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Title:	BA capped CdSe Quantum Dot Sensitized Solar Cell
Author(s):	Nobuhiro Fuke, Laura B. Hoch, Alexey Y. Koposov, Virginia W. Manner, and Milan Sykora*
Intended for:	ACS Meeting, Denver, CO, 8/28-9/1, 2011

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Form 836 (7/06)

BA Capped CdSe Quantum Dot Sensitized Solar Cell.

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Quantum Dot sensitized solar cells (QDSSCs) have been recently studied because of their potential to yield higher efficiencies than dye sensitized solar cells. One important challenge in development of QDSSCs is the optimization of the QD/TiO_2 interface with respect to the electron transfer. In the talk we present studies of QD→TiO_2 electron injection in structures prepared by direct adsorption of pre-synthesized CdSe QDs on nanocrystalline TiO_2 films. The QDs were passivated with two types of ligands: tri-n-octylphosphine oxide (TOPO) and n-butylamine (BA). Using nanosecond transient absorption (TA) spectroscopy, we show that the change of QD passivation from TOPO to BA leads to enhancement of electron injection and injection efficiency. Studies of Internal Quantum Efficiencies (IQEs) of devices prepared using these films will also be discussed. Consistent with the TA result, we find that use of BA passivation leads to enhancement in device performance, with ~100% IQE achieved for best devices.

BA capped CdSe Quantum Dot Sensitized Solar Cell

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ACS fall meeting 2011 at Denver

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Outline

- Motivation
- Measurement methods
  - Photocurrent measurement
  - Transient absorption (TA) measurement
- CdSe QD solar cell
  - Sample preparation
  - Optical properties
  - Device studies
  - Electron injection
- Electron injection in multi exciton regime in CdSe solar cell

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Activity for solar in Japan after EQ on 3/11

- **Prime minister of Japan**

  "Renewable energy will account for 20% of total electricity consumption in Japan in 2020s"

- **Softbank Co.(Communication), Mitsui& Co. Ltd.(Trading)**
  - **Investment in "Mega" Solar project.**
- **Nissan, Honda (Car manufacturing)**
  - **Smart house project using their battery technology.**

Expanding investment in "Solar"

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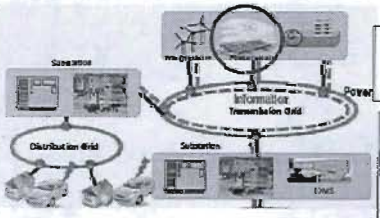
Activity for solar at Sharp

Smart Grid project in Hawaii*



STATE OF HAWAII

U.S. DEPARTMENT OF ENERGY

NEDO **

*the Japan-U.S. Clean Energy Technologies Action Plan

**New Energy and Industrial Technology Development Organization

73MW installation in the Kingdom of Thailand

Eco House project

State

Residence

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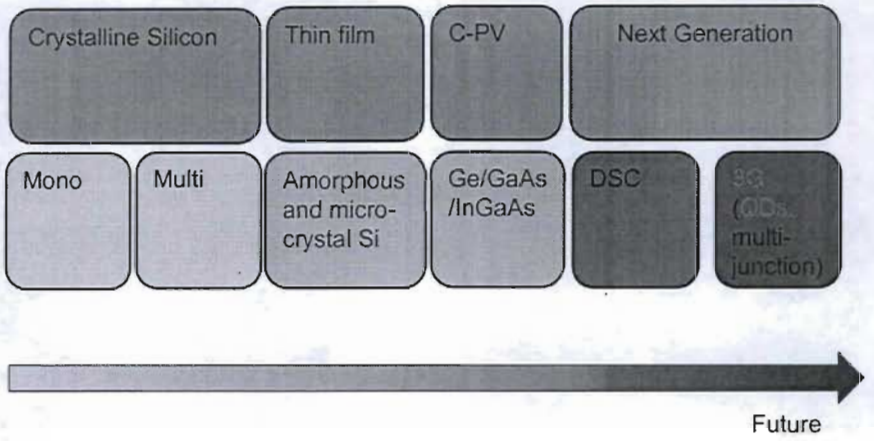
Sharp Solar Cell Technology Portfolio



