Photosensitization of nanostructured TiO$_2$ electrodes with CdSe quantum dots: effects of microstructure in substrates

Q. Shen$^{1,2}$ and T. Toyoda$^{1,2}$

Department of Applied Physics and Chemistry$^1$, and
Course of Coherent Optical Science$^2$

The University of Electro-Communications
Chofu, Tokyo 182-8585, Japan
Nanocrystalline TiO$_2$ has received much attention in numerous fields of applications (e.g., photocatalysis, photoelectrochemical solar cell and gas sensor).

Dye-Sensitized Solar Cell (DSSC) with high energy conversion efficiency exceeding 10 has been developed by (a) preparation of highly porous, nanostructured TiO$_2$ electrodes to increase the surface area; (b) dye or semiconductor quantum dot sensitization to extend the photoresponse of TiO$_2$ to the visible region.

For higher efficiency, further research on the nanostructured TiO$_2$ electrodes (morphology, optical absorption, charge injection, transport and recombination) is essential.
**RESEARCH OBJECTIVES**

**TiO\(_2\) electrodes**

- Anatase-type TiO\(_2\) nanoparticles made from TiCl\(_4\) hydrolysis and oxidation processes.
- Composition of different size anatase-type TiO\(_2\) nanoparticles.
- Composition with rutile-type content on anatase-type TiO\(_2\) nanoparticles.
- TiO\(_2\) nanotubes and nanowires.
- TiO\(_2\) photonic crystals.

**Sensitizer**

- CdSe quantum dots.
Advantages of semiconductor quantum dots

- Quantum confinement allows for energy gap tunable across the solar spectrum.
- Large extinction coefficient resulting from quantum confinement.
- Large intrinsic dipole moment which may lead to rapid charge separation.
- Robust inorganic nature.
- Impact ionization occurs with the possibility of high efficiency.
In order to investigate morphological dependence, two types of nanostructured TiO$_2$ electrodes were prepared and CdSe quantum dots with various sizes were adsorbed on TiO$_2$ as sensitizer.

TiO$_2$ electrodes were characterized using SEM, XRD, photoacoustic (PA) and photoelectrochemical current (PEC) methods.

**PA method** is powerful for the investigation of optical absorption of optically opaque or scattering solid materials.
Nanocrystalline TiO$_2$ powder (30 wt %)
- Pure water
- Acetylacetone 10 wt\%)
- Polyethylene glycol (PEG) (MW:500000)
  (40 w vs TiO$_2$)

Stirring for one hour

TiO$_2$ paste

Depositing TiO$_2$ paste on FTO using squeegee method.

Heating in air at 450 for 30 min.

Two types of TiO$_2$ electrodes

A (15 nm)
B (27 nm)
Chemical solution deposition (CD) method of CdSe quantum dots on the TiO₂ electrode


- 80mM CdSO₄
- 120mM N(CH₂COONa)₃ (NTA)
- 80 mM Na₂SeSO₃

Mixed (1:1:1) Chemical Deposition (CD) Solution

For some Time

TiO₂

Sample

CD Solution

1h 3h 5h 9h 23h 49h
SEM micrographs of TiO$_2$ electrodes

Electrode A

Size of TiO$_2$ in the paste:
15 nm

Electrode B

Size of TiO$_2$ in the paste:
27 nm
SEM micrographs of CdSe-quantum dots adsorbed on TiO$_2$ electrodes
X-Ray diffraction patterns

Intensity (Arb. Units)

2θ (Degrees)

CdSe (111)

CdSe (220)

CdSe (311)

TiO₂

FTO
Scherrer equation:

\[ D = \frac{0.9 \lambda}{\beta \cos \phi} \]

- \( D \): CdSe quantum dot size
- \( \beta \): half-width of the diffraction peak
- \( \phi \): diffraction angle
- \( \lambda \): 0.154 nm

