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Nanostructured ZnO thin films by SDS-assisted electrodeposition for dye-sensitized solar cell applications

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Abstract

A novel ZnO with a sheet-like nanoporous morphology has been synthesized on ITO substrates by a sodium dodecyl sulfate (SDS) assisted electrodeposition method. X-ray powder diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) were used to characterize the structures and the morphologies of ZnO nanostructures. A dye-sensitized solar cell (DSSC) is assembled with the as-prepared ZnO film electrode, and shows a power conversion efficiency of 1.969%.

Keywords: Nanostructured ZnO thin film; SDS-assisted electrodeposition; Dye-sensitized solar cells

1. Introduction

Dye-sensitized solar cells (DSSCs) are attractive due to their potentially low-cost fabrication, easy production and flexibility compared to conventional photovoltaic cells [1]. In DSSCs, the dye-sensitized nanocrystalline semiconductor film as a photoanode plays a significant role in converting photons into electrical energy. Up to now, the best performances reported in the literature have been obtained with cells composed of a titania (TiO_2) nanoparticulate thin film sensitized by a ruthenium polypyridine complex dye (N3 and other derivatives) [2,3]. Besides TiO_2, zinc oxide (ZnO) is also investigated as another promising candidate for anode materials [4–7]. The band gap energy and conduction band edge of ZnO are similar to those of TiO_2 [8,9]. Additionally, ZnO showed an order of magnitude higher electron mobility and the corresponding electron diffusion coefficient [10]. Recently, many studies have been focused on the quasi one-dimensional nanostructured ZnO electrodes with an understanding that the use of single crystal nanorods may allow electron transport via extended sites in the conduction band, rather than a series of hoppings between the traps [11–13]. DSSCs fabricated with ZnO nanowire arrays [14], nanotetrapods [15], nanorods [16], nanoflowers [17] and branched nanowire arrays [18,19] have been reported. However, it should be noted that the highest conversion efficiency of ZnO-based DSSCs is achieved by ZnO nanoparticles [20].

Much effort has been made to control the size and shape of ZnO nanomaterials. ZnO nanostructures with different morphologies have been prepared by different physical, chemical and electrochemical methods [21–24]. Among them, electrochemical methods featuring low temperature, simplicity, and large-scale production are of special interest in the synthesis of nanostructures.

In this work, nanostructured ZnO thin films were prepared on ITO substrates by a sodium dodecyl sulfate (SDS)-assisted electrodeposition method. The influence of SDS on the morphologies of ZnO nanostructured films was studied and is discussed. The cell performances of DSSC based on ZnO nanostructured film have been measured.

2. Experimental

2.1. Synthesis of nanostructured ZnO thin films

Nanostructured ZnO thin films were fabricated by one-step cathodic electrochemical deposition from an aqueous

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solution of zinc nitrate and SDS. A Zn foil (99.99% purity) and an ITO-coated glass substrate (pretreated by sonication in absolute ethanol and de-ionized water successively, then dried in air at 40 °C) were used as the counter electrode and the working electrode, respectively. The concentration of the zinc nitrate aqueous solution was varied from 0.01 M to 0.1 M. Then SDS was added in appropriate proportions to the aqueous precursor solution. The concentration of SDS in the final solution was kept constant at 0.05 M. The initial pH value of the solution was about 6, and the deposition temperature was fixed at 70 °C by a water bath. The deposition time was 4 h, and the deposition current was fixed at 0.9 mA. For comparison, electrodeposition was carried out in the same conditions without adding SDS. After deposition, the products were rinsed with distilled water and dried at room temperature for 24 h. The surface morphology of the as-deposited nanostructured ZnO thin films was characterized by a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800FEG). The crystal structure and phase identification were examined by X-ray diffraction (XRD, Philips X′Pert with Cu Kα radiation).

2.2. Cell fabrication and photoelectrochemical measurements

Nanostructured ZnO film photoelectrode was then immersed in a 0.25 mM ethanol solution of dye N719 for 2 h. When loaded with dye molecules, the electrode was washed with ethanol and dried in air. An electrodeposited platinum conductive glass was used as the counter electrode. The photo and counter electrodes were clipped together and one drop of liquid electrolyte was kept between them. Finally, a piece of cyano-acrylate adhesive (30 mm) was used as a sealant. Bisphenol A epoxy resin was used for the further sealing process. The liquid electrolyte contained 0.4 M sodium iodide, 0.1 M tetrabutyl ammonium iodide, 0.5 M 4-tert-butylpyridine and 0.05 M iodine in an acetonitrile solution. Photoelectrochemical tests were carried out by measuring the *J–V* characteristic curves under simulated AM 1.5 solar illumination at 100 mW cm^{-2} from a xenon arc lamp (CHF-XM500, Trusttech Co., Ltd., China) in an ambient atmosphere and recorded using a CHI 660 C electrochemical workstation (CH Instrument Inc., China).