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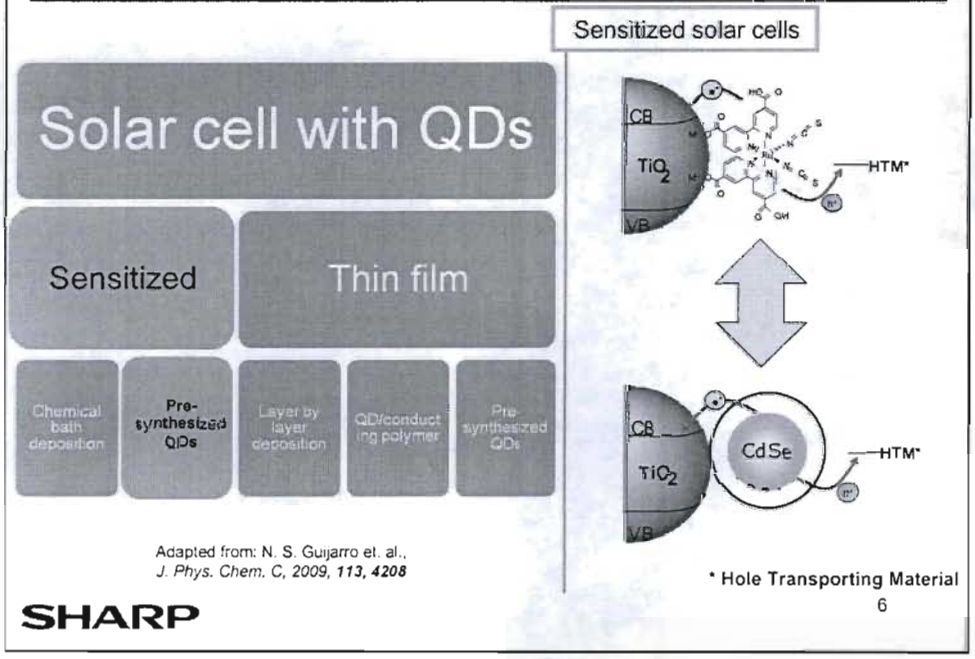
QD solar cells



Adapted from: N. S. Guijarro et. al., *J. Phys. Chem. C, 2009, **113, 4208***

* Hole Transporting Material

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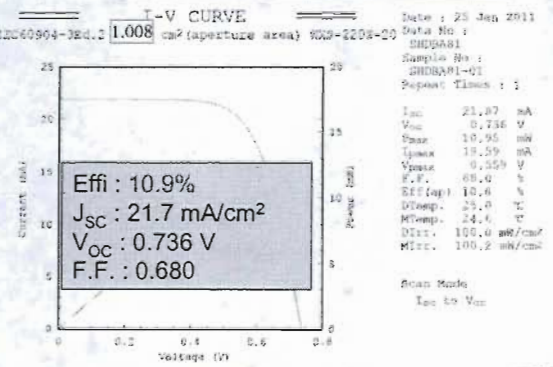
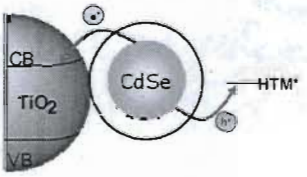
Why QDs in sensitized solar cells?

The highest confirmed efficiency of Dye Sensitized solar cell (DSCs, 1cm²)



Prog. Photovolt: Res. (2011),19,565

AIST



DSC tech. with QDs

Eff(QDSSC)>Eff(DSC)

Our goal is to achieve higher conversion efficiency with QDs than with dyes.

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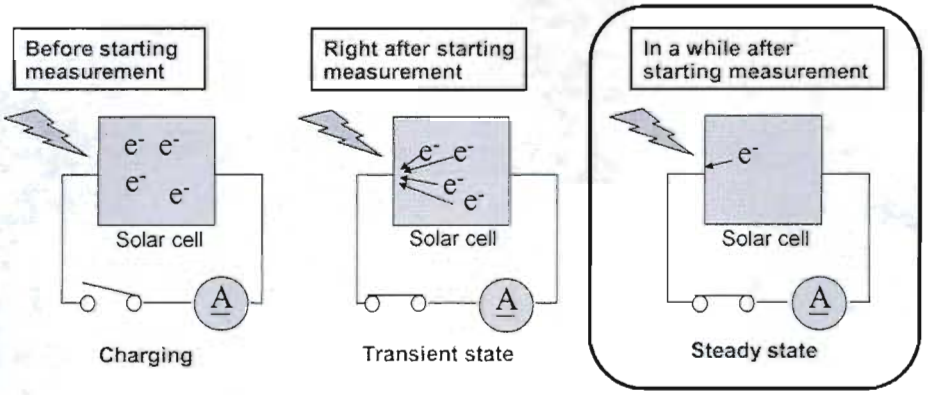
Photocurrent measurement in DSC



To avoid distortions in photocurrent measurement due to transient current, waiting time before the measurement must be **over 200ms** in Dye sensitized solar cell*.

