RAPID COMMUNICATION

The role of ZnO-coating-layer thickness on the recombination in CdS quantum-dot-sensitized solar cells

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Abstract
To prevent recombination at the interface of TiO\textsubscript{2}/polysulfide-electrolyte, a ZnO layer was deposited on a TiO\textsubscript{2} electrode. The optimized ZnO-coated solar cell exhibited a ~32\% increase in the power-conversion efficiency compared to the bare cell. The coating layer acts as an energy barrier, which plays an important role in reducing the charge recombination from the TiO\textsubscript{2} electrode to the electrolyte. Moreover, CdS quantum-dot adsorption was enhanced by employing the ZnO-coated layer. The thicker ZnO layer (more than 8-cycle deposition), however, led to a less porous electrode, as confirmed by electrolyte diffusivity, and also deteriorated the cell efficiency by introducing defect states verified by electron lifetime and chronoamperometric reduction current.

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Introduction
Quantum-dot-sensitized solar cells (QDSCs) have been investigated as one of the most promising approaches for third-generation photovoltaic devices [1,2]. In comparison with dye sensitizers, quantum dots have particular advantages, such as tunability of the bandgap by controlling the quantum-dot size, high extinction coefficient (10\textsuperscript{5} – 10\textsuperscript{6}/M cm), and ability for multielectron generation [3-7].

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Despite these advantages, the efficiency of QDSCs is much lower than that of dye-sensitized solar cells (DSSCs) [7]. The main drawback in QDSCs is charge recombination at the TiO2/polysulfide-electrolyte interface [8-10]. One of the common methods of minimizing the recombination is to build up a thin energy barrier between the TiO2 and redox electrolyte [11-16].

As shown in Figure 1, the ZnO layer behaves as an energy barrier by taking advantage of the higher conduction band than that of TiO2 [12,17]. Using the ZnO barrier layer, enhanced photovoltaic properties were reported previously in QDSCs [17-19], with evidences of enhanced injection efficiency and reduced leakage current. However, demonstrations for the origin of reduced recombination are insufficient in previously-reported results.

Therefore, more systematic approach is necessary to analyze reactions at the TiO2/polysulfide-electrolyte interface. We carried out the measurements of chronoamperometric reduction current and electron lifetime in order to understand the role of ZnO-coating layers with considerations of the interfacial-recombination mechanisms. The effects of the coating-layer thicknesses were studied in terms of the amount of quantum-dot sensitizer, defect states of the coating layer, and electrolyte diffusivity through a porous electrode.

**Experimental procedure**

Nanoporous TiO2 electrodes were prepared on fluorine-doped tin oxide (FTO, TEC 8: Pilkington, Japan) substrates from Ti-Nanoxide D (Solaronix, Switzerland) paste by a doctor blade method. Electrodes were then post-annealed at 450 °C for 30 min in ambient air [20-23]. The ZnO-coating layers were formed using the successive ionic-layer adsorption and reaction (SILAR) method [24]. A 0.01 M ZnCl2 complex with an ammonia solution was prepared as a precursor solution. The TiO2 electrodes were immersed in the precursor solution for 15 s, and then immersed again in distilled water at 90 °C for 30 s. Various thicknesses of ZnO-coating layers were formed by varying the number of coating cycles (4, 8, 12, and 16 cycles).

The CdS quantum dots were deposited on the nanoporous TiO2 electrodes by the SILAR method [25]. The TiO2 electrode was dipped into a methanol solution containing CdCl2 (0.04 M, Aldrich) for 1 min, rinsed with methanol, then dipped for another 1 min into a Na2S methanol solution (0.04 M, Aldrich), and rinsed again with methanol. This dipping process was repeated seven times. For a counter electrode, two holes were drilled in FTO substrate, and Au thin film was deposited by rf magnetron sputtering [26]. Thermoplastic foil (Dupont, thickness: 25 μm) was used as a spacer and the polysulfide electrolyte was prepared by dissolving 0.5 M Na2S, 1.0 M S, and 0.02 M KCl in methanol and water at a ratio of 7:3 [10].

The photocurrent-voltage (J-V) curves of QDSCs were obtained with a potentiostat (CHI 608C: CH Instrumental Inc., Austin, USA) under AM 1.5 illumination (K3000: McScience, Korea, intensity at 100 mW/cm²) with an active cell area of 0.28 cm². An incident photon-to-current conversion efficiency (IPCE) measurement system (K3100: McScience, Korea) was used to obtain the external quantum efficiency [27], and optical properties of CdS quantum dots.
were measured by a UV–vis spectrophotometer (Lambda 35: Perkin-Elmer). An inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima-4300 DV: Perkin-Elmer) was used to measure the amount of Cd atoms loaded on TiO2 electrode. The electrochemical impedance spectra were obtained by a potentiostat under dark condition by applying open-circuit voltage ($V_{oc}$) with frequencies ranging from $\sim 10^{-1}$ to $\sim 10^{4}$ Hz.

