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PHOTOANODE FOR DYE-SENSITIZED SOLAR CELL BASED ON ELECTROPHORETICALLY DEPOSITED ZnO LAYER

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Electrophoretic deposition (EPD) method is employed to obtain a thick ZnO layer on a ZnO nanorod array prepared in a hydrothermal-electrochemical process. ZnO nanorods have the role to improve the mechanical stability and adherence of ZnO layer deposited by electrophoretic technique. D149 dye is used as sensitizer for ZnO semiconductor. The thus prepared ZnO layer is used for the photoanode of dye-sensitized solar cell (DSC). Performance parameters were extracted from standard current-voltage characteristic (I-V) and charge transfer phenomena occurring at ZnO/dye/electrolyte was evaluated by electrochemical impedance spectroscopy (EIS).

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1. Introduction

Dye-sensitized solar cells continue to attract much interest due to their properties [1] such as relatively high energy conversion efficiency, transparency and/or multicolor options, easy integration into building architecture, etc. Recently, DSCs based on nanoporous TiO_2 electrode on rigid glass substrate have shown a conversion efficiency of 12.3% under air mass 1.5 global sunlight [2]. On the other hand, the DSC type of solar cells, unlike the p-n junction type is a majority carrier transport device, and therefore the stringent requirement of high purity materials can be relaxed, with anticipated lower cost of unit power produced. The improvement of DSC efficiency is connected with the optimizing of each component of the solar cell including structure of the photoanode. An alternative to TiO_2 as electron conductor in DSC is ZnO, a wide band gap semiconductor which presents an electron mobility [3] larger than that of anatase TiO_2.

ZnO thin films are prepared by different techniques such as pulsed laser deposition (PLD), spray pyrolysis, magnetron sputtering, MOCVD, etc. Lincot et al. [4-6] and Izaki et al. [7, 8] have initially been introduced the electrochemical deposition of ZnO films by using tin oxide/glass and GaN substrates, respectively. In addition to thin films, ZnO exhibits a large family of nanostructures [9-18].

DSC photoanode consists of nanocrystalline, mesoporous, thick layer of a wide bandgap semiconductor, covered with a monolayer of dye molecules. The semiconductor is deposited on a transparent electrode (FTO, ITO, etc) which the cell is illuminated. The dye sensitized solar cell also contains a redox electrolyte (usually iodide/tri-iodide) and a counter-electrode. The operating principle of DSC for conversion of sunlight into electricity assumes the following stages: dye

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molecule absorbs the photon which will excite an electron from the molecular orbital HOMO (highest occupied molecular orbital) into the molecular orbital LUMO (lowest unoccupied molecular orbital). Then, the electron is injected in the conduction band of the semiconductor and it moves through the nanocrystalline semiconductor network to the external circuit. The hole created after the excitation of dye molecule is recovered by an electron from iodide ion in the redox electrolyte. This oxidized iodide ion turns into tri-iodide ion which reduces to counter-electrode in another step. This system will work as solar cell if the energy of molecular orbital LUMO is higher than that of the conduction band of the semiconductor and the energy of the orbital HOMO is lower than the energy that corresponds to the redox potential of the electrolyte.

Electrophoretic deposition is a useful method for the preparation of thick binder-free layers on conductive substrates in a very short time, compared to the other techniques. However the layer adherence to the substrate is poor and it cannot be handled without exfoliation.

In this contribution, we report the fabrication of a DSC photoanode based on three ZnO superposed layers: a thin layer deposited on FTO substrate, used as blocking layer, an array of ZnO nanorods and an electrophoretically deposited ZnO layer. ZnO nanorods have the role to improve the mechanical stability and adherence of ZnO layer deposited by electrophoretic technique. The complete cell with the ZnO photoanode was constructed and tested.