*N. Koide et. al, Rev. Sci. Instrum., 2004, 75, 2828

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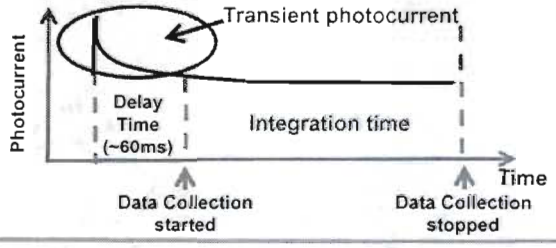
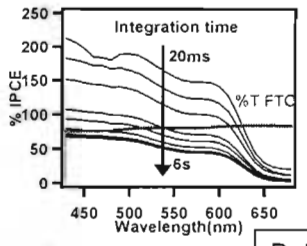
Photocurrent measurement in QDDSCs

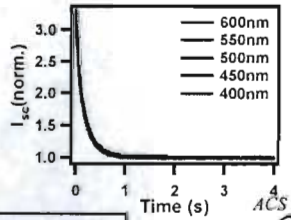
Sequence of the photocurrent measurement



Integration time dependence



Transient photocurrent



ACS Nano, 2010, 4 , 6377

Delay time 60ms → 2s

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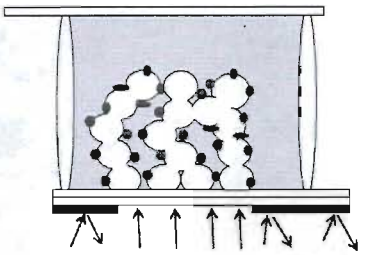
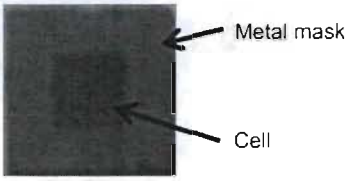
Photocurrent measurement – Mask effect



→ Path of incident light

▬ Metal mask



Photocurrent difference using mask*

Cell size	w/o mask	w/ mask
5mm sq	24.1 mA/cm^2	20.7 mA/cm^2
10mm sq	22.8 mA/cm^2	20.8 mA/cm^2

*Sharp tech. Journal vol.25 (2005)

Masks are needed to prevent overestimation of photocurrent.

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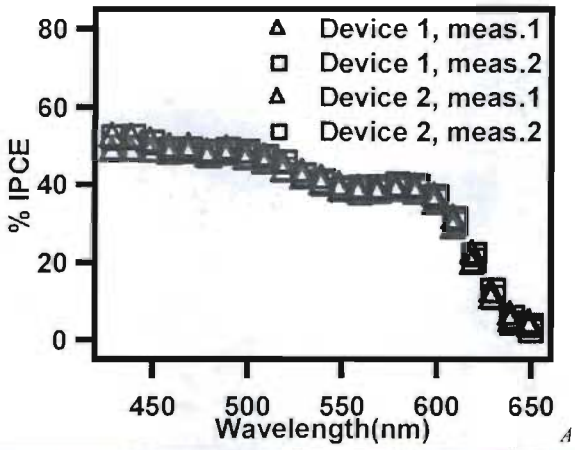
Photocurrent measurement – IPCE



ACS Nano, 2010, 4 , 6377

IPCEs of samples fabricated using the same procedure are very reproducible.

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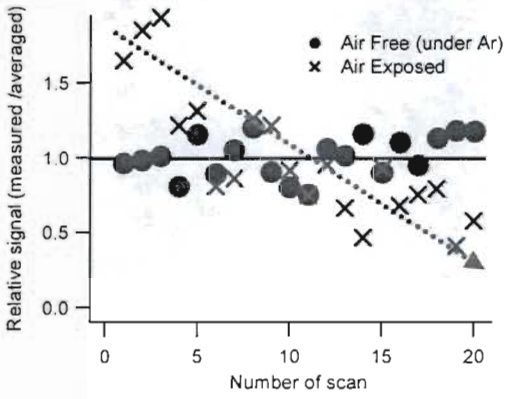
TA measurement (sample degradation)



TA signal at the peak of the 1s bleach (590nm) for TOPO-CdSe-QD/TiO_2 film as a function of number of scans.
The excitation energy was 3.1 eV, $<N_{abs}>$~3 AF, $<N_{abs}>$~0.3 AE

Chem. Commun., 2011, **47**, 6437

The degradation of CdSe-QD/TiO_2 films during the TA measurement can be avoided by using air free conditions and a translating stage.

