

A new ZnO photoanode for dye-sensitized solar cell

M. SIMA*, M. SECU, M. SIMA, E. VASILE^a

National Institute of Materials Physics, P.O. Box MG 7, 077125 Magurele, Romania

^aMETAV-CD, 31 CA Rosetti Street, 020015 Bucharest, Romania

The present work reports the preparation of nanostructured ZnO nanorods in a hydrothermal-electrochemical process and preliminary attempt to fabricate a dye-sensitized solar cell using this material as photoanode. Synthesis of ZnO nanorods in solutions with and without eosin Y dye, used as nanostructuring agent, was studied. ZnO nanorod arrays were characterized by photoluminescence spectroscopy, scanning electron microscopy and X-ray diffraction analysis. Fabricated dye-sensitized solar cell comprised a photoanode prepared with nanostructured ZnO nanorods and eosin Y dye, a platinum counter electrode and an electrolyte consisting of 0.5M KI + 0.03M I₂ in acetonitrile/ethylene carbonate (v/v=1/4). Performance parameters of dye-sensitized solar cell were extracted from standard current-voltage characteristic.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are a low-cost alternative to conventional solid-state solar cells [1-4]. They are composed of a nanostructured semiconductor material with a wide band gap, usually TiO₂, a dye sensitizer, an electrolyte, a counter electrode and transparent conducting substrates. A monolayer of dye is chemically adsorbed on this semiconductor material. Photoexcitation of dye causes injection of electrons into the conduction band of semiconductor from where they diffuse towards a transparent conducting oxide substrate. The dye is regenerated through electrons from an iodide/triiodide redox couple dissolved in the electrolyte. After passing through a desired load, the electrons enter the cell through a counter electrode to reduce the triiodide ions and thus complete the circuit. A 11% efficiency has been achieved with small size cells based on TiO₂ photoanode.

ZnO-based photoanode for DSSCs have 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 TiO₂. In addition, ZnO exhibits most of the configurations of nanostructures that one material can form [5-9]. ZnO films have been prepared by 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. 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 [10,11] and the loaded eosin Y molecules were completely removed by the alkaline treatment. On the other hand, electron transport in the single crystalline rod is expected to be several orders of magnitude faster than that in a random polycrystalline network [12]. In this paper, we investigated the

electrodeposition of an array of ZnO nanorods in the presence of eosin Y as nanostructuring agent in order to obtain porous ZnO nanorods; the feasibility of employing such array of ZnO porous nanorods as photoelectrode material for DSSCs was studied.

2. Experimental

The hydrothermal-electrodeposition processes of ZnO and ZnO/eosin Y nanorods were investigated using the aqueous solutions 1 and 2 from the Table 1; for linear voltammograms measurements the working electrodes were a platinum foil and fluorine doped SnO₂ glass substrate (FTO). The sheet resistance of the FTO layer was ~15 ohm/square and its transmission was > 80% from 400 to 700 nm. The electrochemical cell also contained a zinc foil (20 cm² surface area) 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 PC computer. The microstructures of deposits were imaged by scanning electron microscopy (SEM), using both Zeiss EVO 50 and 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 using a lock-in technique and a standard luminescence set-up consisting in two monochromators for excitation and emission, a Xe-150 W lamp as light source and a photomultiplier as light detector.

Cell performance was measured using a laser diode with wavelength 406 nm. A Thorlabs FDS100 Si photodiode was used for measuring of the incident light power. Photocurrent-voltage (I-V) measurements were performed using an Autolab PGSTAT30 Potentiostat/Galvanostat (Eco Chemie).

Table 1. Chemical composition of the used aqueous solutions.

Solution	Composition
1	5 mM Zn(NO ₃) ₂ + 5 mM hexamethylenetetramine (C ₆ H 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

3. Results and discussion

ZnO nanorods have been prepared without a template in a chemical process in aqueous solution with Zn(NO₃)₂ and C₆H₁₂N₄ as precursors [13]. 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 Zn²⁺ ions will be quickly precipitated and their contribution to the growth of the nanorods will be reduced. In our method the substrate has not been seeded with ZnO nanocrystallites before chemical bath growth of nanorods.

