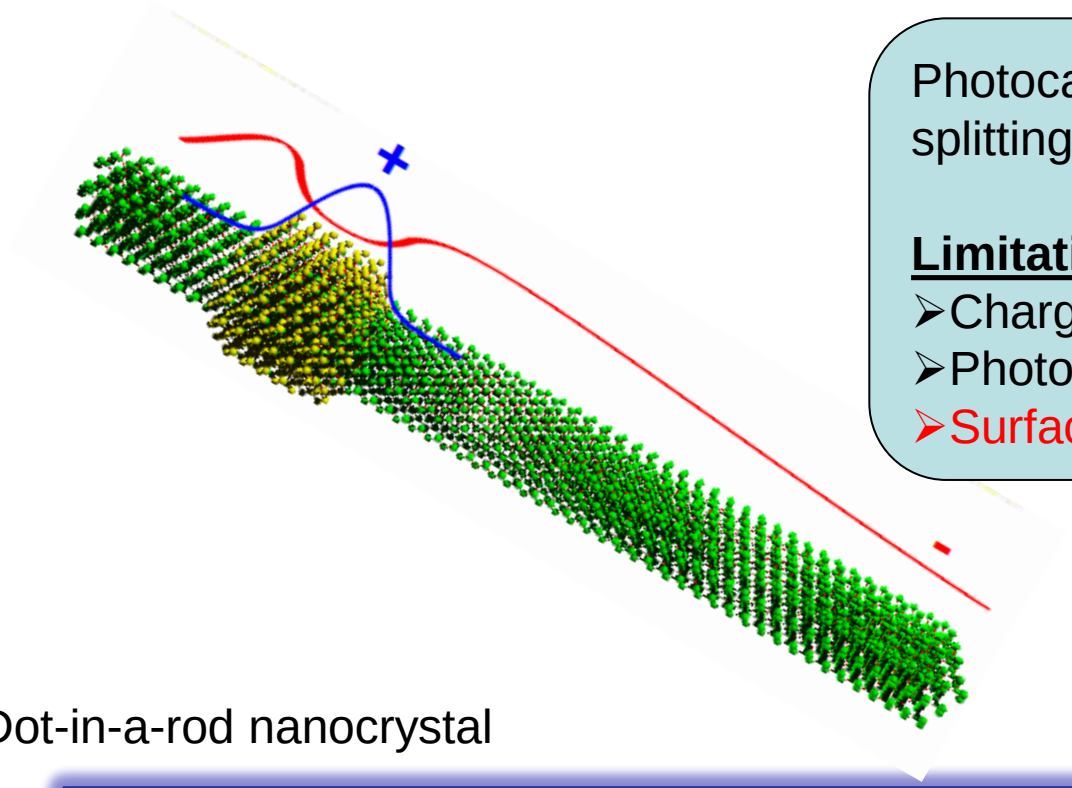
Part III

Semiconductor Metal Heterostructured Nanorods for Charge Separation/H_2 production



Dot-in-a-rod nanocrystal

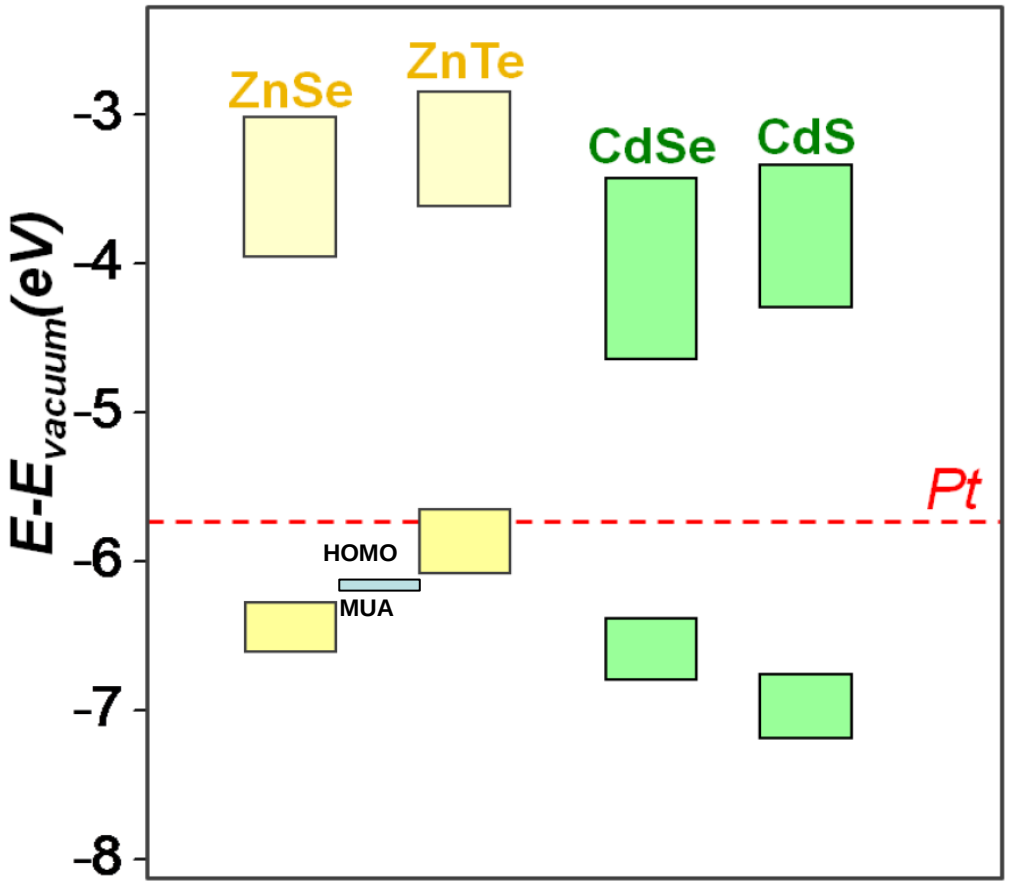
Photocatalytic production of H_2 by splitting water using sunlight

