Effect of Ultrathin Al$_2$O$_3$ Layer on TiO$_2$ Surface in CdS/CdSe Co-Sensitized Quantum Dot Solar Cells

Sang Do Sung, Iseul Lim, Myung Soo Kim,† and Wan In Lee*†

Department of Chemistry, Inha University, Incheon 402-751, Korea. *E-mail: wanin@inha.ac.kr
†School of Chemistry, Seoul National University, Seoul 151-742, Korea

Received October 14, 2012, Accepted November 12, 2012

In order to enhance the photovoltaic property of the CdS/CdSe co-sensitized quantum dot sensitized solar cells (QDSSCs), the surface of nanoporous TiO$_2$ photoanode was modified by ultrathin Al$_2$O$_3$ layer before the deposition of quantum dots (QDs). The Al$_2$O$_3$ layer, dip-coated by 0.10 M Al precursor solution, exhibited the optimized performance in blocking the back-reaction of the photo-injected electrons from TiO$_2$ conduction band (CB) to polysulfide electrolyte. Transient photocurrent spectra revealed that the electron lifetime ($\tau_e$) increased significantly by introducing the ultrathin Al$_2$O$_3$ layer on TiO$_2$ surface, whereas the electron diffusion coefficient ($D_e$) was not varied. As a result, the $V_{oc}$ increased from 0.487 to 0.545 V, without appreciable change in short circuit current ($J_{sc}$), thus inducing the enhancement of photovoltaic conversion efficiency ($\eta$) from 3.01% to 3.38%.

Key Words: Quantum dot sensitized solar cells (QDSSC), CdS/CdSe, Al$_2$O$_3$, Blocking layer, Open circuit voltage ($V_{oc}$)

Introduction

Quantum dot sensitized solar cells (QDSSCs) attract augmenting attentions for the last a few years due to their low cost in fabrication and the possibility of boosting the energy conversion efficiency beyond the traditional Shockley and Queisser limit of 31%. Thus far various kinds of inorganic quantum dots (QDs) with tunable bandgaps and high absorption coefficient have been applied as sensitizers for QDSSCs. CdS/CdSe co-sensitized system is regarded as one of the most popular and promising candidates, because of its relatively high photovoltaic conversion efficiency ($\eta$) and facile fabrication process.

In general, CdS/CdSe QDSSCs exhibit quite high short circuit current density ($J_{sc}$), but its open circuit voltage ($V_{oc}$) is low, since the redox potential of the polysulfides (S$^2-/S_{n2}^-$), used as the electrolyte mediating the charges between the quantum dots (QDs) and counter electrode (CE), is located relatively high, compared to that of the 1/1 couple used in the dye-sensitized solar cells (DSSCs). If the $V_{oc}$ of the CdS/CdSe co-sensitized system is increased, its conversion efficiency will be enhanced to a great extent. Herein, we report a simple process increasing the $V_{oc}$ by coating an ultrathin Al$_2$O$_3$ layer on the surface of nanoporous TiO$_2$ film. Previously, Al$_2$O$_3$ has been used as the blocking layer for DSSCs. Due to considerably higher CB level of Al$_2$O$_3$ than that of TiO$_2$, the electrons injected from the dye molecules to the CB of TiO$_2$ will not be moved to the Al$_2$O$_3$ layer, which is directly facing the electrolyte solution. Resultantly, the back-reaction from TiO$_2$ CB to electrolyte could be blocked significantly.