3. Results and Discussion

Fig. 1a–c shows FE-SEM micrographs of the surface morphologies of ZnO films which can be tuned by varying the Zn-precursor concentration (0.01–0.1 M) without SDS additive. As shown in Fig. 1a, large-area arrays of uniform ZnO nanorods with planar ends have been grown on the ITO substrate. ZnO film composed of hexagonal columns or plates was obtained at higher $Zn(NO_3)_2$ concentration from 0.05 M to 0.1 M, as shown in Fig. 1b and c. The possible growth mechanism has been suggested in our previous paper [25]. Fig. 1d–f displays typical ZnO nanostructured films printed on the ITO substrates with the same SDS concentrations added to the $Zn(NO_3)_2$ electrolyte at different concentrations ranging from 0.01 M to 0.1 M. The ZnO nanostructured films were actually composed of a random growth of seemingly flexible sheet-like structures that can be bent and connected with each other. It is obvious that in the presence of SDS surfactant the morphologies are completely different from that obtained without adding SDS. The mechanism for the formation of ZnO sheet-like nanoporous structures is still under investigation. It was recently reported that SDS was a peculiar surfactant, which acted like a template and catalyzed the self-assembled growth of lamellar nanostructures [26,27]. The adsorption of SDS molecules onto the electrode surface during electrodeposition significantly modifies the crystal structure of ZnO.

Fig. 2 shows XRD patterns of the as-prepared samples electrodeposited under different electrolyte solutions. As indicated in the XRD patterns, all diffraction peaks can be well indexed to hexagonal Wurtzite ZnO (JCPDS, No. 36-1451), and no peaks for other phases indicate that the samples are highly pure Wurtzite phase. When $Zn(NO_3)_2$ concentration was 0.01 M and SDS was not added, the sharp and intense peaks (002) indicate that ZnO nanorods are oriented perfectly with their *c*-axis being perpendicular to the ITO substrates as shown in Fig. 2a. With increasing zinc nitrate concentration in the electrodeposition process (0.05–0.1 M) or adding SDS, the resultant samples exhibited similar XRD patterns. The XRD pattern of the sample electrodeposited from aqueous solution containing 0.05 M $Zn(NO_3)_2$ and 0.05 M SDS is shown in Fig. 2b. The intensity ratio of typical ZnO peaks (100), (002), and (101) is similar to that of ZnO powders, indicating its nearly random orientation.

The photocurrent density–voltage (*J–V*) curves for DSSCs based on ZnO nanostructured films electrodeposited under different electrolyte solutions are plotted in Fig. 3. The performance parameters are collected in Table 1. Apparently, when SDS is added into the electrolyte solution, the short circuit current density (J_{sc}), filling factor (*FF*) and photoelectric conversion efficiency (η) increase. The performance of DSSC reaches a higher photoelectric conversion efficiency of 1.969% with J_{sc} of 3.463 mA/cm^2 and *FF* of 0.648 when the electrolyte solution contains 0.05 M $Zn(NO_3)_2$ and 0.05 M SDS. The relatively high efficiency observed for the present ZnO nanostructured film can be attributed to the sheet-like nanoporous structure itself, which has high dye adsorption compared with ZnO film composed of hexagonal columns or plates.

4. Conclusions

In summary, a novel ZnO sheet-like nanoporous structure has been synthesized on ITO substrates by a SDS-assisted electrodeposition method. FE-SEM images reveal