Limitations:

- Charge carriers recombination
- Photo-corrosion
- Surface back reaction

- **Long lived charge separated state**: Suppress recombination, surface back reaction
- **Reduce photo-corrosion:** More stable

Materials Combination



I. ZnSe/CdS/Pt

II. CdTe/CdS/Pt

How the dynamics of hole is varied with the position of valance band of the core relative to HOMO level of ligand?

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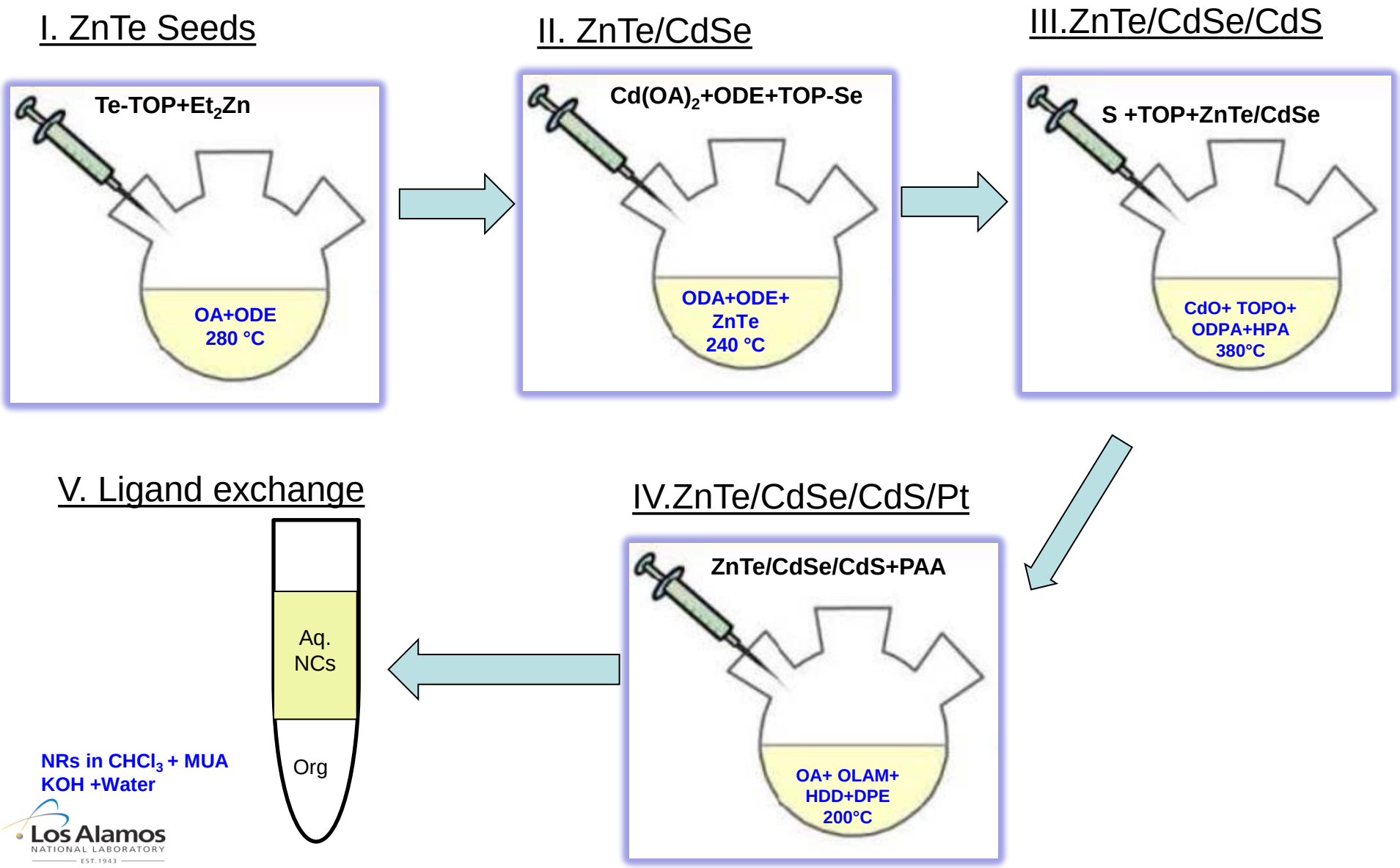
Synthetic Scheme of Semiconductor Metal Heterostructured Nanocrystals