In fabricating QDSSCs, the inorganic QDs are deposited on the surface of TiO$_2$ by successive ionic layer adsorption and reaction (SILAR) process, but, in general, only ~50% of TiO$_2$ surface is covered by CdS/CdSe QDs. Since ~50% of TiO$_2$ surface is exposed to the electrolyte, there is a high possibility of electron back-reaction from TiO$_2$ to polysulfide electrolytes. Therefore, the passivation of TiO$_2$ surface will be a crucial issue in developing efficient QDSSCs. The TiO$_2$ surface was often passivated or anchored by organic capping agents or antenna groups, and the cell efficiencies of QDSSCs were appreciably enhanced as a result. Thus far, however, passivation of TiO$_2$ surface with inorganic material such as Al$_2$O$_3$ or other metal oxides has not been reported in fabricating the QDSSCs. In this work, we applied the ultrathin Al$_2$O$_3$ layer as a blocking layer and investigated its effect in retarding charge recombination in CdS/CdSe co-sensitized QDSSCs.

Experimental Section

The viscous TiO$_2$ paste, employed to the fabrication of nanoporous oxide electrode, was prepared by following procedure. 0.2 g ethyl cellulose, 0.1 g lauric acid and 4.0 g terpineol were added to the 10 mL ethanol solution of 1.0 g TiO$_2$ (Degussa P25), and the ethanol was removed from the solution by rotary evaporator to obtain viscous paste. It was then blended at 1200 rpm for 90 min in a paste mixer (PDM-300, Dae-Wha Tech.). The prepared TiO$_2$ paste was coated on the FTO layer with a doctor-blade method, and the coated films were baked at 150 °C for 30 min, followed by calcination at 500 °C for 15 min.

Stoichiometric amounts of aluminum tri-sec-butoxide (97%, Aldrich) were dissolved in 20 mL 2-propanol to obtain the Al precursor solutions with different concentrations. Nanoporous TiO$_2$ films were immersed in the prepared Al
precursor solutions for 15 min under Ar atmosphere, and the dried samples were subsequently heat-treated at 450 °C for 15 min to obtain the Al2O3-coated TiO2 films (TiO2/Al2O3).

Inorganic QDs were deposited on the surface of TiO2 or TiO2/Al2O3 layer by SILAR process.17-19 To deposit CdS, TiO2 or TiO2/Al2O3 substrate was immersed in an ethanol solution containing Cd(NO3)2 (0.05 M) for 30 min, and rinsed with ethanol. It was then immersed in a Na2S methanol solution (0.05 M) for another 30 min, and rinsed with methanol. Above dipping procedure is defined as one cycle, and this deposition cycle was repeated three times. For the deposition of CdSe, sodium selenosulphate (Na2SeSO3, Aldrich) was used as Se source. The Na2SeSO3 aqueous solution (0.6 M) was prepared by refluxing Se (Aldrich) in an aqueous solution of Na2SO3 at 70 °C for ~12 h. The above deposition cycle was repeated four times. Finally, a ultrathin layer of ZnS was deposited on the TiO2/Al2O3/CdS(3)/CdSe(4) photoelectrode to protect the CdS/CdSe ultrathin layer of ZnS was deposited on the TiO2(3)/CdSe(4) QDs were then deposited by SILAR process over the prepared TiO2/Al2O3 photoanodes. As shown in Figure 1(c), about half of the TiO2/Al2O3 surface is covered by CdS/CdSe QDs, whose sizes are estimated to be ~5 nm.

As shown in UV-visible absorption spectra in Figure 2, the deposited CdS(3)/CdSe(4) QDs on TiO2 and TiO2/Al2O3 exhibit profound absorption over entire visible range up to ~700 nm, whereas the bare TiO2 and TiO2/Al2O3 do not show appreciable absorbance in this spectral range. It is also indicated that the absorbance spectrum of the deposited

using an IPCE system (PV Measurements, Inc.). The electron diffusion coefficient (D0) and the electron lifetime (τe) were measured by a laboratory-made SLITMP equipment, which is described in detail elsewhere.22-26

Results and Discussion

TEM images in Figure 1(a) and (b) show the Al2O3-coated TiO2 (TiO2/Al2O3), prepared by dip-coating the surface of the nanoporous TiO2 film with a 0.10 M Al precursor solution, followed by subsequent calcination at 450 °C. Most TiO2 surfaces were covered with amorphous Al2O3 layer with a thickness of a few nanometers or less. The CdS(3)/CdSe(4) QDs were then deposited by SILAR process over the prepared TiO2/Al2O3 photoanodes. As shown in Figure 1(c), about half of the TiO2/Al2O3 surface is covered by CdS/CdSe QDs, whose sizes are estimated to be ~5 nm.

