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Preparation and Photoelectrochemical Performance Research of ZnO Nanorod Arrays

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Abstract: ZnO nanorod arrays were prepared by chemical bath deposition (CBD) method on fluorine doped tin oxide (FTO) conducting glass substrate. X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were used to characterize the ZnO nanorod arrays. As-prepared ZnO nanorods are single-crystalline hexagonal wurtzite structure. The individual ZnO nanorod is about 50nm diametric and 1micro long. The nanorod arrays are dense oriented and uniform. Dye-sensitized solar cell device was prepared with ZnO nanorods array film sensitized by eosin Y as the photoelectrode. Their open-circuit photovoltage, short-circuit photocurrent density and the overall conversion efficiency were analied.

Keywords: ZnO; Nanorod arrays; Chemical bath deposition; Eosin Y; Dye-sensitized solar cell

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Introduction

ZnO is an important wide bandgap semiconductor material, it has direct wide band gap (3.370 eV) at room temperature, large exciton binding energy (60 meV) and high field electron mobility rate. In recent years, due to its unique physical and optical properties, one-dimensional nano-ZnO was increasingly concerned and was widely applied in solar cells [1-3], ultraviolet laser [4], light emitting diode [5], ultraviolet detector [6], gas sensor [7], and so on. Oriented and uniform ZnO nanorod array is one of the most popular hotspot in nanomaterials research. At present, there are many methods about the preparation of ZnO nanorod arrays, such as chemical vapor deposition [8], thermal evaporation [9-10], electrochemical deposition [11], template method [12]. However, compared with these methods, chemical bath deposition (CBD) method is easy to scale up at low reaction temperature without any template, surfactant and electric field.

ZnO nanorod has excellent optical property and electronic transport capacity. Gratzel solar cell of ZnO nanorod arrays could separate photogenerated electrons and holes faster and reduce the recombination more greatly, compared with that of ZnO nanoparticles, so as to improve the photoelectric conversion efficiency [13]. In this work, dense, oriented and uniform ZnO nanorod arrays was prepared with CBD method on the FTO substrate. Then the ZnO nanorod array was made into photoelectrode of dye-sensitized solar cell sensitized by the eosin Y. Meanwhile, its photoelectric performance was also studied preliminarily.

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Experimental

Preparation of ZnO nanorod arrays

First, a small piece of FTO (SnO_2:F, resistance of 15Ω/cm^2) conducting glass (2.500×2.500 cm^2) were ultrasonic cleaned 30 min with acetone, ethanol, deionized water stepwise, then dried in the oven. A certain quality of zinc acetate dihydrate was dissolved in 2-methoxyethanol, and ethanolamine equimolar amount of zinc acetate dehydrate was added. The transparent solution with Zn^{2+} concentration 0.750 mol/L was obtained at 60° after 30 min magnetic stirring. The solution was dropped on the conductive substrate on the vacuum suction cups of spin coating machine (2500 r/min) for 30 s. Then a layer of ZnO nanoparticle film on the substrate was obtained after heating at 450° for 2 h [14-15].

The substrate with ZnO nanoparticle film was put into growth solution with Zn^{2+} concentration of 0.025 mol/L respectively made by zinc nitrate hexahydrate and hexamethylene tetramine mixed in equal molar ratio, and was took out after 3h heat preservation at 90℃. Then the substrate was washed 5-times with deionized water repeatedly in order to remove excess ions and amine salts, and then dried in the air. Thus the ZnO nanorod array film is prepared.

Characterization of ZnO nanorod arrays

The phase and the crystallography of the products was characterized by X-ray diffraction (XRD, D/MAX-2550, Cu as target radiation source, Kα line, λ = 0.154056 nm). The morphology and microstructure of the samples was analyzed by field emission scanning electron microscopy (FESEM, FEI, Quanta 450) and transmission electron microscope (TEM, TECNAI G2 S-TWIN). Transmission spectra of the samples were recorded in the range of 300∼800 nm using UV-Vis spectrophotometer (Perkin Elmer Lambda 750, PE-USST joint lab).

