Research Article

Aluminum-Doped SnO₂ Hollow Microspheres as Photoanode Materials for Dye-Sensitized Solar Cells

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Al doped SnO₂ microspheres were prepared through hydrothermal method. As-prepared SnO₂ microspheres were applied as photoanode materials in dye-sensitized solar cells (DSCs). The properties of the assembled DSCs were significantly improved, especially the open-circuit voltage. The reason for the enhancement was explored through the investigation of dark current curves and electrochemistry impedance spectra. These results showed that the Al doping significantly increased the reaction resistance of recombination reactions and restrained the dark current. The efficient lifetime of photoexcited electrons was also obviously lengthened.

1. Introduction

Dye-sensitized solar cells (DSCs) have been actually promoted by the development of nanocrystal materials, especially the preparation of TiO₂ nanocrystals with different morphology [1, 2]. High photoelectric conversion efficiency up to 14.3% has been obtained [3]. However, the band gap of TiO₂ is about 3.2 eV which causes obvious catalyzing properties under UV light. The organic solvent in DSCs might be slightly decomposed by TiO₂ nanoparticles on the photoanode under sunlight. As an alternative to TiO₂, SnO₂ has been extensively investigated as a photoanode material in DSCs. SnO₂ has a wider band gap (about 3.6 eV) than that of TiO₂ which was inactive to the organic solvent in DSCs. And SnO₂ has high electron mobility (about 150 cm²V⁻¹s⁻¹) which is a benefit for the collection of the photoexcited electrons in the photoanode [4, 5]. However, the band edge of conduction band edge of SnO₂ is ~4.5 eV (vacuum level) which causes serious back reaction between the electrons in the conduction band and the oxide ions in the electrolyte. It is an efficient way to inhibit these back reactions by doping SnO₂ with other metal elements. Duan et al. doped SnO₂ nanoparticle with Al and found the tuning of the conduction band and suppression of charge recombination [6]. Li et al. prepared Zn-doped SnO₂ nanocrystals to obtain longer electron lifetimes and higher dye loading [7].

In this work, we prepared Al doped SnO₂ hollow microspheres. The electron recombination was efficiently restrained and the photoelectrical conversion efficiency was significantly enhanced compared with that of pure SnO₂.

2. Experimental

2.1. Preparation of Pure SnO₂ Power and Al Doped SnO₂ Power. SnO₂ microspheres were synthesized using the hydrothermal method as follows. For the preparation of SnO₂ power, 0.8 g of stannous chloride dihydrate (SnCl₂·2H₂O) was dissolved in 80 mL deionized water. D-Glucose was used as the soft template. The content of D-glucose was 7.024 g. The former mixture was stirred for 30 min. at room temperature. The resulting well-distributed mixture was transferred into a 100 mL autoclave for hydrothermal reaction at 180°C. The hydrothermal reaction time was 16 h. After the autoclave was cooled to room temperature, the product was collected by centrifugation and washed with distilled water and ethanol several times. The obtained sample was dried at 60°C overnight. The resulting brown power was calcined at 550°C for 1 h in air to obtain the final product. For preparing the
Al doped SnO$_2$ sample, aluminum(III) chloride (AlCl$_3$) was added to the precursor solution. The addition amount of Al was controlled to be 0.5%, 1.0%, 1.5%, and 2.0% (at%) of Sn content in the solution. The preparation processes of Al doped SnO$_2$ powder were controlled to be the same as that described above except for the addition of AlCl$_3$. The obtained samples of pure SnO$_2$ and Al doped SnO$_2$ powder were denoted as pure SnO$_2$, 0.5% Al doped SnO$_2$, 1.0% Al doped SnO$_2$, 1.5% Al doped SnO$_2$, and 2.0% Al doped SnO$_2$, respectively.

2.2. Fabrication of DSSC Based on Pure SnO$_2$ and Al Doped SnO$_2$. To prepare the working electrode, SnO$_2$ or Al doped SnO$_2$ slurry was covered on fluorine-doped tin oxide (FTO) glass ($1 \times 2$ $\text{cm}^2$, $15$ $\Omega$ $\text{sq}^{-1}$, Opvtech) using a doctor blade technique and then sintered at $450^\circ \text{C}$ for 30 min. After cooling to $80^\circ \text{C}$, the samples were immersed in $5 \times 10^{-4}$ mol L$^{-1}$ ethanol of N719 dye for 24 h. Pt counter electrode was prepared by spreading 5mM H$_2$PtCl$_6$ aqueous solution on an FTO glass substrate, followed by pyrolyzation at 390$^\circ \text{C}$ for 15 min. The mixture of 0.6 M dimethylpropylimidazolium iodide, 0.1M iodine, 0.5 M 4-tert-butylpyridine, and 0.1 M lithium iodide in methoxyacetonitrile was prepared as the electrolyte of DSCs.

