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The effect of TiO2-coating layer on the performance in nanoporous ZnO-based dye-sensitized solar cells

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HIGHLIGHTS

- Correlation between photovoltaic properties and TiO2-coating thicknesses.
- Suppression of Zn2+/dye-complex formation and carrier recombination.
- Enhancement of power-conversion efficiency by a factor of three.

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ABSTRACT

Polydisperse ZnO spheres consisting of ~43-nm-sized nanoparticles are facilely synthesized for dye-sensitized solar cells. A uniform TiO2-coating layer on the ZnO surface improves both the open-circuit voltage and short-circuit current, and the power-conversion efficiency is consequently enhanced by a factor of approximately three. A thin coating layer suppresses the formation of Zn2+/dye complexes due to the enhanced chemical stability against the acidic dye, and also reduces charge recombination at the ZnO/dye/electrolyte interface.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been regarded as potential candidates for next-generation solar cells due to their low cost, high durability, large flexibility in shape, and transparency [1–3]. While TiO2 is the most commonly used oxide semiconductor, ZnO has also been considered as a promising candidate for DSSCs. The main reasons are carrier mobility of single-crystal ZnO (115–155 cm² V⁻¹ s⁻¹), which is 2 orders of magnitude higher than that in TiO2 (1–4 cm² V⁻¹ s⁻¹), its direct bandgap (~ 3.2 eV), and the position of the conduction band similar to that of TiO2 [4–8]. Furthermore, various ZnO nanostructures can be obtained by easy and low-cost techniques [9–18]. Despite these advantages, the performances of ZnO-based DSSCs are typically lower (7.5% as a world record) [19] than those of TiO2-based DSSCs (12.3% as a world record) [3]. The limited performance may be explained by the formation of Zn2+/dye complexes and recombination at the ZnO/dye/electrolyte interface [20,21]. The Zn2+/dye complexes are attributed to the poor chemical stability of ZnO in acidic dye solution, and are responsible for the inefficient electron injection from dye to semiconductor [22].

To overcome these problems, several coating layers such as Al2O3, MgO, Nb2O5, SiO2, and TiO2 have been studied [23–28]. Among these materials, TiO2 has been attractive owing to its best performance in the optimized system with iodide-based electrolyte and organometallic dye. While TiO2-coated ZnO electrodes have been reported by atomic-layer deposition (ALD) or corrosive TiCl4 treatment [29–31], in this paper, a thin layer of TiO2 is coated by a facile wet-chemical method that is inexpensive and noncorrosive. In addition, the involved mechanisms between the photovoltaic properties and TiO2-coating thicknesses were identified in a nanoporous ZnO-based solar cell.
2. Experimental procedure

For the fabrication of polydisperse ZnO aggregates, zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O: Sigma–Aldrich) was added to diethylene glycol ((HOCH$_2$CH$_2$)$_2$O: Sigma–Aldrich), and heated in an autoclave at 160 °C for 6 h [32]. Then, the as-synthesized solution was centrifuged at 3000 rpm for 15 min, and dried at 60 °C. One gram of as-prepared ZnO powder, 0.45 g of cellulose ((C$_6$H$_{10}$O$_5$)$_n$: Aldrich), and 5 ml of terpineol (C$_{10}$H$_{18}$O: Aldrich) were mixed, and stirred for one day. Terpineol is an organic solvent with high boiling point and cellulose acts as a binder, preventing cracks during heat treatment and increasing adhesion among the ZnO nanospheres [33]. The resulting paste was spread on a fluorine-doped tin oxide substrate (FTO, TEC 8: Pilkington) by a doctor-blade method. The as-deposited films were subsequently annealed at 350 °C for 1 h.

The TiO$_2$-coating layer on ZnO was prepared by a facile wet-chemical method. The as-prepared ZnO films were immersed in 10 mM titanium butoxide (Ti(O(CH$_2$)$_3$CH$_3$)$_4$: Aldrich) in 2-propanol ((CH$_3$)$_2$CHOH: Sigma–Aldrich) at room temperature (RT). The thickness of the coating layer was controlled by changing the deposition time (30, 60, and 120 min). The TiO$_2$-coated films were post-annealed at 450 °C for 30 min, and the bare film was also sintered as a control set. After annealing, the films were sensitized with 0.5 mM of N719 dye (RuL$_2$(NCS)$_2$:2TBA, L = 2,2′-bipyridyl-4,4′-dicarboxylic acid, TBA = tetrabutylammonium: Solaronix) for 6 h at RT, followed by rinsing with ethanol and drying under a nitrogen stream. To prepare the counter electrode, Pt thin film was deposited by rf-magnetron sputtering on the pre-drilled FTO substrate with two holes. The sensitized electrode and platinized counter electrode were sealed with thermoplastic foil (25 μm: Dupont, U.S.A.), and the gap between the two electrodes was filled with an ionic-based redox electrolyte (AN-50: Solaronix, Switzerland).

