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Fabrication of Length Tunable ZnO Nanowire Arrays and Investigation on Their Effect for Dye-Sensitized Solar Cells

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Abstract

A series of ZnO nanowire arrays were grown on seeded fluorine-doped tin oxide (FTO) substrates by hydrothermal method. The effect of reaction solution concentration on the length and morphology of ZnO nanowire arrays, as well as cell performance in dye-sensitized solar cell (DSSC) was investigated. It was found that with the increase of growth solution concentration, the ZnO nanowires became longer in length, but with the bottom of nanowires gradually interconnected to each other. The enlarged ZnO nanowire length lead to increased power conversion efficiency and achieved the highest efficiency of 1.54% with nanowire length of 8.6 µm; however, the further increased nanowire length and connected bottoms of nanowires restrained the further efficiency improvement due to the increased electron recombination and reduced surface area.

Keywords: ZnO nanowires; Dye-sensitized solar cell; Photoanode

Introduction

As the third generation solar cells, dye-sensitized solar cells (DSSC) have attracted a lot of attention for their low cost, large-scale solar energy conversion and wide-spread commercialization [1,2]. Successful operation of the DSSC depends on the minimization of the possible recombination process occurring at injected electron/oxidized dye or electrolyte interface, allowing efficient electron transport and subsequent electron collection. Although TiO, nanoparticle porous network based DSSC has achieved the solar efficiency over 11% [3], the further enhancement in efficiency is difficult due to multiple trapping/detrapping events occurring within grain boundaries [4-6]. Efforts have been made to improve the charge transport in the photoanode, and replacing TiO, nanoparticle porous network with one-dimensional (1D) nanostructures, including ZnO nanorods and nanowires and TiO, nanorods and nanotubes [7-11], has expected of great potential to boost the DSSC performance. However, the power conversion efficiency of such solar cells are disappointed, especially the efficiency of DSSCs based on 1D ZnO nanostructures is still at a relatively low level. The key point which limited the efficiency of 1D ZnO DSSCs has considered to be insufficient surface area for dye adsorption. Therefore, extensive research has been specially conducted on investigating the synthesis parameters on the length and quality of 1D ZnO nanostructures in the past decades [7,12-16], aimed to fabricate ultralong ZnO NW arrays with high surface area. Among the available methods, the most attractive synthesis technique for obtaining 1D ZnO nanostructures photoanode is the hydrothermal method for its low cost and easy control. Supan Yodyingyong et al have synthesized ZnO nanowire arrays with length of 1.7 μ m, 5.1 μ m and 11 µm on seeded substrate by refreshing the hydrothermal growth solution every 12 h, and the corresponding DSSC efficiency of 0.94%, 1.16% and 1.58% were obtained [17]. Qiu jijun et al have fabricated ZnO nanowire arrays photoanodes with length of 10 μ m, 20 μ m, 30 μ m and 40 µm by adjusting the polyethylenimine concentration in the hydrothermal solution, and the obtained DSSC efficiency were 0.73%, 0.97%, 1.13% and 1.31% [18]. Because of the different hydrothermal synthesize conditions, the crystalline quality and density of the obtained ZnO nanowires were changed, and it is not comparable of the efficiency from different literatures. No matter how different the photovoltaic efficiency in various literatures were, it is clear that, in the same hydrothermal system, the device efficiency were improved with increasing the ZnO nanowire length. If the further increase of ZnO nanowire length can improve the DSSC efficiency? In principle, there should be exist the optimal ZnO nanowire length for DSSC application, just like the TiO_2 -DSSC exhibits the best performance with network thickness of 15~20 µm [1,2]. In order to make clear the secret of ZnO nanowire length and DSSC efficiency, people should understand the change trend of every DSSC performance parameter with increasing the ZnO nanowire length, but seldom investigation on the relationship between ZnO nanowire length and DSSC performance parameters were found.

Herein, in this work, ZnO nanowire arrays photoanodes with various length have been hydrothermally fabricated by adjusting the reaction solution concentration, and the effect of ZnO nanowire length on DSSC performance parameters has been systematically investigated and the reason for this was detailed discussed.

