Quantum Dot-Sensitized Solar Cells —Photovoltaic Properties and Photoexcited Carrier Dynamics—

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Main Research Plan

- **In order to achieve higher photovoltaic conversion efficiency of quantum dot-sensitized solar cell (QDSSC),**

further basic research on *1) nanostructured TiO_2 electrode* and *2) sensitizer*
is important and essential
(with characterizations of *morphology, structure, optical absorption, charge transfer, energy transfer, recombination processes*, and so on).

Advantages of Semiconductor Quantum Dot as Sensitizer

- Quantum confinement allows for ***energy gap tunable*** across the solar spectrum.
- ***Higher optical absorption*** resulting from quantum confinement.
- ***Larger intrinsic dipole moment*** which may lead to rapid charge separation and band alignment.
- ***Inorganic*** nature.
- Possibility of ***multiple exciton generation***.

The Journal of Physical Chemistry Letters

Perspective

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Breakthroughs in the Development of Semiconductor-Sensitized Solar Cells

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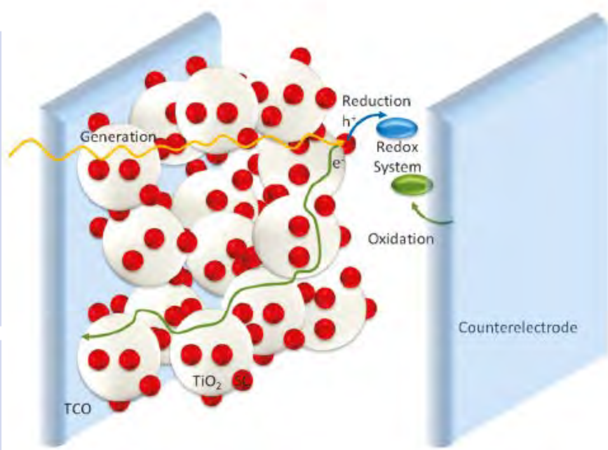
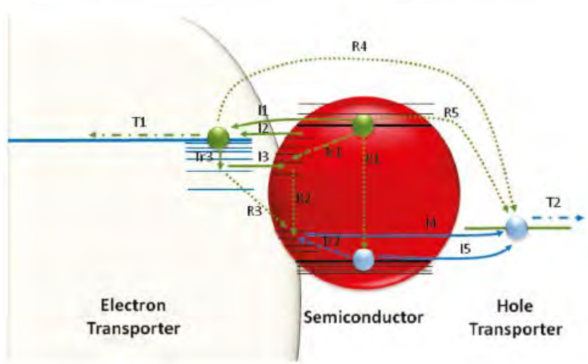
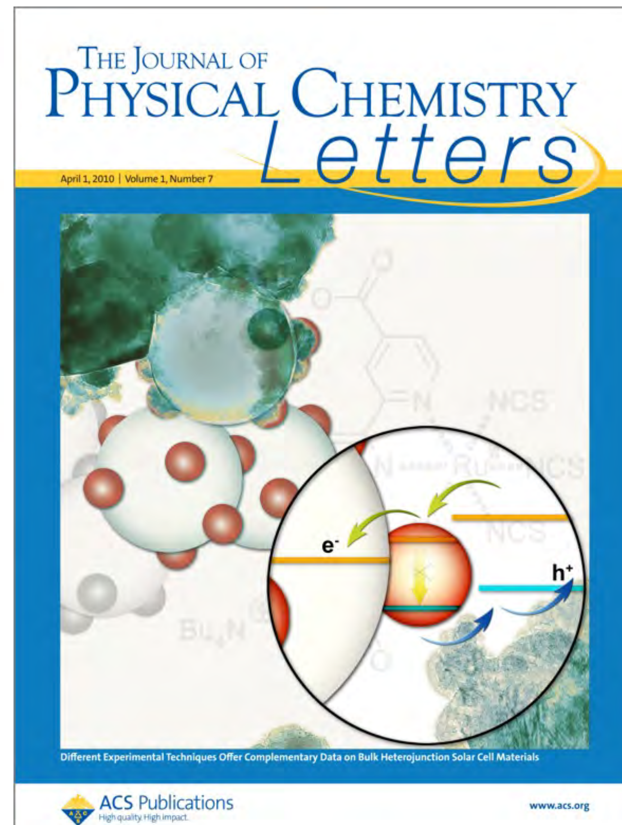
Starting from quite low conversion efficiencies, these semiconductor sensitized solar cells have grown very rapidly to values around 4−5%.

Breakthroughs will come from (i) materials, (ii) surface treatments, and (iii) nanocomposite absorbers.

The semiconductor light-absorber properties dictate the requirements that the other components of the device need to satisfy.







Motivations

- Morphologies of TiO_2 electrodes and choices of sensitizers are important factors for sensitized solar cells.

  → In this study, *we prepare* *inverse opal TiO_2 (& TiO_2 nanotube) electrodes* adsorbed with *multilayered semiconductor quantum dots of CdS/CdSe*.

- Relaxation processes in photoexcited carriers are important factors not only for basic studies but applied research in solar cells.

  → In this study, we characterize *the* *ultrafast photoexcited carrier dynamics* of inverse opal TiO_2 electrodes with multilayred semiconductor quantum dots.

Preparation of CdS/CdSe QDs on *NC* and *IO* TiO_2

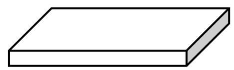
1. Nanostructured TiO_2 electrodes

- TiO_2 nanoparticles (15 nm)
- PEG (Molecular weight : 500000)
- Acetylaceton
- Pure water

⇩

- Mix and Paste applied onto FTO glass
- Annealed at 450 ºC for 30 min

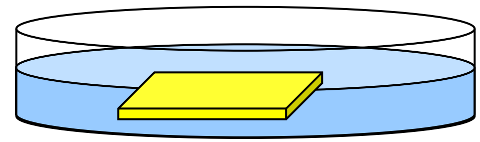
⇨



Nanostructured TiO_2 electrodes

2. Adsorption with CdS QDs [1)]

at 10 °C

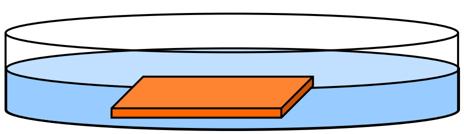


20 mM $CdCl_2$
66 mM NH_4Cl
140 mM Thiourea
230 mM Ammonia

1) R. Jayakrishnan et al., *Semicond. Sci. Technol.* 11 (1996) 116.

3. Adsorption with CdSe QDs [2)]

at 10 °C



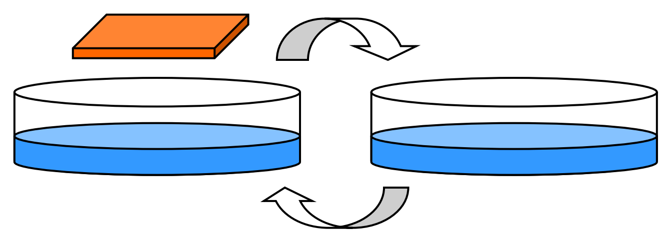
80 mM $CdSO_4$
120 mM $N(CH_2COONa)_3$
80 mM Na_2SeSO_3

2) S. Gorer and G. Hodes, *J. Phys. Chem.* 98 (1994) 5338.

4. Passivation with ZnS [3)]

In order to improve its photo-stability

2 cycles

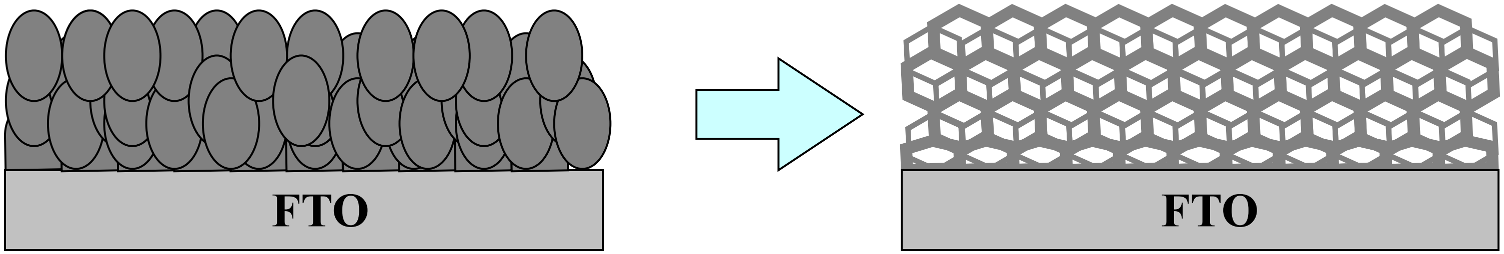


0.1 M $Zn(CH_3COO)_2$ 0.1 M Na_2S

3) S.M.Yang et al., J. Mater. *Chem.* 12 (2002) 1459.