The crystal structure of the electrode was analyzed by X-ray diffraction (XRD, M18XHF-SRA: MAC Science, Japan). Field-emission scanning electron microscopy (FE-SEM, SU70: Hitachi, Japan) was carried out to observe the morphology of the nanostructures. The photocurrent–voltage ($I$–$V$) curves were obtained on a solar cell measurement system (K3000: McScience, Korea) under a solar simulator (Xenon lamp, air mass (AM) 1.5, 100 mW cm$^{-2}$). High-resolution transmission electron microscopy (HRTEM, JEM-3000F: JEOL, Japan) and a focused ion beam (FIB, SMI3050SE: SII Nanotechnology Inc., Japan) were used to identify the uniform coating of TiO$_2$ through the nanoporous ZnO spheres. The elemental compositions and distribution were examined using energy-dispersive X-ray spectroscopy (EDX, ISIS-300: Oxford Instruments). An inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima-4300 DV: Perkin–Elmer, MA, U.S.A.) was employed to determine the atomic ratio of Ti/Zn in the electrode. In order to investigate the electrochemical reactions at the interfaces [34–36], electrochemical impedance spectroscopy (EIS) and open-circuit voltage decay (OCVD) were measured from a potentiostat (CHI 608C: CH Instrumental Inc., Austin, U.S.A.). The absorption spectra of the unloaded dye molecules were recorded on a UV/Vis spectrophotometer (Lambda 20: Perkin–Elmer, Waltham, U.S.A.), and incident photon-to-current conversion efficiency (IPCE) spectra were measured on an IPCE measurement system (K3100: McScience, Korea).

3. Results and discussion

To clearly identify the mechanisms of the TiO$_2$-coating layers with various thicknesses, the experiment was performed with
The ZnO nanoparticle has hexagonal wurtzite structure (JCPDS #36-1451), with no zinc-blende phase (JCPDS #77-0191), and TiO$_2$ is not detected due to the subnanometer-scale coating (XRD analysis in Fig. 1). Grain size is obtained from the Williamson–Hall plot [41], and that of 60-min-coated film after 450 °C annealing is ~ 43 nm, consistent with the cross-sectional TEM image of Fig. 2. The nanocrystallites are able to provide relatively large surface area, and the submicrometer-sized particles can provide effective light scattering [19,32].

The TiO$_2$-coating layer on the ZnO surface improves both the open-circuit voltage ($V_{oc}$) and short-circuit current ($J_{sc}$), as shown in the $J$–$V$ curves of Fig. 3. In particular, the 60-min-coated cell shows an optimum power-conversion efficiency of 1.27%, an increase by a factor of three compared with that of the bare cell. As the coating layer becomes thicker, $V_{oc}$ gradually increases while $J_{sc}$ decreases, as summarized in Table 1.

The amount of dye in the DSSCs was measured by UV–visible absorption, as shown in Fig. 6, considering the molar absorption coefficient of N719 dye ($\sim 10^4$ M$^{-1}$ cm$^{-1}$ at 543 nm) [45]. While the dye loading of all the coated films is higher than that of the bare film, the 60-min-coated film shows the optimum value. The increase in dye loading is attributed to the suppression of Zn$^{2+}$/dye-complex formation at the outer surface of ZnO sphere, which can block the dye diffusion into the nanoporous sphere. In the 120-min-coated film, the amount of dye is slightly decreased. A possible reason is the loss of surface area due to the coating on the nanoporous connections among ZnO nanoparticles.

Impedance analysis was performed at the open-circuit condition under AM 1.5 [46–48], and the resistance (between $\sim 10^9$ and $\sim 10^3$ Hz) increases with the thickness of the coating layer (Fig. 7).