As shown in UV-visible absorption spectra in Figure 2, the deposited CdS(3)/CdSe(4) QDs on TiO2 and TiO2/Al2O3 exhibit profound absorption over entire visible range up to ~700 nm, whereas the bare TiO2 and TiO2/Al2O3 do not show appreciable absorbance in this spectral range. It is also indicated that the absorbance spectrum of the deposited
Effect of Ultrathin Al$_2$O$_3$ Layer on TiO$_2$ Surface in CdS/CdSe

Cds(3)/CdSe(4) QDs was not appreciably modified by coating the ultrathin Al$_2$O$_3$ on TiO$_2$ surface, suggesting that the presence of Al$_2$O$_3$ layer does not change the deposition affinity toward CdS QDs during SILAR process.

In depositing the Al$_2$O$_3$ on the surface of porous TiO$_2$ layer, the concentration of Al precursor solution was varied to 0.05, 0.10, and 0.20 M, in order to determine the optimum thickness of Al$_2$O$_3$ layer in passivating the TiO$_2$ surface. Figure 3(a) shows the I-V curves of the CdS(3)/CdSe(4)/ZnS(1) QDSSCs deposited on the bare TiO$_2$ and several TiO$_2$/Al$_2$O$_3$ layers. Since the electrons generated in the CdS(3)/CdSe(4) QDs are transported to the TiO$_2$ CB via the Al$_2$O$_3$ layer with relatively higher CB level than that of CdS and TiO$_2$, the presence of Al$_2$O$_3$ layer will not be beneficial for the electron transport. In this work, however, when the Al$_2$O$_3$ layer was formed by 0.05 or 0.10 M Al precursor solution, the short circuit current ($J_{sc}$) was not appreciably changed, as shown in Figure 3(a) and Table 1, suggesting that the ultra-thin Al$_2$O$_3$ layers have not prevented the electron transport. In contrast, the Al$_2$O$_3$ layer, derived from 0.20 M Al precursor solution, significantly reduced the $J_{sc}$, clearly indicating that the electron transport is critically dependent on the thickness of Al$_2$O$_3$ layer and that the Al$_2$O$_3$ layer exceeding the critical thickness blocks the electron transport from QDs to TiO$_2$.

Differently from the trends of $J_{sc}$, $V_{oc}$ was enhanced significantly by depositing the Al$_2$O$_3$ layer, and its enhancement was maximized when the Al$_2$O$_3$ layer was formed by 0.10 M solution. It is suggested that the presence of Al$_2$O$_3$ layer with high CB level successfully protects the photo-injected electrons in the TiO$_2$ CB from the back-reaction and the thickness of the Al$_2$O$_3$ layer prepared from the 0.10 M solution is appropriate for this purpose. The TiO$_2$ surface may not be fully passivated by more dilute Al precursor solutions than 0.10 M, whereas the Al$_2$O$_3$ layer derived from 0.20 M solution would be too thick for the efficient transport of electrons. As a result, the $V_{oc}$ was increased from 0.487 to 0.545 V, with noticeable improvement of $\eta$ from 3.01% to 3.38%.

IPCE spectra, as shown in Figure 3(b), indicate that the external quantum efficiency (EQE) over the whole spectral range was not appreciably modified by introducing the ultrathin Al$_2$O$_3$ layer on the TiO$_2$ surface, suggesting that the coated Al$_2$O$_3$ did not induce appreciable light scattering effect, nor brought out other optical interferences.

