Dye-sensitized Solar Cell Based on ZnO Nanorod Arrays

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Abstract: ZnO nanorod arrays were fabricated on the fluorine-doped SnO2 transparent conducting oxide (FTO) glass substrates and used as the wide band gap semiconductor in dye-sensitized solar cells. Our objectives are to introduce and demonstrate new possibilities in designing the semiconductor morphology. The best performance with this cell structure produced an open circuit voltage ($V_{oc}$) of 0.64 mV, a short circuit current density ($J_{sc}$) of 5.37 mA/cm$^2$, a fill factor (FF) of 0.49, and conversion efficiency ($\eta$) of 1.69%, primarily limited by the surface area of the nanorod array.

Keywords: Zinc Oxide, Nanorod Arrays, Dye-sensitized Solar Cell, High Surface Area, One-dimensional

1. INTRODUCTION

Solar cell is one of the most promising renewable energy technologies for this century because it has possibility for solving environmental problems and insufficient energy problem. Dye-sensitized solar cell (DSSC) using inorganic semiconductor is being studied as a new type of solar cell and expected as a low cost alternative to conventional solid-state device. One important limiting factor in the DSSC cell performance is electron transport. During its traversal to the photoelectrode, an electron is estimated to cross 10$^3$ to 10$^6$ nanoparticles [1]. The disorder structure of the nanoparticles film leads to enhanced scattering of free electrons, thus reducing electron mobility and causing electron recombination especially at the grain boundaries between the nanoparticles[2]. The replacing of the nanoparticle film with an array of oriented single-crystalline nanorod offers the potential for improved electron transport leading to higher photoefficiencies. The pathways provided by the nanorods ensure the rapid collection of carriers generated throughout the device as the nanorod provide a direct path from the point of photogeneration to the conducting substrate. This greatly reduces the electron recombination losses of the photogenerated charge-carriers due to the fewer grain boundaries in charge transportation process. Moreover, electron transport in the crystalline rod is expected to be several orders of magnitude faster than percolation through a random polycrystalline network [3].

In this study, we have fabricated transparent ZnO nanorod arrays on the fluorine-doped SnO$_2$ transparent conducting oxide (FTO) glass substrates and used them as the wide band gap semiconductor in dye-sensitized solar cells.

2. METHODOLOGY

2.1 Synthesis

Arrays of ZnO nanorods were chemically synthesized on FTO substrate. The procedure consists of two steps. Firstly, zinc acetate solution was dropped onto substrates by spin coating, and then the substrates were dried and annealed in order to form the nanocrystal seeds on the substrates. Secondly, vertical ZnO nanorod arrays from the nanocrystal seeds were grown by immersing the seeded substrates in precursor solution containing Zn(NO$_3$)$_2$ and 0.80 M NaOH at 110$^\circ$C with different growth time interval.

2.2 Characterization

The crystalline structure of the samples was evaluated by X-ray diffraction (XRD, RIGAKU RINT 2100). The microstructure of the prepared materials was analyzed by scanning electron microscopy (SEM, JEOL JSM-6500FE).

2.3 Dye-sensitized solar cell measurement

The ZnO electrodes were soaked in 0.3 mM of ruthenium (II) dye (known as N719, Solaronix) in a t-butanol/ acetonitrile (1:1, in vol %) solution. The electrodes were washed with acetonitrile, dried, and immediately used for measuring photovoltaic properties. The electrolyte was composed of 0.6 M dimethylpropylimidazolium iodide, 0.1 M lithium iodide (Li$_2$), 0.05 M iodide (I$_2$), and 0.5 M 4-tert-butylpyridine in acetonitrile.

3. RESULTS AND DISCUSSION [4]

3.1 Characterization results

Figure 1 shows typical SEM images of the ZnO nanorods arrays grown on FTO substrate. The low-magnification images (A, C) show a well-aligned high-density ZnO nanorods growing uniformly in large area on the substrate. From the high magnification image (D), it can be seen that high-density ZnO nanorods with well-defined hexagonal facets were grown vertically on the substrate. The cross-sectional view (B) of nanorods arrays demonstrated that the ZnO grew vertically from the substrate. In this work, we could grow ZnO nanorods in the wafer scale implied that our method is applicable to mass production of well-aligned ZnO nanorod arrays.

