Highly Efficient CdSe-Sensitized TiO_2 Photoelectrode for Quantum-Dot-Sensitized Solar Cell Applications

Yuh-Lang Lee,* Bau-Ming Huang, and Huei-Ting Chien

Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan

Received August 21, 2008
Revised Manuscript Received October 7, 2008

Dye-sensitized solar cells (DSSC) are considered to be a promising alternative to conventional solid-state solar cells due to their characteristics of low cost, surrounding friendly, and high energy conversion efficiency. On the basis of photosensitization of mesoporous TiO_2 films using ruthenium complex sensitizers, power conversion efficiency up to 11% has been achieved by DSSCs.[1] In addition to the organic sensitizers, semiconductor materials which absorb light in the visible region are alternative light harvesters of DSSCs. Metal chalcogenide semiconductors such as CdS,[2−4] CdSe,[5] PbS,[6,7] and PbSe[8] have received interest in this application. When the sizes of these materials were decreased down to the quantum-dot (QD) region, the quantum confinement effect makes it possible to generate multiple electron−hole pairs per photon through the impact ionization effect.[9] By using this advantage, the efficiency of a solar cell may exceed the limit calculated by Shockley and Queisser (31%).[10]

Although QDs have specific advantages over organic materials to be sensitizers of DSSCs, there are relatively fewer studies devoted to the QD-sensitized solar cells (QD-SSCs), and their energy conversion efficiencies are still low. The poor performance of the QD-SSCs may be ascribed to the difficulty of assembling the QDs into the mesoporous TiO_2 matrix to obtain a well-covered QD layer on the TiO_2 crystalline surface. The other problem one would encounter is the selection of an efficient electrolyte in which the metal chalcogenide can run stably without serious degradation. In our previous papers, CdS was assembled into a TiO_2 film using a method coupling self-assembled monolayer (SAM) and chemical bath deposition (CBD),[11] as well as a modified CBD process performed in an alcohol system.[12] Furthermore, a polysulfide electrolyte considering simultaneously the penetration of the electrolyte in a mesoscopic TiO_2 film and the ion dissociation in the solution was developed for application in a CdS-sensitized solar cell (CdS-SSC).[13] These modified processes have proved to be efficient for the CdS-SSC, and the energy conversion efficiencies achieved by a CdS-SSC are 1.84% and 1.15% respectively for iodide/triiodide (I^-/I_3^-) and polysulfide electrolytes.[12,13]

One of the reasons limiting the performance of CdS-SSC is its relatively higher band gap (ca. 2.25 eV in bulk)[14] which limits its absorption range below the wavelength of ca. 550 nm. In comparison with CdS, CdSe has a wider absorption range (<ca. 720 nm) which is advantageous to the light harvest. By using a CdSe-sensitized nanocrystalline TiO_2 photoelectrode in a photoelectrochemical cell, Niitsoo et al.[15] achieved a 2.8% conversion efficiency under 1 sun illumination. Although this efficiency is high for a CdSe-sensitized photoelectrochemical cell, it was performed in a three-electrode configuration. For the sandwich structure solar cell, Diguna at al.[16] prepared a CdSe-sensitized potoelectrode based on a TiO_2 inverse opal (about 400 nm in pore size), and an energy conversion efficiency of 2.7% was obtained. This efficiency is relatively higher for QD-SSCs; however, the preparation of an opal structure is supposed to limit the real application of this system.

In this work, CdSe was assembled into nanocrystalline TiO_2 films using a technique coupling SAM and CBD. Colloidal CdS-QDs were first self-assembled on TiO_2 surface by using a bifunctional linker, 3-mercaptopropyl trimethyoxysilane (MPTMS). The pre-self-assembled CdS-QD (SAM-CdS-QD) layer acts as a seed layer in the following CBD process, inducing the nucleation and growth of CdSe. The present strategy was proved to have a great enhancement to the performance of a CdSe-SSC.