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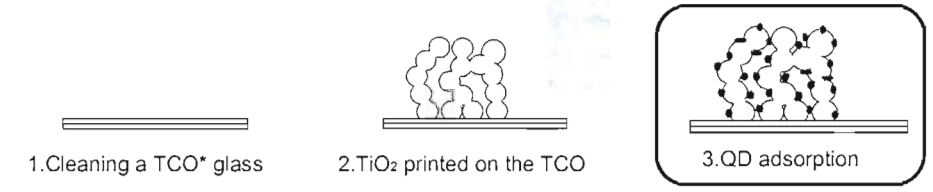
  - Device studies
  - Electron injection
- Electron injection in multi exciton regime in CdSe solar cell

Device Fabrication

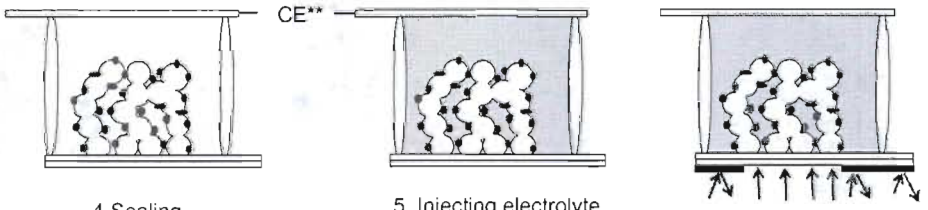


1.Cleaning a TCO* glass

2.TiO_2 printed on the TCO

3.QD adsorption

*TCO: Transparent conducting oxide



4.Sealing

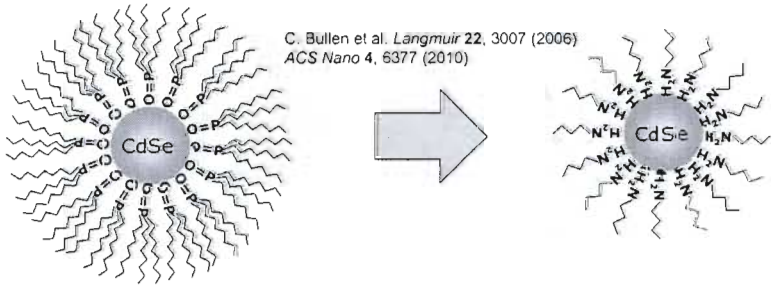
5. Injecting electrolyte

6. Placing black metal mask on the glass

**CE: Counter electrode

→ Path of incident light

Surface ligand exchange



C. Bullen et al. *Langmuir* **22**, 3007 (2006)
ACS Nano **4**, 6377 (2010)

TOPO: O=P

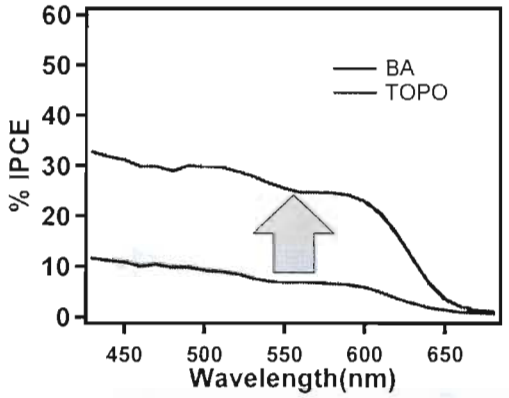
~1.1 nm

BA: H_2N

~0.4 nm

C. B. Murray et al. *J. Am. Chem.* Soc. **115**, 8706 (1993).

Device studies – IPCE



IPCE of QDSSC improved using BA instead of TOPO as a ligand.