2. Experimental

ZnO films and nanorods were deposited by electrodeposition from aqueous solutions 1 and 2, respectively from the Table 1. The working electrode was a commercial FTO/glass substrate with a sheet resistance of ~15ohm/square and its transmission was > 80% from 400 to 700nm. The substrate was thoroughly cleaned in an ultrasonic bath with isopropanol for 15 min prior to use. The electrochemical cell also contained a platinum foil as auxiliary electrode and a Ag/AgCl electrode in saturated KCl as reference electrode. The electrochemical processes were performed using an Autolab PGSTAT 30 potentiostat digitally controlled by a PC computer. For EPD tests an electrophoresis power supply Consort EV233 was used. 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.

The parameters of the solar cell were determined from I-V measurements carried out under standard illumination conditions using an AM1.5 solar simulator (L.O.T.-Oriel GmbH & Co.KG, Model LS0306 with a 300W Xe-Arc lamp and an AM1.5-Global filter (LSZ189) with the specification: 1sun at 18cm working distance). Photocurrent-voltage (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. The electrochemical impedance spectra were obtained at a bias of open-circuit voltage in $0.05Hz \leq f \leq 10^5$ Hz frequency range with ac voltage amplitude of ±5 mV, under 100mWcm^{-2} illumination.

Table 1. Chemical composition of the used solutions.

Solution	Composition (working temperature)
1	80mM $Zn(NO_3)_2$ (70^0C)
2	5mM $Zn(NO_3)_2$+5mM hexamethylenetetramine ($C_6H_{12}N_4$) (95^0C)

3. Results and discussion

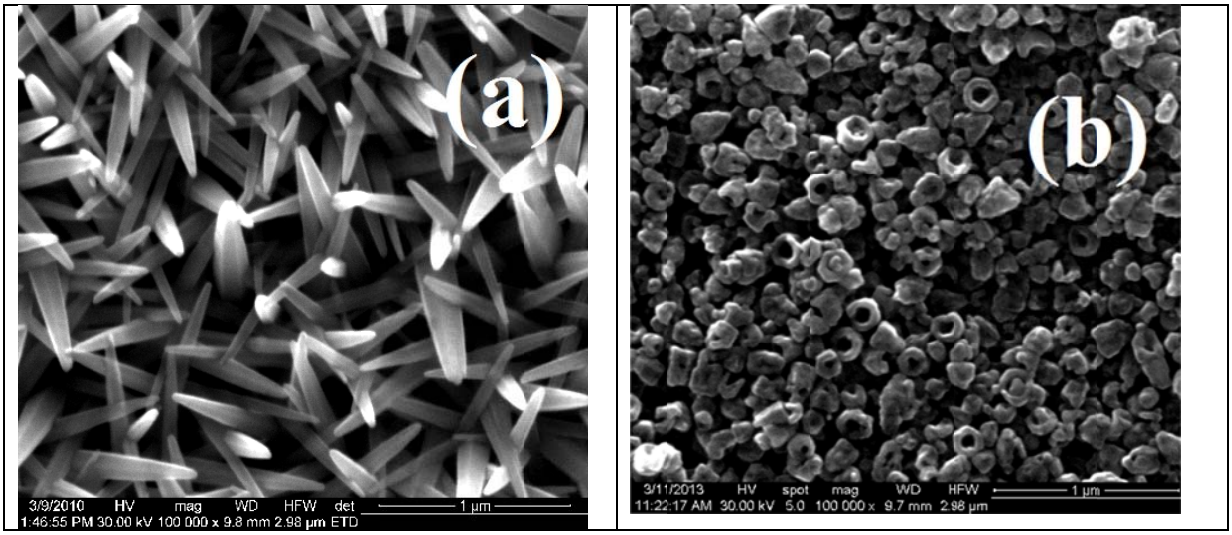

Fig.1. FESEM images of ZnO nanostructures deposited on FTO electrode: a) nanorod array prepared in a hydrothermal-electrochemical process; b) nanopowder for electrophoretic deposition treated at 450^{0}C for 30min.

