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Photoelectrochemical Properties of Highly Oriented ZnO Nanotube Array Films on ITO Substrates

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Abstract: Highly oriented ZnO nanotube array films on the conducting substrates have been synthesized by a simple hydrothermal method and characterized by scanning electron microscopy (SEM) and UV-Vis spectroscopy. The thin films consisting of laterally fragmentized ZnO nanotubes with controlled orientation have been tested as photoanode in Grätzel-type solar cell. For a sandwich-type cell, with 0.5 mol/L LiI and 0.05 mol/L I_2 in propylene carbonate electrolyte, the overall solar energy conversion efficiency reaches 2.3%.

Keywords: ZnO nanotube, hydrothermal deposition, photoelectrochemistry.

Zinc oxide is a wide band gap semiconductor which is one of the ideal materials to be used as electrodes for dye-sensitized solar cells[1]. However, for the nanostructured ZnO electrodes based on interconnected spherical particles, it is difficult to further improve the photocurrent efficiency due to charge-carrier recombination losses at grain boundaries between the nanoparticles in the film[2]. To avoid the recombination losses, one feasible method is to synthesize nanostructures which have a higher order degree compared to the random fractal-like assembly of nanoparticles. A desirable morphology of the thin film should have the mesoporous channels in parallel to each other and vertically with respect to the substrate[2] such as nanorod/tube arrays. Since the nanotubes have higher specific areas than that of the nanorods with the same diameters, well-aligned nanotube arrays are expected to have higher conversion efficiency when used as photoanodes. Recently, Vayssieres *et al.* developed a hydrothermal deposition method to prepare ZnO microtube arrays[3]. The prepared ZnO microtubes have diameters of about 1-2 μm, which is too large to be used in solar cells. Herein, we report the hydrothermal growth of densely packed and well-aligned ZnO nanotube array films. We find that the resulting film shows relatively high photoconversion efficiency when employed as photoanodes in dye-sensitized solar cells.

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Experimental

Preparation and characterization: The ZnO nanotubes were prepared from zinc nitrate in a neutral aqueous solution under hydrothermal conditions. The procedure is a modification of the approach developed by Vayssieres *et al*[3]. Equimolar aqueous solutions (0.5 mol/L) of zinc nitrate (1 mL) and methenamine (1 mL) were added dropwise to 1.5 × 3.0 cm^2 ITO substrates. After 5 min deposition and subsequent spin coating, the substrates were modified with ZnO nanocrystal seeds. At least three cycles were needed for the dense and uniform dispersion of ZnO nanoparticles on ITO substrates. The hydrothermal growth was then carried out at 90°C in a sealed kettle by immersing the modified substrates in the aqueous solution (60 mL) containing $Zn(NO_3)_2$ (0.05 mol/L)and methenamine (0.05 mol/L). The morphology and size distribution of the nanotubes were characterized using scanning electron microscopy (SEM) (Philips FEI XL30 SFEG operated at 10 KeV).

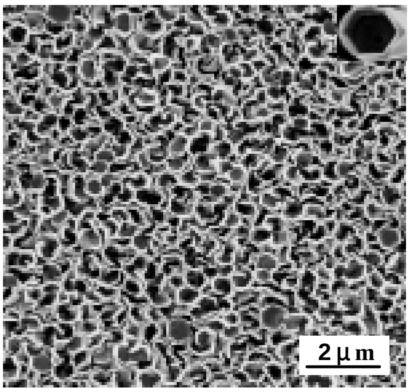
Photoelectrochemical measurement: Dye-coating of the ZnO electrode was done by soaking it in 0.5 mmol/L $Ru(dcbpy)_2(NCS)_2$(dcbpy=4,4'-dicarboxy-2,2'-bipyridine) for 2 h. For two-electrode measurements, the dye-sensitized ZnO electrodes were mounted in a sandwich-type system with a platinum sheet as a counter electrode. The electrolyte was 0.5 mol/L LiI and 0.05 mol/L I_2 in propylene carbonate. Overall efficiency measurements were carried out with a 150 W xeron lamp, furnished with a 10 cm water filter.

Results and Discussion

1. Characterization of highly oriented ZnO nanotubes on ITO substrate by SEM

SEM was employed to characterize the morphology of ZnO nanotubes grown on the modified ITO substrates. The SEM images at low magnification indicate that well-aligned ZnO nanotubes grow uniformly in large area. A typical top view SEM image is shown in **Figure 1**, from which the laterally incomplete nanotubes with average diameter of about 500 nm can be observed. Although most of the nanotubes are

Figure 1 A top view of SEM image of ZnO fragmentized nanotubes.



Inset: SEM top view of the single ZnO nanotube. Growth time: 60 h.

incomplete and intercrossed, the hexagonal crystal plane can be clearly identified from the fragmentized tube walls. The inset in **Figure 1** shows a integrated ZnO nanotube, which suggests that the tube or tube walls are hexagonal phase ZnO nanocrystals. This is further supported by the X-ray diffraction pattern of as prepared ZnO film, which is well indexed to the standard diffraction pattern of wurtzite ZnO. Furthermore, the thickness of the ZnO films is about 1 μm.