**D** 5-6 nm (CdSe120h)
**Photoacoustic Spectroscopy (PAS)**

- **Light source**: 300W xenon arc lamp
- **Normalization**: carbon black sheet
- **Wavelength range**: 250nm–800nm
- **Modulation frequency**: 33Hz
PA spectra of TiO$_2$ electrodes A (TiO$_2$:15nm) deposited with CdSe quantum dots for various times.
Effective mass approximation:

\[ \Delta E = E_1 - E_g = \frac{\hbar^2}{8 \mu a^2} \quad (D = 2a) \]

Dependence of CdSe quantum dot size on deposition time.
PA spectra of TiO₂ electrodes B (TiO₂: 27nm) deposited with CdSe quantum dots for various times.
Photoelectrochemical Current (PEC) Spectroscopy

Light source: 300W xenon arc lamp
Normalization: carbon black sheet
Material of the PEC cell: quartz
Wavelength range: 250nm - 800nm
Electrolyte: 1M KCl + 0.1M Na₂S
PEC spectra of TiO$_2$ electrodes A (TiO$_2$:15nm) deposited with CdSe quantum dots for various times.
PEC spectra of TiO$_2$ electrodes B (TiO$_2$: 27nm) deposited with CdSe quantum dots for various times.
IPCE: incident photon-to-current conversion efficiency for monochromatic radiation

\[
\text{IPCE}(\%) = \frac{\text{injected electron numbers}}{\text{incident photon numbers}}
\]

\[
= \frac{1240 \text{ (eV \cdot nm)} \times \text{photocurrent density (\(\mu A \cdot \text{cm}^{-2}\))}}{\text{wavelength (nm)} \times \text{photoflux (\(\mu W \cdot \text{cm}^{-2}\))}}
\]
IPCE spectra of TiO$_2$ electrodes A (TiO$_2$: 15nm) deposited with CdSe quantum dots for various times.
IPCE spectra of TiO₂ electrodes B (TiO₂:27nm) deposited with CdSe quantum dots for various times.
Two types of nanostructured TiO$_2$ electrodes A (15nm) and B (27nm) deposited with CdSe quantum dots by chemical deposition, have been characterized using PA, PEC spectra and IPCE measurements.

- Photosensitization by CdSe quantum dots was demonstrated and red shift of the spectra with increasing CdSe sizes can be clearly observed.

- PEC and IPCE spectra in the visible region are quite different for the two types of TiO$_2$ electrodes, even for the same deposition time of CdSe quantum dots.
The electron diffusion coefficient of the TiO$_2$ electrode A was found to be two times larger than that of electrode B using transient photocurrent responses.

PEC and IPCE in the visible region in the CdSe-sensitized TiO$_2$ nanostructured electrodes largely depend on both the microstructure and electron transport property in the TiO$_2$ electrodes as well as the size and quantity of CdSe nanoparticles.

**Future studies:**
- TiO$_2$/CdSe interfacial property;
- Energy conversion efficiency;
- Ultrafast relaxation dynamics etc.
The *ultrafast carrier dynamics* were investigated by using lens-free heterodyne detection transient grating (LF-HD-TG) technique.

One kind of optical pump and probe technique:

Measurements of the decay of excited carrier densities after pulsed injection.
By approaching a sample to the grating, 1: Grating excitation
2: Heterodyne detection
→ Easy TG method without lenses (No daily setup)

K. Katayama et al., APL 82, 2775 (2003).
Lens-free heterodyne detection transient grating technique (LF-HD-TG)

Titanium/sapphire laser
Wavelength: 800 nm; Pulse width: 150 fs; Intensity: 5 µJ/pulse

