Hollow SnO₂ microspheres for high-efficiency bilayered dye sensitized solar cell

Jing Chen,‡*a Chen Li,†*a Feng Xu,‡†b Yidan Zhou,a Wei Lei,a Litao Sunb and Yan Zhanget al.

Received 11th May 2012, Accepted 27th June 2012
DOI: 10.1039/c2ra20909h

We synthesized hollow SnO₂ microspheres using a hydrothermal method and fabricated bilayered dye sensitized solar cells (DSSCs) with hollow SnO₂ microspheres as the top layer and TiO₂ as the bottom layer. Due to the reduced transfer resistance, faster diffusion constants, and enhanced light harvesting, the performance of the bilayered DSSC with SnO₂ top layer was better than that without SnO₂ top layer. A maximum power conversion efficiency (PCE) of 4.15% was obtained for this bilayered DSSC under illumination of one sun (AM 1.5 G, 100 mW cm⁻²), which exhibited a 19% improvement compared to the QDSSC without a SnO₂ layer.

1. Introduction

Dye sensitized solar cells (DSSC) have received considerable research interest due to their low cost, simple fabrication process and relatively high conversion efficiencies. It is well accepted that the performance of DSSCs can be dominated by several factors, for example, the light harvesting ability of dyes, the electron transport rate at the semiconductor interface and the diffusion velocity of electrolyte. Compared to TiO₂, SnO₂ has a faster electron diffusion rate due to its higher electron-mobility. Meanwhile, the bilayered photoanode can help improve the energy conversion efficiency by tuning the film structure from monolayer to multilayer. The hollow SnO₂ microspheres were synthesized by a hydrothermal method. A power conversion efficiency (PCE) for the bilayered DSSC of 4.15% was obtained in this work.

2. Experimental

SnO₂ was synthesized through a hydrothermal method and the procedure was described elsewhere. Briefly, 1.75 g TiN(V) chloride, 1.71 g D-(-)glucose, 10 ml deionized water, and 1 mmol or 5 mmol sulfuric acid were mixed together and reacted at 190 °C for 24 h. The precipitates were obtained and dried at 600 °C for 3 h. Two kinds of SnO₂ hollow microspheres with sizes of 200 nm and 600 nm were prepared. 0.5 g ethylcellulose was added to 5 ml ethanol and stirred for 30 min to form a clear gel. After that, 0.1 g SnO₂ powder and 0.4 g tert-pineol were added into the gel, and then stirred continually to form a homogenous white paste. A 10 μm thick TiO₂ film (Sn-Nanoxide T/SP, Solaronix) and a 2.0 μm thick SnO₂ film were deposited on FTO glass (SnO₂: F, Solaronix) sequentially by the doctor blading method. A bare 12 μm thick TiO₂ film was fabricated for comparison. Then, the electrodes were immersed into a 0.3 mM acetonitrile: tert-butyl alcohol (1:1) solution of cis-bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato) (2,2'-bipyridyl-4,4'-dinonyl) ruthenium(II) (commercially called Z907 dye) for 3 h. The TiO₂/SnO₂ photoelectrodes were assembled with a 20 nm platinum-coated indium tin oxide (ITO) substrate as the counter electrode. The cell gap was maintained by a 60 μm thermal-plastic spacer. The iodide electrolyte consisting of 0.05 M I₂, 0.6 M 1-methyl-3-propylimidazolium iodide (MPII), and 0.5 M 4-tert-butyl-pyridine (TBP) in acetonitrile was injected into the cells by the capillary effect. The photoanodes fabricated with TiO₂/SnO₂ (200 nm), TiO₂/SnO₂ (600 nm) and TiO₂ were named cell A, B and C, respectively. X-ray diffraction (XRD) patterns were obtained on a D8 Advance X-ray diffractometer (Bruker AXS, USA) using Cu-Kα irradiation.
Nitrogen adsorption–desorption isotherms were obtained on AS-6B apparatus (Micromeritics Instrument Corp.). All the samples were degassed at 150 °C prior to Brunauer–Emmett–Teller (BET) measurements. The thickness of the film was measured by TENCOR P-10 Surface Profiler. The absorption spectra were recorded using a SHIMADZU MPC-2200 UV-VIS Spectrometer. The current density-voltage (J–V) characteristics were measured with a Keithley 2440 Sourcemeter and the cell was subjected to the irradiation of a solar simulator (Abet-technologies, USA) operating at 100 mW cm\(^{-2}\) (AM 1.5 G). The incident photon to current conversion efficiency (IPCE) was measured with QE/IPCE Measurement Kit (Oriel, USA) in the wavelength range of 350 to 800 nm. Electrochemical impedance spectra (EIS) were measured under open circuit potential with oscillation potential amplitudes of 10 mV from \(10^{-2}\) to \(10^{6}\) Hz.