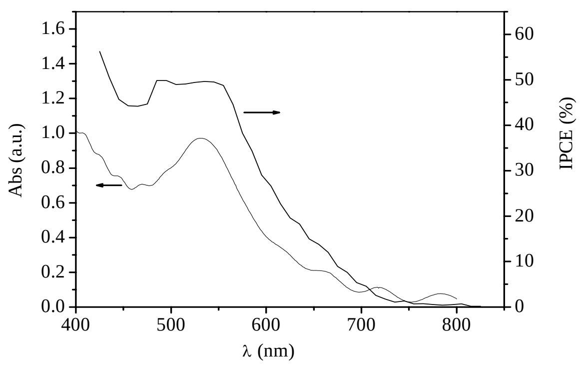
In our previous works[4,5], we have demonstrated that perpendicularly-oriented ZnO nanorods can be fabricated on ITO substrates that are pre-modified with ZnO nanocrystals. The only difference in preparing procedure between ZnO nanorods and nanotubes is that the hydrolysis time is much longer for nanotubes. According to the Vayssieres' report, well-aligned ZnO nanotubes result from the preferential chemical dissolution of the metastable (001)-ZnO planes of highly oriented nanorods in an aging process[3]. Therefore, it is reasonable to believe that the ZnO nanotube walls are vertically with respect to the substrates.

The density of the ZnO nanotube is estimated to be about 5.4×10^6 nanotubes per square centimeter, which is much larger than the value calculated from Vayssieres reported[3]. This implied that the as-prepared ZnO nanotube array films had high porosity and large surface area which would be of benefit to adsorption of more dyes, when the ZnO nanotube array films were used as photoanode of dye sensitized solar cell, the light harvest efficiency can be improved.

2. Photoelectrochemical characteristics of the dye-sensitized oriented ZnO electrode

The absorption spectrum of the dye $Ru(dcbpy)_2(NCS)_2$ attached to the ZnO nanotube array films is found to match the photocurrent action spectrum when the dyed ZnO electrodes were used in a solar cell, as shown in **Figure 2**. From **Figure 2** we can see that the maximum value of IPCE is about 50% at around 535 nm in accordance with the absorption spectrum of $Ru(dcbpy)_2(NCS)_2$ on ZnO electrode. Under the illumination of simulated solar light (42 mW/cm^2) from 150 W Xe lamp, a sandwitched-type solar cell,

Figure 2 Absorption and photocurrent action spectra of the ZnO electrodes sensitized by $Ru(dcbpy)_2(NCS)_2$ for 15 min.



Electrolyte: 0.5 mol/L LiI / 0.0 5 mol/L I_2 in propylene carbonate.

which is fabricated with $Ru(dcbpy)_2(NCS)_2$ sensitized ZnO nanotube photoanode, 0.5 mol/L LiI/0.05 mol/L I_2 propylene carbonate (PC) electrolyte, and a platinized ITO glass counter electrode, shows a short-circuit current of 3.4 mA/cm^2 and a open-circuit voltage of 0.54 V. The fill factor in this experiment is 0.53, and the overall efficiency of the dye-sensitized ZnO electrode is calculated to be 2.3%.

It is well known that the photoconversion efficiency increases, in a certain range, with the increasing of nanocrystalline film thickness because thicker films provide larger amount of absorbed dyes and more photon-capturing changes. The IPCE value obtained in our experiments is quite close to that of the solar cells based on ZnO nanoparticle films with a thickness of 7-9 μm under the same conditions[6]. However, when considering the facts that the thickness of ZnO film used in our experiments is only 1 μm, it may be concluded that the photoconversion efficiency of the dye-sensitized ZnO nanotube electrode may be higher when the film thickness is the same.

The relatively high efficiency observed for ZnO nanotube films can be ascribed to the as-synthesized film nanostructure. Since every laterally fragmentized nanotube wall is a single crystal that can provide electron transportation channel to the conducting substrate, the incompleteness of nanotube will not, in principal, decrease the photoconversion efficiency of the solar cell. On the contrary, the intercrossed tube walls can make good use of space and may provide higher porosity and specific area for ZnO films. As a result, the densly-packed ZnO nanotube walls can adsorb enough dyes to improve the light harvest efficiency. Furthermore, the photogenerated electrons can transport directly through the oriented tube walls to the conducting substrates. This greatly reduces the recombination losses of the photogenerated charge–carriers due to fewer grain boundaries in charge transportation process.

In summary, well-aligned and laterally incomplete single-crystalline ZnO nanotubes arrays have been prepared and used as photoanode in Grätzel solar cell. Relatively high photoconversion efficiency has been obtained with rather thin ZnO films, which suggests that thicker ZnO nanotube film might result in higher overall efficiency. The preparation of thicker ZnO nanotube films and the study of their photoelectrochemical properties are in progress in our group.

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