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Preparation of nanostructured ZnO nanorods in a hydrothermal–electrochemical process

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ABSTRACT

An array of ZnO nanorods, each nanorod being covered with a shell of porous ZnO was prepared in two steps by hydrothermal–electrochemical processes. The growth of ZnO nanorods was achieved in a zinc nitrate and hexamethylenetetramine aqueous solution on fluorine-doped tin oxide film. The porous ZnO shell was grown from a similar solution in the presence of eosin Y as nanostructuring agent. A dye-sensitized solar cell was assembled using as photoanode an eosin Y sensitized ZnO nanorod/shell layer.

1. Introduction

Ordered arrays of 1D ZnO nanowires and nanorods have attracted increasing attention due to promising applications in electronic and optoelectronic devices arising from their physical properties. Some improving in the performance of various ZnO based nanodevices such as nanostructured solar cells [1,2], field-emission devices [3], short-wave lasers [4], gas sensing [5] are expected. ZnO-based photoanode for dye-sensitized solar cell (DSSC) has attracted considerable interest during the past several years due to the similarity of the energy bandgap and the electron-injection process of ZnO to that of TiO_2, the primary photovoltaic material for DSSCs; in addition, ZnO has higher electron mobility. However, only a maximum conversion efficiency of 5.4% have been obtained with films of well-packed polydisperse ZnO aggregates and Ru complex dye [1] or of 5.56% using indoline dyes [6], while a 11% efficiency has been achieved with small size cells based on TiO_2 photoanode [7]. An array of ZnO nanorods could provide a direct path from the point of photogeneration of carriers to the conducting substrate, thus increasing electron diffusion length and effectively reducing the electron recombination losses. Zinc oxide has been prepared into various nanostructures [8–12] such as, nanowires, nanotubes, tetrapods, nanoparticles using a wide variety of techniques. The electrodeposition method has advantages over other processes because of its simplicity, low cost equipment and the possibility in making large area thin films. It is a low-temperature synthetic approach which permits use of plastic substrates for the fabrication of flexible and light in weight DSSCs. However, the electrodeposited ZnO is highly crystallized and that means it has a small surface area, so that no appreciable amount of dye could be adsorbed. In order to prepare a nanoporous ZnO film, it was electrodeposited a ZnO/eosinY hybrid thin film [13,14] and the loaded eosinY molecules were completely removed by the alkaline treatment.

In this paper, we investigated the fabrication of an array of ZnO nanorods, each nanorod being covered with a shell of porous zinc oxide; combined hydrothermal–electrochemical processes were used for the deposition of a ZnO nanorod/shell layer. The feasibility of employing such ZnO layer as photoelectrode for DSSCs was studied.

2. Experimental details

ZnO nanorods and ZnO/eosin Y shell were prepared using the aqueous solutions 1 and 2 from the Table 1; for linear voltammograms measurements the working electrodes was fluorine doped SnO_2 glass substrate (FTO). The sheet resistance of the FTO layer was ~15 Ω/square and its transmission was >80% from 400 to 700 nm. The electrochemical cell also contained a zinc foil as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. Linear voltammetry measurements were performed using an Autolab PGSTAT 30 potentiostat digitally controlled by a computer. The microstructures of deposits were imaged by field emission scanning electron microscopy (FESEM), using FEY Quanta Inspect scanning electron microscopes. X-ray diffraction (XRD) analyses were performed on a Bruker D8 Advance type X-ray diffractometer, in focusing geometry, equipped with copper target X-ray tube and LynxEye one-dimensional detector. Photoluminescence spectra have been recorded at room temperature using an Edinburgh Instruments FL 920 spectrometer (200–900 nm) equipped with a Xe lamp 450 W and double monocromators; the photoluminescence was excited at 350 nm.

The parameters of the solar cells were determined from photocurrent–voltage (I–V) measurements carried out under standard

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Table 1
Chemical composition of the used aqueous solutions.

Solution	Composition
1	5 mM $Zn(NO_3)_2 + 5$ mM hexamethylenetetramine ($C_6H_{12}N_4$)
2	5 mM $Zn(NO_3)_2 + 5$ mM hexamethylenetetramine + 0.32 mM eosin Y
3	80 mM $Zn(NO_3)_2$

illumination conditions using an AM1.5 solar simulator (L.O.T.-Oriel GmbH & Co.KG, Model LS0306 with a 300 W Xe-Arc lamp and an AM1.5-Global filter (LSZ189) with the specification: 1sun at 18 cm working distance).

I–V measurements were performed using an Autolab PGSTAT 30 Potentiostat/Galvanostat (Eco Chemie). The Autolab PGSTAT 30 potentiostat with Frequency response analysis software, version 4.9 was used to conduct the electrochemical impedance spectroscopy (EIS) study, in order to determine the electron transport performance of the solar cell. The electrochemical impedance spectra were obtained at a bias of open-circuit voltage in 10^{-1} Hz $\leq f \leq 10^5$ Hz frequency range with ac voltage amplitude of ±5 mV, under 100 mW/cm^2 illumination.

3. Results and discussion

It is well-known that ZnO nanorods can be prepared in a chemical process [15] in aqueous solution with $Zn(NO_3)_2$ and $C_6H_{12}N_4$ as precursors. Hexamethylenetetramine molecules act like a weak base which hydrolyzes slowly in the hot aqueous solution and, as a result, increases the pH of the solution and induces ZnO formation. It is important that the increase of the pH to go slow, otherwise Zn^{2+} ions will be quickly precipitated and their contribution to the growth of the nanorods will be reduced. If the chemical process takes place at the same time with electrochemical reduction of nitrate ions the deposition process of ZnO nanorods will change; the electrochemical process contributes to precipitation of ZnO nuclei on the cathode surface and to the growth of nanorods by permanent supplying of hydroxyl ions.