Improvement

Electrode Structure



Disordered Structure
(Nanocrystalline TiO_2)

Ordered Structure
(Inverse Opal TiO_2)

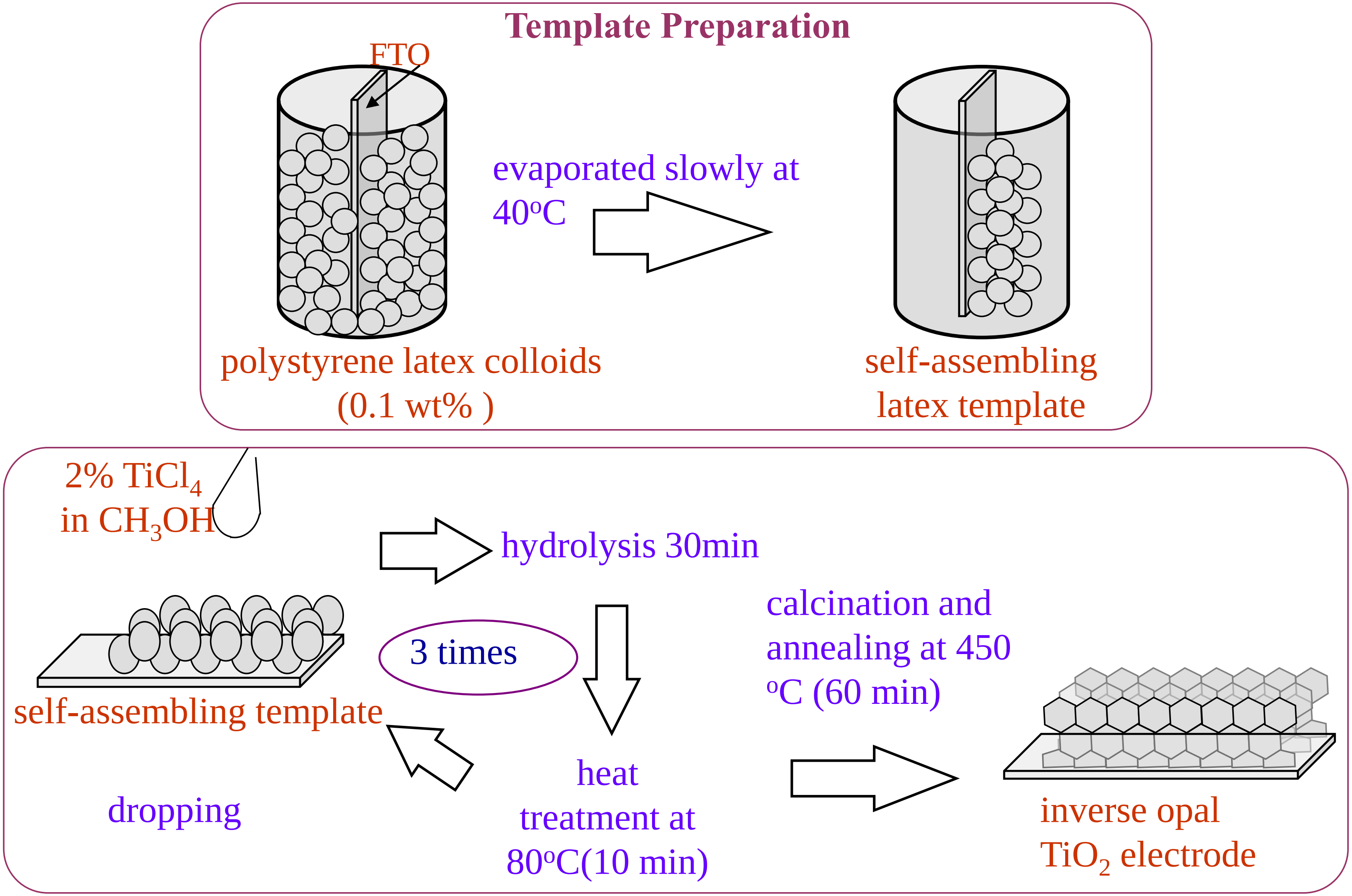
Advantages of *inverse opal structure* in solar cell application are,

(1) *Smooth electron transport* owing to topological inter-connected material.

(2) *Better penetration of sensitizer* owing to macroporous structure.

(3) *Enhancement of optical absorption* owing to photon localization.