The components of IPCE

Electron injection into TiO_2 from QDs Electron/hole transport

$$IPCE = LHE \cdot \Phi_{INJ} \cdot \Phi_{COLL}$$

Incident photon-to-current conversion efficiency

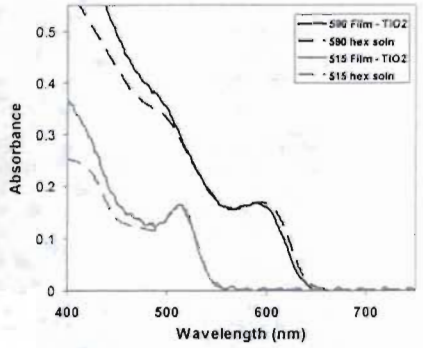
Light Harvesting efficiency

Electron injection efficiency

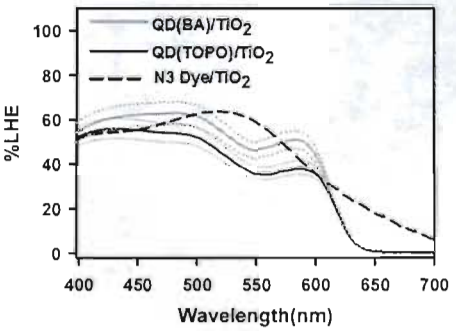
Carrier collection efficiency

Optical properties of QD/TiO_2 films -LHE

Absorption spectra



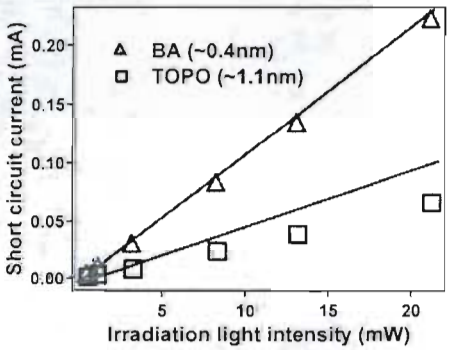
LHE



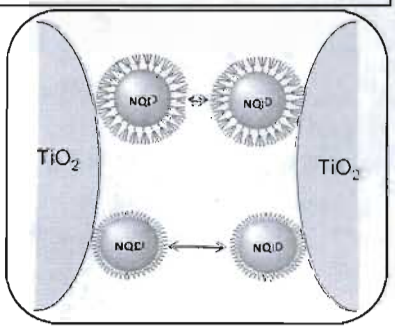
- QD/TiO_2 films have optical properties similar to QD solutions.
- LHE improvement using BA is attributed to the reduction in ligand length, which allows higher QD loading.

Device studies – hole transport

J_{sc} dependence on light intensity



Structure of pores in QD/TiO_2 films

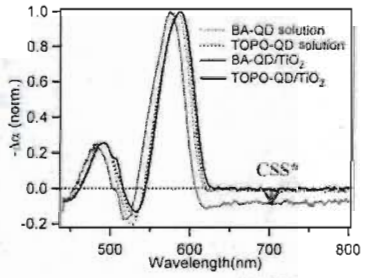


hole transport (BA capped dots) > hole transport (TOPO capped dots)

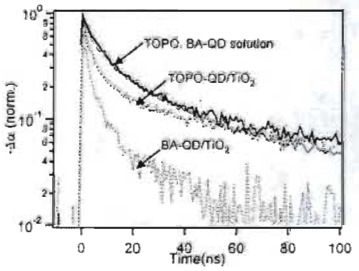
- Hole (Mass) transport limitation are observed using TOPO capped QDs.
- This is likely due to more room for hole transporter to diffuse within TiO_2 pores with BA capped QDs.

Electron injection studies – 1S feature in TA

TA spectra at 0ns



Dynamics of 1S bleaching (at 580nm)



*CSS: Charge Separated State

Ref: Martı´nez-Ferrero et al,
Phys. Chem. Chem. Phys., 2010, 12, 2819

$\tau_{BA} << \tau_{TOPO}$

Electron injection from BA-QDs is more efficient than from TOPO-QDs.

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Electron injection dynamics

Lifetime of 1S bleaching

	τ (ns)	β
TOPO-QD Solution	8.71 ± 0.21	0.57 ± 0.008
TOPO-QD/TiO2	3.47 ± 0.14	0.42 ± 0.008
BA-QD Solution	8.39 ± 0.13	0.55 ± 0.005
BA-QD/TiO2	1.49 ± 0.05	0.48 ± 0.009

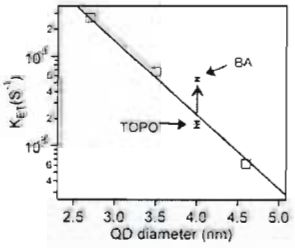
Stretched exponential

$$\Delta A(t) = \Delta A(0) \times \exp[-(t/\tau)^{\beta}]$$

Rate constant

$$K_{ET} = 1/\tau_{QD/TiO2} - 1/\tau_{QD\,Solution}$$

Electron transfer rate vs QD diameter



□ :I. Robel, *et al*, *J. Am. Chem. Soc.*, 2007, **129**, 4136

Using linker (mercaptopropionic acid) for QD adsorption

Electron injection from BA-QDs is faster than from TOPO-QDs without or with the use of linkers.

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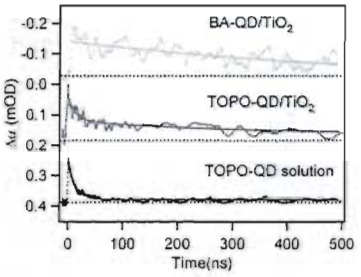
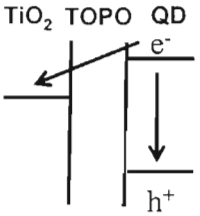
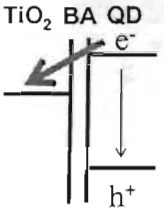
Electron injection studies – TA in NIR