Mesoscopic TiO_2 films were prepared by spin coating of TiO_2 paste (Degussa P25) on indium-doped tin oxide (ITO, about 13 Ω/sq, Solaronix SA) substrates, followed by sintering at 450 °C for 30 min. The thickness of the TiO_2 film was measured to be 8.5 μm. Colloidal CdS-QDs were synthesized in a reversed micelle system,[11] and the diameters of the CdS-QDs were about 3−5 nm measured by a transmission electron microscope. TiO_2 films were surface-modified by immersing in a 1 wt % MPTMS/toluene solution for 5 min, followed by dipping into a butanol solution containing CdS-QDs at 50 °C for 12 h. The electrode obtained is termed as TiO_2/SAM-CdS-QD. In the following CBD process of CdSe, sodium selenosulphate (Na_2SeSO_3) was used as the Se source. The Na_2SeSO_3 aqueous solution was prepared by refluxing Se (0.3 M) in an aqueous solution

---

* Corresponding author. E-mail: yllee@mail.ncku.edu.tw.

(1) Nazeeruddin, M. K.; Angelis, F. D.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grältzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 16835.
(2) Peter, L. M.; Riley, D. J.; Tull, E. J.; Wijayantha, K. G. U. *Chem. Commun.* **2002**, *10*, 1030.
(3) Wijayantha, K. G. U. L.; Peter, M.; Otley, L. C. *Sol. Energy Mater. Sol. Cells* **2004**, *83*, 263.
(4) Chen, S.; Paulose, M.; Ruan, C.; Mor, G. K.; Varghese, O. K.; Kouzoudis, D.; Grimes, C. A. *J. Photochem. Photobiol., A* **2006**, *177*, 177.
(5) Robel, I.; Subramanian, V.; Kuno, M.; Kamat, P. V. *J. Am. Chem. Soc.* **2006**, *128*, 2385.
(6) Plass, R.; Serge, P.; Krüger, J.; Grätzel, M. *J. Phys. Chem. B* **2002**, *106*, 7578.
(7) Hoyer, P.; Könenkamp, R. *Appl. Phys. Lett.* **1995**, *66*, 349.
(8) Schaller, R. D.; Klimov, V. I. *Phys. Rev. Lett.* **2004**, *92*, 186601.
(9) Nozik, A. J. *Inorg. Chem.* **2005**, *44*, 6893.
(10) Shockley, W.; Queisser, H. J. *J. Appl. Phys.* **1961**, *32*, 510.
(11) Lin, S. C.; Lee, Y. L.; Chang, C. H.; Shen, Y. J.; Yang, Y. M. *Appl. Phys. Lett.* **2007**, *90*, 143517.
(12) Chang, C. H.; Lee, Y. L. *Appl. Phys. Lett.* **2007**, *91*, 053503.
(13) Lee, Y. L.; Chang, C. H. *J. Power Sources* **2008**, *185*, 584.
(14) Grältzel, M. *Nature* **2001**, *414*, 338.
(15) Niitsoo, O.; Sarkar, S. K.; Pejoux, C.; Rühle, S.; Cahen, D.; Hodes, G. *J. Photochem. Photobiol., A* **2006**, *181*, 306.
(16) Diguna, L. J.; Shen, Q.; Kobayashi, J.; Toyoda, T. *Appl. Phys. Lett.* **2007**, *91*, 023116.

10.1021/cm802254u CCC: $40.75

of Na_2SO_3 (0.6 M) at 70 °C for 7 h. In the CBD process of CdSe, the TiO_2/SAM-CdS-QD (or bare TiO_2) electrode was dipped first into an ethanol solution containing $Cd(NO_3)_2$ (0.5M) for 5 min at room temperature, rinsed with ethanol, and then dipped into a Na_2SeSO_3 solution for 1 h at 50 °C, and rinsed again with pure water. The two-step dipping procedure is termed as one CBD cycle. Repeating the CBD cycle would increase the incorporated amount of CdSe. The CBD method was also used to deposit the ZnS passivation layer. The electrode was dipped sequentially into a 0.5 M Zn (NO_3) ethanol solution and a 0.5 M Na_2S methanol solution. The optimal dipping time was found to be 1 min for both solutions.

A QD-SSC was assembled by sandwiching a sensitized TiO_2 photoelectrode and an Au-coated counter electrode using 60 μm thick sealing material (SX-1170-60, Solaronix SA). A polysulfide electrolyte prepared using water/methanol (7:3 by volume) solution was used in this work. The electrolyte contains 0.5 M Na_2S, 0.1 M S, and 0.2 M KCl. The active area of the cell was 0.16 cm^2.