The electron diffusion coefficient ($D_{e}$) and the electron lifetime ($\tau_{e}$) of the photo-injected electrons in the TiO$_2$ or TiO$_2$/Al$_2$O$_3$ layer during QDSSC operation were analyzed by a stepped light-induced transient measurements of photocurrent (SLITMP) technique.\textsuperscript{22-26} The electron diffusion coefficient was determined by the equation,

\[ D_{e} = \frac{L^2}{2.77 \times \tau_{e}} \]

where $L$ and $\tau_{e}$ are the thickness of the TiO$_2$ layer and the time constant, respectively.\textsuperscript{22} $\tau_{e}$ can be obtained by fitting the decay of transient photocurrent as a function of time ($t$) with a single-exponential function, $\exp(-t/\tau_{e})$. Figure 4(a) plots the $D_{e}$ as a function of the $J_{sc}$ for the CdS/CdSe QDSSCs prepared on TiO$_2$ and TiO$_2$/Al$_2$O$_3$. The $D_{e}$ value was not altered by the introduced Al$_2$O$_3$ layer, clearly indicating that the presence of ultrathin Al$_2$O$_3$ layer does not influence at all the electron transport through the TiO$_2$ CB.

The electron lifetime ($\tau_{e}$) can also be determined by fitting the decay of a transient photocurrent with $\exp(-t/\tau_{e})$. Figure 4(b) plots the $\tau_{e}$ as a function of the $J_{sc}$, illustrating that the $\tau_{e}$ values increased significantly by coating the ultrathin Al$_2$O$_3$ layer on TiO$_2$ surface. The longer electron lifetime indicates that the photo-injected electrons in the TiO$_2$ CB were

\begin{table}
\centering
\caption{Parameters obtained from I-V curves of the CdS(3)/CdSe(4)/ZnS(1) QDSSCs depending on the photoanodes}
\begin{tabular}{|c|c|c|c|c|}
\hline
Photoanode & $V_{oc}$ (mV) & $J_{sc}$ (mA/cm$^2$) & FF (%) & $\eta$ (%) \\
\hline
Bare TiO$_2$ & 487.2 & 12.984 & 47.63 & 3.01 \\
Al$_2$O$_3$-coated by 0.05 M & 528.3 & 12.606 & 47.91 & 3.19 \\
Al$_2$O$_3$-coated by 0.10 M & 545.1 & 12.785 & 48.45 & 3.38 \\
Al$_2$O$_3$-coated by 0.20 M & 499.6 & 12.043 & 48.08 & 2.89 \\
\hline
\end{tabular}
\end{table}
Coating the TiO$_2$ successfully protected by the Al$_2$O$_3$ layer. The fabricated TiO$_2$ layer was coated by 0.10 M Al precursor solution.

...whereas the polysulfide electrolyte, thus inducing the blocking of back-reaction spectra indicated that $\tau_e$ was increased considerably, which is clear evidence for the efficient blocking of electron back-reactions by the ultrathin Al$_2$O$_3$ layer.

Conclusions

The optimum Al$_2$O$_3$ layer, in blocking the back-reaction of the photo-injected electrons from TiO$_2$ CB to polysulfide electrolyte (S$_2^2$/S$_n^2$), was successfully prepared by dip-coating the TiO$_2$ surface with 0.10 M Al precursor solution. The fabricated TiO$_2$/Al$_2$O$_3$/CdS(3)/CdSe(4)/ZnS exhibited the significantly increased $V_{oc}$ (from 0.487 to 0.545 V), whereas $J_{sc}$ was not appreciably altered. Transient photocurrent spectra indicated that $\tau_e$ was increased considerably, whereas $D_e$ was not appreciably changed, which are clear evidence for the efficient blocking of electron back-reactions by the ultrathin Al$_2$O$_3$ layer.

Acknowledgments. This work has been supported by the Pioneer Research Program (2012-0001065), and the Converging Research Center Program (2009-0082141) through National Research Foundation funded by the Ministry of Education, Science, and Technology, Korea.

References