Preparation of Inverse Opal TiO_2 Electrode

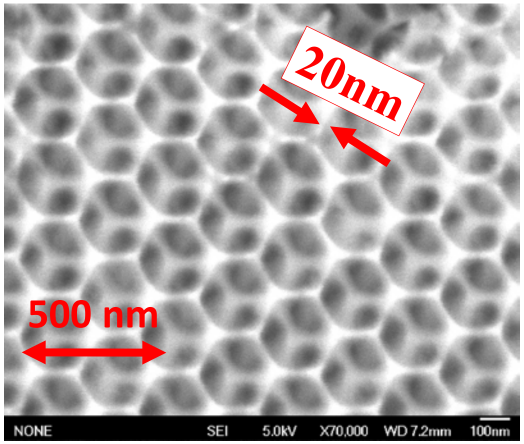


L. J. Diguna et. al., ***Jpn. J. Appl. Phys.*** **45 (2006) 5563.**

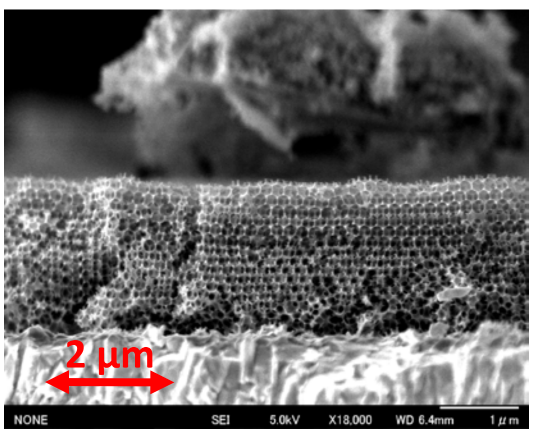
SEM Images

Inverse Opal (IO) TiO_2

Top View



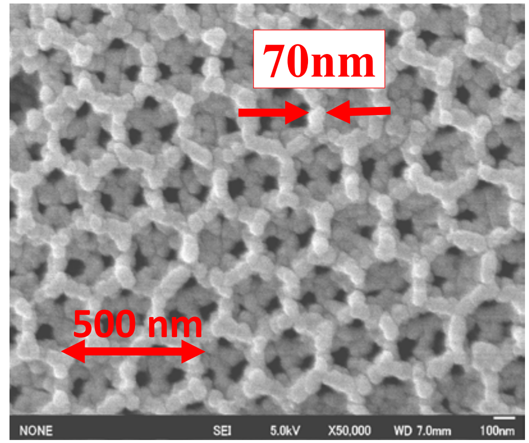
Cross Section

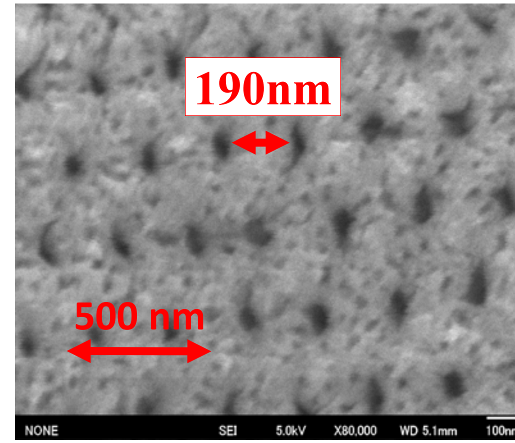


Chemical adsorption

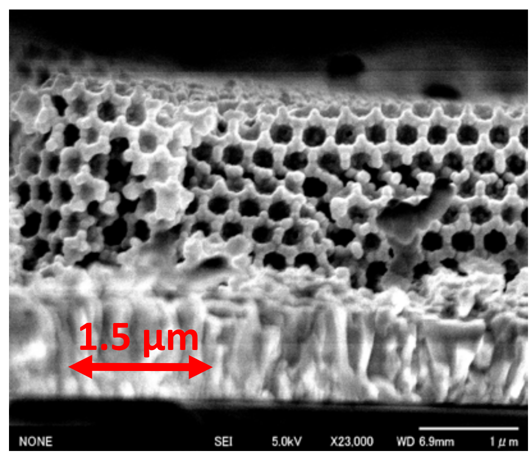
IO TiO_2 adsorbed with CdSe QDs

8 h Top View **24 h**





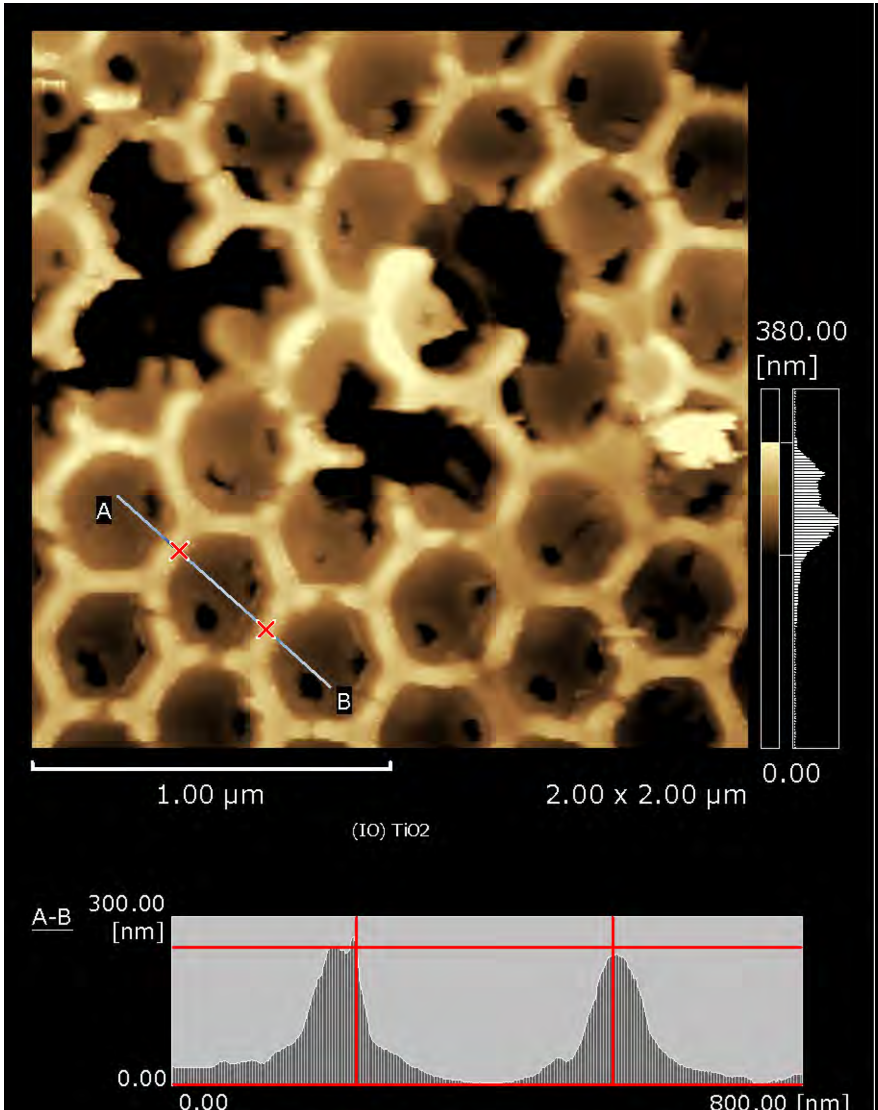
8h Cross Section



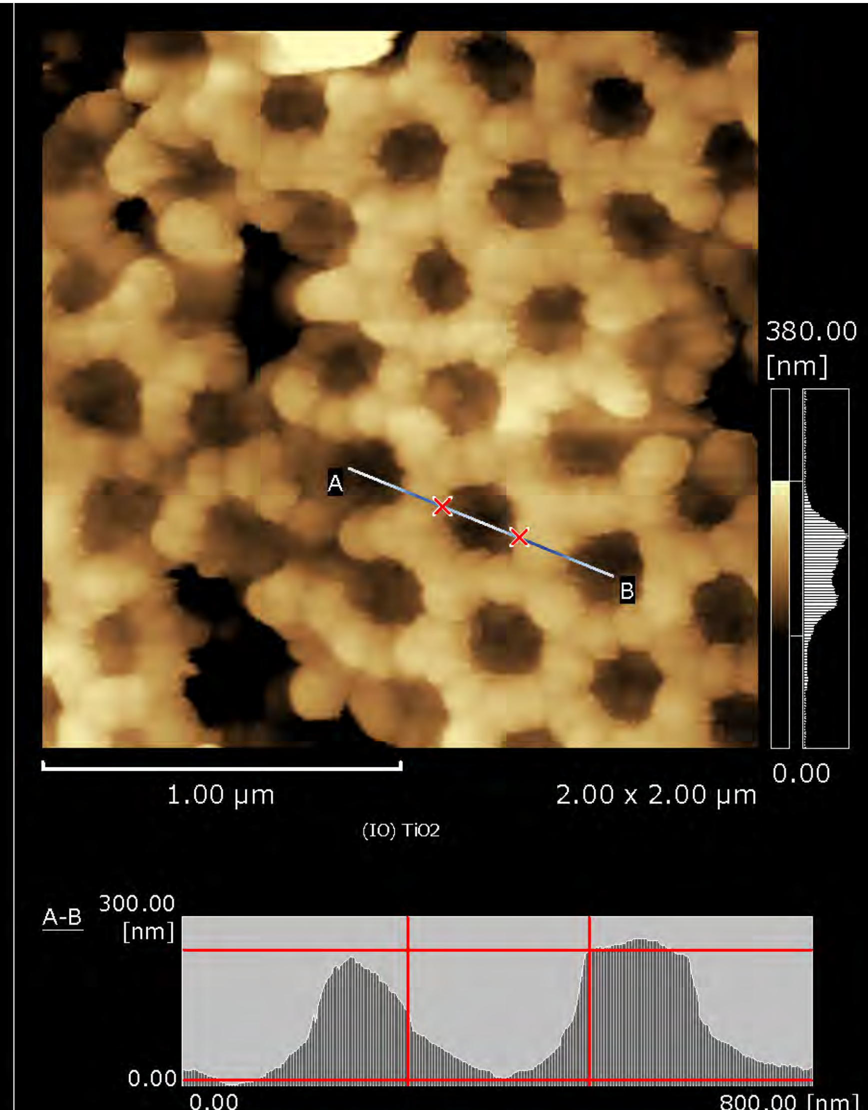
For longer adsorption,

- *increase of CdSe QD size and amount.*

(ＩＯ)



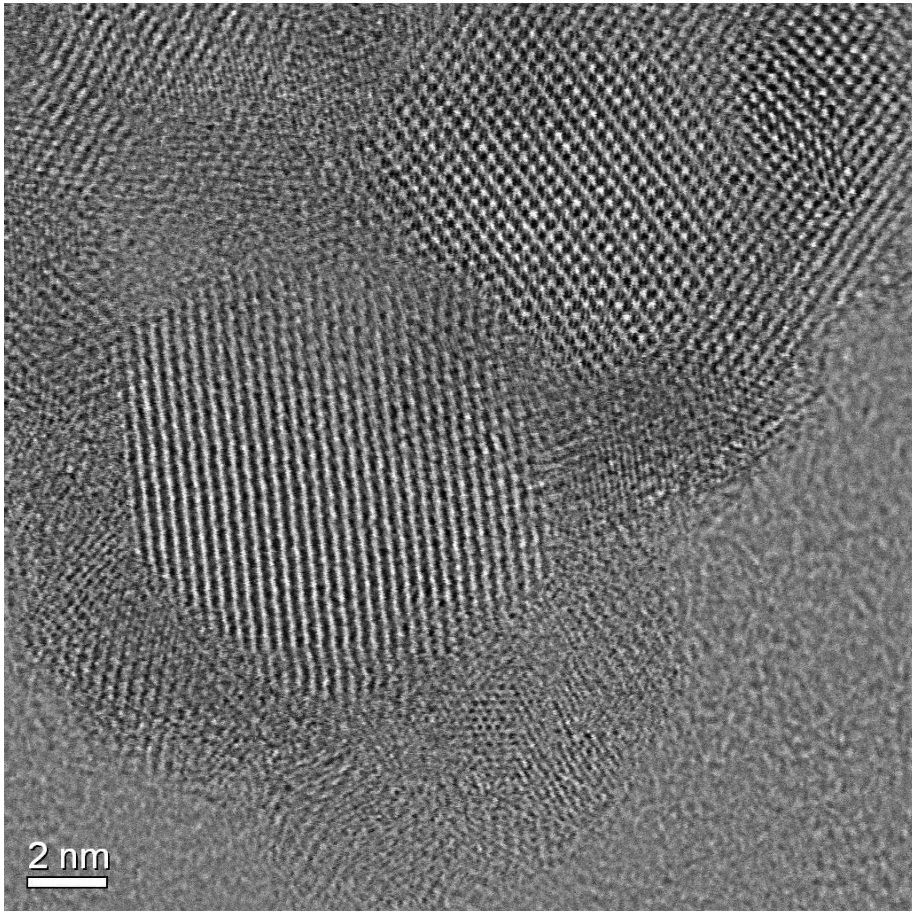
	距離[nm]	高さ[nm]	角度[°]
—	326.06	247.06	37.15