Table 1

<table>
<thead>
<tr>
<th>Coating</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>1.50</td>
<td>0.595</td>
<td>43.9</td>
<td>0.38%</td>
</tr>
<tr>
<td>30 min</td>
<td>3.02</td>
<td>0.645</td>
<td>54.2</td>
<td>1.06%</td>
</tr>
<tr>
<td>60 min</td>
<td>3.30</td>
<td>0.663</td>
<td>58.3</td>
<td>1.27%</td>
</tr>
<tr>
<td>120 min</td>
<td>2.55</td>
<td>0.679</td>
<td>57.2</td>
<td>0.99%</td>
</tr>
</tbody>
</table>

The nanoparticle size of the bare film without TiO$_2$ coating (Fig. 4(a)) is bigger than that of the coated film after 450 °C annealing (Fig. 4(c)), indicating that the TiO$_2$-coating layer inhibits the coarsening behavior of ZnO nanoparticles (before dye loading) [42]. This is also supported by the larger full-width at half-maximum (FWHM) of the coated film from diffraction (Fig. 1) [43,44]. Therefore, 60-min-coated film has relatively large surface area. After dye loading, the bare film (Fig. 4(b)) is covered with Zn$^{2+}$/dye complexes. However, no significant morphological change is observed in the coated film, confirming that the TiO$_2$ layer efficiently restrains the formation of Zn$^{2+}$/dye complexes.

Fig. 5 confirms the homogeneous coating of TiO$_2$, from the spatial distribution of Zn and Ti elements throughout the nanopores. With the atomic ratios of Ti/Zn measured by ICP-AES, the coating thickness is in the subnanometer range if assumed uniform coating. Most of the generated electron carriers from dye would transfer through the ZnO nanoparticles because TiO$_2$ layer is too thin to transfer electrons effectively, and also ZnO is a preferred electron channel due to the high mobility [4,5]. The detailed description about the thickness calculation is provided in the supplemental materials (Table S1).

The device performance under AM 1.5 is summarized in Table 1, where, for example, Bare shows the performance without coating, 30 min, 60 min, and 120 min show the performance after coating for 30 min, 60 min, and 120 min, respectively. The device performance improves with increasing coating time, and the 60 min coating is higher than that of the bare device. However, the 120 min coating decreases the device performance compared with the 60 min coating.

Fig. 4. Plan-view FE-SEM images of nanoporous ZnO spheres with/without TiO$_2$-coating layer (60 min) followed by 450 °C annealing, and before/after dye loading.
This indicates that the TiO$_2$-coating layer suppresses back electron transfer, and consequently improves $V_{oc}$ [49,50]. Thicker coating, however, also suppresses forward electron injection, resulting in a decreased current density [51–54]. The bare cell shows the highest resistance due to the formation of resistive Zn$^{2+}$/dye complexes.

Reduction of charge recombination was also observed (Fig. 8) [55–57]. The decay response of the coated cell is slower than that of the bare cell, indicating that recombination is effectively reduced. The electron-carrier lifetime ($\tau$) is obtained from Ref. [55]:

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

where $k_B T$ is the thermal energy, $e$ is the elementary charge, and $t$ is time (Fig. 8(b)). The electron-carrier lifetime of the coated cell is approximately one order of magnitude higher in comparison with the bare cell.

The TiO$_2$-coated cells show higher IPCE values than the bare cell in the whole visible region due to the reduction of recombination by TiO$_2$ coating, as shown in Fig. 9. Even in the lower wavelength region (below $\sim 390$ nm) where light is mainly absorbed by ZnO, the IPCE of the bare cell is still lower than that of the coated cell because of the formation of Zn$^{2+}$/dye complexes, while the degree of enhancement among the coated cells becomes insignificant. The bandgap of ZnO nanoparticle aggregate is expected to be similar to that of the bulk ($\sim 3.2$ eV), because the size of nanoparticle ($\sim 43$ nm) is much larger than the excitonic diameter of ZnO ($\sim 5.6$ nm) [58]. The IPCE value dropped to zero at wavelength around 300 nm due to the absorption of FTO [59].

The shorter dye-adsorption time (30 min) is also performed for higher efficiency, and the corresponding photocurrent density–voltage ($J$–$V$) characteristics are presented in Fig. 10. These results
indicate similar tendency with that of the longer dye-immersion time (6 h) that \( V_{oc} \) increases while \( J_{sc} \) decreases, as the coating-layer thickness increases (Table 2). The optimum power-conversion efficiency of 2.54% is obtained in the 60-min-coated cell, which is \( \sim 26\% \) higher than that of the bare cell (1.87%). The interface stability of TiO\(_2\)-coated cell is investigated for two weeks, as shown in Fig. 11. In the first several days, both \( V_{oc} \) and fill factor (FF) increase while \( J_{sc} \) decreases, resulting in the 15% decrease in efficiency. The former may be attributed to adsorption of electrolyte additives on the electrode surface, and the latter may result from the dissolution of Zn into the electrolyte [60,61]. The efficiency, however, remains relatively constant after several days, indicating good stability of the interfaces. Schematic representations illustrate the effect of the TiO\(_2\)-coating layer (Fig. 12). This coating layer not only reduces the recombination and formation of Zn\(^{2+}\)/dye complexes, but also preserves the relatively large surface area. These

Fig. 8. (a) Experimental decay results of \( V_{oc} \) for the bare and coated cells. (b) Electron lifetime from Eq. (1) as a function of voltage.