2.3. Characterization and Optical Measurements. The crystalline phase of the samples was characterized by DX-2700 X-ray diffractometer (XRD) with monochromatized Cu K$_\alpha$ irradiation. The morphology was studied using a JSM-7001F field emission scanning electron microscope (FE-SEM) and JEM 2100 transmission electron microscope (TEM). XPS measurements were performed on Thermo Scientific ESCALAB 250 station (Thermo Fisher Scientific, Massachusetts, USA). Photocurrent density-voltage ($J-V$) characteristics were measured using a Keithley 2440 Source Meter under AM 1.5 G illumination from a Newport Oriel Solar Simulator with an intensity of one sun. The incident light intensity was calibrated with a standard Si solar cell provided by Newport Oriel. The active cell area of the assembled DSCs was 0.25 $\text{cm}^2$. An electrochemistry workstation (IM6) was used to investigate the electrochemical impedance spectra (EIS) of DSCs. This measurement was also carried out with the same structured DSCs as that used in the former experiments. The impedance measurement of DSCs was recorded under dark condition at the bias potential of $-0.6$ V over a frequency range of 0.1-1 MHz with an AC amplitude of 10 mV.

3. Results and Discussion

Figure 1(a) shows the morphology of the prepared Al doping SnO$_2$ microspheres. The diameter is 300–500 nm. These SnO$_2$ microspheres were piled up with homogeneous nanoparticles. The size of the particles is 20–40 nm. There are some broken microspheres which indicate that the prepared SnO$_2$ is hollow microspheres. This structure is a benefit for the absorbing of dye and the diffusion of the electrolyte in DSCs. TEM was also carried out to confirm the hollow spheres structure of SnO$_2$. The TEM of SnO$_2$ microspheres is shown in Figure 1(b). The whole SnO$_2$ spheres show almost the same darkness which indicates that the thickness at the center of SnO$_2$ spheres is almost the same as that of edge. Therefore, the as-prepared SnO$_2$ should be hollow spheres.

Figure 2 shows the XRD spectra of SnO$_2$ microspheres doped with different Al content. The prepared SnO$_2$ microspheres correspond to the cassiterite structured SnO$_2$ (JCPDS database card number 41-1445). There is almost no change in the XRD spectra with the addition of Al element which might be because the content of added Al element is too little to change the structure of SnO$_2$. The crystalline particle size ($D$) could be estimated from the 110, 101, and 211 diffraction peak using the Scherrer equation [8]:

$$D = \frac{0.89\lambda}{\beta \cos \theta},$$

where $\lambda$ is the wavelength of the X-ray, $\beta$ is the full-width at half-maximum (FWHM), and $\theta$ is the Bragg angle in the
Table 1: Detailed photovoltaic parameters of the SnO\textsubscript{2} hollow microspheres doped with different Al content.

<table>
<thead>
<tr>
<th>Al content/at%</th>
<th>$V_{OC}$/mV</th>
<th>$J_{SC}$/mA cm\textsuperscript{-2}</th>
<th>FF/%</th>
<th>Efficiency/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>179</td>
<td>8.05</td>
<td>32.2</td>
<td>0.46</td>
</tr>
<tr>
<td>0.5</td>
<td>347</td>
<td>9.40</td>
<td>51.7</td>
<td>1.69</td>
</tr>
<tr>
<td>1.0</td>
<td>412</td>
<td>10.71</td>
<td>53.4</td>
<td>2.36</td>
</tr>
<tr>
<td>1.5</td>
<td>474</td>
<td>11.48</td>
<td>55.8</td>
<td>3.04</td>
</tr>
<tr>
<td>2.0</td>
<td>442</td>
<td>9.56</td>
<td>55.2</td>
<td>2.34</td>
</tr>
</tbody>
</table>

Figure 2: XRD of SnO\textsubscript{2} hollow microspheres doped with different Al content.

The characteristic frequencies of these photoanodes, SnO\textsubscript{2} and Al doped SnO\textsubscript{2}, are 3.1 and 1.2 Hz, respectively. According to (2), the electron lifetimes ($\tau_e$) were calculated to be about 51 ms and 132 ms for the SnO\textsubscript{2} and Al doped SnO\textsubscript{2} electrodes, respectively. It can be seen that Al doping can enhance the efficient electron lifetime of SnO\textsubscript{2} electrodes. This result is in accordance with that of dark current experiments (shown in Figure 4).

4. Conclusions

Al doped SnO\textsubscript{2} microspheres were prepared through hydrothermal method using glucose as template. The SnO\textsubscript{2} microspheres were piled up with SnO\textsubscript{2} nanoparticles. As-prepared SnO\textsubscript{2} microspheres were applied as photoanode materials in dye-sensitized solar cells. The results showed that the Al doping significantly restrained the dark current and improved the open-circuit voltage of the cells. Electrochemistry impedance spectra showed that the reaction resistance of recombination reactions increased sharply after doping of Al and the efficient
Figure 3: XPS of SnO$_2$ hollow microspheres doped with 1.5% Al and pure SnO$_2$ hollow microspheres (given in the insert): (a) full spectra; (b) high resolution of O 1s; (c) high resolution of Sn 3d; (d) high resolution of Al 2p.

Figure 4: $J$-$V$ characteristic of the DSCs based on the SnO$_2$ hollow microspheres doped with different Al content (a) and the corresponding dark current-voltage curves (b).
lifetime of photoexcited electrons was lengthened. The total photoelectrical conversion efficiency was improved from 0.46% to 3.04% after Al doping.

**Competing Interests**

The authors declare that they have no competing interests.

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**References**


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