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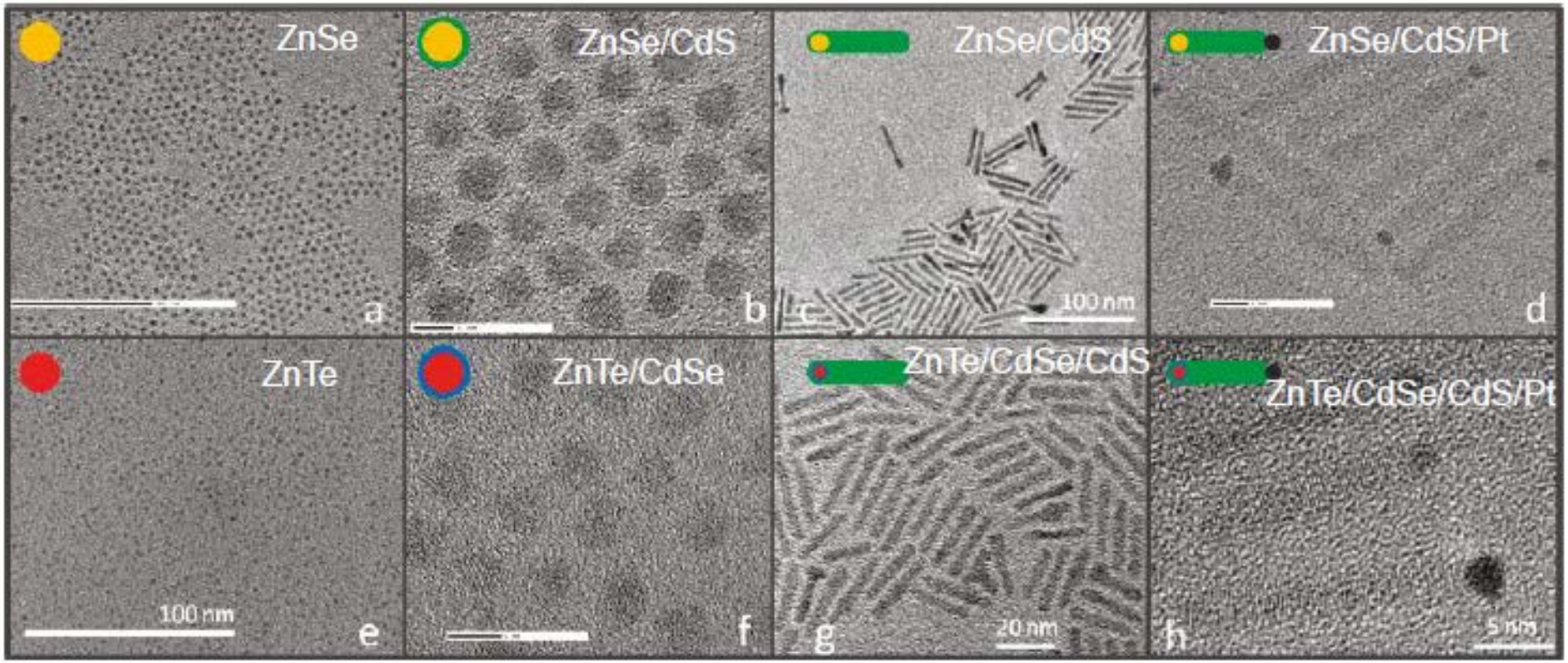