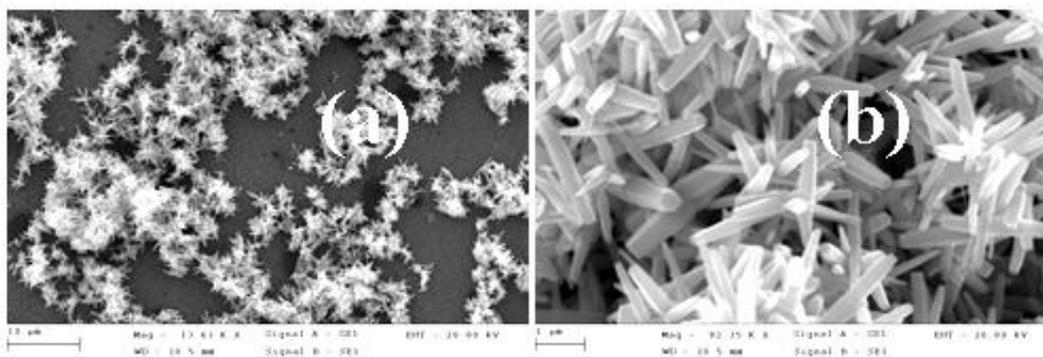
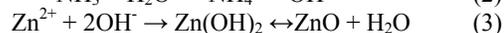
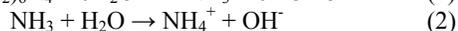


Fig. 1. SEM images (at two magnifications) of ZnO nanorods obtained by hydrothermal method in the solution 1 (Table 1) at 90 °C on a FTO support.

The chemical reactions which take place in the solution at 95 °C [14] are expressed by the following equations:



Our measurements showed (Fig. 1) that ZnO nanorods obtained by hydrothermal method are rather uniform in dimension but are not well dispersed onto FTO coated glass; these nanorods having 2 μm length exhibit essentially pyramid trunk-like shapes.

In a hydrothermal-electrochemical process in the solution 1 from Table 1, at the same time with the chemical process it takes place electrochemical reduction of nitrate ions followed by the precipitation of ZnO nuclei distributed uniformly on the surface of electrode, used as cathode (see equations (4) and (5)); the electrochemical process also contributes to the growth of nanorods by permanent supplying of hydroxyl ions on the electrode surface. The as-synthesized ZnO nanorods with length of about 2 μm become thinner from the root to the top end and form a sharp edge at the tip (Fig. 2a). Voltammetric curves from Fig. 3 show an irreversible cathodic current attributed to nitrate ions reduction; the ZnO deposition process takes place even at a potential of -1.5 V, without cathodic reduction of Zn²⁺ ions to metallic zinc, both at platinum and FTO electrodes.

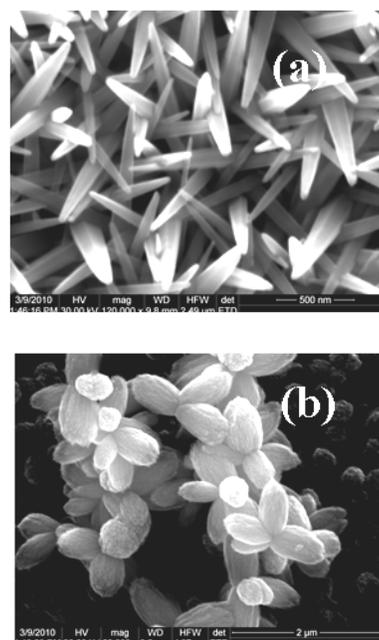


Fig. 2. SEM images of ZnO nanorods prepared in hydrothermal-electrochemical processes in the solutions 1 (a) and 2 (b) from Table 1 on a FTO electrode; electrodeposition current = -0,25 mA/cm², t=90 °C, deposition time 3500s. SEM image of the sample (b) was obtained after extraction of eosin Y by soaking in diluted KOH aqueous solution.

Small Zn^{2+} concentration and large concentration of hydroxyl ions which result in hydrothermal-electrochemical process could be reasons of this behaviour.

