The effect of a blocking layer on the photovoltaic performance in CdS quantum-dot-sensitized solar cells

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A R T I C L E   I N F O

Article history:
Received 12 June 2011
Received in revised form 9 August 2011
Accepted 10 August 2011
Available online 17 August 2011

Keywords:
Quantum-dot-sensitized solar cells
Cadmium sulfide
Blocking layer
Charge-transfer kinetics
Trap states

A B S T R A C T

In order to reduce the surface recombination at the interface between the fluorine-doped tin oxide (FTO) substrate and the polysulfide electrolyte in CdS quantum-dot-sensitized solar cells (QDSCs), compact TiO2 is deposited on the FTO electrode by sputtering. The TiO2-coated CdS-sensitized solar cell exhibits enhanced power-conversion efficiency (0.52%) compared with a bare CdS-sensitized solar cell (0.23%). Charge-transfer kinetics are analyzed by impedance spectroscopy, open-circuit decay, and cyclic voltammetry. The TiO2 layer deposited on the FTO substrate acts as a blocking layer, which plays a significant role in reducing the electron back transfer from the FTO to the polysulfide electrolyte. Interestingly, with respect to the incident photon-to-current conversion efficiency (IPCE) data, asymmetric enhancement is observed from the sample with a thicker blocking layer. This is because CdS quantum dots absorb ultraviolet light completely with the TiO2 layer because of the high extinction coefficient of the CdS quantum dots compared with dye molecules.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been considered as one of the most renewable solar energy sources due to their low cost, high durability, and potential use as flexible devices. Since Grätzel and O’Regan invented the dye-sensitized nanocrystalline TiO2 solar cell structure [1], enormous progress has been made in the power conversion efficiency of DSSCs, and maximum efficiencies of up to 11% have been achieved [2].

Recently, semiconductor quantum dots have been considered as a fascinating alternative to organic dye molecules. Quantum-dot-sensitized solar cells (QDSCs) have potential advantages over DSSCs, such as higher absorption coefficients compared with dye molecules, tailored absorptions by changing the size of quantum dots, and the possibility of exceeding the Schottky–Queisser limit by using multiple-electron generation [3–7].

Nevertheless, the QDSCs still exhibit lower efficiencies compared with DSSCs [8]. One of the main reasons is the recombination loss due to various defects at the interfaces [9,10]. Therefore, to obtain the improved photovoltaic performance of QDSCs, studies on interface quality are necessary [11,12].

Several groups have examined the surface-treatment effects on QDSC performance [13–16], even though the exact enhancement mechanisms have not been clarified yet.

In DSSCs, the compact blocking layer was used to prevent the backward electron transfer from FTO to the conventional iodide electrolyte, and many groups have studied several materials for this layer, including TiO2 and Nb2O5 [17–19]. The blocking-layer incorporation, however, induces little effect on the photovoltaic performance, because the shunt resistance of DSSCs is on the order of 10^3 Ω cm^2 when using an iodide electrolyte [20], and this magnitude of resistance is high enough to operate DSSCs.

In the case of QDSCs, to solve the corrosion problem of quantum dots in the electrolyte [21], a polysulfide solution was used as an alternative for the 3I^-/I_3^- electrolyte. The fill factor of QDSCs using the polysulfide electrolyte is lower than those of DSSCs due to both the low shunt resistance of the interfaces and the high series resistance of the electrolyte [22]. One of the possible reasons for the low shunt resistance is the loss caused by the recombination at the FTO/polysulfide electrolyte interfaces. Nevertheless, the mechanisms and charge-transfer kinetics of the FTO/polysulfide electrolyte have not yet been studied. In this article, we examined the influence of a TiO2 blocking layer on the photovoltaic performance of QDSCs. The electron recombination and charge-transfer kinetics were analyzed for the recombination reactions at the FTO/polysulfide electrolyte interfaces.
2. Experimental procedure

The TiO₂ blocking layer on the FTO electrode was prepared using a rf-magnetron sputtering system. The deposition was performed at room temperature (RT) under an Ar atmosphere with an operating pressure of 3 mTorr and rf power of 100 W. The thickness of the blocking layer was controlled by changing the deposition time in the range of 5–120 min. Commercial TiO₂ nanopowder (Ti-Nanoxide D; Solaronix, Switzerland) was used as a host material for QDSCs. The paste was spread with a one-step doctor blade method on the fluorine-doped tin oxide (FTO, TEC 8; Pilkington, Japan) electrode, and the paste-coated electrodes were subsequently annealed at 450 °C for 30 min in ambient air. The thickness of the TiO₂ nanoparticle layer was approximately 5 μm, and the active area of the photoelectrode was 0.28 cm².

