Chemical Structure of ZnO Nanorod Array on a DSSC Photoanode


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ABSTRACT

The main objective of the present work was to study speciation of ZnO nanorods during the photoexcited electron transfer between photosensitive dyes and the ZnO nanorod arrays on the photoanode of a dye-sensitized solar cell (DSSC) by X-ray absorption (near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)) spectroscopy. The least-square component fitted XANES spectra show that the main zinc species in the ZnO-nanorod photoanode are nanosize ZnO (88%) and Zn(OH)₂ (12%). An enhanced adsorption of the dyes N₃ (C₂₆H₂₀O₁₀N₆S₂Ru) and mercurochrome (C₂₀H₈Br₂HgNa₂O₆) on the ZnO nanorods is found, of which 6-10% of the nanosize ZnO involve in the chemical interaction with the dyes. Their EXAFS spectra also indicate that the bond distance and coordination number of Zn-O in the ZnO nanorods is 1.95 Å (which is less than that in the ZnO seedlayer by 0.01 Å) and in the range of 4.6-4.8, respectively. The efficiencies of the DSSCs containing the N₃ and mercurochrome dispersed ZnO nanorods on the photoanodes are 0.33-0.92%. The relatively less \( J_{sc} \) (photocurrent density) of the DSSC with the N₃-dispersed ZnO nanorod may be due to the formation of a N₃-Zn²⁺ complex. A rapid recombination of the photoexcited electrons with I₃⁻ in the electrolyte of the DSSC containing the N₃ dispersed ZnO nanorods is also found, which causes a reduction of its \( FF \) (fill factor) value.

Keywords: DSSC, ZnO, XANES, EXAFS

1 INTRODUCTION

Dye-sensitized solar cells (DSSCs) have been attracted increasing attention in recent decades, due to their low fabrication cost, relatively simple process, and high efficiency [1, 2]. The typical DSSC is consisted of a dye adsorbed on a nanostructure films made up of metal oxide nanoparticles, an electrolyte as a charge transportation layer containing iodide/tri-iodide redox couples, and a platinum coated transparent conducting oxide glass as a counter electrode [3-5]. Dye sensitizers adsorbed on the surfaces of photoactive metal oxide nanoparticles are used for absorbing incident sunlight. During illumination of solar irradiation, the photoexcited electrons are migrated from the dye sensitizers to the conduction band of photoactive metal oxide and transported to the transparent conducting oxide (TCO) glass. The dye sensitizers are regenerated with electrons from the platinum counter electrode through the redox couple in the electrolyte [6, 7]. Tens of thousands of the grain boundary in a traditional DSSC may restrain electron transportation from dye sensitizer to a TCO glass. Therefore, promoting the electron transfer efficiency of photoactive metal oxide nanoparticle photoanode is an essential issue [8-10].

Zinc oxide possessing an effective band gap (3.37 eV), high electron mobility and good optical characteristic has attracted extensive attention in UV light emitters, field emissions, gas/chemical sensors, and field effect transistors [11]. Very recently, it has been found that an improvement of the electron transportation in the photoanode of a DSSC can be achieved by using single crystal and vertical ZnO nanowires or rods on a TCO glass [10, 12-14].

Coordination number (CN), bond distance, and oxidation state of select element in the complex matrix can be determined by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. By EXAFS, it was observed that copper oxide clusters played an important role in catalytic oxidation of chlorophenols (in supercritical water) and decomposition of NO [16, 17]. The photoactive sites in the nanosize TiO₂ during photocatalytic degradation of CHCl₃ and methylene blue have also been formed by in situ XANES [18, 19].

Speciation of zinc in the ZnO nanorod photoanode adsorbed with dye sensitizers is still lacking in the literature.
The molecule-scale understanding of photoactive species can facilitate development of new DSSC technologies. Hence, the main objective of this work was to study chemical structure of zinc in the ZnO nanorod photoanode adsorbed with dye sensitizers such as mercurochrome and N3.