Assembling cells and performance test

After heating at 300℃ for 1 h and cooling down to 80℃ for another hour, ZnO nanorod arrays were dipping in the solution of eosin Y - absolute ethylene alcohol for 24 h in the dark. And then, ZnO–eosin Y hybrid film-based Dye Sensitized Solar Cells(DSSCs) was obtained, assembling with the dye sensitized ZnO nanorod arrays electrode, the counter electrode made by FTO conducting glass plating Pt, electrolyte synthesized from Propylene Carbonate (0.3 mol/L LiI, 0.03 mol/L I_2). The photocurrent–photovoltage curves of ZnO–eosin Y hybrid film-based DSSCs was tested with electrochemistry workstation (CHI 604C), under the condition of light source with xenon lamp (120w), incident intensity at 100 mW/cm^2, and cell effective area with 1 cm^2.

Results and discussion

X-ray diffraction (XRD) analysis

Figure 1 shows the XRD pattern of ZnO nanorod arrays on the FTO substrate with ZnO nanoparticle. It can be seen from the Fig. 1 that all diffraction peaks match with the hexagonal wurtzite ZnO (cell parameters: a=0.3249 nm, c=0.5206 nm, JCPDS NO. 36-1451). Another view from the diffraction intensity, the intensity of the peak (002) is much stronger than others. The ratio of the intensity of peak (0002) to that of peak (10-10) and (10-11) is 200:1 and 60:1. According to the standard XRD pattern of ZnO, as-grown ZnO nanorod arrays along the c-axis are of preferential orientation.

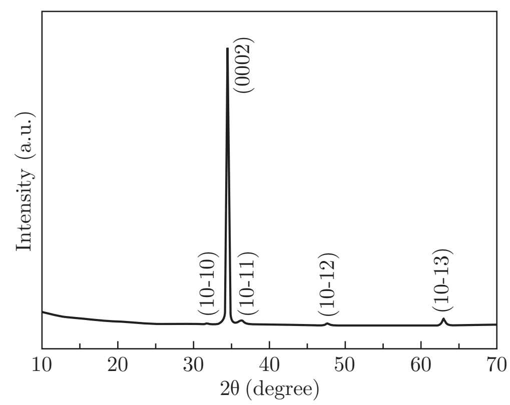

Fig. 1 XRD pattern of ZnO nanorod array film.

Scanning Electron Microscopy (SEM) analysis

The morphology, size and microstructure of the samples are investigated in detail from FESEM observations. Fig. 2(a) is the typical FESEM image of ZnO nanoparticle film on the FTO substrate, and shows that ZnO nanoparticle is compact and uniform with diameter about 50 nm. ZnO nanoparticle film which is deposited on the FTO substrate in advance reduces the lattice mismatch between the ZnO nanorod array and the substrate and helps ZnO nanorod grow oriented [16]. The low magnification FESEM image Fig. 2(b), magnified SEM image Fig. 2(c) of ZnO nanorod array films clearly show that ZnO nanorod arrays on a large scale is denser, more uniform and more orientated with average diameter of 50 nm and length of 1 micro with the top of ZnO nanorod hexagonal shape.

Transmission Electron Microscopy (TEM) analysis

The microstructure of the sample was investigated in detail from TEM observation. Fig. 3 shows the typical TEM image of the single ZnO nanorod arrays. It's indicated that the single ZnO nanorod is about 50 nm in diameter and accorded with SEM observation. The clear diffraction spots in the illustrations for the electron diffraction pattern indicated that the ZnO nanorod array is single crystal. From the High-Resolution Transmission Electron Microscopy (HRTEM) image Fig. 3(b), it can be seen that only one orientation lattice fringe is clear and the interplanar spacing of 0.520nm which corresponds of (0001) planes, indicates that ZnO nanorod grows along the [0001] direction.