TA signals probed at 1200nm

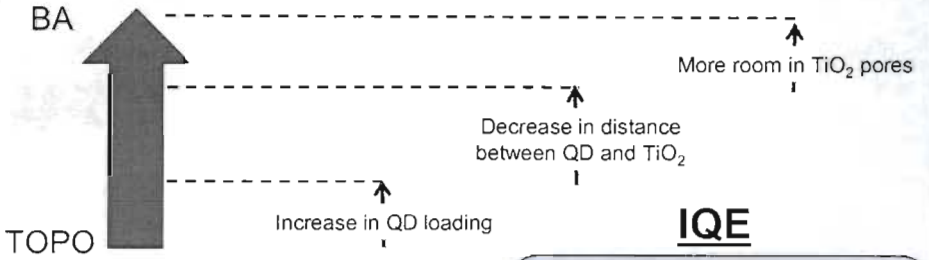






Electron injection from BA-QDs is faster than from TOPO-QDs without the use of linkers.

Summary – BA effect on IPCE



IQE

$$IPCE = LHE \cdot \Phi_{INJ} \cdot \Phi_{COLL}$$

Incident photon-to-current conversion efficiency

Light Harvesting efficiency

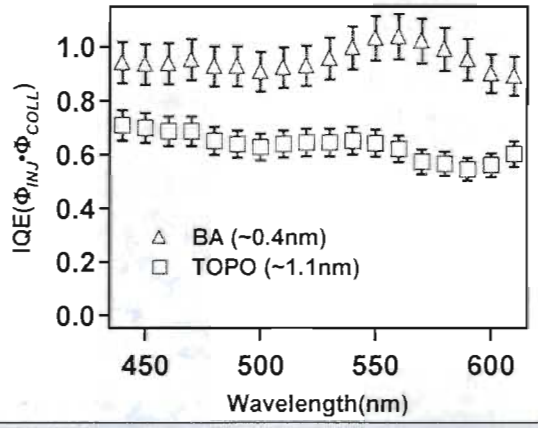
Electron injection efficiency

Carrier(Hole) collection efficiency

BA improves three components of IPCE.

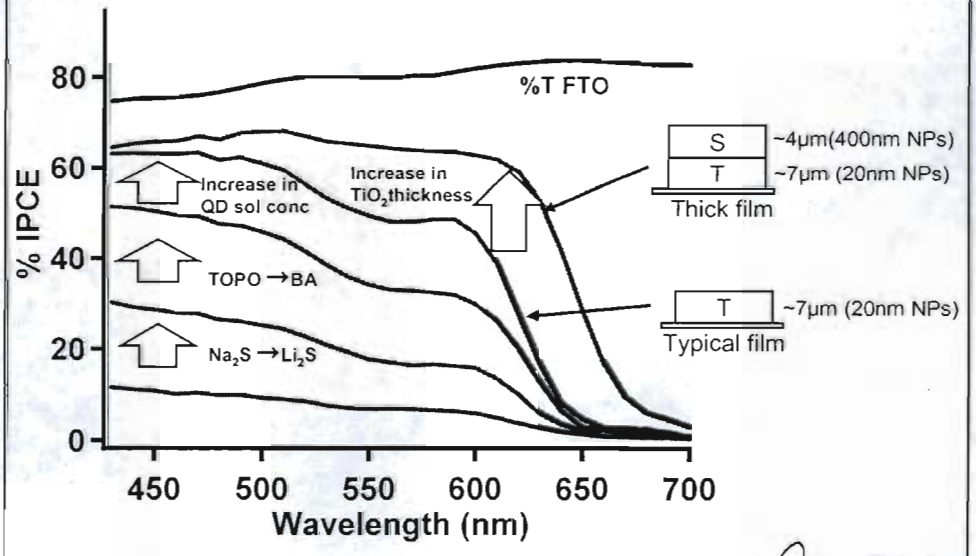
Device studies – IQE

$$IQE = IPCE/(\%T(FTO)\cdot LHE) = \Phi_{INJ}\cdot\Phi_{COLL}$$



Best devices show IQEs ~1: both electron injection efficiency and charge collection efficiency are close to 100%.

Device studies – IPCE improvement



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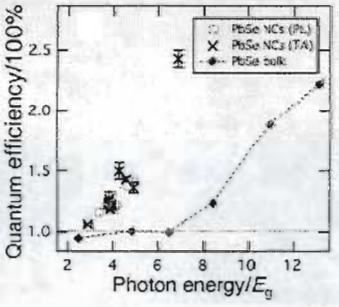
- Electron injection efficiency from CdSe QDs to TiO_2 in multi exciton regime.