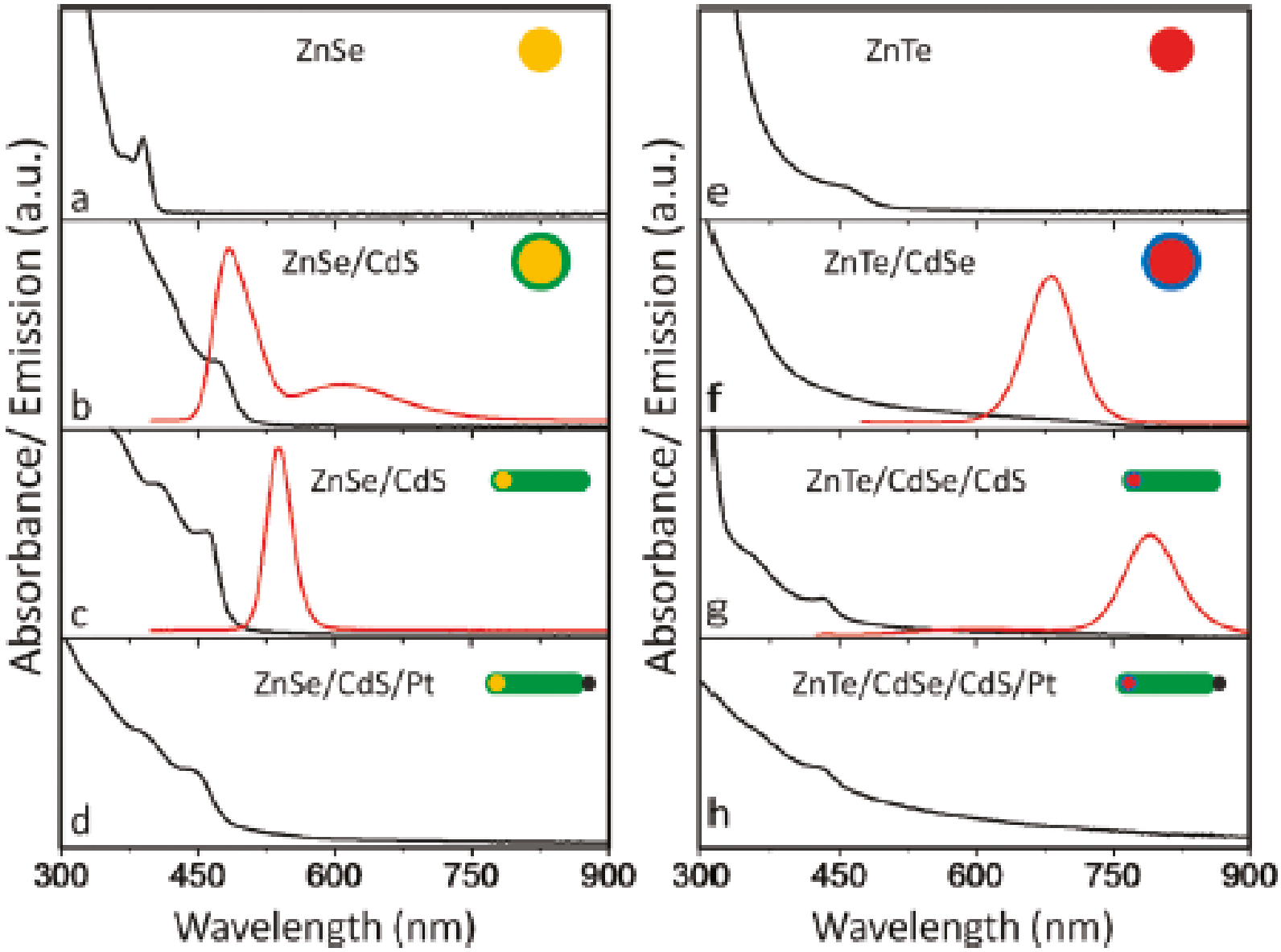
ZnSe/CdS/Pt & ZnTe/CdSe/CdS/Pt Morphology



