Quantum-dot-sensitized solar cells: Assembly of CdS-quantum-dots coupling techniques of self-assembled monolayer and chemical bath deposition

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Two methods, coupling self-assembled monolayer and chemical bath deposition (CBD), were utilized to assemble cadmium sulfide (CdS) quantum dots (QDs) onto mesoporous TiO₂ films for dye-sensitized solar cell (DSSC) applications. Colloidal CdS QDs were first self-assembled on the TiO₂ surface. CBD was then introduced to replenish the incorporated amount and increase the coverage ratio of CdS QDs on the TiO₂ surface. The preassembled CdS QDs act as nucleation sites in the CBD process, forming a CdS nanofilm with an interfacial structure capable of inhibiting the recombination of injected electrons. An efficiency as high as 1.35% for the QD-sensitized DSSC was achieved using the present strategy. © 2007 American Institute of Physics. [DOI: 10.1063/1.2721373]

Due to its renewable and clean-energy characteristics, solar energy is destined to be an important energy source for the next generation. Recently, dye-sensitized solar cells (DSSCs) have attracted a lot of attention due to their potential application as low-cost photovoltaic cells. DSSCs are based on the photosensitization of nanocrystalline TiO₂ semiconductor electrodes by absorbed dyes. The absorption spectrum of a sensitizer plays an important role in determining the energy conversion efficiency of a DSSC cell. In addition to organic dyes, semiconductor quantum dots (QDs) which absorb light in the visible spectrum are also good candidates to be a sensitizer of a DSSC cell. Some specific advantages of using semiconductor QDs as light absorbers exist. Due to the quantum confinement effect, the optical property and the band gap of a QD can be adjusted by changing the size of the QDs. In addition, the QDs open up a way to utilize hot electrons and to generate multiple electron-hole pairs with a single photon through impact ionization.

Recently, sensitization of mesoporous TiO₂ using CdS, CdSe, and PbS QDs has been performed. However, the energy conversion efficiencies reported were still low (less than 0.5%). One possible reason for the poor efficiency of a QDs-sensitized DSSC is the difficulty of assembling the QDs into the mesoporous TiO₂ matrix to obtain a firmly anchoring and completely covered monolayer of QDs on the TiO₂ crystalline surface. Two methods are commonly employed for the assembly of QDs. The first is the in situ synthesis of the QDs in the mesoporous TiO₂ substrate using the chemical bath deposition (CBD) technique. The other is the self-assembled binding of the preprepared CdS QDs to the TiO₂ surface through the linking of a bifunctional molecule [termed as self-assembled monolayer (SAM) technique hereafter].

In this study, a method of combining techniques of SAM and CBD is employed to assemble the CdS QDs onto the mesoporous TiO₂ electrode. A bifunctional surface modifier, 3-mercaptopropyl trimethoxysilane (MPTMS), is used as a linker molecule to anchor a CdS-QD monolayer on the TiO₂ surface. Then, the CdS-QDs-modified TiO₂ electrode (TiO₂/SAM CdS QD) is further subjected to a CBD process to increase the coverage ratio and incorporation amount of CdS. In this letter, this strategy is proven to have a great enhancement to the energy conversion efficiency of QDs-sensitized DSSCs.

CdS QDs were synthesized in a reverse micelle system, with the details reported in a previous paper. F-doped tin oxide substrate (about 8 Ω/sq, Solaronix SA) was used as transparent conducting substrates to prepare TiO₂ photoelectrode. TiO₂ paste (Degussa P25) was spin coated on the substrate and sintered at 450 °C for 30 min. The thickness of the TiO₂ film was measured to be 5.5 µm. Surface modification of the TiO₂ substrate was performed by immersing the TiO₂ electrode into a 1 wt % MPTMS/toluene solution for 5 min. CdS QDs were assembled onto the MPTMS-modified TiO₂ electrode by immersing the electrode in a pyridine solution containing CdS QDs at 50 °C for 12 h. The CBD process followed, in which the TiO₂/SAM-Cds-QD electrode was dipped for 5 min into a 2M Cd(NO₃)₂ aqueous solution, rinsed with pure water, and then dipped for another 5 min into a 0.5M Na₂S solution and rinsed again with pure water. The two-step dipping procedure is termed as one full cycle of CBD. Repeating the CBD cycle would increase the incorporated amount of CdS.

The CdS-modified TiO₂ electrode and a Pt-coated counter electrode were sandwiched using 60 µm thick sealing material (SX-1170-60, Solaronix SA). 3-methoxypropionitrile solution consisting of 0.1M lithium iodide, 0.05M iodine, 0.6M 1-propyl-2,3-dimethylimidazolium iodide, and 0.5M 4-tert-butylpyridine was used as the redox electrolyte of the DSSC cells. The active area of the cell was 0.16 cm². The photocurrent-voltage (I-V) curves were measured under an illumination of a solar simulator (Newport, Oriel class A, 91160A) at 100% sun (AM1.5, 100 mW/cm²). An Autolab, Eco Chemie potentiostat/galvanostat was used to record the current-voltage (I-V) characteristics. An Oriel 500 W xenon arc lamp and Keithley 2400 electrometer were used during
the measurements of incident photon to current conversion efficiency (IPCE).