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The crystallinity of the grown ZnO nanorods was investigated using XRD. A typical XRD pattern is shown in Figure 2, the intensity of the peak assigned to the (002) plane of wurtzite ZnO was markedly strong and the diffraction peaks of other crystal planes disappeared or very weak revealing that ZnO nanorods were formed through elongation along the $c$-axis perpendicularly to the substrate.

In addition, we found that the length of ZnO nanorod could be freely modified by controlling the reaction time. The nanorod lengths increased from 2.6 to 4.0 and 5.1 µm when the reaction times increase from 1 to 2 and 4 h, respectively. By the multiple-step growth, the nanorod length can be increased up to 10.8 µm when the total reaction time of 18 h.
3.2 Dye-sensitized solar cell characteristics

Figure 3 shows the absorption spectra of N719 dye adsorbed onto the ZnO nanorods array with different film thickness. All samples have the same maximum values around 308, 377, and 511 nm. The intensities of the absorption peaks of N719 were decreasing gradually with decreasing film thickness, suggesting that fewer dyes have been adsorbed onto the thinner films than onto the thicker films.

![Absorption spectra](image)

**Fig. 3** Absorption spectra of adsorbed N719 dye onto ZnO nanorods array films at different nanorods length: (a) 2.6 µm, (b) 4.0 µm, (c) 5.1 µm, and (d) 10.8 µm.

In order to examine the device performance, the photocurrent-voltage characteristics of the DSC using ZnO nanorod as the electrode have been measured under illumination as shown in Figure 5. The fundamental results have been summarized in the Table 1. The short circuit current density and cell performance significantly increase as the nanorod length increases. A higher amount of the adsorbed dye on longer nanorods, resulting in improving photon absorption and carrier generation with increased rod length [5]. These results suggest that cell performance is strongly depending on the electrode surface area. The increasing in the nanorod length provides larger amount of surface area, more adsorbed dyes, and resulting in higher conversion efficiency. The best-worked cell gave a conversion efficiency (η) of 1.69 %, an open circuit voltage (Voc) of 0.64 mV, a short circuit current density (Jsc) of 5.37 mA/cm², a fill factor (FF) of 0.49 in case of the ZnO obtained from the reaction time of 18 h. The use of nanorods with high crystallinity instead of nanoparticles contributes to the decreased number of grain boundaries, which act as electron traps [6]. This greatly reduces the electron recombination losses of the photogenerated charge-carriers due to the fewer grain boundaries in charge transportation process. The nanorod arrays also provide a direct path from the point of photogeneration to the conducting substrate. These pathways ensure the rapid collection of carriers generated throughout the device. Moreover, electron transport in the crystalline rod is expected to be several orders of magnitude faster than percolation through a random polycrystalline network [7].

<table>
<thead>
<tr>
<th>Samples</th>
<th>Reaction time (h)</th>
<th>Nanorod length (nm)</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>2.6</td>
<td>2.88</td>
<td>0.60</td>
<td>0.54</td>
<td>0.94</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
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<td>3.97</td>
<td>0.59</td>
<td>0.54</td>
<td>1.27</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>5.1</td>
<td>4.84</td>
<td>0.61</td>
<td>0.48</td>
<td>1.42</td>
</tr>
<tr>
<td>D</td>
<td>18</td>
<td>10.8</td>
<td>5.37</td>
<td>0.64</td>
<td>0.49</td>
<td>1.69</td>
</tr>
</tbody>
</table>
Fig. 5 Photocurrent-Voltage curves of the N719- sensitized ZnO electrodes with different nanorods length: (a) 2.6 µm, (b) 4.0 µm, (c) 5.1 µm, and (d) 10.8 µm.

4. CONCLUSION

In this study, we have fabricated transparent ZnO nanorod arrays FTO glass substrates and used them as the wide band gap semiconductor in dye-sensitized solar cells. The nanorods length can be highly controlled by adjusting the reaction time interval. The short circuit current density and cell performance were mainly determined by the nanorod length. The increasing in the nanorod length provides larger amount of surface area, more adsorbed dyes, and resulting in higher conversion efficiency. The best performance with this cell structure produced an open circuit voltage ($V_{oc}$) of 0.64 mV, a short circuit current density ($J_{sc}$) of 5.37 mA/cm$^2$, a fill factor (FF) of 0.49, and a conversion efficiency ($\eta$) of 1.69 %, primarily limited by the surface area of the nanorod array.

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6. REFERENCES