Acharya et al., *Nano Lett*. *11*, **2011**, 2919.

Optical Properties



Achara et al., *Nano Lett*. *11*, **2011**, 2919.

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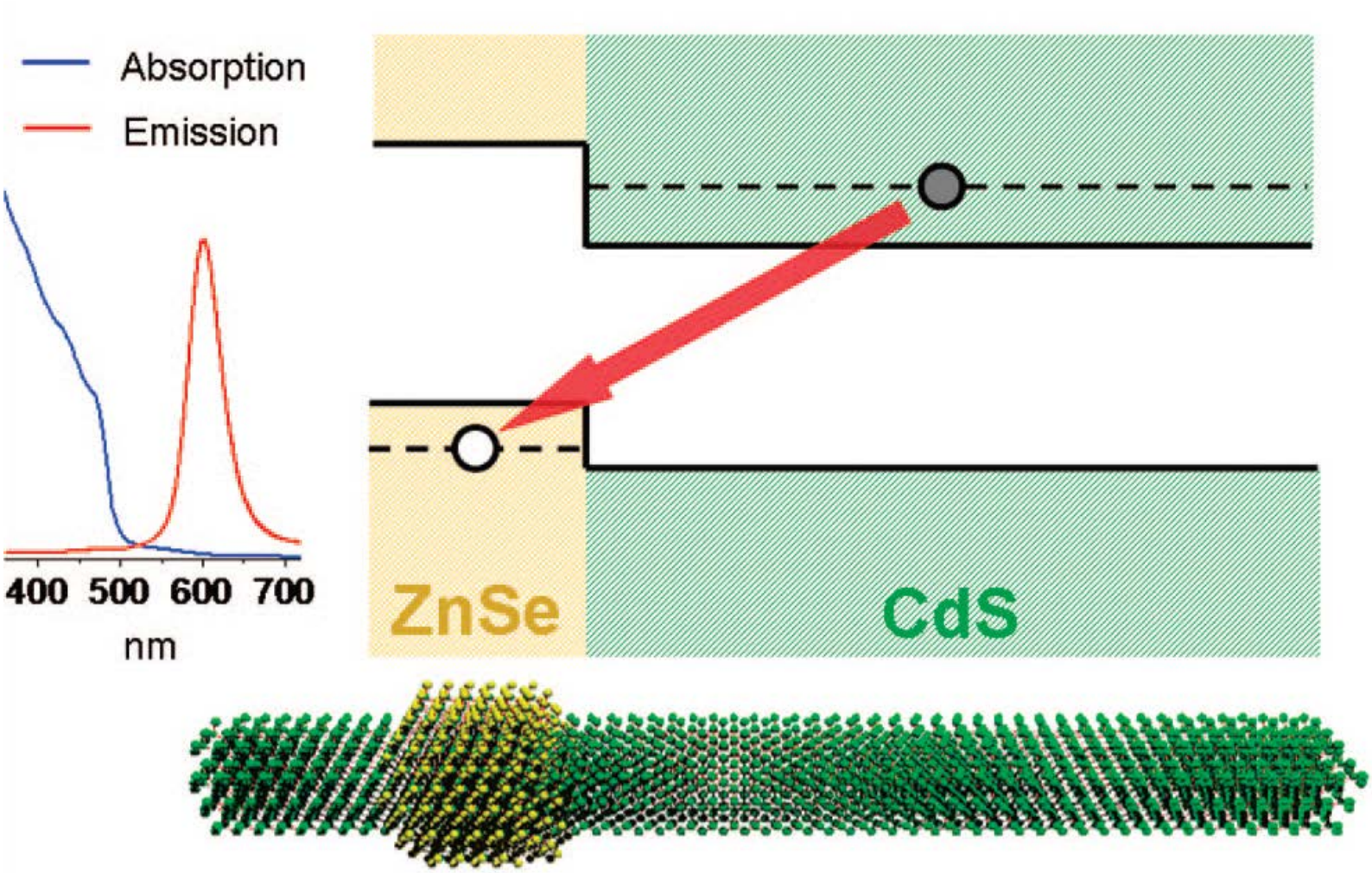
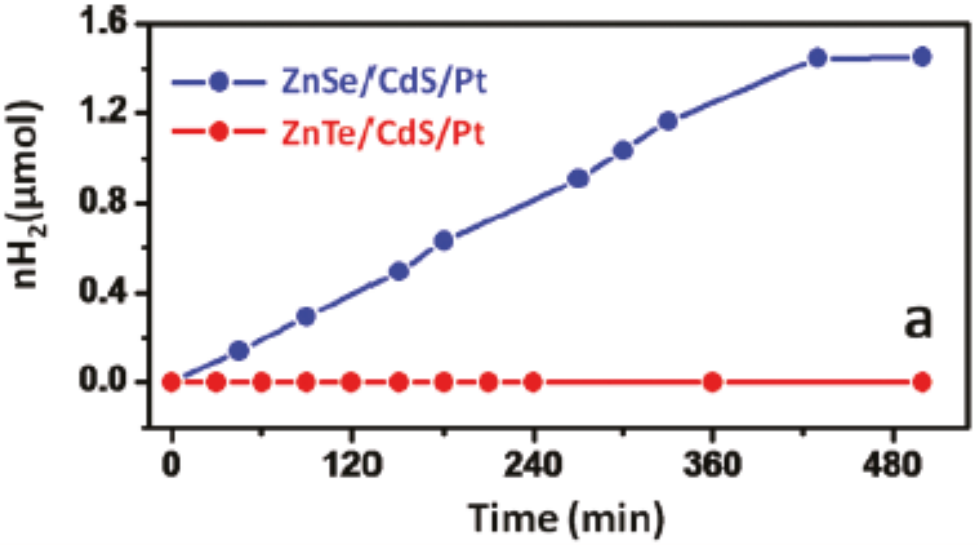
Radiative Recombination of Spatially Extended Exciton