The CdS quantum dots were coated onto the TiO₂ nanoparticle electrode using a successive ionic-layer adsorption and reaction (SILAR) method for fabricating efficient QDSCs with high quantum-dot coverage [23,24]. The as-prepared TiO₂ electrodes were immersed in 0.04 M cadmium chloride (CdCl₂; Aldrich, St. Louis, USA) in methanol for 1 min, and then the same samples were soaked in 0.04 M sodium sulfide (Na₂S; Aldrich, St. Louis, USA) dissolved in methanol. Following each step, the electrodes were rinsed with methanol for 1 min and dried. This coating process was repeated five times. The polysulfide electrolyte was prepared by dissolving 0.5 M Na₂S, 1 M S, and 0.02 M KCl in methanol/water with the ratio of 7:3 solutions [24]. The Pt counter electrode was deposited on the FTO substrate by rf-magnetron sputtering. Thermostatic foil (25 μm; Dupont, France) was used as a spacer for the sandwich-type solar cells.

The photocurrent–voltage (J–V) curves were characterized with a solar cell measurement system (K3000: McScience, Korea) under a solar simulator (Xenon lamp, air mass (AM) 1.5, 100 mW cm⁻²). Impedance spectra and open-circuit decay measurements were performed using a potentiostat (CHI 608C: CH Instrumental Inc., Austin, USA) and solar simulator (PEC-L11: Peccell, Japan) under AM 1.5 illumination. The electrochemical impedance spectra were recorded over a frequency range of 0.1 to 10⁵ Hz. An electrochemical analyzer (CHI 604A: CH Instrumental Inc., Austin, USA) was used for measuring the electrochemical reactions at the FTO/electrolyte interface. Field-emission scanning electron microscopy (FE-SEM, SU70: Hitachi, Japan) was used to characterize the morphology of the blocking layer on the FTO electrode. The absorption spectra of the blocking-layer coated FTO were recorded on a UV/Vis spectrophotometer (Lambda 20: Perkin-Elmer, Waltham, USA) with bare FTO as a reference. Incident photon-to-current conversion efficiency (IPCE) was obtained by using an IPCE measurement system (K3100: McScience, Korea).

3. Results and discussion

Fig. 1 shows the plan-view FE-SEM images of the bare and TiO₂ blocking layer coated on the FTO electrode. The film morphology and coverage changed with the deposition time. The nominal thicknesses of all the blocking layers are 7, 30, and 170 nm, depending on the deposition rate of the TiO₂ film. The island growth is clearly observed from the 30 nm-TiO₂ blocking layer on FTO, and after the 170 nm deposition, the FTO substrate is completely covered with the TiO₂ layer.

From the current density–voltage (J–V) curves of the CdS sensitized solar cells in Fig. 2, the photovoltaic–conversion efficiencies of the cells are enhanced with increases in the TiO₂ blocking-layer thickness, and both the open-circuit voltage and short-circuit current also increased. The fill factor showed maximum with the 7 nm-deposited cell, and gradually decreased with the increasing blocking-layer thickness. The possible reasons are the resistance of the blocking layer itself that impedes electron transport from TiO₂ nanoparticles to the FTO substrate [9,17], or inefficient ion transport of the polysulfide electrolyte as the flux of current increases [25].

As shown in Table 1, the 30 nm-deposited cell exhibits the best efficiency, by more than a factor of two compared to the bare cell. On the other hand, the thick blocking layer results in a decreased conversion efficiency.
The open-circuit voltage ($V_{oc}$) and short-circuit current ($J_{sc}$) were affected by the TiO$_2$ conduction-band position, electron concentration in the TiO$_2$-nanoparticle layer, light-harvesting efficiency, etc. [26–28]. The conduction band of the mesoscopic TiO$_2$ film does not change because the TiO$_2$ nanoparticle/polysulfide electrolyte interface is not affected by the addition of the blocking layer. This demonstrates conclusively that the increase of $V_{oc}$ is attributed to the increase in electron concentration which is influenced by the reduced recombination properties during light harvesting. Thus, the first aim of our study focused on the recombination properties with respect to variation of the blocking-layer thickness.