3. Results and discussion

3.1 Morphology and structure characterization of the photoanode

Fig. 1a and b show the scanning electron microscopy (SEM) images of the hollow SnO\(_2\) microspheres with a size of \(~600\) nm. It is clearly seen that the SnO\(_2\) has a hollow structure. Fig. 1c and d show the SEM images of the bare TiO\(_2\) film and TiO\(_2\)/SnO\(_2\) film. It can be seen that the 2 \(\mu\)m thick SnO\(_2\) microsphere layer was uniformly dispersed on the 10 \(\mu\)m thick TiO\(_2\) layer. Most SnO\(_2\) microspheres have an open hole on the hollow structure after heat-treatment at 600 °C. Fig. 1e and f show the transmission electron microscopy (TEM) images of two kinds of SnO\(_2\) microspheres. It is clear that both SnO\(_2\) microspheres have a hollow structure with inner sphere diameters of 200 and 600 nm, respectively. And it has been reported that this hollow structure enhances light harvesting due its multiple light reflecting and scattering effects in the DSSC\(^{6,9}\).

Fig. 2a shows the XRD spectra of 200 and 600 nm SnO\(_2\) hollow microspheres. It can be seen that all the diffraction peaks of the SnO\(_2\) hollow microspheres are in good agreement with a rutile structure of SnO\(_2\) (JCPDS No.41–1445)\(^{11}\). Fig. 2b shows the reflectance measurement of TiO\(_2\), TiO\(_2\)/SnO\(_2\) (200 nm), and TiO\(_2\)/SnO\(_2\) (600 nm). It can be seen that the reflecting light in hollow SnO\(_2\) is higher than TiO\(_2\). TiO\(_2\) nanoparticles have very weak reflectance, and the light scattering effect is usually ignored due to their size being smaller than 30 nm\(^{12}\). Therefore, hollow SnO\(_2\) can produce a greatly enhanced light harvest due to light multi-reflections and scattering.

3.2 Photovoltaic performances of DSSCs

Fig. 3a and b show I–V characteristics and the IPCE spectra of cells A–C at 100 mW cm\(^{-2}\) (AM 1.5 G), whose related photovoltaic parameters were listed in Table 1. Cell A has a PCE of 4.05% with short-circuit current density \((J_{sc})\) of 8.83 mA cm\(^{-2}\), open-circuit voltage \((V_{oc})\) of 0.679 V, and fill factor (FF) of 67.6%. With 600 nm SnO\(_2\) hollow microspheres (cell B) the DSSC leads to an improved PCE of 4.15% with \(J_{sc} = 9.36\) mA cm\(^{-2}\), \(V_{oc} = 0.662\) V, and FF = 67.0%.
than that of TiO2, which leads to the decreased reflections within the TiO2/SnO2, rather than an increased surface likely because of enhanced light harvesting due to multiple light photoanodes. The and B is due to the suppressed back electron transfer in the bilayered area. Compared to cell C, the improvement in the FF values of cell A because the conduction-band edge of SnO2 is 300 mV more positive than of I3-. It was reported that the middle-frequency peak reflects the properties of the photoinjected electrons with the oxide semiconductor, which can be fitted to a transport resistance (Rw) and a constant phase element. The high-frequency peak can be fitted to a charge-transfer resistance (Rct) and the chemical capacitance, which is due to charge transfer at the interfaces of the redox electrolyte/Pt counter electrode. According to the electric circuit shown in the inset of Fig. 4b, the Rw and Rct can be obtained by Z-view software. The Rw values are 19.6, 17.7 and 21.4 Ω and Rct are 4.03, 2.07 and 4.33 Ω for cells A–C, respectively. Therefore, cell B performs the lowest value of Rw and Rct among the three cells, indicating that more efficient charge transfer process at the interfaces of oxide/dye/electrolyte and electrolyte/Pt electrode. The low resistance and high diffusion.