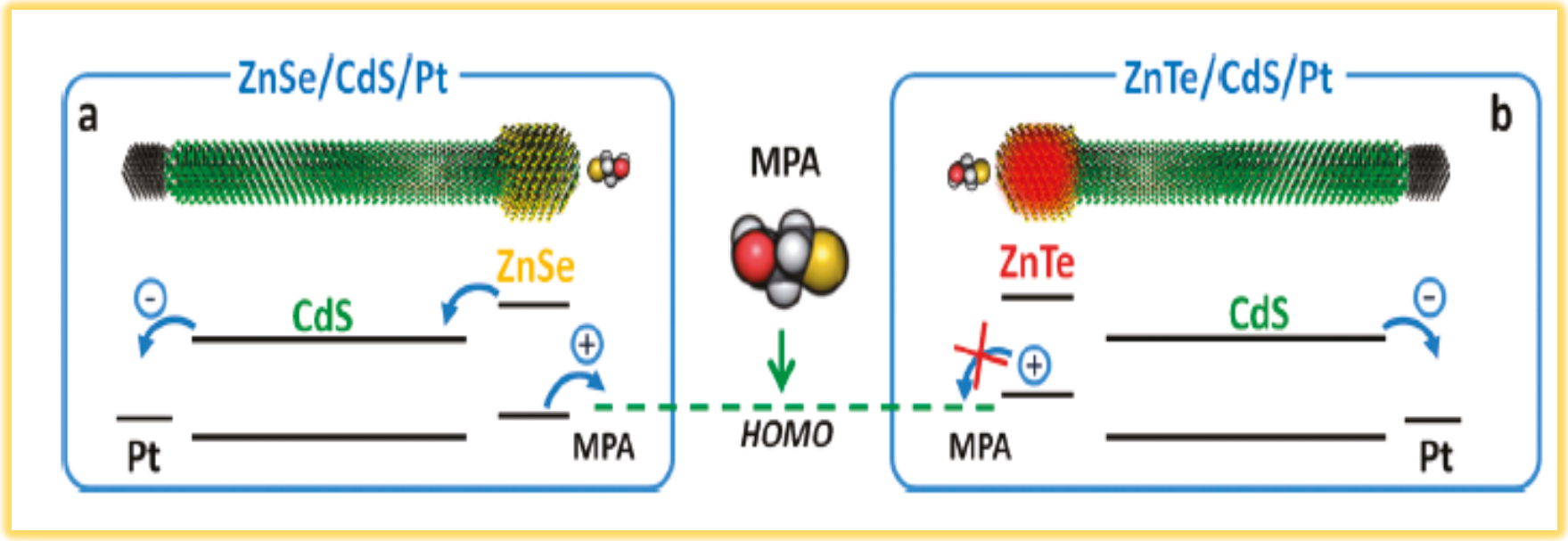


Hydrogen Production Test



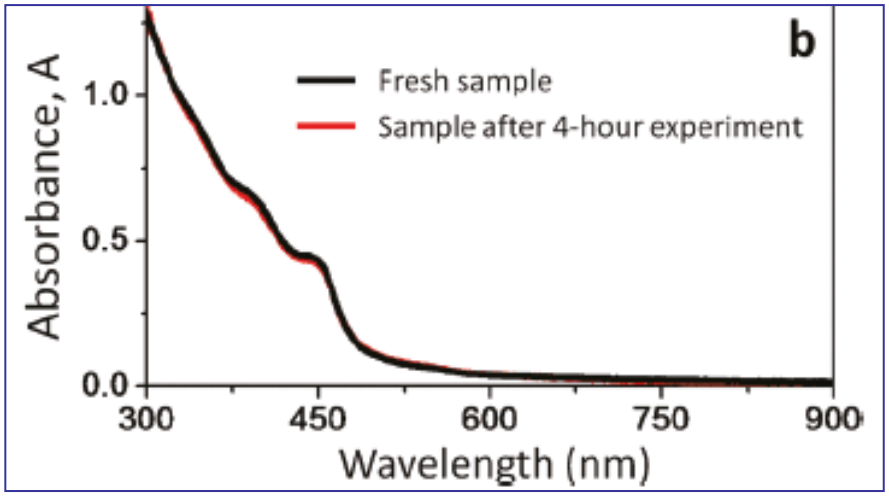
1mg/5mL

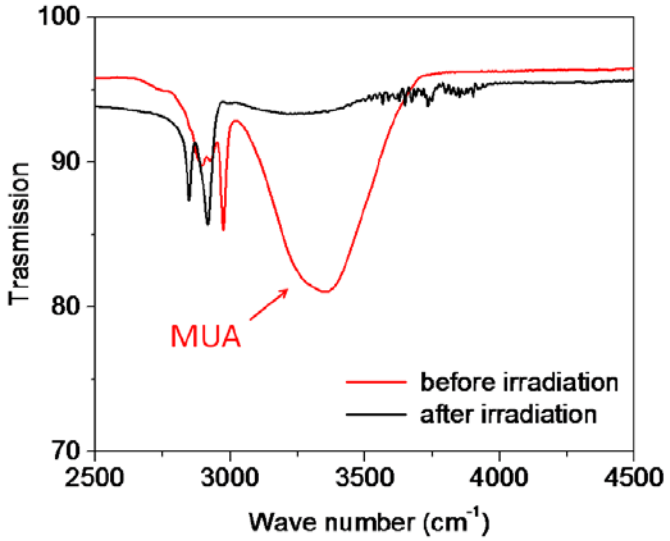
- 1(H_20): CH_3OH)
- 120 mW/cm^2
- Gas chromatograph

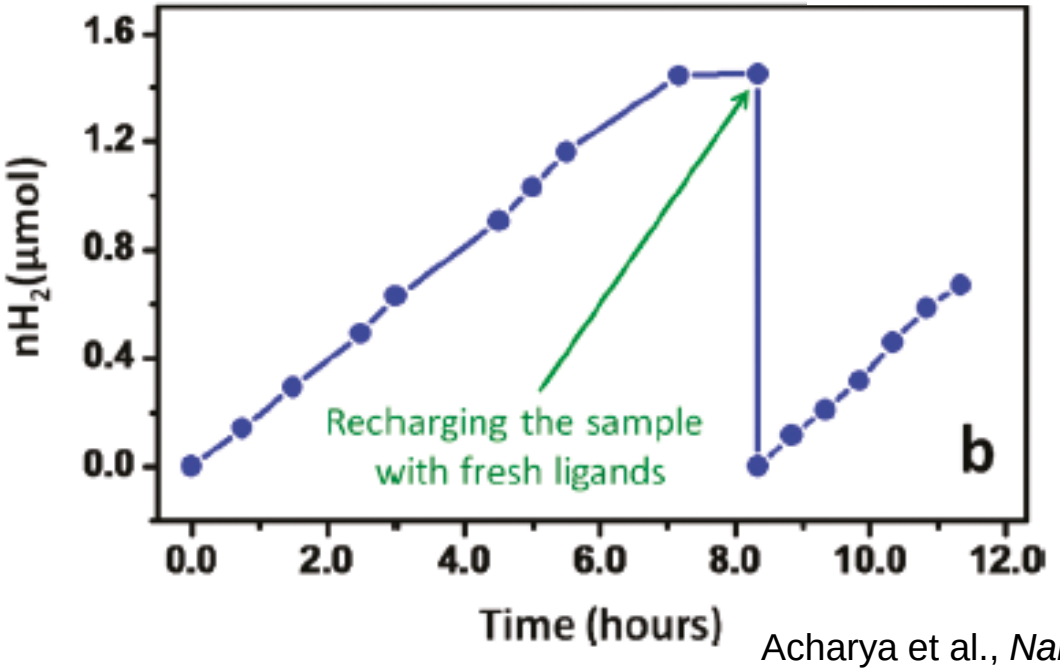


Acharya et al., *Nano Lett*. *11*, **2011**, 2919.

Reusability of Exhausted Hetero-nanorods







Acharya et al., *Nano Lett*. *11*, **2011**, 2919.

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Conclusions

Part I

- Thick-shell ZnSe/CdS & CdSe/ZnSe core/shell were synthesized using SILAR
- ZnSe/CdS forms type-II while CdSe/ZnSe forms type-I electronic structures
- ZnSe/CdS are blinking suppressed and CdSe/ZnSe show high biexciton efficiencies
- Cation exchange and alloying must be considered in thick-shell growth process

Part II

- Pulsed-laser deposited graphite film can be used as a counter electrode
- PbSe and PbS NCs were grown onto isolated TiO_2 NRs and annealed TiO_2 substrates and their photovoltaic properties are demonstrated
- Introduced a new layer-by-layer method to fabricate TiO_2/NWs films
- Devices made using identical mass and conditions show that NWSSC performs better than QDSSC due to enhanced light absorption

Part III

- ZnSe/CdS/Pt & ZnTe/CdS/Pt NRs synthesized and demonstrated their photocatalytic properties
- The position ligand's HOMO and core's valance band level play important role in photocatalysis
- Semiconductor can be charged with fresh ligands after hydrogen production ceases.