The chemical reactions which take place in the solution 1 from Table 1 at 95 °C [16] are expressed by the following equations:

$$(CH_2)_6\,N_4 + 6H_2O \rightarrow 4NH_3 + 6HCHO \tag{1}$$

$$NH_3 + H_2O \rightarrow NH_4{}^+ + OH^- \tag{2}$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \leftrightarrow ZnO + H_2O \tag{3}$$

On the other hand, the electrochemical reduction of nitrate ions can proceed by a two-electron pathway with the pH increasing on the electrode surface followed by the precipitation of ZnO nuclei:

$$NO_3{}^- + 2e^- + H_2O \rightarrow NO_2{}^- + 2OH^- \tag{4}$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO\downarrow + H_2O \tag{5}$$

A typical linear voltammogram for cathodic polarization using solution 1 (containing zinc ions and hexamethylenetetramine molecules, only) is shown in Fig. 1a. An irreversible cathodic current increases gradually starting from cca −0.5 V, when a FTO electrode is used. A ZnO nuclei film is deposited during this process due to the reduction of nitrate ions and base generation on the electrode surface; when the reduction process takes place in the presence of eosin Y dye (Fig. 1b) some details are observed. The first portion of cathodic curve corresponds to ZnO deposition that begins at cca −0.5 V and has a limiting current within $-0.8 \div -1.0$ V potential range. The process involves the electroreduction of nitrate ions leading to ZnO precipitate together with conversion of Eosin Y dye in its reduced form (uncolored) [13]. A continuous increase of current without any other peak is recorded by scanning the potential up to −1.5 V polarization. This continuous current increase at potentials more negatively than −1.0 V may be assigned to the deposition of Zn metal seeds and probably the evolution of hydrogen. However, the aspect of the deposits changes rapidly, owing to oxidation of Zn seeds to ZnO.

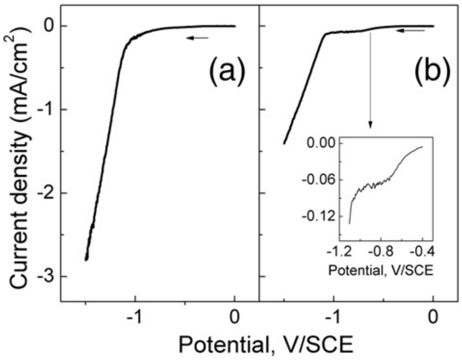

Fig. 1. Linear voltammograms recorded for cathodic process on platinum FTO electrodes using solutions 1 (a) and 2 (b) from Table 1; inset: Details of the linear voltamogram (b) on the potential interval −0.04, −1.1 V; scan rate 5 mV/s, t = 95 °C .

The growth of ZnO nanorods was performed on the surface of FTO electrode in the solution 1 at 95 °C, using an electrodeposition current of −0.25 mA/cm^2. The shell of ZnO/eosin Y was deposited from solution 2, under similar conditions. On linear voltammograms from Fig. 1 a current density of −0.25 mA/cm^2 corresponds to potentials more negative than −1.0 V, assigned to deposition of Zn metal seeds. At the same time with this process it takes place the pH increase on the electrode surface due to nitrate ions reduction. A large number of ZnO nuclei forms on the electrode surface due to Zn seeds instability into the deposition solution; on these nuclei will grow an array with high density of ZnO nanorods. The length of ZnO nanorods (sample NR) deposited in the solution 1 for 2000 s at −0.25 mA/cm^2 was about 2 μm; these nanorods become thinner from the root to the top end and form a sharp edge at the tip (Fig. 2a). They are highly crystallized so that no sufficient amount of dye (eosin Y) could be adsorbed for the preparation of a ZnO photoanode for DSSC. In order to prepare nanoporous ZnO nanorod array we deposited for 1500 s at −0.25 mA/cm^2 a ZnO/eosinY shell from the solution 2 on the surface of the previously prepared ZnO nanorods (NR); the loaded eosin Y molecules were removed by treatment in 0.01 M KOH aqueous solution for 12 h (Fig. 2b).

The pure ZnO nanorods deposited from dye-free solution have hexagonal shapes and their surface is smooth (Fig. 2a). The obtained ZnO nanorod/shell array has a completely different morphology; after dye removing, the electrodeposited ZnO nanorod/shell (sample NR-S1) structures have become porous and show conical shapes (Fig. 2b).

ZnO porous structures presented in the Fig. 2c and Fig. 2d were called NR-S2 and NR-S3 and are prepared by ZnO/eosin Y shell deposition for 4000 s and 8000 s, respectively. The deposition process was performed on ZnO nanorods (NR) and was followed by eosin Y extracting process. Fig. 2c and d shows formation of a ZnO layer by filling of the space between the nanocones with porous zinc oxide; over this layer, new porous ZnO structures have grown. In comparison, ZnO deposition for 3000 s at −0.25 mA/ cm^2 directly on the FTO electrode surface, using the solution 2 led to obtaining of bud shaped structures (S) after dye extracting (Fig. 2e).

The X-ray diffraction pattern of ZnO nanorod array (sample NR) deposited on a FTO electrode is shown in the Fig. 3a. The result shows that all diffraction peaks can be indexed to the wurtzite structure. In comparison with standard powder diffraction data [17], it was found that relative intensity of (002) peak is stronger to others; this demonstrates that nanorods are polycrystal structures with a preferred orientation in the direction of the c-axis. Sample S grown