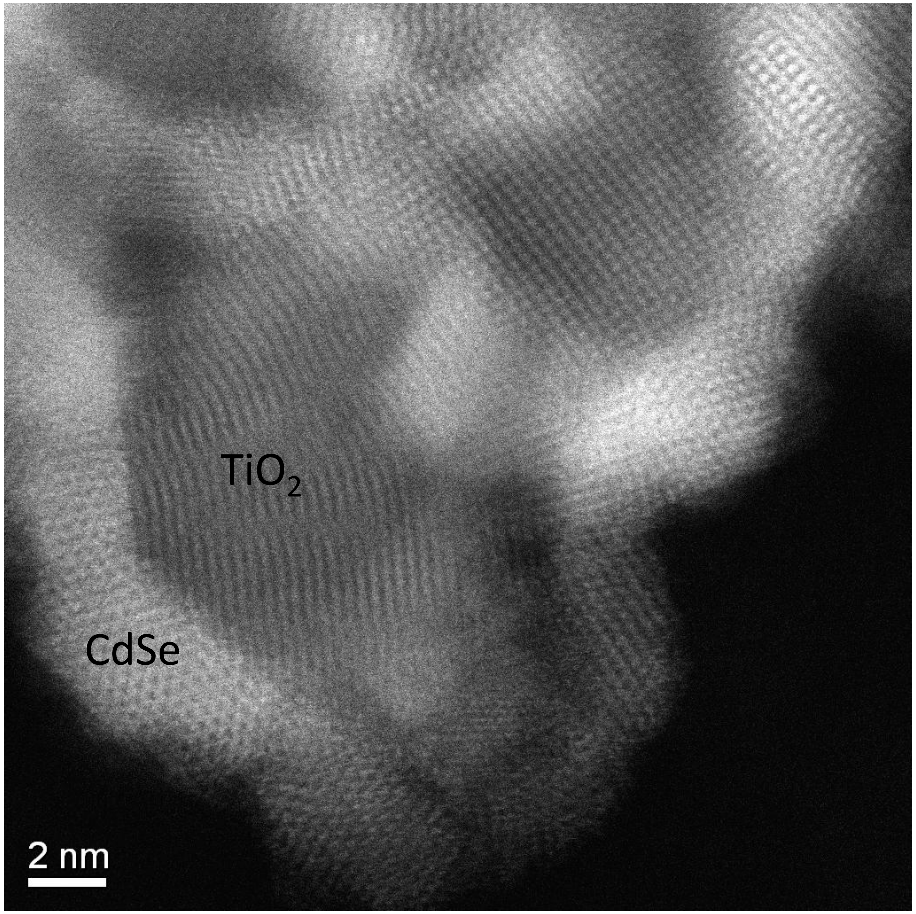
	距離[nm]	高さ[nm]	角度[°]
—	231.63	234.45	45.35

Sample：TiO_2/CdSe/ZnS

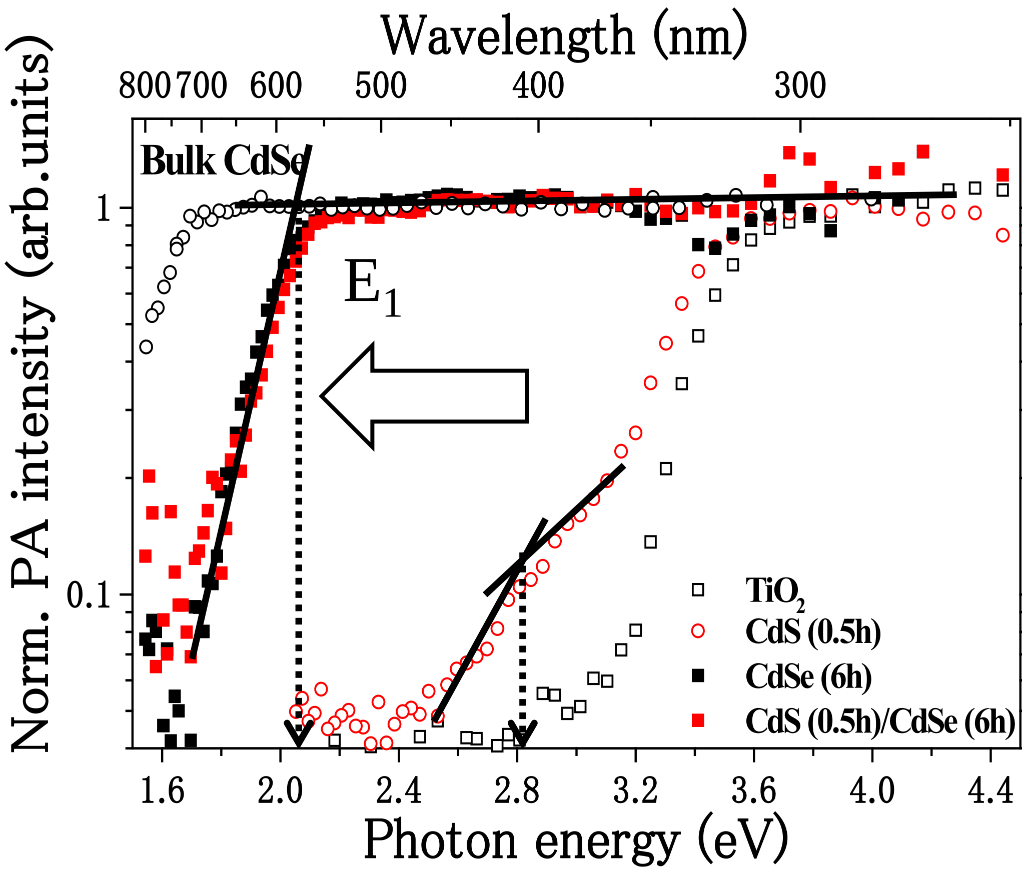
BF-STEM Image



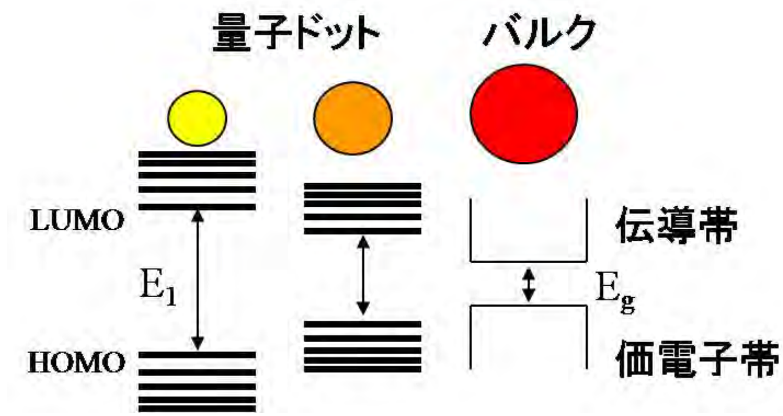
HAADF-STEM Image



Photoacoustic Spectra



CdS (bulk) : Eg= 2.4 eV
CdSe (bulk) : Eg= 1.7 eV



Estimation of average size of each quantum dots

CdS QDs	: 4.4 nm (0.5 h)
CdSe QDs	: 7.0 nm (6 h)

Effective mass apprpximation[1)]