The prepared CdS QDs can be dispersed stably in pyridine for several months as confirmed by the transparency of its yellow solution. The diameters of the QDs estimated from the transmission electron microscopy image were between 4 and 6 nm. The UV-vis spectrum of the CdS QDs self-assembled on the TiO\textsubscript{2} electrode is shown in Fig. 1 (curve 2). A strong absorption shoulder appears at 425 nm for the TiO\textsubscript{2}/SAM-CdS-QD electrode, revealing the optical characteristic of a quantum-sized CdS.

When a subsequent CBD process was performed on the TiO\textsubscript{2}/SAM-CdS-QD electrode, the resulting UV-vis spectra (curves 3 and 4 in Fig. 1) show an increase of the absorbance with the increase of CBD cycle, as well as the redshifts of the absorption shoulder and onset position. These results indicate that more CdS are incorporated into the TiO\textsubscript{2} matrix during the CBD process and besides, the sizes of the CdS QDs increase after the CBD process. The inset in Fig. 1 shows the absorbance of excitonic peaks after various cycles of the CBD process. With increase of the CBD cycles, the absorbance increases more quickly in the early cycles, slows down gradually, and only little increment is observed after six cycles. The higher increment of absorbance in the early cycles is attributed to the higher surface area of the mesoporous matrix available for adsorption. It is inferred that there are pores with a size that is too small to be filled in by the colloidal CdS QDs. It is quite possible that the TiO\textsubscript{2} surface area was not covered completely by the QDs due to the non-uniform assembly of the bifunctional SAM. The CBD process is able to replenish CdS on the empty sites that cannot be accomplished by the self-assembled process. Such replenishment is supposed to finish in the early CBD cycles and simultaneously causes the growth of the CdS films. The surface area of the TiO\textsubscript{2} matrix decreases gradually due to the filling of CdS and the blocking of the mesopores in the TiO\textsubscript{2} matrix. Therefore, a smaller increment of absorbance is observed in the later CBD cycles. The inset figure also shows the result obtained on a bare TiO\textsubscript{2} electrode without the self-assembled CdS-QD layer. Compared with the TiO\textsubscript{2}-SAM-CdS-QD electrode, the absorbance is lower in the early CBD cycles, and a similar absorbance is obtained at about four to six cycles.

The photocurrent-voltage ($I$-$V$) curves for the DSSC cells prepared by the CdS-sensitized TiO\textsubscript{2} photoelectrodes are shown in Fig. 2. The open circuit potential ($V$\textsubscript{OC}), short circuit current ($I$\textsubscript{SC}), fill factor (ff), and the total energy conversion efficiency ($\eta$) of these cells are listed in Table I. For the TiO\textsubscript{2}/SAM-CdS-QD electrode without the CBD process, the $I$\textsubscript{SC} and $V$\textsubscript{OC} are 0.17 mA/cm\textsuperscript{2} and 529 mV, respectively, resulting a very low value of energy conversion efficiency ($\eta$=0.05%). When the CBD process was introduced, both $I$\textsubscript{SC} and $V$\textsubscript{OC} increased with increasing CBD cycles, reaching a maximum value at five cycles, and then decreased with a further increase of CBD cycles. As a result, the overall energy conversion efficiency ($\eta$) increases noticeably after the CBD process, and a maximum value as high as 1.35% is obtained at five CBD cycles. For the present case, the early CBD cycles are supposed to increase the coverage ratio of CdS on the TiO\textsubscript{2} surface by replenishing the uncovered area left by the self-assembled process. Furthermore, CdS film thickness increases after each CBD cycle. Such increment of CdS loading leads to more excited electrons under the illumination of light, which is advantageous to the photocurrent of a DSSC cell. However, as thickness of the CdS film increases, it will be more difficult to inject an excited electron into the conduction band of TiO\textsubscript{2}.