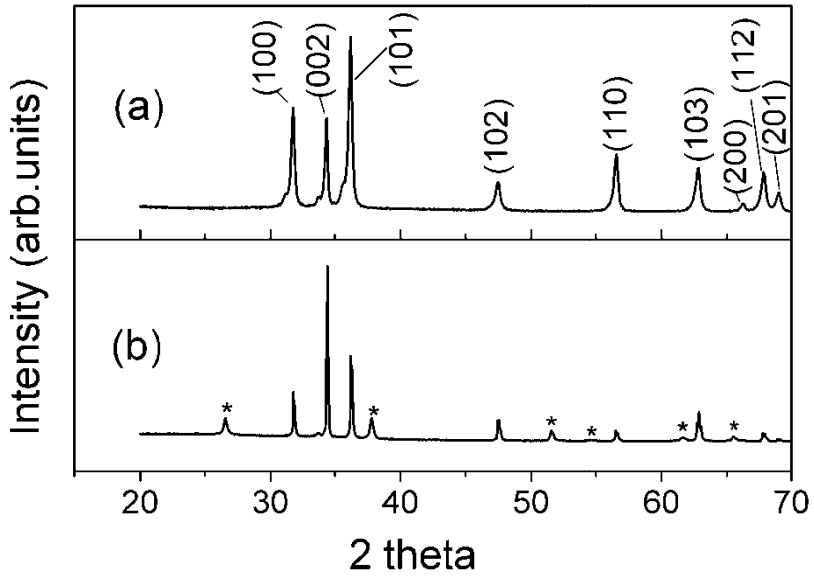

Fig.2. XRD patterns of ZnO (a) nanopowder for electrophoretic deposition treated at 450^{0}C for 30min and (b) nanorod array grown on the FTO electrode. The peaks of the FTO coated glass substrate is indicated by "".*

For photoanode fabrication, a ZnO thin film (~300nm) was prepared using a pulsed-current deposition technique (on time 5s at current density -1.4mA/cm^2, 5s off-time) [19]; solution 1 from Table 1 was used for electrodeposition process. On this film was electrodeposited a ZnO nanorod array (Fig.1,a) from the solution 2 in a hydrothermal-electrochemical process [16] at constant current of -0.25mA/cm^2 for 2000s. The thickness of the ZnO layer was around 1.8µm.

ZnO nanoparticles used in the electrophoretic process were synthesized by direct precipitation [20]. An aqueous solution of zinc acetate (Sigma Aldrich) 0.34M was prepared, and

the precipitation was carried out at pH > 8 by the addition of NaOH 1 M. The resulting precipitate was washed and filtered. A thermal treatment at 200^0C for 3 min was enough to decompose the remaining starting reagents and to obtain ZnO nanopowder. The FESEM image of ZnO powder for electrophoretic deposition is shown in Fig.1,b. Different particle morphologies and sizes (under 300nm) were obtained after thermal treatment at 450^0C for 30min.

The X-ray diffraction (XRD) patterns of ZnO nanopowder and nanorod array deposited on a FTO electrode are shown in the Fig.2. The fact that we are able to index all the peaks according to the wurtzite ZnO structure indicates good crystal quality of ZnO nanopowder and nanorods. The main diffraction peak from XRD pattern of ZnO nanopwder (Fig.2,a) corresponds to the crystalline planes family of Miller indices (101). The nanorods array shows a specific crystalline orientation (Fig.2,b) along a direction perpendicular to the diffraction plane (002).

EPD is an important technology for coating colloidal processes. Under the influence of a DC electric field charged colloids or particles suspended or dispersed in a fluid move to the electrode and are deposited. Originally, EPD was performed using organic suspensions that have several advantages among which: low electrical conductivity and good chemical stability, absence of chemical reactions and Joule heating of the electrodes. This leads to the formation of high-quality coatings. At the initial part of deposition, a linear relationship between the film thickness and time deposition can be observed. On the other hand, the morphology of the film surface can be controlled by potential difference between electrodes [21]. This technique was applied to deposit at room temperature a thick ZnO layer (thickness 5-8μm) on previously deposited ZnO nanorod array from ZnO nanoparticles suspension. In order to prepare a stable suspension of ZnO nanoparticles, the metal oxide was treated with a non-ionic surfactant (acetylacetone) in a polar organic solvent and the suspension obtained was added to a charging solution consisting of iodine, acetone and deionized water in a polar solvent. The particle charging in this sistem is achieved via adsorption of protons, which are formed by keto-enol reaction [22]:

$$CH_3COCH_3 \leftrightarrow CH_3C(OH)CH_2 \quad (1)$$

$$CH_3C(OH)CH_2 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^- \quad (2)$$