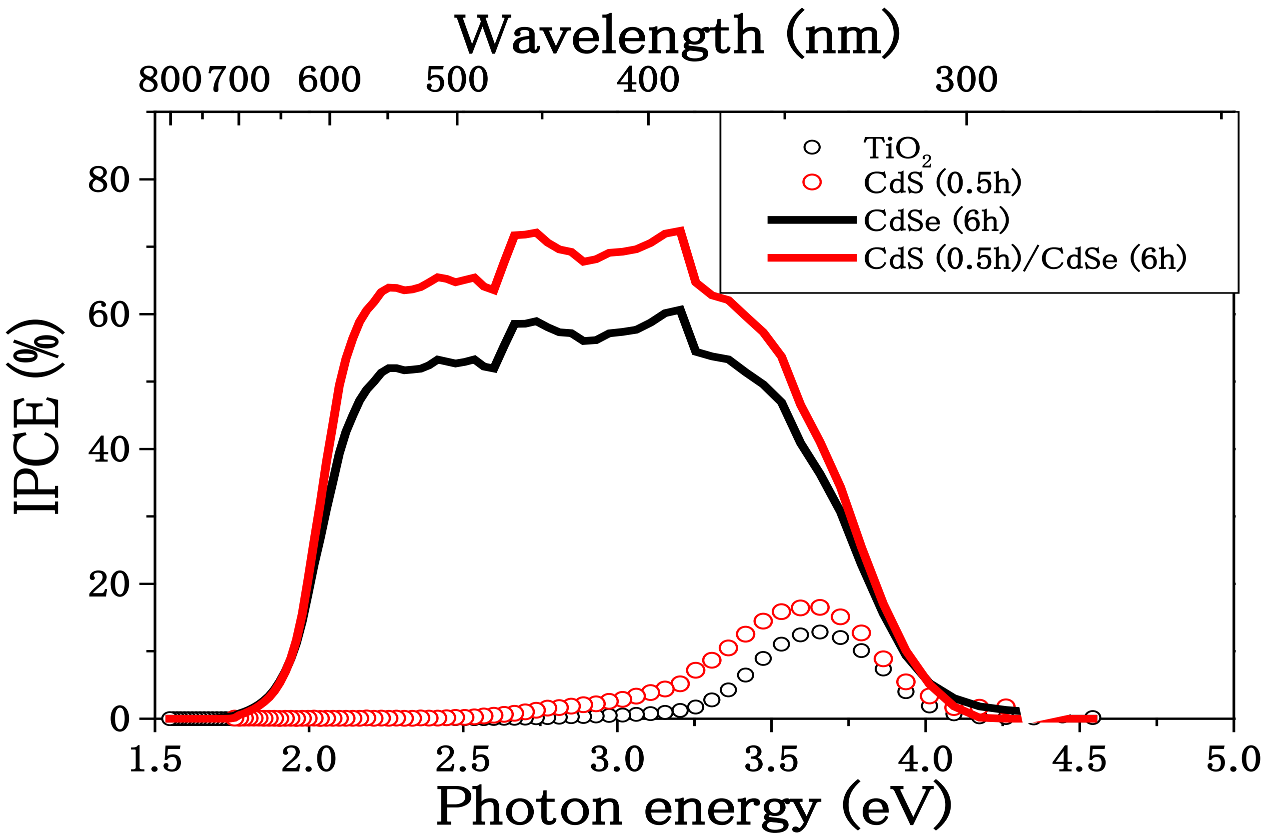
$$\Delta E = E_1 - E_g = \frac{h^2\pi^2}{2\mu a^2} \quad (D = 2a)$$

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$

m_e : electron effective mass
m_h: hole effective mass
E_1 : first excited energy

1) L. E. Brus, *J. Chem. Phys.* **80** (1984) 4403.

IPCE Spectra



Adsoption of CdS QDs at 0.5 hours and CdSe QDs at 6 hours (multi-layered) shows higher IPCE value than CdSe QDs (single-layered) at 6 hours.

55 % → 75 %

Photovoltaic Performance

Short circuit current density(J_{sc})

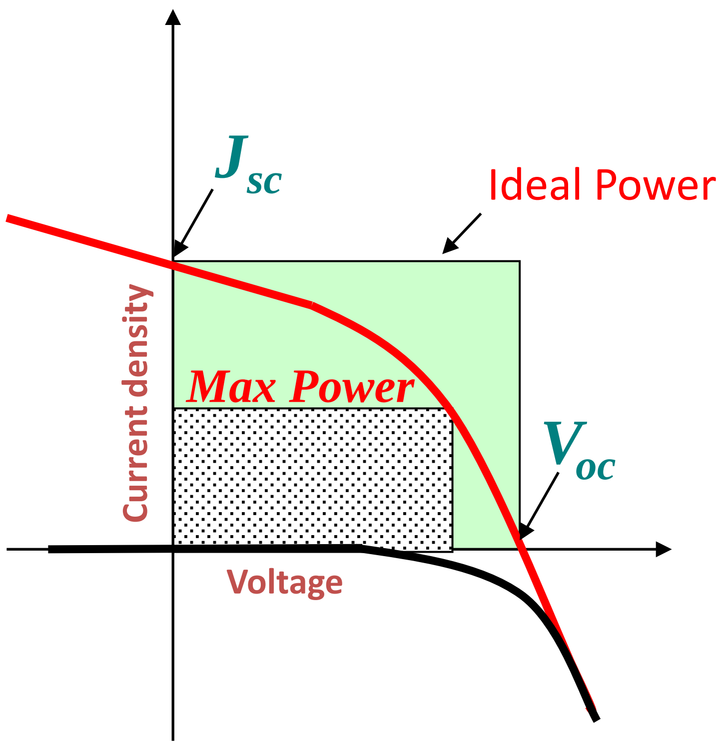
Open circuit voltage (V_{oc})

Fill factor (FF) = $\dfrac{\text{max power}}{\text{ideal power}}$

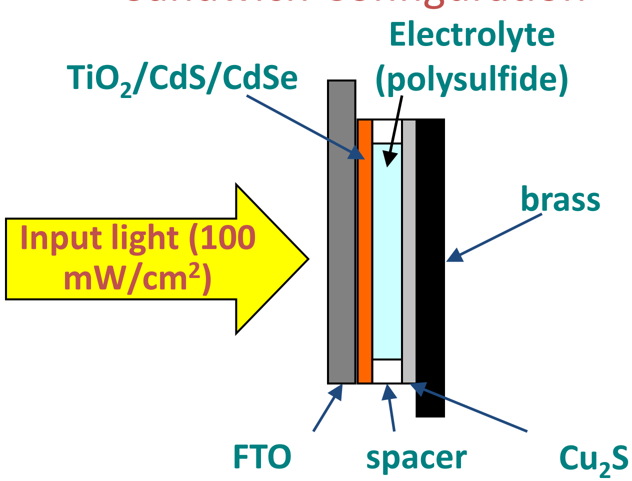
Photovoltaic conversion efficiency (η)

$$\eta = \frac{\text{max power of solar cell}}{\text{power of input light}} \times 100\%$$

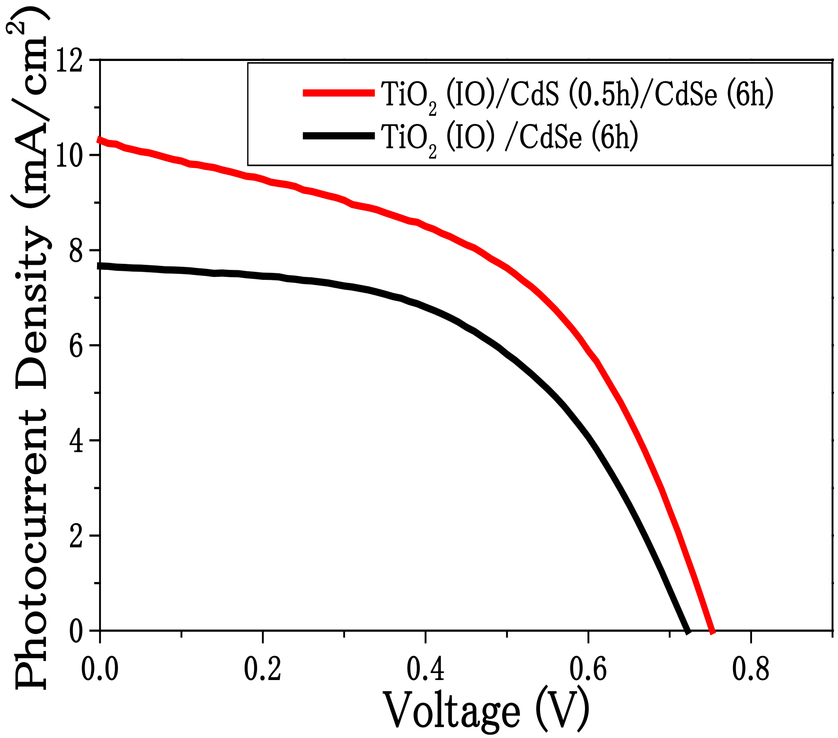
$$= \frac{\text{Jsc x Voc x FF}}{\text{power of input light}} \times 100\%$$