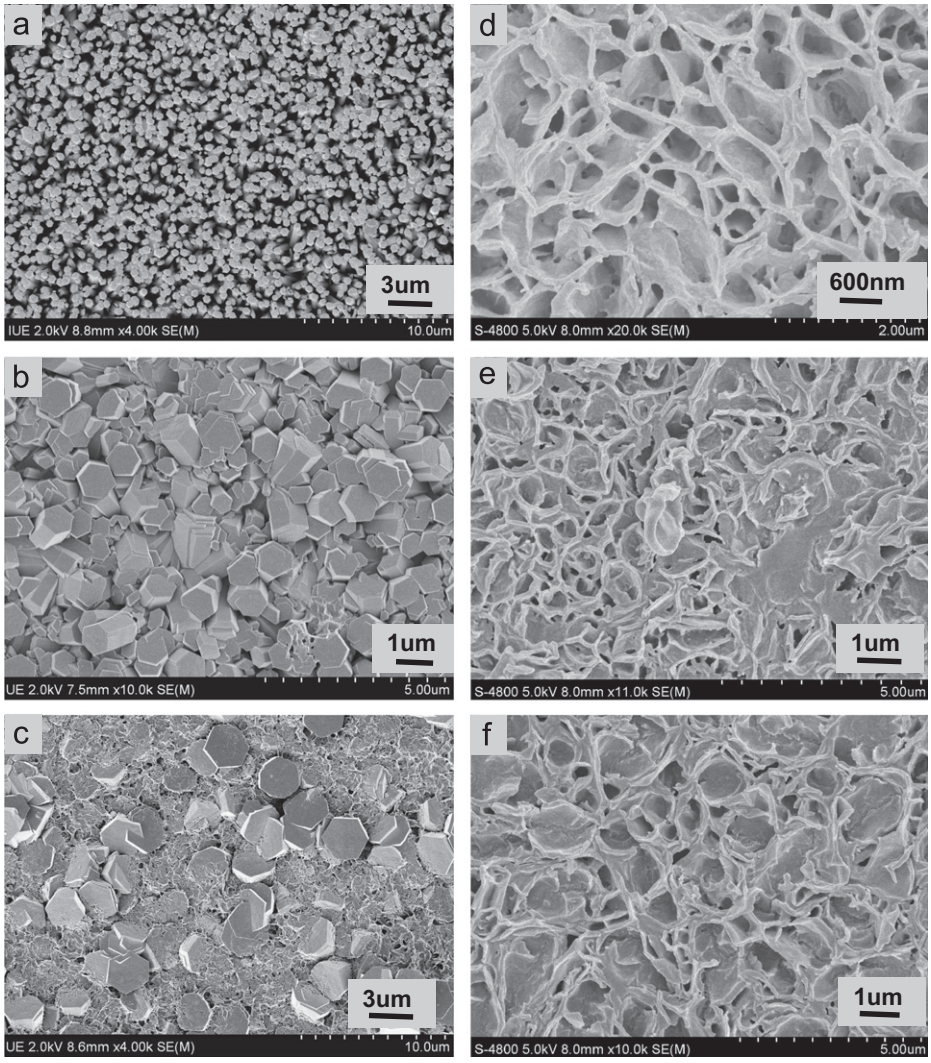

Fig. 1. FE-SEM images of the samples electrodeposited from aqueous solution containing (a) 0.01 M $Zn(NO_3)_2$, (b) 0.05 M $Zn(NO_3)_2$, (c) 0.1 M $Zn(NO_3)_2$, (d) 0.01 M $Zn(NO_3)_2$+0.05 M SDS, (e) 0.05 M $Zn(NO_3)_2$+0.05 M SDS, and (f) 0.1 M $Zn(NO_3)_2$+0.05 M SDS.

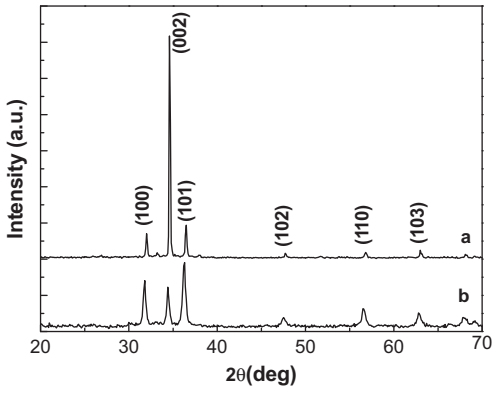

Fig. 2. XRD patterns of the samples electrodeposited from aqueous solution containing (a) 0.01 M $Zn(NO_3)_2$, and (b) 0.05 M $Zn(NO_3)_2$+0.05 M SDS.

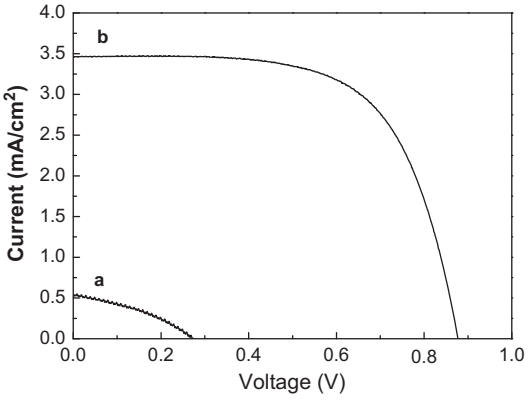

Fig. 3. *J–V* curves of DSSCs based on ZnO nanostructured film electrodeposited from aqueous solution containing (a) 0.05 M $Zn(NO_3)_2$, and (b) 0.05 M $Zn(NO_3)_2$+0.05 M SDS.

that SDS can significantly influence the growth of ZnO films. The dye-sensitized solar cell is assembled with the as-prepared film electrode sensitized by N719 dye, and the performance of DSSC under simulated AM 1.5 solar illumination at 100 mW cm^{-2} from a xenon arc lamp gives a short circuit photocurrent density of 3.463 mA/cm^2, an

Table 1
Performance parameters of DSSCs based on ZnO nanostructured film electrodeposited under different electrolyte solutions.

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF*	η (%)
0.05 M $Zn(NO_3)_2$	0.272	0.535	0.387	0.056
0.05 M $Zn(NO_3)_2$+0.05 M SDS	0.877	3.463	0.648	1.969

open-circuit photovoltage of 0.877 V and a fill factor of 0.648 corresponding to a power conversion efficiency of 1.969%.

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