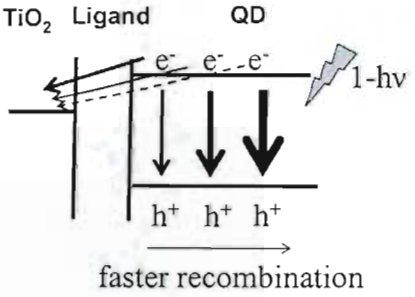
MEG(CM) for Solar Cell

MEG(CM) effect



J. A. McGuire, M. Sykora, J. Joo, J. M. Pietryga, and Victor I. Klimov, *Nano Lett.* **2010**, *10*, 2049–2057

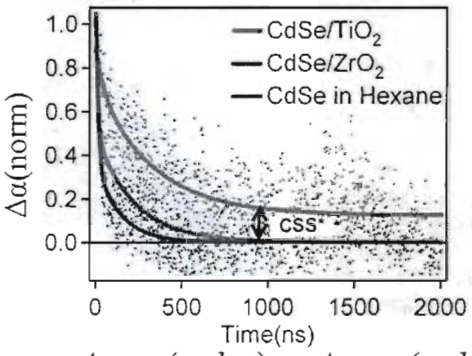
Energy diagram in MEG(CM) regime



Objective is to observe electron injection in multi exciton regime (not MEG(CM)) using CdSe(BA)/TiO_2 interface with efficient electron injection.

TA relaxation dynamics

TA signals probed at 1200nm



E_g(CdSe) = 2.4 eV (515 nm)

CSS:
Charge separated state

$$y = \underbrace{A_1 \exp(-k_1 t)}_{\text{Fast component (Recombination within QDs)}} + \underbrace{A_2 \exp(-k_2 t)}_{\text{Slow component (Recombination of CSS)}}$$

Long-lived component is assigned to the $QD^+/TiO_2(e^-)$ charge separated state (CSS).

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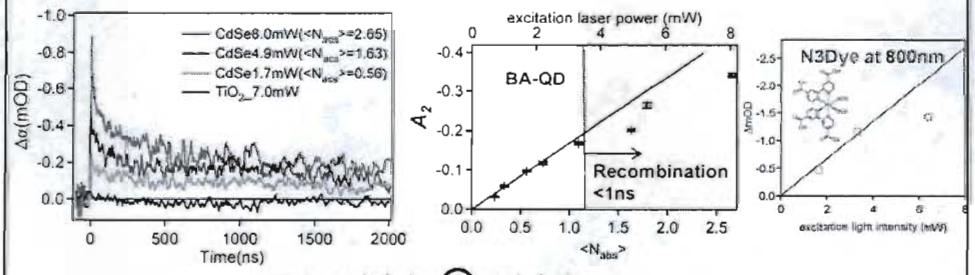
TA -Electron injection study

TA signals probed at 1200nm

A_2 vs excitation light intensity



$$y = A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t)$$

The fraction of CSSs

The fraction of CSSs is likely larger than estimated using A_2.

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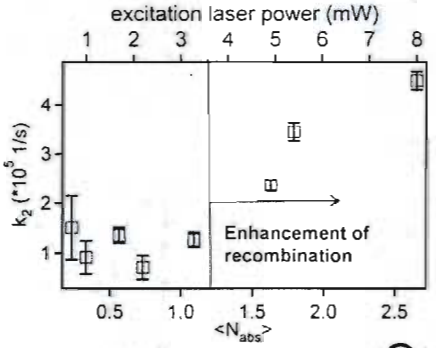
CSS recombination rate

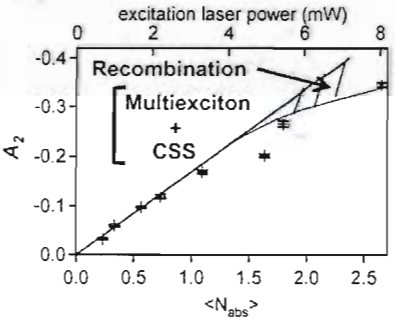
CSS recombination rate vs excitation light intensity



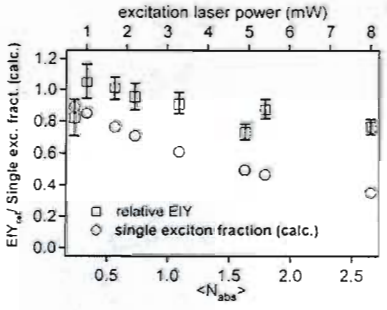
CSS recombination is enhanced as number of CSSs increases, similar to DSSCs.

Estimation of relative electron injection yield

A_2 vs excitation light intensity



Relative electron injection yield



Electrons in multi-exciton regime can be injected to TiO_2.

Summary

- Change of QD surface passivation layer from TOPO to BA leads to significant improvement of IPCE for the CdSe/TiO_2 QDSSC.
- The ligand substitution leads to increase in LHE, Electron injection and hole collection efficiencies.
- Approximately 100% IQE is achievable in the improved QDSSCs
- Electrons in multi exciton regime can be effectively injected into TiO_2 from CdSe QDs.