Experiments

Synthesis of ZnO nanowire arrays

The 1D ZnO nanostructures were fabricated by a two-step method as reported in our previous works [19,20]. Firstly, c-axis oriented ZnO seed layer with thickness of 300 nm was prepared on the fluorine-doped tin oxide (FTO) glass substrate by radio frequency (RF) magnetron sputtering technique. Prior to the seeding, the FTO substrates were ultrasonically cleaned in distilled water, acetone and ethanol for 15 min, respectively. When the FTO substrate was loaded into the chamber the deposition chamber was evacuated down to ~4×10⁻⁴ Pa, high purity argon gas was introduced at a flow rate of 20 SCCM (SCCM denotes

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standard cubic centimeters per minute at STP) and the working pressure in the chamber was fixed at 0.5 Pa. The substrate temperature was 200 °C, and the RF power of 100 W was used to sputter ZnO target (99.99%) for 0.5 hour and the ZnO seed layer was obtained.

Subsequently, ZnO NW arrays were grown on the seed layer by a hydrothermal method. The seeded substrates were vertically immersed in an aqueous solution of $Zn(NO_3)_2$ and NH_3 · H_2O at 95 °C for 6 h. The pH value of the reaction solution was fixed at 10.00 by adjusting the amount of NH_3 · H_2O . In order to fabricate ZnO NW arrays with various nanowire length, the solution concentration of $Zn(NO_3)_2$ was changed from 10 mM to 25 mM, 50 mM, 75 mM and 100 mM. After growth, the resultant samples were removed from the autoclave, rinsed thoroughly with distilled water to remove any residual reactants and dried in air at 80°C for one day.

Fabrication of ZnO nanowire arrays based DSSCs

DSSCs based on ZnO nanowire arrays with various length were assembled in a standard route [19,20]. The prepared ZnO nnaowire arrays photoanodes were immersed into the 0.3mM cis-bis (isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bistetrabutylammonium (N719) ethanol solution for 24 hours to assure complete sensitizer uptake. After washing with ethanol for several times and drying by N2 gas flow, the sensitized photoanodes were assembled with thermally Pt counter electrodes and sealed with hot-melt spacers (25 μ m thick, Bynel, Dupont). The internal space of each cell was filled with liquid electrolyte composed of 1.0 M 1,3-dimethylimidazolium iodide, 0.05 M LiI, 0.1 M guanidinium thiocyanate, 0.03 M I₂, and 0.5 M tert-butylpyridine in the mixture of acetonitrile and valeronitrile (85/15, v/v) by vacuum backfilling through the hole in the counter electrode. Finally, the hole was sealed with a hot-melt sheet and covered with a thin glass (0.1 mm).

Characterization

The morphologies of the samples were characterized by field emission scanning electron microscopy (FE-SEM JEOL JSM 6700F). The crystal structure of the products was characterized on a Rigaku-Dmax2500 X-ray diffractometer (XRD) with high intensity Cu Ka $(\lambda = 1.5418 \text{ Å})$ incident radiation. Transmission electron microscope (TEM) images, high-resolution TEM (HR-TEM) and electron diffusion (ED) images were taken on a JEOL JEM-2010 transmission electron microscope. Photovoltaic measurements were performed using an Oriel AM 1.5G solar simulator with an irradiance of 100 mW cm⁻² [19,20]. The current-voltage characteristics of the cells were measured by applying external potential bias to the cell and measuring the generated photocurrent with a Keithly model 2400 digital source meter (Keithly, U.S.A.). Under full computer control, light from a 300 W Xe lamp (ILC Technology, U.S.A.) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., U.K.) onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum to generate the incident photon to current conversion efficiency (IPCE). Photovoltaic performance was measured by using a metal mask with an aperture area of 0.158 cm².

Results and Discussion

Figure 1a-e shows the cross-section scanning electron microscopy (CS-SEM) images of ZnO nanostructures with various solution concentration, indicating that 1D ZnO nanostructures with various length were aligned perpendicularly to the seeded FTO substrate. It is clear that the ZnO nanowire length increased from 0.8 μ m to 1.5 μ m,

 $6.8 \ \mu m$, $8.6 \ \mu m$ and $11.3 \ \mu m$ with increasing the hydrothermal solution concentration from 10 mM to 25 mM, 50 mM, 75 mM and 100 mM. It is also noted that the diameter of the nanowires were always in the range of 80-120 nm with neglectable change, while, the bottom part of the nanowires became thicker and were gradually interconnected with increasing the reaction solution concentration, which would hamper electron transport and decrease surface area of the photoanode. Figure 1f shows the XRD pattern of the ZnO nanostructure with solution concentration of 75 mM. The nanowire arrays photoanode exhibits a high crystallinity with very well defined (100), (002), (101) diffraction peaks. The dominating (002) diffraction peak is attributed to the wurtzite structure of aligned ZnO NW arrays with c-axis oriented, which coincides with the SEM observation.