The photocurrent−voltage ($I-V$) curves were measured under an illumination of a solar simulator (Newport, Oriel class A, 91160A) at one sun (AM1.5, 100 mW/cm^2). An Eco Chemie Autolab potentiostat/galvanostat was used to record the current−voltage ($I-V$) characteristics. An Oriel 500W xenon arc lamp and Keithley 2400 electrometer were used during the measurements of IPCE (incident photon to current conversion efficiency).

The incorporated amount of CdSe in a TiO_2 film was evaluated using the absorbance of the UV−vis spectrum. Figure 1 shows the variation of the spectra with CBD cycles. For the CBD process performed on a bare TiO_2 film, the growth of CdSe is slow as inferred from the lower absorbance of the TiO_2/CdSe films. The absorbance increases slowly with increasing CBD cycle with a slight red-shift of the absorption shoulder and onset position. At the presence of a SAM-CdS-QD seed layer, the growth of CdSe is greatly enhanced as demonstrated by the higher absorbance shown in Figure 1b. For the TiO_2 film containing only a SAM-CdS-QD layer (trace "s" in Figure 1b), the absorption edge, obtained from the intersection of the baseline with the tangent line of the sharply decreasing region of the spectrum, is approximately 490 nm, corresponding to a band gap of 2.53 eV. The size of CdS particles estimated from the excitonic peak (ca. 425 nm) is 4.2 nm,[17] close to the value obtained from TEM. When CdSe was assembled on the TiO_2/SAM-CdS-QD electrode, the absorbance increases quickly especially at the first CBD cycle. These results demonstrate the growth enhancement effect of the seed layer on the deposition of CdSe. It is inferred that CdS-QD has a catalytic effect to the synthetic reaction of CdSe, leading to a high deposition rate of CdSe in the early CBD cycles. For the TiO_2/SAM-CdS-QD/CdSe (5) electrode, the band gap measured from the absorption edge (680 nm) is 1.82 eV, higher than the value reported for CdSe in bulk (1.7 eV). The mean size of CdSe crystallites estimated from the excitonic peak (620 nm) is 5.6 nm. These results indicate that the sizes of CdSe are in the range of QDs.

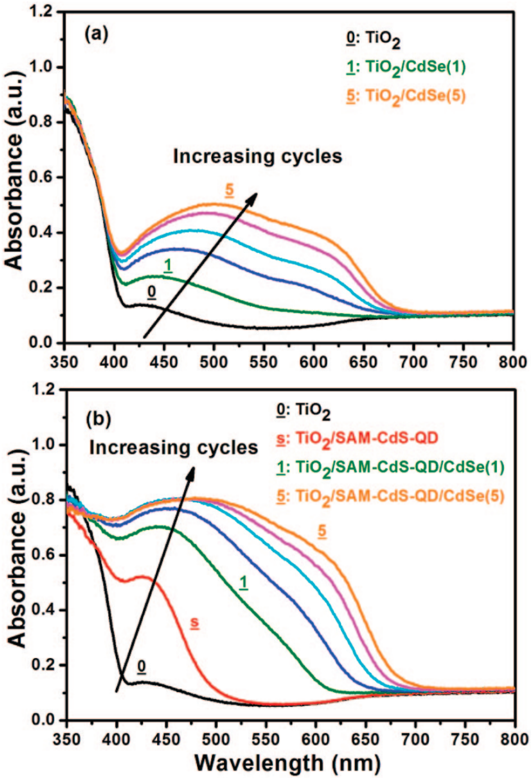

Figure 1. UV−vis absorption spectra of CdSe-sensitized TiO_2 films prepared by various cycles of CBD process in the absence (a) or in the presence (b) of a self-assembled layer of CdS-QD. The number on each curve corresponds to the CBD cycle introduced to assemble the CdSe.