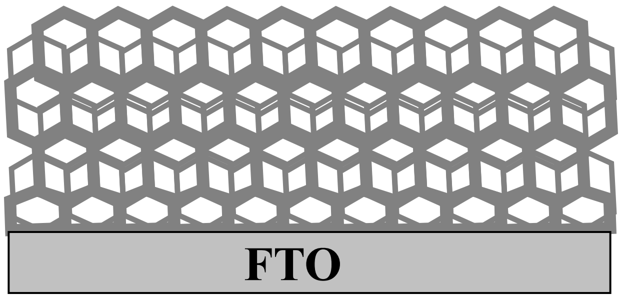


Sandwich Configuration



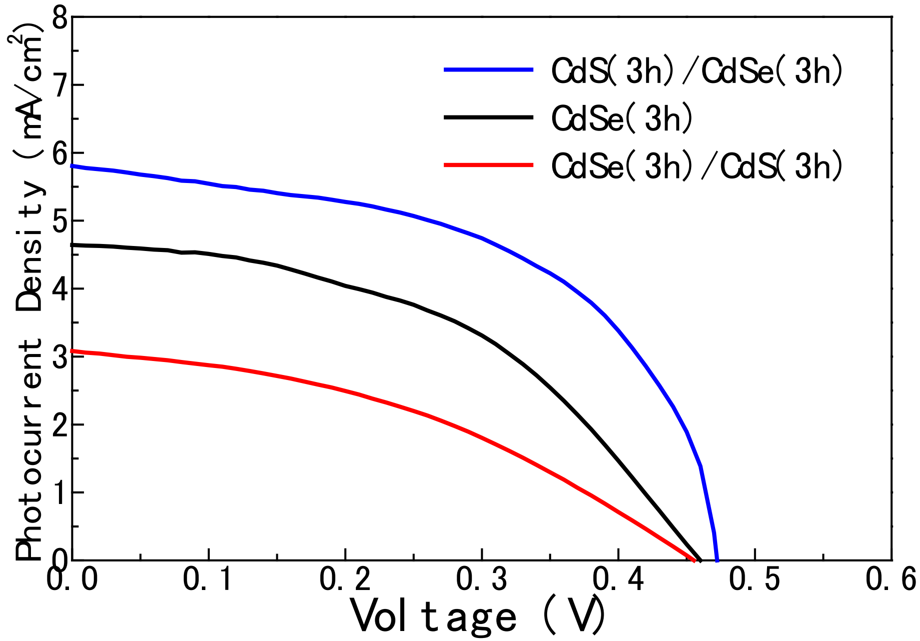
J-V Characteristics

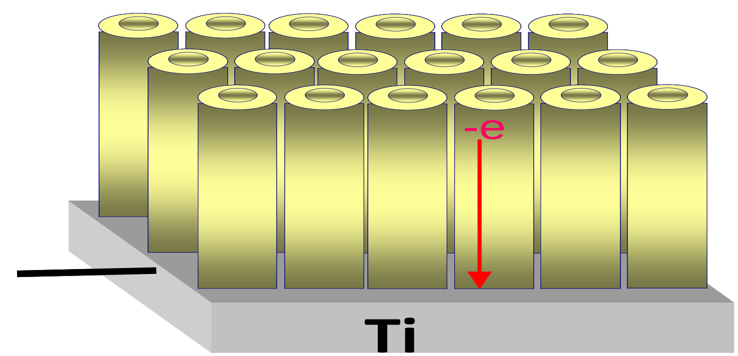




Sample	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
CdSe (6h)	7.7	0.72	0.53	2.9
CdS (0.5h)/CdSe(6h)	10.3	0.75	0.49	3.8

CdS/CdSe QDs on TiO_2 nanotube electrodes

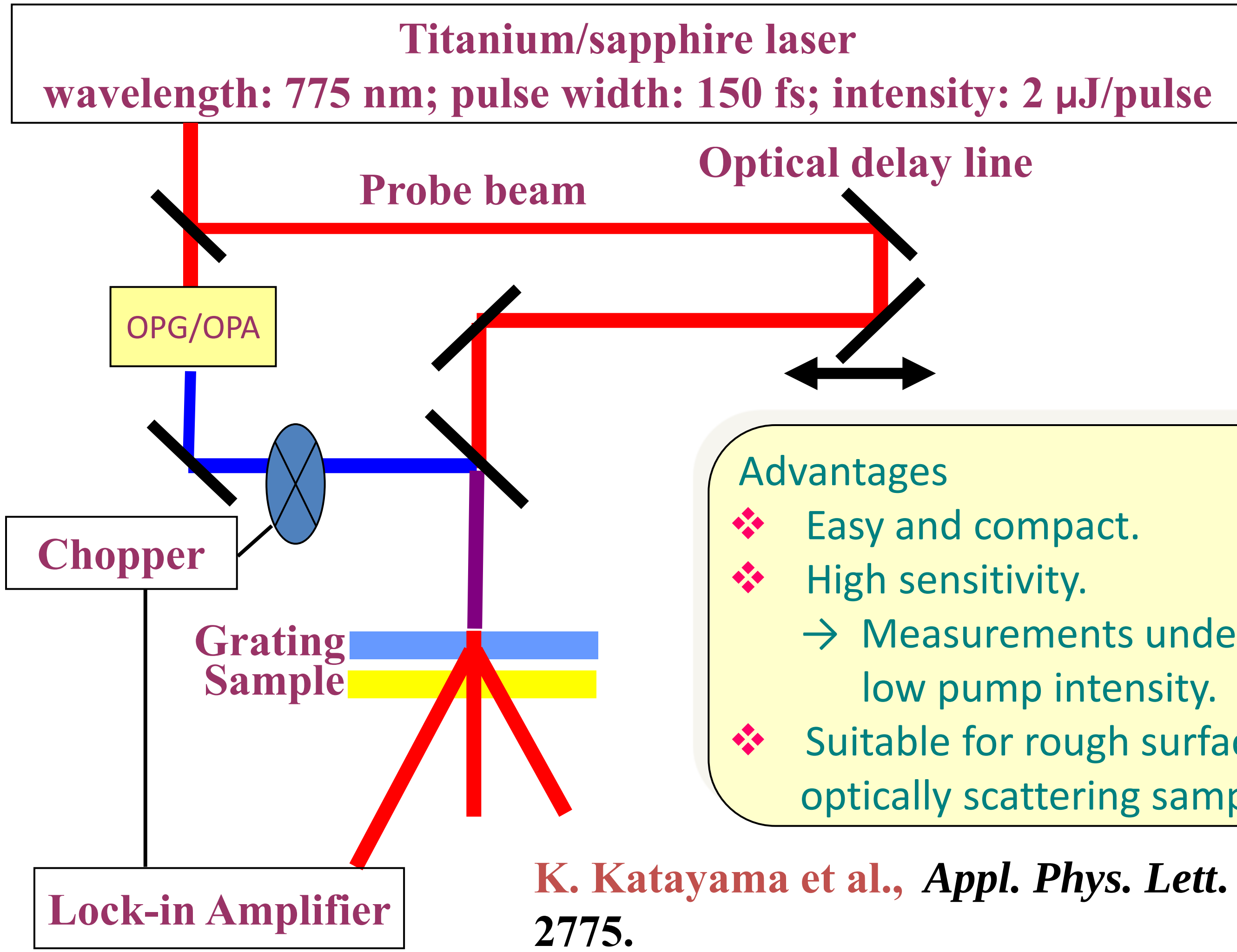




	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)	R_{sh} $(k\Omega \cdot cm^2)$	R_s $(\Omega \cdot cm^2)$
CdS/CdSe	5.8	0.47	0.54	1.48	0.4	7
CdSe(3h)	4.6	0.46	0.46	0.99	0.9	4×10
CdSe/CdS	3.1	0.46	0.40	0.56	0.3	7×10

Improved Transient Grating (TG) Technique

Detailed understanding of photoexcited carrier dynamics is required to understand and improve photovoltaic properties of solar cells, that is satisfied using ultrafast transient grating technique.