(Figure 2 a-c) shows the transmission electron microscopy (TEM), high resolution TEM (HRTEM) and electron diffraction (ED) images of the obtained ZnO NW fabricated with solution concentration of 75 mM. As shown in (Figure 2a and b), the ZnO nanowires exhibit smooth surface and clear lattice planes. The obtained ZnO NW has single crystalline wurtzite structure with growth direction along the [0001] direction, which can be further confirmed by the (0001) interface space of 0.52 nm in (Figure 2b) and the bright diffraction spots in (Figure 2c). It is demonstrated that the 1D single crystalline structure would help to electron transport and collection in DSSC application.

Because there are little change in the nanowire diameter with various reaction solution concentration, in our work, we compared the effect of nanowire length on the cell performance in an ideal case, that is, the nanowires are with the same diameter. The DSSCs with nanowire length of 0.8 μ m, 1.5 μ m, 6.8 μ m, 8.6 μ m and 11.3 μ m were



Figure 1: (a-e) CS-SEM images of ZnO nanowire arrays with solution concentration of 10 mM, 25 mM, 50 mM, 75 mM and 100 mM, and (f) the XRD pattern of the ZnO nanostructure with solution concentration of 75 mM: \blacklozenge indicates the wurtzite phase of ZnO, * indicates the SnO₂ from the FTO substrate.

fabricated and they were denoted as DSSC-a, b, c, d and e. (Figure 3) shows the IPCE curves of DSSCs with various ZnO nanowire length as photoanodes. It is clear that the IPCE curves exhibit a continuous enhancement in the spectral region from 350 to 650 nm with the ZnO nanowire length increasing from 0.8 to 8.6 μ m, but a sharp drop with ZnO nanowire of 11.3 μ m. This can be explained by the SEM results in (Figure 1a-e), with the nanowires increasing from 0.8 to 8.6 μ m, the ZnO nanowire grew longer quickly with little diameter change, and thus the surface area of the corresponding photoanode became larger which lead to more dye absorption and photoelectrons. As the nanowire increasing to 11.3 μ m, most bottom part of the nanowires were interconnected which hampered the electron transport and decreased the surface area in the photoanode, and thus resulted in the less photoelectrons and lower IPCE.

(Figure 4 a and b) show the compared light and dark photocurrent density-voltage (J-V) characteristics of these DSSCs, which are measured under the irradiance of AM 1.5G sunlight of 100 mW cm⁻² and in the dark. As shown in (Figure 4a), the short-circuit current density (J_{sc}) was gradually enhanced with ZnO nanowire arrays increasing from 0.8 to 8.6 µm, but was largely decreased with nanowire length of 11.3 µm, according to the IPCE results. As shown in (Figure 4b), with the nanowires increasing from 0.8 to 11.3 µm, only the dark current of DSSC with nanowire length of 6.8 µm was largely suppressed. Because



Figure 2: TEM (a), HRTEM (b) and ED (c) images of ZnO nanowire fabricated with solution concentration of 75 mM.



the light and dark J-V curves are crossed to each other, no obvious relationship between ZnO NW length and DSSC performance has been found from these curves.

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To further understand the effect of ZnO nanowire length on the photovoltaic performance, the DSSC parameters of open-circuit voltage (V_{0c}) , J_{sc} , fill factor (FF) and overall efficiency (η) for these DSSCs are compared, as shown in (Figure 5a-d). With gradually increasing the ZnO NW length from 0.8 to 6.8 µm, all DSSC parameters were continuously improved, which was mainly attributed to the improvement in surface area and electron transport. As further increasing the nanowire length from 6.8 to 8.6 µm, the total efficiency for DSSC with 8.6 µm NW length arrived at the peak of 1.54%, 0.02% higher than that of 6.8 µm nanowire based DSSC. The increased efficiency is mostly due to the improvement in J_{sc} which can be explained by the enlarged surface area (Figure 5b). However, the $V_{_{oc}}$ and FF of 8.6 μm nanowire based DSSC were largely decreased compared with that of 6.8 µm nanowire DSSC (Figure 5 a&c), especially for the V_{oc}. When the ZnO nanowire length increased to 11.3 µm, all device performances were dramatically decreased and a efficiency as low as 1.05% was obtained. Different from previous literatures [17,18], the DSSC efficiency was not endless enhanced with increasing the ZnO NW length, but decreased when the ZnO NW length reached at a given value.