The suspension for electrophoretic deposition [23] was prepared by mixing 0.35g ZnO powder with 50ml isopropanol and 0.12ml acetylacetone. In addition, a charging solution containing the following additives: iodine (14.7ml), acetone (2.1ml) and water (1.05ml) in 17.5ml isopropanol and 17.5ml ethanol absolute was prepared. After one hour of stirring ZnO suspension was added to the charging solution and the mixture was sonicated 15min.

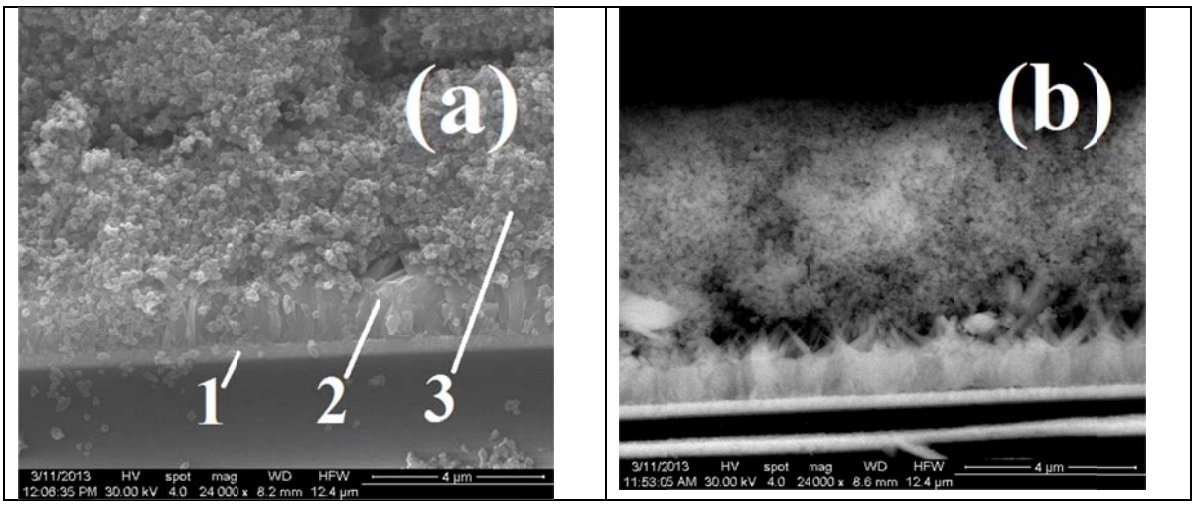

Fig.3. FESEM images of ZnO layer structure used for the fabrication of DSC photoanode: (a) 1-ZnO film; 2-ZnO nanorod array; 3-ZnO layer deposited by electrophoretic technique. (b) Imperfect mechanical contact between ZnO nanorod array and electrophoretically deposited ZnO nanoparticles.

The electrophoretic cell contained two electrodes, one electrode of FTO covered with ZnO thin layer and ZnO nanorod array, used as cathode and another electrode of platinum as counter-electrode. The electrodes were placed vertically at a distance of 1cm in the prepared suspension and the DC power supply was set at 90V. The deposition time was 6min. Zinc oxide layer was thermally treated at 450^0C and it was sensitized by immersing into a D149 dye solution (0.5mM in acetonitrile/tert-butylalcohol (V/V=1/1)). Fig.3,a indicates the structure of ZnO layer after thermal treatment while Fig.3,b shows some bad mechanical connections between nanorod array and nanoparticles into ZnO layer. The basic components of dye sensitized solar cell are the photoanode, the counter-electrode and the electrolyte. The counter-electrode was fabricated by sputtering deposition of a Pt film onto the FTO substrate and the used electrolyte had the following composition: 0.5 M tetrabutylammonium iodide, 0.001 M $LiClO_4$, 0.5 M 4-tert-butylpyridine and 0.1 M I_2 in acetonitrile [24].