We performed dark current experiments, as shown in Fig. S1. As expected, the dark-recombination current decreases as the blocking-layer thickness increases in the positive-bias area, and the exchange current also decreased in the negative-bias region. Furthermore, compared with the poor junction characteristics of the bare sample, the coated sample exhibits good junction quality with a small leakage current [29]. The TiO$_2$ layer acts as the blocking layer which attenuates the charge-transfer rate at the FTO/polysulfide interface. The reduced recombination rate leads to an upward shift of the electron quasi-Fermi level $E_{F0}$ by increasing the electron-carrier concentration, thereby resulting in the improvement of the open-circuit voltage [30].

Fig. 2. Photocurrent density–voltage characteristics of CdS-sensitized solar cells with various blocking-layer thicknesses. The inset shows the power-conversion efficiency of QDSCs as a function of the blocking-layer thickness.

Fig. 3. (a) Equivalent circuit of QDSCs approximated for the low-voltage or high-voltage region [34]. (b) Electrochemical impedance spectroscopy for the bare and blocking-layer coated QDSCs with an applied voltage of 0.1 V, and the corresponding Bode plot. The lines were calculated using the equivalent circuit above. (c) Electrochemical impedance spectroscopy at the open-circuit voltage and the corresponding Bode plot.
Electrical impedance spectroscopy (EIS) is a powerful tool for analyzing the electrochemical reaction at the interfaces [31–33]. At relatively low voltages, the Fermi level of nanoparticle TiO$_2$ electrode is far below the conduction band. So, the electron concentration in the TiO$_2$ electrode is relatively low, and the nanoparticle layer behaves like an insulator. Therefore, charge transfer is dominated by the reaction at the FTO/electrolyte interface [34]. Thus, we can mainly focus on the blocking-layer effect at this low-voltage region. Fig. 3(b) shows the impedance spectroscopy for the bare and blocking-layer coated QDSCs at 0.1 V with AM 1.5 illumination. The charge-transfer resistance was calculated using the equivalent-circuit model represented by Fabregat-Santiago et al. [35], as shown in Fig. 3(a). The $R_t$ is a series resistance of FTO, $R_{FTO}$ is the charge-transfer resistance for the electron recombination from the FTO to the electrolyte, and $C_{FTO}$ is the capacitance for the FTO/electrolyte interface. The $Z_{dsol}$ stands for the impedance of diffusion in the polysulfide electrolyte, $R_p$ is the charge-transfer resistance from the electrolyte to the Pt counter electrode, and $C_p$ is the corresponding interfacial capacitance. The fitting lines are shown as solid/dashed lines in Fig. 3(b), and the fitting parameters are listed in Table 2. The parameters, including $Z_{dsol}$, $R_p$, and $C_p$, remain unchanged with the addition of the blocking layer, so these parameters are fixed. As shown in Table 2, the charge-transfer resistance increases considerably by one order of magnitude with the incorporation of the TiO$_2$ blocking layer, which means that the recombination is reduced at the FTO/electrolyte interface. The 170 nm-deposited sample exhibits a $C_{FTO}$ value that is approximately five times larger than the other samples, due to the capacitive charging/discharging of the thick TiO$_2$ blocking layer on the FTO. As shown in the Bode plot, the peak frequency is shifted from ~100 Hz to ~10 Hz with the addition of the blocking layer, which again indicates a reduced charge-transfer rate [36]. In spite of the low charge-transfer resistance of the 170 nm sample compared with that of the 30 nm sample, the peak-frequency position of the sample is shifted to a much lower region, and this result is in good agreement with the larger $C_{FTO}$ value.

For the open-circuit voltage, the charge-transfer resistance of the blocking-layer coated sample exhibits lower resistance compared with the value measured at 0.1 V (Fig. 3(c)), because the electron-carrier density in the TiO$_2$ nanoparticles is high at the relatively high open-circuit voltage. On the other hand, the bare sample exhibits a similar resistance and Bode-plot characteristics at 0.1 V and at the open-circuit voltage, due to the relatively low open-circuit voltage of the bare sample (0.285 V), so the charge-transfer kinetics do not change significantly [35].