To make clear the above results, the electron transport in single crystalline ZnO nanowire must be taken into account. The electrons in the nanocrystalline photoanode are demonstrated to diffuse in a random walk model [21-23], and the average transit time from the top of one ZnO nanowire to the bottom is approximately expressed as

$$\tau = \frac{l^2}{\pi^2 D} \tag{1}$$

Where τ is the diffuse time, l is the diffuse length, D is the electron diffusion coefficient.

The electron diffusion coefficient *D* can be expressed as [21]

$$D = -\frac{\mu}{q}kT \tag{2}$$

Where μ is the electron mobility rate, *q* is the electronic charge of 1.6×10^{-19} C, *k* is the Boltzmann constant of 1.38×10^{-23} J/K.

So, the diffuse time of electron transferring from the tip to the bottom of a ZnO nanowire photoanode could be expressed as

$$\tau = \frac{l^2 \times q}{\pi^2 \times \mu \times kT} \tag{3}$$

As reported, the lifetime of the light-induced electron is about 10⁻⁸ s [24-26], and the electron mobility rate of single crystalline ZnO is about 200 cm² V⁻¹ s⁻¹ measured at 300 K [21]. Supposing all of the ZnO nanowires were single crystalline, the electron transfer rate will be the fastest and the diffuse length will be the maximum in the identical time. Therefore, at 300 K, the maximum diffuse length of single crystalline ZnO nanowire is calculated to be 7.16 µm, that is, electron can not transfer through the whole nanowire longer than 7.16 $\mu m.$ Therefore, as increasing the nanowire length from 6.8 to 8.6 and 11.3 µm, theoretical speaking, electron can't transfer through the whole ZnO nanowire and will not collect at the FTO substrate, and thus the DSSC performance should be disappointed. In fact, it exhibited that the function of DSSC with ZnO NW photoanode longer than 7.16 μm did not stop immediately. It is deduced that only the 7.16 μm part measured from the FTO glass to ZnO nanowire (P1 in Figure 1d) was effectively functioned in the ultralong ZnO nanowire DSSC, the

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Figure 4: The light (a) and dark (b) J-V curves of N719-sensitized DSSCs measured under the irradiance of AM 1.5G sunlight of 100 mW cm² and in the dark. The DSSCs with ZnO NW length of 0.8 µm, 1.5 µm, 6.8 µm, and 11.3 µm were denoted as DSSC-a, b, c, d and e.



electrons in the top part of the ultralong nanowire (P2 in Figure 1d) were unable to transfer to the FTO glass and so they were recombined with oxidized dye or electrolyte. The more electron recombinations would result in a decrease in electron density at the ultralong ZnO nanowire surface, and subsequently the lower quasi-Fermi level and V_{oc} [27]. When the ZnO nanowire length increased to 11.3 µm, most

part of the bottom 7.16 μ m (which were mainly functioned in DSSC application) were interconnected (Figure 1e), the surface area of the photoanode was decreased, electron transport was hampered, and subsequently the electron recombinations were increased, thus all of the DSSC performances were dramatically decreased, as shown in (Figure 5a-d). In addition, the larger dark current of ZnO nanowire DSSC with

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length of 8.6 and 11.3 μm in (Figure 4b) can also be explained by the more combinations.

Conclusion

In summary, ZnO nanowire arrays with tunable length have been hydrothermal fabricated on the seeded FTO substrates by changing the growth solution concentration. With the increase of solution concentration, the ZnO nanowire arrays grow longer but with the bottom of nanowires become thicker and interconnected with each other. The enlarged nanowire length lead to increased cell efficiency and achieved at a peak of 1.52% based on 8.6 μ m nanowire cell. However, with further increase the nanowire length, the cell performance was decreased, due to the increased electron recombination from ultralong nanowires and reduced surface area from interconnected nanowire bottoms.

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