### Table I. Parameters obtained from the photocurrent-voltage ($I$-$V$) measurement of the DSSCs constructed by various electrodes.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>UV-vis absorption</th>
<th>$I$\textsubscript{SC} (mA/cm\textsuperscript{2})</th>
<th>$V$\textsubscript{OC} (mV)</th>
<th>ff</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2}/SAM CdS QD</td>
<td>0.42</td>
<td>0.17</td>
<td>529</td>
<td>0.59</td>
<td>0.05</td>
</tr>
<tr>
<td>TiO\textsubscript{2}/SAM CdS QD/CBD(1)</td>
<td>0.46</td>
<td>0.89</td>
<td>602</td>
<td>0.53</td>
<td>0.28</td>
</tr>
<tr>
<td>TiO\textsubscript{2}/SAM CdS QD/CBD(3)</td>
<td>0.58</td>
<td>1.93</td>
<td>634</td>
<td>0.56</td>
<td>0.68</td>
</tr>
<tr>
<td>TiO\textsubscript{2}/SAM CdS QD/CBD(5)</td>
<td>0.63</td>
<td>3.44</td>
<td>657</td>
<td>0.60</td>
<td>1.35</td>
</tr>
<tr>
<td>TiO\textsubscript{2}/SAM CdS QD/CBD(7)</td>
<td>0.65</td>
<td>2.52</td>
<td>615</td>
<td>0.52</td>
<td>0.81</td>
</tr>
<tr>
<td>TiO\textsubscript{2}/CBD(5)</td>
<td>0.65</td>
<td>1.70</td>
<td>612</td>
<td>0.68</td>
<td>0.70</td>
</tr>
</tbody>
</table>
generated in the outer layer into the TiO$_2$ matrix. It is also inferred that the CdS/electrolyte contacting area will decrease with an increase of CBD cycles because more pores are probably blocked by the additional loading of CdS. The competition between these effects determines an optimal thickness of the CdS layer to be used as a sensitizer of a DSSC cell.

To study the role of the SAM-CdS-QD layer on the DSSC, the $I$-$V$ characteristics of the electrodes without the SAM-CdS-QD layer were also analyzed, and the maximum energy conversion efficiency was obtained at around five CBD cycles. The $I$-$V$ curve of the TiO$_2$/CBD(5) electrode is shown in Fig. 2 for comparison. The UV-vis absorbance of the TiO$_2$/CBD(5) electrode is nearly identical to the TiO$_2$/SAM-CdS-QD/CBD(5) electrode, indicating a similar amount of CdS incorporated in the TiO$_2$ matrix. However, the $I_{SC}$ and overall efficiency ($\eta$) of the TiO$_2$/CBD(5) electrode are only about half of those of the TiO$_2$/SAM-CdS-QD/CBD(5) electrode. This result indicates that the SAM-CdS-QD layer plays an important role in the energy conversion of a DSSC cell. The different efficiencies between TiO$_2$/SAM-CdS-QD/CBD(5) and TiO$_2$/CBD(5) electrodes are attributed to the difference in the TiO$_2$/CdS interfacial states with and without the presence of a SAM-CdS-QD layer.

To decipher the role of the SAM-CdS-QD layer, the $I$-$V$ characteristic was measured under dark conditions and the result is shown in the lower part of Fig. 2. It shows that the applied voltage required to drive the electrons across the photoelectrodes increases in the order TiO$_2$/CBD(5) < TiO$_2$/SAM CdS QD/CBD(5), which also shows an increase of the energy barrier for an injected electron in the TiO$_2$ to recombine with the oxidized species in the electrolyte.$^{18,19}$ That is, the TiO$_2$/SAM-CdS-QD/CBD(5) electrode has a superior property in retarding interfacial recombination losses of charges, which is also responsible for its higher energy conversion efficiency. It is inferred that the SAM CdS QD acts as a seed layer for the growth of CdS in the CBD process, resulting in an interfacial structure of the CdS film which is superior in retarding the recombination of injected electrons.

The IPCEs of the electrodes were measured from the $I_{SC}$ monitored at different excitation wavelengths. For the TiO$_2$/SAM CdS QD/CBD(5) and TiO$_2$/CBD(5) electrodes shown in Fig. 3, the spectral responses closely resemble the absorption spectra (Fig. 1). An IPCE value as high as 30% is obtained for the TiO$_2$/SAM-CdS-QD/CBD(5) electrode.

Both IPCE measurement and the UV-vis spectrum indicate that only light with a wavelength smaller than 550 nm can be harvested by CdS. However, the energy conversion efficiency of the CdS-sensitized DSSC fabricated by the present strategy is higher than those published for the QD-sensitized DSSCs using QDs of broader absorption spectra such as CdSe, PbS, and InP.$^{5,6,15}$ The present result not only demonstrates the applicability of this methodology to assemble a QD-sensitized DSSC but also implies the potential of QDs to be an efficient sensitizer in DSSCs.

In summary, by coupling the SAM and CBD techniques, it is possible to assemble the CdS QDs onto the mesoporous TiO$_2$ film to prepare an efficient QD-sensitized DSSC. An IPCE value as high as 30% is obtained for CdS. However, the energy conversion efficiency is attributed to the formation of an interfacial structure capable of inhibiting the recombination of injected electrons.

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FIG. 3. Incident photon to current conversion efficiencies (IPCEs) of various electrodes measured as a function of wavelength.