Advantages
1) Easy and compact.
2) High sensitivity.
   → Measurements under low pump intensity.
3) Suitable for rough surfaces or optically scattering samples.
LF-HD-TG response of nanostructured TiO$_2$ electrode without CdSe quantum dots.
LF-HD-TG responses of nanostructured TiO$_2$ electrodes B (TiO$_2$: 27 nm) with CdSe quantum dots for different deposition times.
Pump intensity dependence of the LF-HD-TG response of nanostructured TiO$_2$ electrode B (TiO$_2$: 27 nm) deposited with CdSe quantum dots for 49h. The pump intensity is ranging from 2.5 to 16.5 µJ/pulse.
The pump intensity dependence of the maximum signal intensity for nanostructured TiO$_2$ electrode B (TiO$_2$: 27 nm) deposited with CdSe quantum dots for 49 h.
Analyses of LF-HD-TG response

\[ y = y_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \]

Transient Grating Signal

Delay Time (ps)

<table>
<thead>
<tr>
<th>Transient Grating Signal</th>
<th>cdse20h</th>
<th>fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>y0</td>
<td>0.11043</td>
<td>0.00715</td>
</tr>
<tr>
<td>A1</td>
<td>1.00703</td>
<td>0.03463</td>
</tr>
<tr>
<td>(\tau_1)</td>
<td>2.55526</td>
<td>0.12042</td>
</tr>
<tr>
<td>A2</td>
<td>0.39276</td>
<td>0.00834</td>
</tr>
<tr>
<td>(\tau_2)</td>
<td>27.48046</td>
<td>1.86301</td>
</tr>
</tbody>
</table>
## Results of the Fitting Parameters

<table>
<thead>
<tr>
<th>CdSe deposition time (h)</th>
<th>CdSe size (nm)</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$y_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4.8</td>
<td>1.8</td>
<td>16</td>
<td>0.74</td>
<td>0.34</td>
<td>0.15</td>
</tr>
<tr>
<td>9</td>
<td>5.1</td>
<td>2.1</td>
<td>19</td>
<td>0.68</td>
<td>0.37</td>
<td>0.16</td>
</tr>
<tr>
<td>20</td>
<td>5.8</td>
<td>2.1</td>
<td>20</td>
<td>0.65</td>
<td>0.31</td>
<td>0.20</td>
</tr>
<tr>
<td>44</td>
<td>6.5</td>
<td>2.2</td>
<td>29</td>
<td>0.63</td>
<td>0.28</td>
<td>0.18</td>
</tr>
<tr>
<td>125</td>
<td>6.7</td>
<td>1.9</td>
<td>30</td>
<td>0.60</td>
<td>0.31</td>
<td>0.27</td>
</tr>
</tbody>
</table>
(1) Fast decay process ($\tau_1$): decrease of hole carrier numbers by trapping at the CdSe QD surface states;

(2) Slow decay process ($\tau_2$): photoexcited electron relaxation process, i.e. recombination and/or transfer to the TiO$_2$ electrode;

(3) Base line ($y_0$): thermal diffusion signal owing to thermal grating.

tr: trapped
et: electron transfer
Eg: energy gap
$h\nu$: excitation energy
--- nonradiative
--- radiative
--- excitation
Nanostructured TiO$_2$ electrodes adsorbed with CdSe quantum dots by chemical deposition, have been characterized using LF-HD-TG measurements for the first time.

Three decay processes can be shown with decay time of 2 ps ($\tau_1$), 16-30 ps ($\tau_2$) and larger than a few hundreds ps, respectively.

It is found that $\tau_1$ is independent of quantum dot size, but $\tau_2$ depends on quantum dot size.
Acknowledgements

D. Arae (now at Anritsu)
M. Hayashi (now at CANON)
I. Tsuboya (now at SONY)
Y. Kumagai
K. Katayama (University of Tokyo, now at MIT)
T. Sawada
(University of Tokyo, now at Tokyo University of Agriculture and Technology)

Financial supports:

A Grant-in Aid for Scientific Research (No. 14750645 and No. 15510098) and one on on Priority Area 417 (No. 15033224) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

The 21st Century COE program on “Coherent Optical Science”.