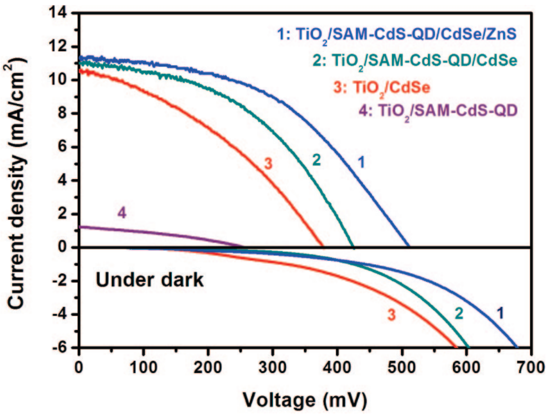

Figure 2. $I-V$ characteristics of various QD-sensitized DSSCs measured under the illumination of one sun (AM1.5, 100 mW/cm^2). The $I-V$ characteristics of the cells measured under dark conditions are shown in the lower part of this figure.

The performance of a QD-SSC is dependent on the CBD cycles introduced to deposit the QD. Overloading of CdS-QD onto a TiO_2 film was reported to be disadvantageous to the cell performance, ascribed to the blocking of the mesopores by additional loading of the CdS.[11,12] The effect of CBD cycles on the device performance has been carefully studied in the present work, and the optimum cycles found for the TiO_2/CdSe and TiO_2/SAM-CdS-QD/CdSe are all around 4. The $I-V$ curves measured for these electrodes, as well as for the electrode with only CdS-QD (TiO_2/SAM-CdS-QD), are shown in Figure 2. The open circuit potential (V_{OC}), short circuit current (I_{SC}), fill factor (FF), and total energy conversion efficiency (η) corresponding to these cells

---

[17] Yu, W. W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003**, *15*, 2854.

Table 1. Parameters Obtained from the $I-V$ Curves of QD-DSSCs Using Various Electrodes

structure	I_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η (%)
TiO_2/SAM-CdS-QD	1.33	260.4	0.33	0.1
TiO_2/CdSe	10.61	378.5	0.36	1.4
TiO_2/SAM-CdS-QD/CdSe	11.00	425.6	0.46	2.1
TiO_2/SAM-CdS-QD/CdS	6.50	459.6	0.47	1.4
TiO_2/SAM-CdS-QD/CdSe/ZnS	11.66	502.6	0.49	2.9

are list in Table 1. When only the SAM-CdS-QD layer was present on a TiO_2 electrode, the I_{SC} (1.33 mA/cm^2) and V_{OC} (260 mV) are small, and a low energy conversion efficiency ($\eta = 0.1\%$) is obtained. The small I_{SC} and FF (0.33) indicate that only a small amount of CdS-QDs was incorporated on the TiO_2 film, which also implies that this seed layer takes little contribution to the light harvest in the following TiO_2/SAM-CdS-QD/CdSe electrode.

Figure 2 shows that the performances of the CdSe-SSCs are much higher than that of the TiO_2/SAM-CdS-QD cell. Furthermore, the efficiency achieved by the cell with a SAM-CdS-QD seed layer (2.1%) is significantly higher than that without a seed layer (1.4%). The higher performance of the TiO_2/SAM-CdS-QD/CdSe cell is mainly attributed to the higher values of V_{oc} and FF induced by the presence of the SAM-CdS-QD seed layer. The higher V_{oc} and FF of the TiO_2/SAM-CdS-QD/CdSe cell imply that this electrode has a superior ability, compared to TiO_2/CdSe, in inhibiting the charge recombination at the electrode/electrolyte interface. This inference is sustained by the $I-V$ characteristics measured under dark conditions (shown in the lower part of Figure 2), which shows a smaller dark current for the TiO_2/SAM-CdS-QD/CdSe cell. The effect of the SAM-CdS-QD seed layer on the performance enhancement of the TiO_2/SAM-CdS-QD/CdSe cell is associated with its effect on the growth enhancement in the CBD process. Therefore, it is inferred that the presence of this seed layer contributes an interfacial structure with superior ability in collecting the excited electron and retarding the recombination of injected electrons.