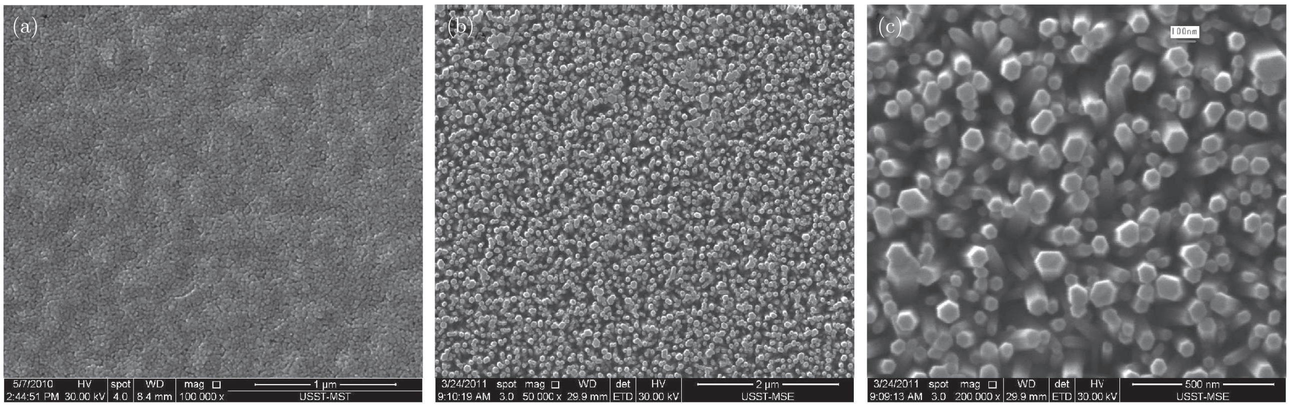

Fig. 2 (a) SEM image of the ZnO nanoparticle film; (b) Low magnification SEM images of the ZnO nanorod array films: (c) Magnified magnification SEM images of the ZnO nanorod array films.

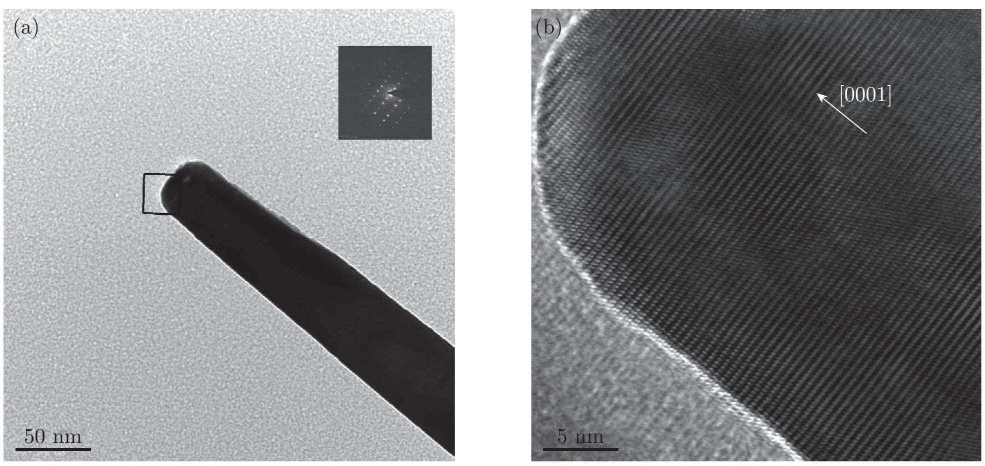

Fig. 3 (a) TEM image of a single ZnO nanorod and its corresponding SAED pattern (insert); (b) High-resolution TEM image of the ZnO nanorod.

UV-vis absorption spectrum

UV-vis absorption spectra of sensitized ZnO nanorod array films and unsensitized ones are shown in Fig. 4. From fig.4 (a), it is shown that a main absorption of unsensitized ZnO sample is in the ultraviolet region, and its absorption band is at 380nm. However, from Fig.4(b), it can be seen that the sensitized ZnO has stronger absorption in the visible-light region than unsensitized one, and the absorption band is at 530nm. This suggests that the ZnO nanorod arrays sensitized with eosin Y which can expand absorption range from ultraviolet to the visible-light region, and meanwhile hopefully improve the photoelectric conversion efficiency of ZnO nanorod arrays used as photoelectrode.

Photoelectrochemical Properties

Figure 5 is photocurrent–photovoltage curves of ZnO–eosin Y film-based DSSCs. The filling factor (FF) of the fabricated solar cell can be calculated using the following equation;

$$FF = \frac{P_{\max}}{V_{oc} \cdot I_{sc}} = \frac{V_{\max} \cdot I_{\max}}{V_{oc} \cdot I_{sc}} \tag{1}$$

where $P_{\max}$ is the battery's maximum output power, V_{oc}, I_{sc} are battery's Open-circuit voltage and short-circuit current, $V_{\max}$, $I_{\max}$ are the voltage and current respectively obtained at the maximum power point on the photovoltaic power output curve.