### Table 1: Detailed photovoltaic parameters of cell A–C

<table>
<thead>
<tr>
<th>Cells</th>
<th>Jsc (mA cm⁻²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell A</td>
<td>8.83</td>
<td>0.679</td>
<td>67.6</td>
<td>4.05</td>
</tr>
<tr>
<td>Cell B</td>
<td>9.36</td>
<td>0.662</td>
<td>67.0</td>
<td>4.15</td>
</tr>
<tr>
<td>Cell C</td>
<td>9.23</td>
<td>0.706</td>
<td>53.6</td>
<td>3.49</td>
</tr>
</tbody>
</table>

Compared to cell C, the PCE of cell B has improved 19%, which is due to the increased Jsc and FF. The larger Jsc value for cell B is most likely because of enhanced light harvesting due to multiple light reflections within the TiO2/SnO2, rather than an increased surface area. Compared to cell C, the improvement in the FF values of cell A and B is due to the suppressed back electron transfer in the bilayered photoanodes. The Voc for cells A and B were a little decreased. It is because the conduction-band edge of SnO2 is 300 mV more positive than that of TiO2, which leads to the decreased Voc of cells with SnO2 layer. Meanwhile, higher Jsc value for cell B than cell A should result from the larger dye absorption amount due to the enhanced surface areas, light scattering and reflection abilities. Therefore, cell B has the best performance among the three cells.

Fig. 3b presents the IPCE of cells A–C, which were measured in iodide electrolyte. The corresponding values of FF and η are shown in the format of (FF, η) in (a).

**Fig. 3** (a) I–V characteristics (b) IPCE spectra of cell A–C measured under simulated solar illumination (AM 1.5 G) with an intensity of 100 mW cm⁻² in iodide electrolyte. The corresponding values of FF and η are shown in the format of (FF, η) in (a).

**Fig. 4** (a) steady-state current–voltage curves of cells A–C. (b) Nyquist plots of cells A–C. The electric circuit is shown in the inset of Fig. 4b.

### 3.3 Diffusion constants and EIS measurements

Lastly, to reveal the kinetics of interfacial reactions of photoexcited electrons in DSSCs, we measured the EIS spectra of the as-prepared DSSCs. Fig. 4a shows the steady-state current–voltage curves of samples A–C. The diffusion-limited current density (jlim) eqn (1) is shown as follows:

\[
 j_{\text{lim}} = 2nFD_{I_3^-}c_{I_3^-}/l
\]

Where F is Faraday's constant (96 484 C mol⁻¹), \( c_{I_3^-} \) is the concentration per volume unit of I3⁻, \( D_{I_3^-} \) is the diffusion constant of I3⁻, \( n \) is the number of electrons transported in the each reaction (in general, \( n = 2 \)) and \( l \) is the distance between electrodes. The diffusion constants of I3⁻ are estimated as 2.0 × 10⁻⁶, 2.9 × 10⁻⁶ and 1.6 × 10⁻⁶ cm² s⁻¹, respectively. Cell B has the highest diffusion constant among the three cells, which can be beneficial to the charge transfer in cell B.
constant in the DSSC can facilitate electron transfer and reduce electron recombination, leading to a higher FF value. As a result, the improved performance of DSSCs based on TiO\textsubscript{2} coated with hollow SnO\textsubscript{2} is ascribed to rapid charge transport with less diffusive hindrance by the presence of hollow SnO\textsubscript{2} microsphere layer.

4. Conclusion

Z907 dye sensitized solar cells based on SnO\textsubscript{2} hollow microspheres were studied in this work. A TiO\textsubscript{2}/SnO\textsubscript{2}/dye bilayered cell has a better performance than a TiO\textsubscript{2}/dye cell, which is attributed to the multiple light reflection and scattering in the DSSCs by the presence of the SnO\textsubscript{2} hollow structure. EIS measurements demonstrated a lower resistance and faster diffusion constant for TiO\textsubscript{2}/SnO\textsubscript{2}/dye than TiO\textsubscript{2}/dye, leading to the reduction of electron recombination and a lower FF value. As a result, a PCE of 4.15\% was achieved for TiO\textsubscript{2}/SnO\textsubscript{2}/dye, which accounts for a 19\% improvement compared to the TiO\textsubscript{2}/dye cell.

References