Acknowledgements

LANL Team



BGSU Team



- Minh: Blinking and Blinking statistics
- Joanna Casson: Nanoparticle TEM

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- **NIH**

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ity

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I. Synthesis

High PLQY, Robust and Air Stable QDs

- **Red emitter**: CdSe/CdS, SILAR and continuous injection method
- **Green emitter**: ZnSe/CdS elongated core/shell; seeded methods
- **Blue emitter**: ZnCdSe/CdS or ZnCdSSe/ZnSe/ZnS
- SILAR: Injection automation using syringe pumps

Other Synthesis

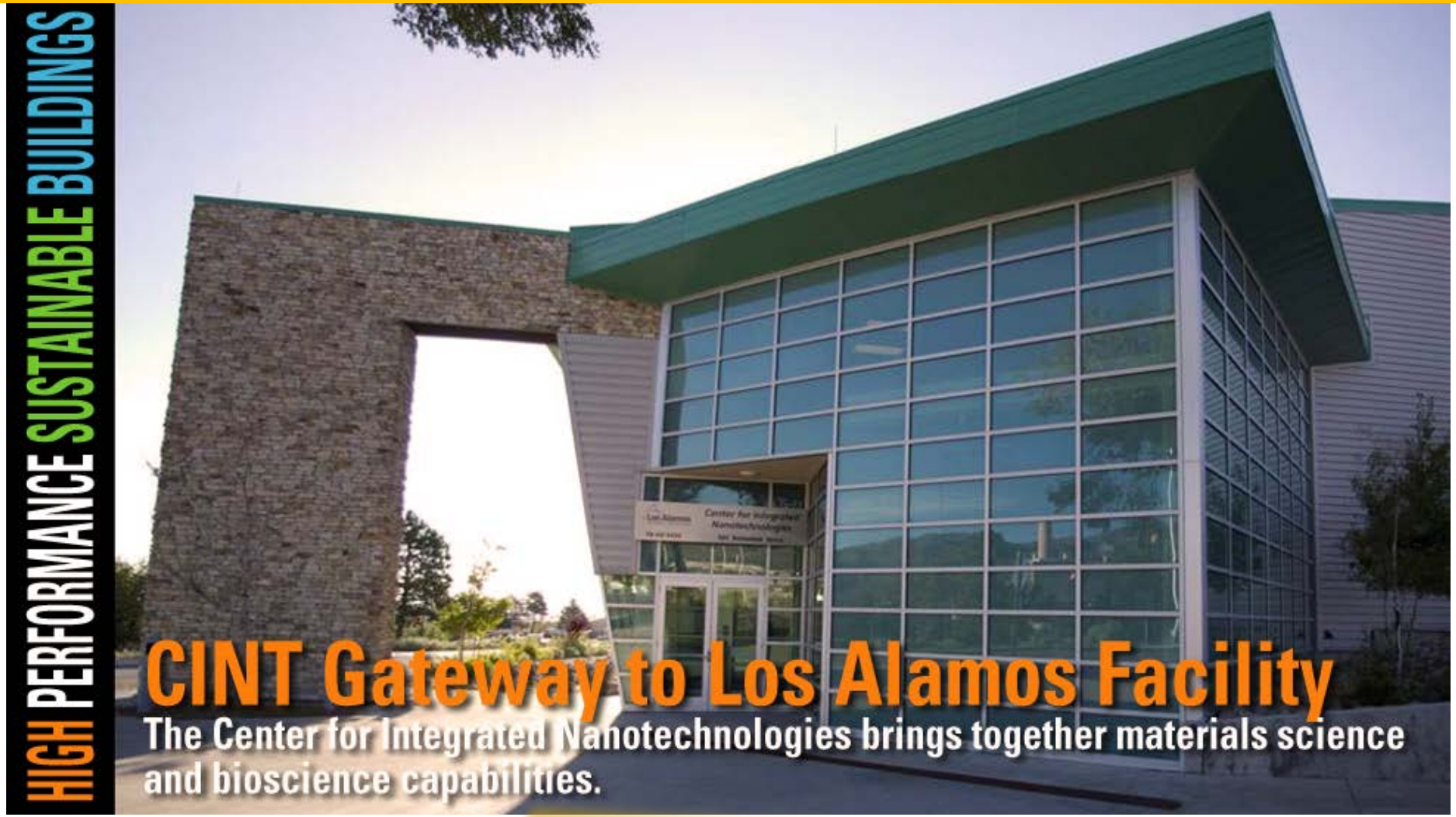
ZnTe/ZnSe; CdTe/CdS

InP/ZnSeS; CIS_2/ZnSe

II. Devices

If we are to achieve results never before accomplished, we must expect to employ methods never before attempted.

- Sir Francis Bacon


HIGH PERFORMANCE SUSTAINABLE BUILDINGS
CINT Gateway to Los Alamos Facility
The Center for Integrated Nanotechnologies brings together materials science and bioscience capabilities.

Thank you