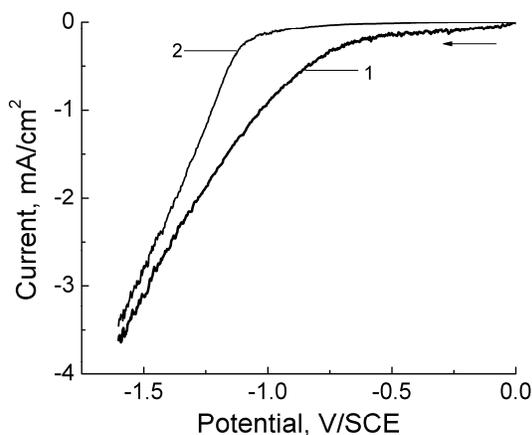
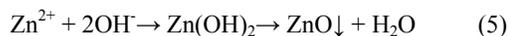


Fig. 3. Linear voltammograms recorded for cathodic process on platinum (1) and FTO (2) electrodes using solution 1 (Table 1); scan rate 5 mV s^{-1} , $t=90 \text{ }^\circ\text{C}$.

The electrodeposited ZnO nanorods are highly crystallized so that no sufficient amount of dye (eosin Y) could be adsorbed for the preparation of a ZnO photoanode for DSSC. The x-ray diffraction (XRD) pattern of ZnO nanorod array deposited on a ZnO thin film is shown in the Fig. 4; FTO was used as supported electrode. The fact that we are able to index all the peaks according to the wurtzite ZnO structure indicates good crystal quality of ZnO nanorods. The nanorods array shows a specific crystalline orientation along the (002) diffraction plane. In order to prepare nanoporous ZnO nanorod array we electrodeposited ZnO/eosinY nanorods and the loaded eosinY molecules were removed by treatment in 0.01M KOH aqueous solution for 12 hours (Fig. 2b). The pure ZnO nanorods electrodeposited from dye-free solution have hexagonal shapes and their surface is smooth (Fig. 2a). The ZnO/eosin Y hybrid obtained with a small quantity of eosin Y (solution 2, Table 1) have a completely different morphology; after dye removing the electrodeposited ZnO layer shows conical shapes with fibrous internal nanostructure aligned in the direction of the nanocone growth (Fig. 2b).

Fig. 5 compares the photoluminescence spectra of ZnO nanorods and ZnO nanocones prepared in the solutions 1 and 2 (Table 1), respectively; ZnO nanorod array shows a strong free exciton emission at 380 nm (3.26 eV) and a weak, broad deep level emission centered at 600 nm (2.07 eV) which was attributed to the lattice defects.

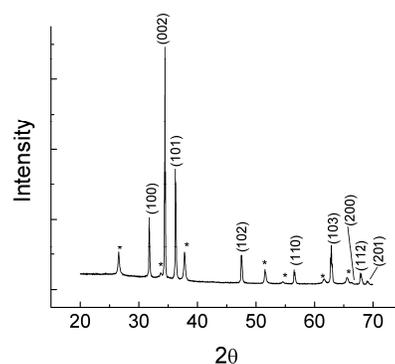


Fig. 4. XRD patterns of ZnO nanorod array electrodeposited from the solution 1 (see Fig. 2a) on a ZnO thin film (thickness $\sim 400 \text{ nm}$) prepared in the solution 3 (Table 1) using a pulsed-current deposition technique (on time 5s at current density -1.4 mA/cm^2 , 5s off-time) [15]. The peaks of the FTO coated glass substrate is indicated by "*".

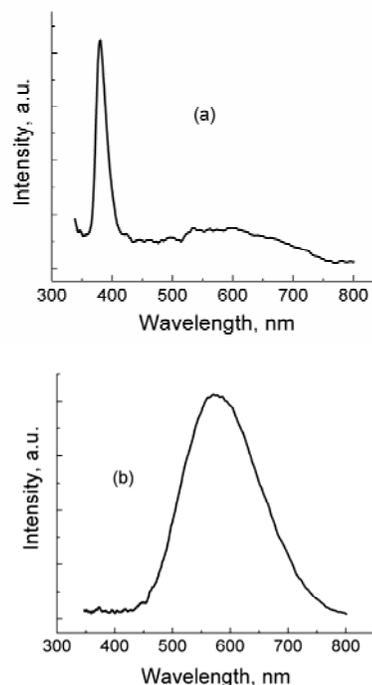


Fig. 5. Photoluminescence spectra of ZnO nanorods (a) and ZnO nanocones (b) (see Fig. 2) prepared from solutions 1 and 2 (Table 1) respectively on FTO glass substrate; photoluminescence excitation at 550 nm.

On the other hand, the intensity of the defect related band of ZnO nanocone array increased significantly in comparison with similar band observed in the case of ZnO nanorods; it was found to be situated around 573 nm (2.16 eV). The UV near-band edge emission was not observed in this case. These spectra show that the growth of ZnO nanostructures in the presence of eosin Y dye produces a very high density of defects in semiconductor material.