Fig. 9. Incident photon-to-current conversion efficiency (IPCE) spectra of bare and coated cells.

Fig. 10. Photocurrent density–voltage characteristics of the TiO\(_2\)-coated ZnO-based DSSCs (dye-adsorption time: 30 min), and the inset shows the power-conversion efficiency of DSSCs with respect to the TiO\(_2\)-coating time.

Table 2

<table>
<thead>
<tr>
<th>( J_{sc} ) (mA cm(^{-2}))</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>5.44</td>
<td>0.601</td>
<td>57.2%</td>
</tr>
<tr>
<td>30 min</td>
<td>6.64</td>
<td>0.605</td>
<td>58.7%</td>
</tr>
<tr>
<td>60 min</td>
<td>6.77</td>
<td>0.627</td>
<td>59.9%</td>
</tr>
<tr>
<td>120 min</td>
<td>4.63</td>
<td>0.635</td>
<td>60.4%</td>
</tr>
</tbody>
</table>

Fig. 11. The changes of short-circuit current, open-circuit voltage, fill factor, and power-conversion efficiency of the 60-min-coated cell for two weeks (dye-adsorption time: 30 min).
results directly influence the improved $V_{oc}$, $J_{sc}$, and FF compared with the bare cell.

4. Conclusions

The effect of TiO$_2$-coating layers on the performance of ZnO-based DSSCs is systematically investigated with various TiO$_2$-coating thicknesses. The TiO$_2$ layers play an important role in the suppression of the formation of Zn$_2^+$-dye complexes and recombination at the ZnO/dye/electrolyte interface. As a result, the power-conversion efficiency is enhanced by a factor of approximately three.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2013.01.042.

References

The effect of TiO₂-coating layer on the performance in nanoporous ZnO-based dye-sensitized solar cells

Highlights

- Correlation between photovoltaic properties and TiO₂-coating thicknesses.
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- Enhancement of power-conversion efficiency by a factor of three.

Ab initio design of GaN-based photocatalyst: ZnO-codoped GaN nanotubes

Graphical abstract

Highlights

- GaN nanotubes codoped with ZnO.
- Chirality-dependent doping effects.
- Wide tunable band gap and enhanced mobility.
- High efficiency for solar energy conversion.

Errata

Corrigendum to “Nb-doped TiO₂/carbon composite supports synthesized by ultrasonic spray pyrolysis for proton exchange membrane (PEM) fuel cell catalysts” [J. Power Sources 220 (2012) 1–8]

Keerthi Seneviratne, Vladimir Neburchilov, Vanessa Alzate, Ryan Baker, Roberto Neagu, Jiujun Zhang, Stephen Campbell, Harmeet Chhina, Siyu Ye
Supplemental Materials

Table S1. Atomic ratios of Ti/Zn in the films, as measured by ICP-AES, and the thicknesses of TiO$_2$ layer, with the assumption of uniform coating on each nanoparticle.

<table>
<thead>
<tr>
<th>Time</th>
<th>Ti/Zn</th>
<th>TiO$_2$ Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td>0.81%</td>
<td>0.04 nm</td>
</tr>
<tr>
<td>60 min</td>
<td>2.67%</td>
<td>0.23 nm</td>
</tr>
<tr>
<td>120 min</td>
<td>3.63%</td>
<td>0.32 nm</td>
</tr>
</tbody>
</table>

The thicknesses of TiO$_2$ coating layers are estimated with a simple back-of-an-envelope calculation. Because we confirmed from the EDX analysis that TiO$_2$ is coated relatively uniformly throughout the ZnO nanopores, we assume that each nanoparticle is covered with a uniform TiO$_2$ layer. Heterogeneous nucleation of TiO$_2$ on ZnO may cause nonlinear increase of thicknesses. The TiO$_2$-coating thicknesses are obtained without considering the three-dimensional necking of nanoparticles, and the actual thicknesses may be thicker than the calculated values. Although the atomic ratios of Ti/Zn are also measured by EDX, ICP-AES method is used due to its reliability of quantitative analysis.