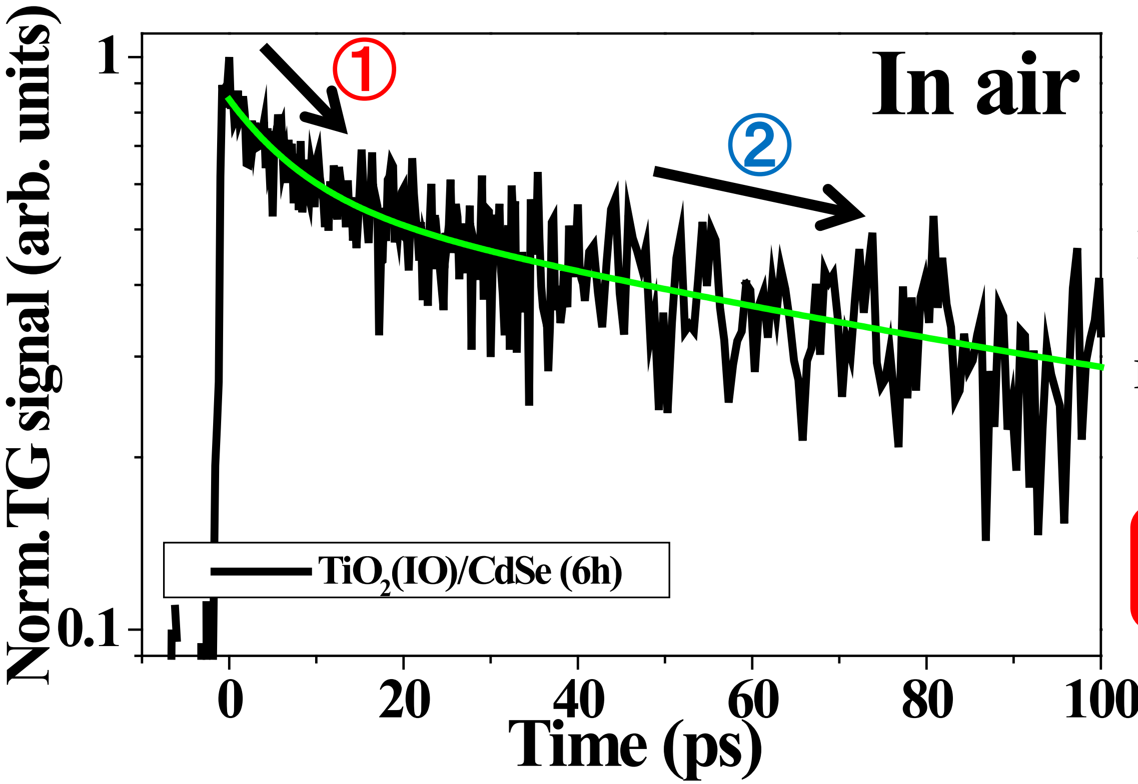


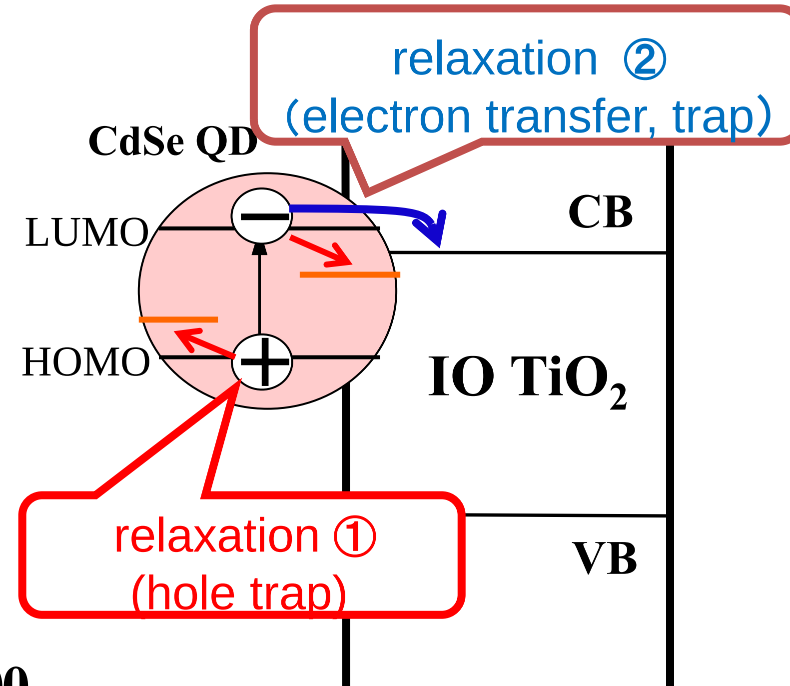
Advantages

- Easy and compact.
- High sensitivity.
  → Measurements under low pump intensity.
- Suitable for rough surfaces or optically scattering samples.

K. Katayama et al., *Appl. Phys. Lett.* **82 (2003) 2775.**

TG response in IO TiO_2/CdSe electrode[1)]





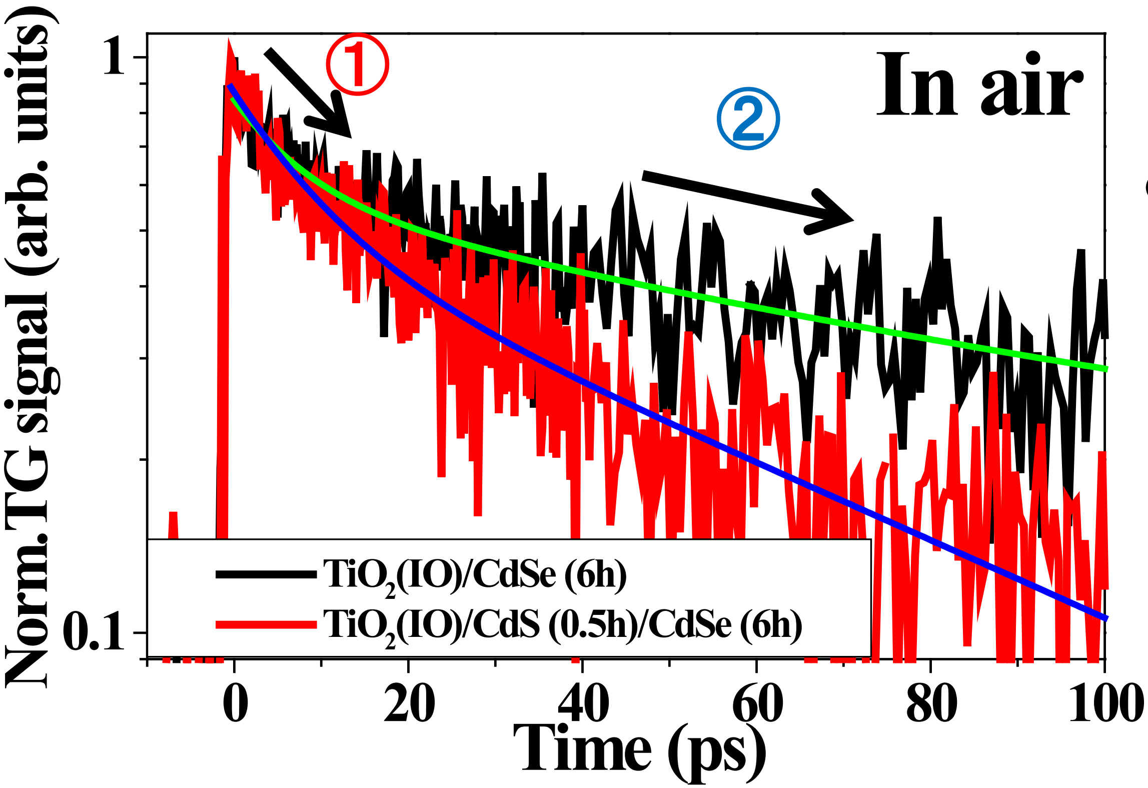
$$y(t) = \underbrace{A_1 e^{-t/\tau_1}}_{①} + \underbrace{A_2 e^{-t/\tau_2}}_{②} + y_0$$

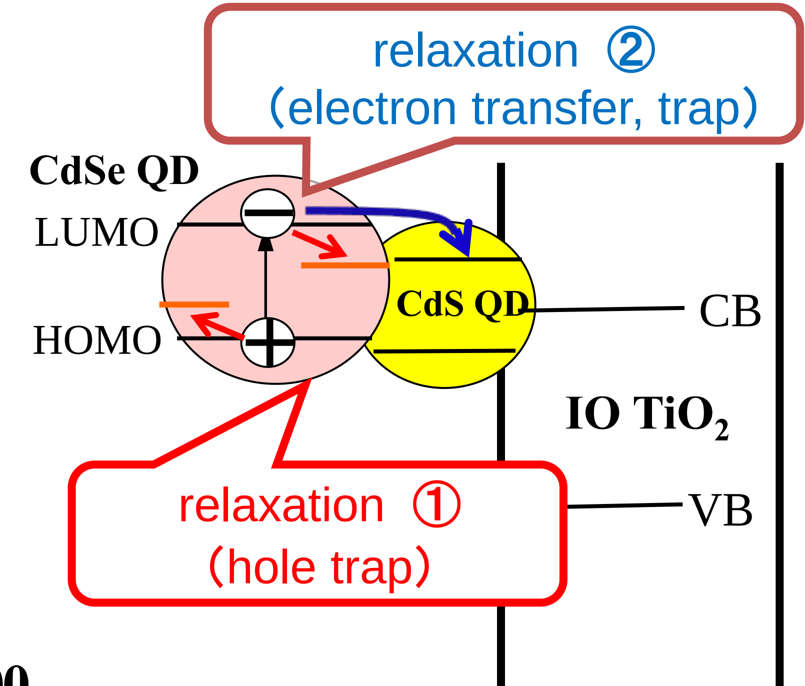
①　:　Relaxation in fast process　　→　hole trap

②　:　Relaxation in slow process　　→　electron transfer and/or trap

1) Q. Shen, Y. Ayuzawa, K. Katayama, T. Toyoda, *Appl. Phys. Lett.* **97** (2010) 263113.