A preliminary attempt to fabricate a dye-sensitized solar cell based on ZnO nanocones-eosin Y hybrid layer prepared by electrodeposition was performed.

For photoanode fabrication, a ZnO thin film (~400 nm) was prepared using a pulsed-current deposition technique (on time 5s at current density -1.4 mA/cm^2 , 5s off-time) [15]; solution 3 from Table 1 was used for electrodeposition process. On this film was electrodeposited ZnO nanocone-eosin Y array from the solution 2 (electrodeposition current = -0.25 mA/cm^2 , $t=90^\circ\text{C}$, deposition time 3500s).

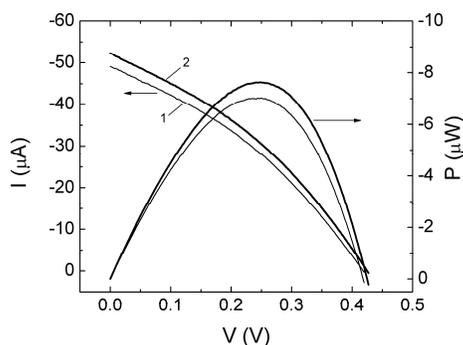


Fig. 6. Photocurrent-voltage and power profile obtained with a an Autolab PGSTAT30 Potentiostat/Galvanostat and a laser diode with wavelength 406 nm for illumination intensities: 1) $453 \text{ } \mu\text{W/cm}^2$; 2) $466 \text{ } \mu\text{W/cm}^2$ (cell surface area = 1.75 cm^2).

Table 2. The values of the parameters of dye-sensitized solar cell derived from the IV curves from Fig. 6.

Incident light power ($\mu\text{W/cm}^2$)	Short-circuit current (μA)	Open-circuit voltage (V)	Maximum power ($\mu\text{W/cm}^2$)	Fill factor	Efficiency (%)
453	49	0.42	4.076	0.34	0.9
466	52	0.427	4.358	0.34	0.93

4. Conclusions

In this study, nanostructured ZnO nanorods samples have been successfully synthesized using a hydrothermal-electrochemical precipitation method in aqueous solution. In this process Eosin Y dye was used as nanostructuring agent. The ZnO/eosin Y hybrid have a completely different morphology in comparison with ZnO nanorods prepared in a solution without Eosin Y; after dye removing the electrodeposited ZnO layer shows conical shapes with fibrous internal nanostructure aligned in the direction of the nanocone growth.

Photoluminescence spectra show that the growth of ZnO nanostructures in the presence of eosin Y dye produces a very high density of defects in semiconductor material.

A dye-sensitized solar cell based on ZnO nanocones-eosin Y hybrid layer as photoanode was fabricated. This cell based on a $2 \text{ } \mu\text{m}$ length ZnO nanocones deposited on 400nm thick compact nanocrystalline ZnO film yielded a conversion efficiency of about 0.9% under an illumination with a laser diode centered at 406 nm (incident light power

EosinY was extracted by soaking for 12 hours in a 0.01M KOH aqueous solution and it was re-absorbed in a monomolecular layer on the large surface of ZnO nanocones from a solution containing $3.2 \times 10^{-4}\text{M}$ eosin Y in ethanol. This photoanode, prepared on a FTO electrode, a platinum counter electrode and an electrolyte consisting of 0.5M KI + 0.03 M I_2 in acetonitrile/ethylene carbonate ($v/v=1/4$) were used to fabricate the photoelectrochemical cell.

The performance of cell was quantified by measuring its photocurrent-photovoltage curve under an illumination with a laser diode (10 mW) centered at 406 nm. The power of the incident radiation was $453 \text{ } \mu\text{W/cm}^2$ in a case and $466 \text{ } \mu\text{W/cm}^2$ in another case. From these measurements the parameters like fill factor, efficiency and maximum power were derived (Table 2).

The photocurrent-voltage measurements (IV-curves) were obtained by applying a potential scan, from 0 V (short-circuit conditions) to the open-circuit potential, under constant illumination. Fig. 6 shows the measured IV curves with increasing light intensity; as the light intensity increases, the maximum short-circuit current and the open-circuit voltage increase.

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*Corresponding author: msima@infim.ro