**Results and discussion**

The ZnO-coated layer between CdS and TiO2 is verified by electron energy loss spectroscopy (EELS) mapping (Figure 2(a)). It can be seen that the ZnO layer has a thickness of approximately 3 nm, and is uniformly coated onto the TiO2. The formation of crystalline CdS quantum dots is also confirmed with various orientations (Figure 2(b)).

The change in the amount of CdS quantum dots, most likely due to the prior ZnO coating, is demonstrated by absorption spectra. The absorption edge is shifted to a longer wavelength, and the overall absorption is enhanced in the ZnO-coated electrodes, as shown in Figure 3. The optical bandgap is estimated through $\alpha^2$ vs. $h\nu$ plot in Figure 3, and it can be seen that the optical bandgap of 8-cycle-deposited electrode (2.47 eV) is smaller than that of the bare electrode (2.54 eV). Furthermore, when the average size of CdS quantum dots is obtained from Brus equation, describing the effect of exciton confinement [28–30], the increase in size (diameter) of 8-cycle-deposited electrode ($\sim 9$ nm) with respect to the bare sample ($\sim 7$ nm) can be easily verified (Table 1).

A quantitative analysis by ICP-AES also demonstrates that the amount of CdS quantum dots is increased. The Cd/Ti atomic ratios stood at 0.20, 0.26, 0.29, and 0.17, respectively, for the bare, 4-cycle, 8-cycle, and 16-cycle ZnO-coated electrodes. In particular, Cd atoms loaded on 8-cycle-deposited electrode increased by $\sim 69\%$ compared to the bare electrode. It can be estimated that the amount of adsorbed CdS increases by $\sim 47\%$ with the consideration of increased sensitizer size.

A possible demonstration for increases in both the amount and size of CdS can be justified by the grown morphology of ZnO-coating layer. It was observed by Mane et al. [24] that when ZnO is deposited by SILAR method, the ZnO layer forms in a conical shape. Following this result, the cone-like shape of ZnO increases the quantum-dots

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**Table 1** Short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor ($FF$), power-conversion efficiency ($\eta$), CdS quantum-dot size, and electrolyte diffusivity ($D$) of CdS-QDSCs with various ZnO-coating-layer thicknesses.

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$</th>
<th>$\eta$</th>
<th>CdS Size</th>
<th>$D$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>3.48</td>
<td>0.423</td>
<td>36.0%</td>
<td>0.53%</td>
<td>6.9 nm</td>
<td>7.15 x 10$^{-7}$</td>
</tr>
<tr>
<td>4 Cycles</td>
<td>3.98</td>
<td>0.451</td>
<td>35.1%</td>
<td>0.63%</td>
<td>8.4 nm</td>
<td>6.55 x 10$^{-7}$</td>
</tr>
<tr>
<td>8 Cycles</td>
<td>4.26</td>
<td>0.471</td>
<td>34.9%</td>
<td>0.70%</td>
<td>9.4 nm</td>
<td>5.76 x 10$^{-7}$</td>
</tr>
<tr>
<td>16 Cycles</td>
<td>3.18</td>
<td>0.416</td>
<td>31.7%</td>
<td>0.42%</td>
<td>6.0 nm</td>
<td>4.82 x 10$^{-7}$</td>
</tr>
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nucleation sites where CdS deposition can be consequently promoted [19,24,31]. In order to see whether the diffusion behavior of polysulfide electrolyte can be affected by the porosity of TiO2 [20,32], the diffusivities of polysulfide electrolyte through the nanoporous TiO2 electrode were confirmed by impedance spectroscopy (Figure 4). The diffusivities of the electrolyte were obtained by fitting the Warburg impedance based on the equivalent circuit in the inset of Figure 4. With increasing ZnO-deposition times, the pore size within the TiO2-nanoparticle film decreases, and the electrolyte diffusion through nanopores thus becomes difficult. The diffusivity of the 16-cycle-deposited electrode particularly decreases by a factor of 1.5 compared to that of the bare electrode. Certainly, the reduced diffusivity is associated with less porosity, and this can be also observed in Figure 3 where the absorption edge of 12 or 16-cycle-deposited sample shifts to shorter wavelength. The consideration of both Figures 3 and 4 leads us to the conclusion that the enhanced roughness by ZnO coating is more noticeable until 8-cycle deposition, and ZnO coating with more than 8-cycle deposition blocks the pores in TiO2, resulting in decreased inherent porosity of TiO2. The ZnO-coated cell exhibits both higher short-circuit current density ($I_{sc}$) and open-circuit voltage ($V_{oc}$) compared to the bare cell, as shown in Figure 5. Among the cells measured, the 8-cycle-deposited cell shows the best power-conversion efficiency of 0.70%, which is ~32% higher than that of the bare cell (0.53%). The corresponding photovoltaic parameters of all the cells are listed in Table 1. Though the efficiency reported here is lower than 4.6% by Chen et al. [17], the enhancement of cell performance is quite reasonable for the purpose of this study, namely, to evaluate the effect of ZnO coating on the CdS-QDSCs. The increase in photocurrent arises from both an increase in the absorption from the CdS quantum dots and a decrease in the carrier recombination. The reduced charge recombination increases the electron-carrier concentration, resulting in an upward shift of the electron Fermi level, and accordingly, $V_{oc}$ is higher than that of the bare cell. In contrast, 16-cycle-deposited ZnO layer exhibits lower efficiency, which might be caused by both the decreased amount of CdS quantum dots and diffusivity of polysulfide electrolyte. The recombination rate at the TiO2/polysulfide-electrolyte interface was confirmed by the open-circuit voltage decay, as shown in Figure 6(a). The slow decay response of the ZnO-coated cell confirms the reduced recombination between electrons in the TiO2 conduction band and a redox couple in the electrolyte. From the voltage decay curves, the electron-carrier lifetime ($\tau$) can be obtained by using following equation [33,34]:

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

At all voltages, the electron-carrier lifetime of the 8-cycle-deposited cell is improved by approximately one order of magnitude compared with the bare cell (Figure 6(b)). Since the recombination of carrier electrons is significantly diminished by the ZnO layer, the overall charge-collection efficiency is enhanced, as shown in Figure 7. It is interesting that the IPCE-enhancement ratio increases at wavelengths over 450 nm (inset of Figure 7). This result is in line with the increased amount of adsorbed CdS quantum dots, as shown by the absorption spectra (Figure 3) and ICP-
AES data. The less-porous 16-cycle-deposited cell results in reduction in the size of CdS, and therefore, the IPCE-enhancement ratio at wavelength above 450 nm is observed to be lower than that of the bare one.

The chronoamperometric reduction current is a measure of showing the recombination rate of electrons near the TiO2 conduction bandedge [35]. The applied potential was set to $-1.1 \text{ V vs. NHE}$, above the TiO2 conduction band. The position of TiO2 conduction band is estimated to be $-0.83 \text{ V vs. NHE}$, which was calculated from pH value in the polysulfide electrolyte (pH 12.1). The smaller reduction current of ZnO-coated TiO2 indicates that the recombination rate is significantly reduced by the ZnO potential barrier, as shown in Figure 8.

However, the reduction current is generated more severely from the 8-cycle-deposited ZnO layer than from that of the 8-cycle-deposited ZnO. When an epitaxial growth occurs, the early stage well follows defect-free epitaxial growth (below the critical thickness) [36-40]. Above the critical thickness, the lattice mismatch is accumulated with subsequent defect formation inducing strain relaxation. In other words, 16-cycle-deposited ZnO grows beyond a critical thickness, and several defect states (e.g., dislocations) are formed by which carrier electrons can easily recombine. Consequently, the degraded efficiency observed in 16-cycle-deposited cell is attributed to two factors: the decrease in both diffusivity and amount of deposited CdS by ZnO coating reducing the porosity of TiO2, and more frequent recombination induced by defect states generated inside the ZnO-coating layers.

Possible effects of the ZnO-coated layer in CdS-QDSCs are summarized in Figure 9. The ZnO potential barrier at the interface of TiO2/electrolyte effectively prohibits injected electrons in TiO2 from recombining with the redox couple in electrolyte. Also, the ZnO-coated layer allows for a substantial increase in size and a larger amount of CdS. However, the cell efficiency of the 16-cycle-deposited ZnO layer is lower than that of the bare cell, because of defect states and reduced porosity of the TiO2 electrode.

Figure 7 Incident photon-to-current conversion efficiency (IPCE) spectra of CdS-QDSCs with various ZnO-coating-layer thicknesses. The inset shows IPCE-enhancement ratios compared with the bare cell.

Figure 8 Chronoamperometry of bare and ZnO-coated electrodes measured at $-1.1 \text{ V vs. NHE}$ in polysulfide electrolyte. The inset shows cyclic voltammetric curves with various ZnO-coating-layer thicknesses, and the TiO2 conduction-band position is denoted by a short-dashed line.

Conclusions

The effects of ZnO-coating thicknesses on the photovoltaic properties were systematically investigated. The enhanced efficiency by the nanoscale coating was attributed to the increased adsorption of CdS quantum dots, and reduced charge recombination at the TiO2/polysulfide-electrolyte interface. The role of the coating layer was reflected in the longer electron lifetime than that of the bare cell, leading to a 32% increase (0.53% to 0.70%) in the efficiency of the corresponding QDSC.

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References


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