2 EXPERIMENTAL

The ZnO sol-gel precursor was prepared by dissolving zinc acetate dihydrate (Zn(CH3COO)2·2H2O) (OSAKA) in a mixture of containing 2-aminoethanol (NH2CH2CH2OH) (WAKO) (0.75 M) and 2-methoxyethanol (CH3OCH2CH2OH) (Fluka) at a 1:1 molar ratio of zinc acetate dihydrate to 2-aminoethanol. The solution was mixed with stirring at 333 K for 30 min to yield a clear solution which was dropped onto an ITO substrate for spin coating on a spin coater at 30 00 rpm for 30 sec. The thin film was dried at 353 K and annealed at 623 K for one hour. The film was self-assembled at 363 K. The as synthesized ZnO nanorod photoanode was washe with deionized water and dried at 353 K for 24 hour.

Chemical structure of the ZnO nanorod photoanode was determined by X-ray diffraction spectroscopy (D8 advance, Bruker) with a Cu Kα (1.542 Å) radiation. The microstructure of the ZnO nanorod on the photoanode was studied by scanning electron microscopy (SEM) (PHILIPS, S3000N). After dehydration at 373 K, the photoanode was immersed in 0.04 mM of N3 dye (C26H20O10N6S2Ru) (Solaronix) or mercurochrome (C20H8Br2HgNa2O6) (Fluka) in C2H5OH (99.5%) at 298 K for 24 hours in the dark. The Pt counter electrode was prepared by spin-coating of a H2PtCl6 solution (a drop) on the ITO and annealed at 373 K for 10 minutes. After infusion electrolyte into the spacer, the channels between two electrodes were sealed by epoxy resin.

The dye-sensitized ZnO nanorod photoanode was illuminated through a conducting glass by with an AM 1.5 simulated light irradiation (300W Xenon lamp and AM 1.5 filter). The current-voltage characteristics of the DSSCs were investigated on a solar simulator (Newport, 91160A).

3 RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the ZnO seedlayer and nanorod on the ITO substrate. The characteristic diffraction peaks at (100), (002) and (004) that are attributed to wurtzite (JCPDS card no. 36-1451) are observed. A sharp diffraction peak (002) at 2θ = 34.8° suggests that ZnO nanorod on the photoanode has a high crystallinity. Remarkably, the enhanced diffraction peak (002) is much more intensive than the (100) and (004) peaks, indicating that the ZnO nanorods are oriented perpendicular to the substrate surface perfectly and grown along the c-axis, which is similar to observation of Cheng and Samulski [20]. The (002) diffraction peak for the ZnO seedlayer may be attributed to the well establish ZnO nanorod in the crystal growth process.

The SEM image of the ZnO nanorod on the photoanode is shown in Figure 2. The vertically well-aligned arrays of ZnO nanorod with a high density are uniformly formed on the substrate. The length, diameter and aspect ratio of nanorods are about 900, 50 nm and 18, respectively.

XANES can provide information including oxidation state of an excited atom, coordination geometry and bonding of local environment in the complex matrix. XANES spectra of model compounds such as nanosize ZnO, Zn(OH)2, and metallic Zn have also been determined. The XANES spectra of zinc were expressed mathematically in a LC XANES fit vectors, using the absorption data within the energy range of 9640-9700 eV. The least-square fitted XANES spectra of zinc in the ZnO nanorod are shown in Figures 3. The main zinc species in the ZnO seedlayer is nanosize ZnO (100%). Zinc species in the ZnO nanorod are mainly nanosize ZnO (88%) and Zn(OH)2 (12%). Adsorption of N3 (C26H20O10N6S2Ru) and mercurochrome (C20H8Br2HgNa2O6) dyes on the ZnO nanorod photoanode causes decreasing of nanosize ZnO fractions to 83 and 80%, respectively.

The EXAFS spectra of zinc were recorded and analyzed in the k range of 3.5-12.5 Å⁻¹. The Debye-Waller factors (Δσ²) are less than 0.01 Å² in all refined EXAFS data (see Table 1). In the ZnO seedlayer and nanorod, the bond distances of Zn-O are 1.96 and 1.95 Å, respectively. The coordination numbers (CNs) of the ZnO nanorod photoanode adsorbed with N3 and mercurochrome are 4.6 and 4.8, respectively.