Acknowledgements

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•We thank Dr. Victor Klimov of Los Alamos National Laboratory for equipment use.

Thank you!

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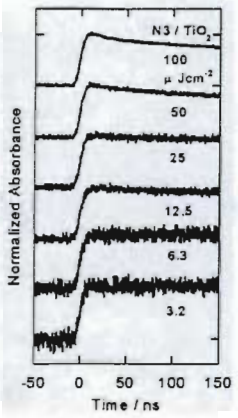
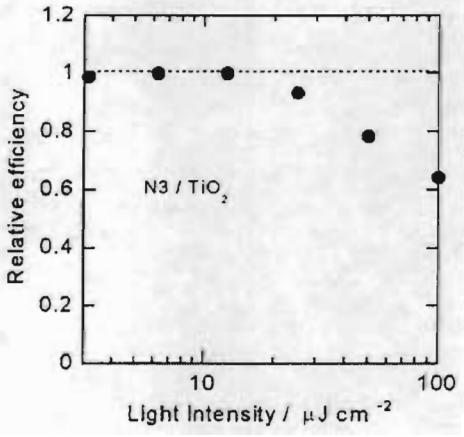
"Sincerity and Creativity"

Electron injection efficiency of DSC





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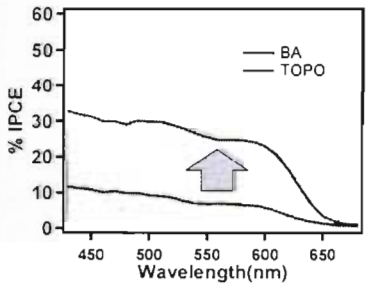
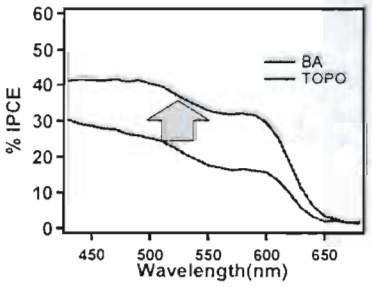
Device studies – IPCE

Na_2S



Li_2S



IPCE of QDDSC improved using

- Li_2S instead of Na_2S
- BA instead of TOPO

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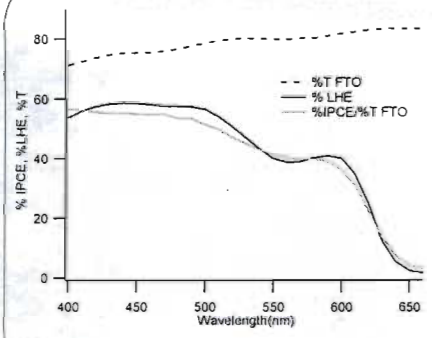
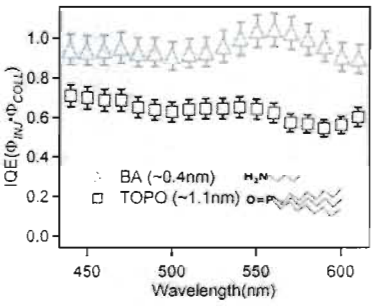
IQE studies

$$IPCE / \%T(FTO) = LHE \cdot \Phi_{INJ} \cdot \Phi_{COLL}$$



IPCE using BA capped QD/TiO_2 (5μm)

$$IPCE / (\%T(FTO) \cdot LHE) = \Phi_{INJ} \cdot \Phi_{COLL}$$



·Internal quantum yield ~1

- In most devices we observe IPCEs to be comparable with LHEs, which indicates high Internal quantum yield (IQE)
- Best devices show IQEs ~1, which means that both electron injection efficiency and charge collection efficiency is close to 100%.
- The best performance is observed in devices using BA-capped QDs

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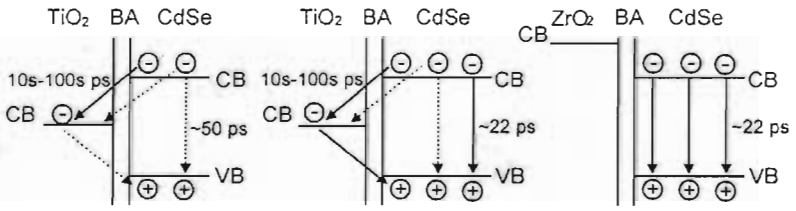
Electron injection in multi exciton regime

Scheme of electron injection in multi exciton regime



- Redox (Mass) transport limitation are observed using TOPO capped QDs.
- This is likely due to more room for redox transport in TiO_2 pores with BA capped QDs.

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