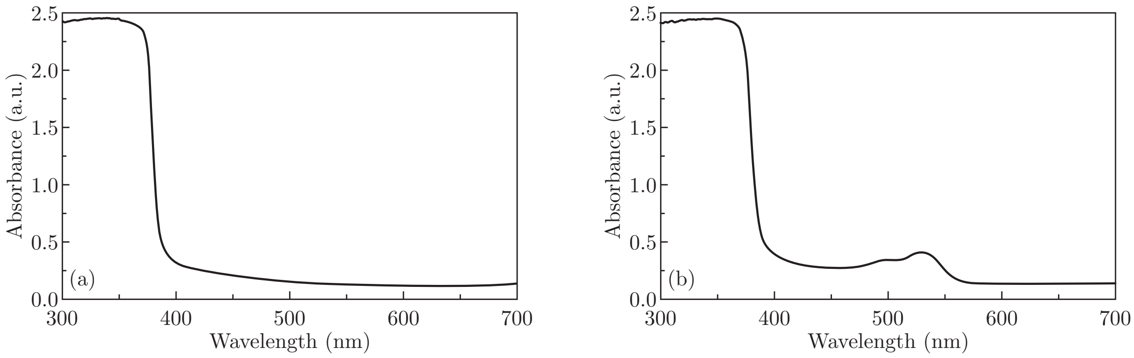

Fig. 4 The UV-Vis absorption spectra of (a) the sensitized ZnO nanorod array film and (b) unsensitized ZnO nanorod array film with eosin Y.

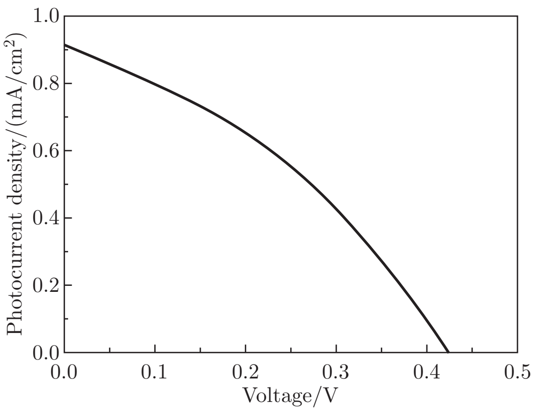

Fig. 5 The photocurrent-voltage curve of eosin Y sensitized ZnO nanorod array film as photoanode for Dye-Sensitized Solar Cell

The photovoltaic efficiency (η) is calculated using the following equation;

$$\eta = \frac{FF \cdot V_{oc} \cdot I_{sc}}{P_{in}} \tag{2}$$

P_{in} is the input power of DSSCs. From Fig. 5, some data is obtained as follows: I_{sc}=0.917 mA/cm^2, V_{oc}=0.424 V, *FF*=0.356, η=0.138%. The overall photovoltaic conversion efficiency (η) is lower than that of DSSCs prepared by Fujihara [17]. There may be several reasons after analysis: (1) nanometer ZnO rod array could accelerate to separate photogenerated electrons and holes fast and reduce the recombination, however, because the thickness of the as-prepared ZnO photoanode is very thin ($\leq 1\,\mu$m), thereby, the adsorption quantity of the dye is so little that the photoelectric conversion efficiency decreases. (2) The orientation of ZnO nano rod array needs to be further enhanced. (3) The face resistance of FTO conductive glass increased due to high temperature treatment. It increases from 14.4 Ω/cm^2 to 66.7 Ω/cm^2 after an hour by heat treatment [18].

Conclusion

Dense, orientated and uniform ZnO nanorod array film growing on the FTO conductive glass substrate was prepared with chemical bath deposition method. ZnO nanorod was hexagonal single crystal wurtzite structure growing along with [0001] crystallographic orientation preferentially, with average diameter of 50 mm and length of 1 micro. Dye-sensitized solar cell, of which anode was made by ZnO nanorod arrays sensitized with eosin Y, was assembled and tested in photoelectric property on condition that light intensity was 100 mW/cm^2. It is shown that the total photoelectric conversion efficiency was 0.138% (open-circuit voltage was 0.424 V, short-circuit current was 0.917 mA/cm^2).

Acknowledgements

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