The recombination rates of QDSCs were determined by photovoltaic-decay measurements. The photovoltaic-decay rate of the cell with a blocking layer exhibits much slower rate than that of the bare sample, as shown in Fig. 4(a). The electron recombination rate at the FTO/electrolyte decreased due to the compact TiO$_2$ blocking layer. Therefore, more electrons accumulated in the TiO$_2$ nanoparticle layer, thereby resulting in higher photovoltaic voltage concurrently. The decay-time constants were calculated to quantify the decay rate from equation [37]:

$$\tau = \frac{k_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1}. \quad (1)$$

The decay-time constant of the blocking-layer (30 nm) coated sample is approximately one order of magnitude higher compared with bare sample at all the voltages, as shown in Fig. 4(b).

To examine the electrolyte reactions with FTO, cyclic voltammetry was performed in the same polysulfide electrolyte used in our QDSCs, as shown in Fig. 5. The TiO$_2$ blocking layer effectively suppresses oxidation/reduction reactions of the polysulfide electrolyte with the FTO. On the other hand, in the middle of the potential range, the capacitive current increases as the blocking layer becomes thicker, as clearly shown in the magnified inset of Fig. 5. The TiO$_2$ conduction-band position in the polysulfide electrolyte is estimated to be −0.83 V vs. NHE, based on measuring the acidity of the electrolyte (pH 12.1) with −0.12 V vs. NHE at pH 0.

### Table 1

Open-circuit voltage, short-circuit current, fill factor, and power-conversion efficiency of the CdS-QDSCs with various blocking-layer thicknesses.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>V$_{oc}$ (V)</th>
<th>J$_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>0.285</td>
<td>2.43</td>
<td>33.6%</td>
<td>0.23%</td>
</tr>
<tr>
<td>7</td>
<td>0.390</td>
<td>2.70</td>
<td>36.2%</td>
<td>0.38%</td>
</tr>
<tr>
<td>30</td>
<td>0.451</td>
<td>3.24</td>
<td>35.7%</td>
<td>0.52%</td>
</tr>
<tr>
<td>170</td>
<td>0.435</td>
<td>3.04</td>
<td>35.0%</td>
<td>0.46%</td>
</tr>
</tbody>
</table>

### Table 2

Charge-transfer resistance and capacitance for the FTO/electrolyte interface of the CdS-QDSCs obtained by using an equivalent circuit at an applied voltage of 0.1 V with various blocking-layer thicknesses, based on fitting the impedance spectroscopy in Fig. 3(b).

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$R_{FTO}$ (Ω)</th>
<th>$C_{FTO}$ (μF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>181</td>
<td>32.6</td>
</tr>
<tr>
<td>7</td>
<td>1881</td>
<td>29.4</td>
</tr>
<tr>
<td>30</td>
<td>2768</td>
<td>50.0</td>
</tr>
<tr>
<td>170</td>
<td>1511</td>
<td>198.7</td>
</tr>
</tbody>
</table>
for the conduction band of TiO₂ [38]. Therefore, we conclude that the capacitive current observed above −0.83 V is attributed to the filling of conduction-band states. Also, in the more positive potential region, capacitive current is still observed, due to a reversible filling of charge-trap states within the TiO₂ bandgap of the blocking layer [39,40]. These defects can act as recombination centers, which give rise to electron leakage by transferring photoexcited electrons from the TiO₂ blocking layer to the polysulfide electrolyte before reaching the FTO. In Fig. S2, the trap states are also observed in the absorption spectrum below the TiO₂−bandgap energy (3.2 eV), exhibiting an increased value with the thick blocking layer.