In a previous work reported by Niitsoo et al. using the TiO_2/CdS/CdSe electrode, the presence of CdS prelayer was also found to improve the performance of a photoelectrochemical cell.[15] Several possibilities were proposed to explain this effect including the passivation effect of CdS on the TiO_2 surface, the formation of different nature of CdSe on CdS, and so forth. The role of the SAM-CdS-QD seed layer used in this work seems to have a function similar to the CdS layer used by Niitsoo.[15] However, the effect of SAM-CdS-QD seed layer is mainly on the increase of V_{oc} and FF in this work, which is different from the result of Niitsoo.[15]

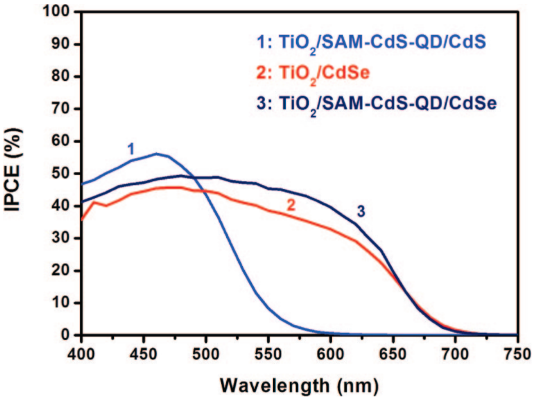

Figure 3. Incident photon to current conversion efficiencies (IPCE) of various electrodes measured as a function of wavelength.

When CdS was used instead of CdSe as sensitizer, the best efficiency obtained for the TiO_2/SAM-CdS-QD/CdS cell is only 1.4% (shown in Table 1). The higher performance of the TiO_2/SAM-CdS-QD/CdSe cell is mainly resulted from its higher I_{sc} (11.00 mA/cm^2), in comparison with that of the TiO_2/SAM-CdS-QD/CdS cell (6.50 mA/cm^2), attributed to the broader light harvest range of CdSe. To decipher this inference, the incident photon to current conversion efficiency (IPCE) was measured for various devices (Figure 3). In the short wavelength range (<480 nm), the TiO_2/SAM-CdS-QD/CdS device has a slightly higher IPCE than the TiO_2/SAM-CdS-QD/CdSe device, attributable to the higher conduction band edge of CdS. However, the IPCE spectra of the TiO_2/SAM-CdS-QD/CdSe device shows a much wider light harvest range, which is responsible for its higher I_{sc} and efficiency. It is also found that the IPCE values obtained for the TiO_2/CdSe and TiO_2/SAM-CdS-QD/CdSe devices are very similar, consistent with the close I_{sc} values of the two devices. This result also sustains the previous inference that the performance enhancement effect of the SAM-CdS-QD layer is mainly on the inhibition of charge recombination at the electrode/electrolyte interface.

It was known that ZnS can be used as a passivation layer of CdS or CdSe to enhance the performance of a photoelectrode.[16,18−20] A ZnS layer was therefore assembled on the optimum electrode to prepare the TiO_2/SAM-CdS-QD/CdSe/ZnS electrode. The corresponding $I-V$ characteristics and related parameters for this cell are also demonstrated in Figure 2 and Table 1, respectively. The results show that introduction of a ZnS layer leads to an increase of cell efficiency from 2.1 to 2.9%, mainly attributed to the increase of FF and V_{oc}. The dark current measurement (Figure 2) shows that a smaller dark current was obtained at the presence of ZnS, indicating that the ZnS layer can further inhibit the recombination of the excited electron at the electrode/electrolyte interface.

In summary, the growth of CdSe on a mesoporous TiO_2 film can be induced by a pre-self-assembled layer of CdS-QDs, leading to a higher deposition rate and an interfacial structure with superior ability in inhibiting the charge recombination at the electrode/electrolyte interface. The presence of the SAM-CdS-QD layer significantly increases the V_{oc} and FF of the CdSe-SSC, and an efficiency as high as 2.9% was achieved for the TiO_2/SAM-CdS-QD/CdSe/ZnS device.

Acknowledgment. The support of this research by the National Science Council of Taiwan through Grant NSC-94-2120-M-006-006 and NSC-95-2120-M-006-001 is gratefully acknowledged.

CM802254U

---

(18) Yang, S. M.; Huang, C. H.; Zhai, J.; Wang, Z. S.; Jiang, L. *J. Mater. Chem.* **2002**, *12*, 1459.

(19) Russak, M. A.; Reichman, *J. Electrochem. Soc.* **1982**, *129*, 542.

(20) Hodes, G.; Cahen, D.; Manassen, J.; David, M. *J. Electrochem. Soc.* **1980**, *127*, 2252.