The photocurrent density-voltage characteristics of the dye-sensitized solar cell fabricated with the ZnO nanorod
photoanode adsorbed with N3 and mercurochrome dye under an AM 1.5 simulated light irradiation are shown in Figure 4. The solar cell efficiency can be expressed by $\eta = (J_{sc} \times V_{oc} \times FF / P_{in})$, where, $J_{sc}$ is the short-circuit current density, $V_{oc}$ is the open-circuit voltage, $FF$ is the fill factor, and $P_{in}$ is the incident light power. The parameters of the ZnO nanorod photoanode in the DSSC are summarized in Table 2. The $V_{oc}$ value of the ZnO nanorod/N3 on the photoanode of the DSSC is slightly greater than that of the mercurochrome dye. The $J_{sc}$ of the DSSC with the ZnO nanorod adsorbed with N3 is much less than that with mercurochrome, which may be caused by the formation of a N3-Zn$^{2+}$ complex [21]. The less FF value in the ZnO nanorod/N3 on the photoanode of the DSSC suggests that the photoexcited electrons may be more rapidly to be recombined by I$_3^-$ in the electrolyte if compare to the DSSC using the mercurochrome dye. It seems that the mercurochrome has a better performance in the ZnO nanorod on the photoanode of the DSSC.

4 CONCLUSIONS

The main zinc species in the ZnO nanorod photoanode are nanosize ZnO (88%) and Zn(OH)$_2$ (12%). An enhanced adsorption of the dyes N3 ($C_{26}H_{20}O_{10}N_6S_2Ru$) and mercurochrome ($C_{20}H_8Br_2HgNa_2O_6$) on the ZnO nanorods is found, of which 6-10% of the nanosize ZnO involve in the chemical interaction with the dyes. The coordination numbers (CNs) of the ZnO nanorod photoanode adsorbed with N3 is less than that with mercurochrome. Because of the formation of a N3-Zn$^{2+}$ complex, the $J_{sc}$ of the DSSC with the ZnO nanorod adsorbed with N3 is much less than that with mercurochrome. A rapid recombination of the photoexcited electrons with I$_3^-$ in the electrolyte of the DSSC containing the N3 dispersed ZnO nanorods is also found, which causes a reduction of its FF (fill factor) value.

5 ACKNOWLEDGEMENTS

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REFERENCES

Table 1: Structural parameters of the ZnO nanorod photoanode absorbed with mercurochrome and N3.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Bond Distance (Å)</th>
<th>Coordination Number</th>
<th>( \sigma^2 ) (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seedlayer</td>
<td>1.96±0.0001</td>
<td>5.20</td>
<td>0.006</td>
</tr>
<tr>
<td>ZnO nanorod</td>
<td>1.95±0.0001</td>
<td>5.20</td>
<td>0.006</td>
</tr>
<tr>
<td>ZnO NRA /mercurochrome</td>
<td>1.95±0.0001</td>
<td>4.75</td>
<td>0.005</td>
</tr>
<tr>
<td>ZnO NRA/N3</td>
<td>1.95±0.0001</td>
<td>4.55</td>
<td>0.005</td>
</tr>
</tbody>
</table>

\( \sigma^2 \): Debye-Waller.

Figure 1: XRD patterns of the ZnO (a) seedlayer (magnified by 10 times) and (b) nanorod on the ITO substrate.

Figure 2: SEM images of the ZnO nanorod photoanode.

Figure 3: SEM images of the ZnO nanorod photoanode.

Figure 4: Current-voltage curves of the DSSCs containing the ZnO NRA photoanode absorbed with (a) N3 and (b) mercurochrome.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>( V_{oc} ) (V)</th>
<th>( J_{sc} ) (mA/cm²)</th>
<th>( FF )</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO nanorod /</td>
<td>0.52</td>
<td>1.03</td>
<td>0.42</td>
<td>0.92</td>
</tr>
<tr>
<td>Mercurochrome</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO nanorod / N3</td>
<td>0.60</td>
<td>0.57</td>
<td>0.24</td>
<td>0.33</td>
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<tr>
<td>TiO₂ /</td>
<td>0.49</td>
<td>2.84</td>
<td>0.45</td>
<td>0.64</td>
</tr>
<tr>
<td>Mercurochrome</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂ /N3</td>
<td>0.68</td>
<td>11.8</td>
<td>0.40</td>
<td>3.22</td>
</tr>
</tbody>
</table>

\( V_{oc} \): open-circuit voltage; \( J_{sc} \): short-circuit current density; \( FF \): fill factor; \( \eta \): efficiency.

Table 2: Structural parameters of the ZnO nanorod photoanode absorbed with mercurochrome and N3.