In order to characterize the light-harvesting effect of the blocking layer, we performed IPCE measurements, as shown in Fig. 6. Interestingly, asymmetric enhancement of IPCE is observed for the thick blocking-layer sample, which is not observed in the DSSCs. This is due to the absorption natures of the CdS semiconductor, and the trap-state absorption of the TiO₂ blocking layer. In the case of DSSCs, an IPCE below the ∼390 nm region (left region) is mainly affected by the absorption from the bandgap of the TiO₂ nanoparticles [41] because the molar absorption coefficient of the dye (∼10⁴ M⁻¹ cm⁻¹) is much lower than that of the TiO₂ [42]. In contrast, semiconductor quantum dots have much higher absorption coefficients of 10⁵ to 10⁶ M⁻¹ cm⁻¹ [42] above the bandgap energy. Therefore, the values of the IPCE are represented by the summation of the CdS and TiO₂ responses in the UV region. As the TiO₂ blocking-layer thickness increases, more photons are absorbed by the TiO₂ layer. The TiO₂ nanoparticles without the CdS sensitizer in the polysulfide electrolyte, however, exhibit lower solar-cell performance in the UV region (over the TiO₂ bandgap or left region in Fig. 6). Furthermore, as the blocking layer becomes thicker, the slopes of the IPCE spectra become steeper below the bandgap energy (middle region) in Fig. 6. The reason for this is that the thicker blocking layer has much more trap states, which means that the absorption near the conduction band becomes intensified, as shown by the absorption spectra of Fig. S2. In the higher wavelength region (right region), symmetric enhancement of the IPCE is observed because the absorption through the TiO₂ blocking layer becomes insignificant.

Fig. 7 shows a schematic illustration for the effect of the blocking layer. The electron recombination from the FTO electrode to the polysulfide electrolyte is blocked by the addition of the compact TiO₂ blocking layer, thereby improving Voc, Isc, and the fill factor. Consequently, this phenomenon has a direct impact on the improved energy-conversion efficiency of the QDSCs.
Nevertheless, when the blocking layer becomes too thick, the layer acts as trap sites for both recombination of the carrier and absorption of light. Therefore, the performance of the solar cell with the 170 nm blocking layer deteriorates.

4. Conclusions

The addition of blocking layer to QDSCs plays an important role in reducing the electron-carrier recombination at the FTO/electrolyte interface. The TiO2 blocking-layer coated Cds-sensitized solar cell exhibits enhanced conversion efficiency compared with the bare cell by more than a factor of two. In contrast to DSSCs, asymmetric enhancement of the IPCE is also observed, due to the high extinction coefficients of the semiconductor quantum dots compared with that of dye molecules.

Acknowledgments

This research was supported by the National Research Foundation of Korea, through the World Class University (WCU, R31-2008-000-10075-0), and the Korean Government (MEST: NRF, 2010-0029065).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2011.08.052.

References

The effect of a blocking layer on the photovoltaic performance in CdS quantum-dot-sensitized solar cells

Graphical abstract

Highlights

➤ The electron-recombination mechanisms within FTO/electrolyte interface are analyzed.
➤ The TiO₂-coated solar cell exhibits enhanced efficiency by more than a factor of two. ➤ The electron-carrier lifetime is one order of magnitude higher than bare sample. ➤ IPCE shows asymmetric behavior due to high extinction coefficients of quantum dots.

High performance quasi-solid-state dye-sensitized solar cells based on poly(lactic acid-co-glycolic acid)

Highlights

➤ A novel polymer gel electrolyte using poly(lactic acid-co-glycolic acid) of proton-donating groups and low crystallinity. ➤ High conductivity of 10 mS cm⁻¹ at 25 °C. ➤ Higher short-circuit current density than liquid-based cells (the intercalation of proton). ➤ High overall efficiencies of 7.5 and 7.4% with high polymer contents of 20 and 40 wt%, respectively (7.6% for the reference liquid-based cell). ➤ Overall efficiencies lying in ±5% of the initial values during 60 days under ambient conditions.

Precise modification of the interface between titanium dioxide and electrolyte of dye-sensitized solar cells with oxides deposited by thermal evaporation of metals and subsequent oxidation

Graphical abstract

Highlights

➤ Al₂O₃ and MgO were coated by thermal evaporation of metals and subsequent oxidation.
➤ The thickness of the oxide layers can be precisely controlled. ➤ Oxide layers were coated on TiO₂ of DSCs to modify its interface with electrolyte. ➤ The oxide layers remarkably improve the photovoltaic performance of DSCs.
Fig. S1. (Color) Dark current of the bare and blocking-layer coated CdS-sensitized solar cells with various thicknesses.
Fig. S2. (Color) Absorbance of the TiO$_2$ blocking layer with various thicknesses on the FTO substrate. Bare FTO sample is used as a reference.