TG response in IO TiO_2/CdS/CdSe electrode





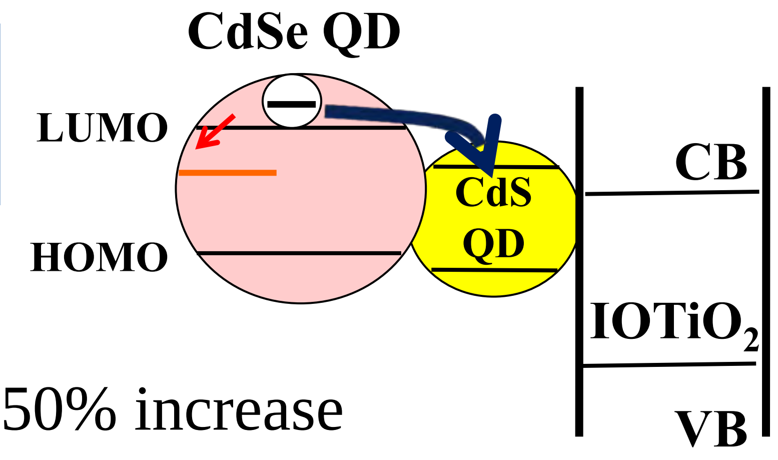
Faster relaxation process can be observed in relaxation ② on TiO_2/CdS/CdSe electrode than that of CdSe.

Sample	τ_1 (ps)	τ_2 (ps)
TiO_2(IO)/CdSe (6 h)	8±1	98 ±10
TiO_2(IO)/CdS (0.5 h)/CdSe(6 h)	9±1	67 ±7

Velocity constant in electron relaxation processes

IO TiO_2/CdS/CdSe electrode

- **decrease in relaxation time τ_2 in CdSe QDs.**



sample	τ_2 (ps)	k_2 ($10^{10}s^{-1}$)
TiO_2/CdSe	98	1.0
TiO_2/CdS/CdSe	67	1.5

50% increase

$$\frac{1}{\tau_2} = k_2 \Rightarrow k_2 = k_r + k_{et}$$

increase in k_{et}

k_2 : electron velocity constant
k_r : velocity constant (trap)
k_{et} : velocity constant (transfer)

Summary (Japan)

- **Quantum confinement effect by multilayerd CdS/CdSe quantum dot on inverse opal TiO_2 electrode can be observed by photoacoustic spectroscopy.**
- **Photosensitization by multilayered CdS/CdSe quantum dot on inverse opal TiO_2 electrode is realized and the suitable adsorption time is existed for the photocurrent.**
- **The maximum photovoltaic conversion efficiency of 3.8% can be achieved on inverse opal TiO_2 electrode adsorbed with multilayered CdS/CdSe quantum dots, having the correlation with ultrafast carrier dynamics (faster electron velocity constant in CdS/CdSe than in CdSe).**

Summary (Spain)

- **TiO_2 <u>morphology</u> and <u>quantum dots adsorption method</u> is the key role on the performance of QDSSCs.**
- **The dependence of <u>the photovoltaic conversion efficiency is different for quantum dots adsorption method</u> (CBD and SILAR).**
- **The recombination and injection analysis indicate that <u>CBD and SILAR methods produce with significantly different properties with photovoltaic properties</u>.**
- **<u>Injection kinetics is also dependent on both the TiO_2 morphology and quantum dots adsorption method</u>, being systematically faster for CBD.**

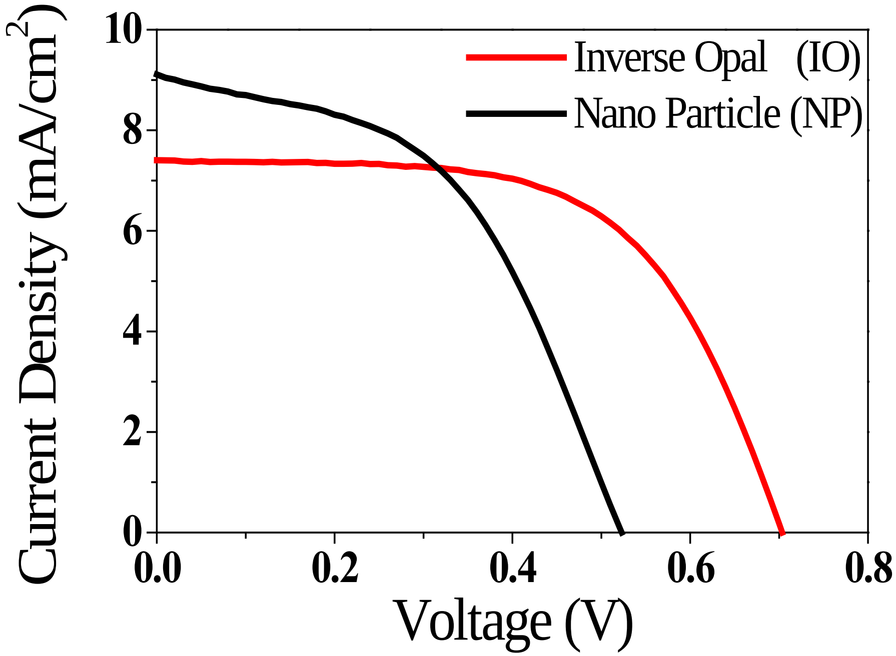
Future Studies

- **Characterization of photoexcited carrier dynamics for wider time domain (femtoseconds to microseconds) with different wavelength of pump beam.**
- **Correlation between electron-phonon interaction with different phonon modes and photovoltaic properties.**
- **Surface coating of quantum dot.**
- **Combined quantum dots (eg. CdSe/CdTe, CdSe/metal quantum dots).**
- **Suitable counter electrode and electrolyte for quantum dot-sensitized solar cell system.**
- **Electrochemical impedance characterization.**

Recent Publications

1. T. Toyoda and Q. Shen: Quantum dot-sensitized solar cells: Effect of nanostructured TiO_2 morphologies on photovoltaic properties, ***J. Phys. Chem. Lett.* 3**, 1885 (2012).
2. M. Samadpour, S. Giménez, P. P. Boix, Q. Shen, M. E. Calvo, N. Taghavinia, A. I. Zad, T. Toyoda, H. Míguez, and I. Mora-Seró: Effect of nanostructured electrode architecture and semiconductor deposition strategy on the photovoltaic performance of quantum dot sensitized solar cells, ***Electrochim. Acta* 75**, 139 (2012).
3. S. Hachiya, Y. Onishi, Q. Shen, and T. Toyoda: Dependences of the optical absorption and photovoltaic properties of CdS quantum dot-sensitized solar cells on the CdS quantum dot adsorption time, ***J. Appl. Phys.* 110**, 054319 (2011).
4. N. Guijarro, J. M. Campiña, Q. Shen, T. Toyoda, T. Lana-Villarreal, and R. Gómez: Uncovering the role of the ZnS treatment in the performance of quantum dot sensitized solar cells, ***Phys. Chem. Chem. Phys.* 13**, 12024 (2011).
5. Q. Shen, Y. Ayuzawa, K. Katayama, T. Sawada, and T. Toyoda: Separation of ultrafast photoexcited electron and hole dynamics in CdSe quantum dots adsorbed onto nanostructured TiO_2 films, ***Appl. Phys. Lett.* 97**, 263113 (2010).
6. Q. Shen, A. Yamada, S. Tamura, and T. Toyoda: Quantum dot-sensitized solar cell employing TiO_2 nanotube working-electrode and Cu_2S counter-electrode, ***Appl. Phys. Lett.* 97**, 123107 (2010).
7. N. Guijarro, Q. Shen, S. Giménez, I. Mora-Seró, J. Bisquert, T. Lana-Villarreal, T. Toyoda, and R. Gómez: Direct correlation between ultrafasrt injection and photoanode performance in quantum-dot sensitized solar cells, ***J. Phys. Chem. C* 114**, 22352 (2010).
8. N. Guijarro, T. Lana-Villarreal, Q. Shen, T. Toyoda, and R. Gómez: Sensitization of titanium dioxide photoanodes with cadmium selenide quantum-dots prepared by SILAR: Photoelectro-chemical and carrier dynamics studies, ***J. Phys. Chem. C* 114**, 21928 (2010).

Inverse Opal versus Nanocrystalline TiO_2



Electrode	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)
Inverse Opal	**7.4**	**0.69**	**0.60**	3.2
Nanocrystal	**9.1**	**0.52**	**0.49**	2.2

Inverse opal TiO_2 (relative to nanocrystalline TiO_2)

- Higher Voc — *Larger amount of CdSe QDs on thinner TiO_2 electrode (highly increase of the quasi Fermi level)*
- Higher FF — *Macroporous structure (efficient hole transport to the electrolyte)*