I-V characteristics for solar cell based on the fabricated photoanode, with an active area of $1.5cm^2$ are exhibited in Fig. 4, a. The values for short-circuit current, open circuit voltage and fill factor were 10.53 mA, 0.57 V and 33.4%, respectively, resulting in a solar cell efficiency of 1.34%. A further evaluation was performed by measuring impedance spectra of the solar cell. These measurements are useful when the experimental data are fitted to representative equivalent circuit. The impedance response of DSC is related to the response of the different components of the device. A transmission line model was proposed by Bisquert to describe this system [25]. The transmission line model is composed of a network of resistive and capacitive elements, which describe the transport and interfacial transfer of electrons that take place in the metal oxide. Fig.5 shows the equivalent circuit model used to fit impedance spectra for dye-sensitized solar cell. The distributed components describing the transmission line are the electron transport resistivity in the photoelectrode consisting of interconnected ZnO nanoparticles r_t (Ωcm), the charge transfer resistance at ZnO/dye/electrolyte interface per unit volume of the electrode r_{rec} (Ωcm^3) and electrode capacitance per unit volume c_μ (Fcm^{-3}). These distributed parameters are related to total resistances and capacitances by $R_t= r_t d$, $R_{rec}= r_{rec} d^{-1}$and $C_\mu= c_\mu d$ with their units Ωcm^2 and Fcm^{-2}, respectively, d being the thickness of the layer. In addition, equivalent circuit model of DSC contains the series resistance R_s, the resistance and capacitance of the substrate/electrolyte interface (R_{su} and C_{su}), the substrate/nanoparticle contact ($R_{co,2}$ and $C_{co,2}$), the counter-electrode/electrolyte interface (R_{CE} and C_{CE}) and Warburg impedance (Z_d) representing the diffusion of redox species in the bulk electrolyte layer.

Fig.4,b shows the Bode and the Nyquist (inset) diagrams of DSC system under study. The Bode plot shows two peaks and the Nyquist plot consists of two semicircles: the smaller semicircle corresponds to the charge-transfer resistance at the platinum electrode/electrolyte interface while the second semicircle represents the kinetics of the transport/recombination processes occurring in the photoelectrode.

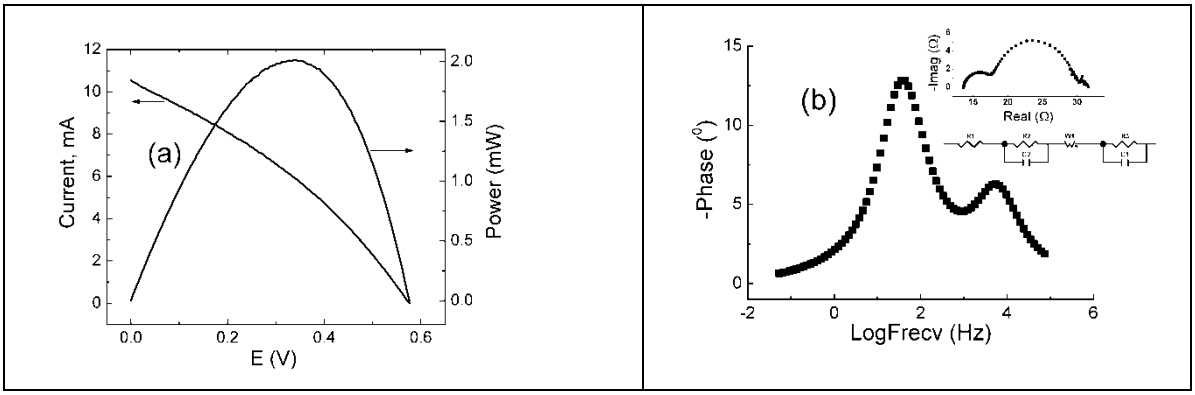

Fig.4. Evaluation of solar cell based on nanostructured ZnO photoanode sensitized with D149 dye under illumination AM 1.5: a) current-voltage characteristics and power profile b) Bode phase representation. The inset shows the equivalent circuit which was fitted the measured spectrum and Nyquist representation of the impedance spectrum.

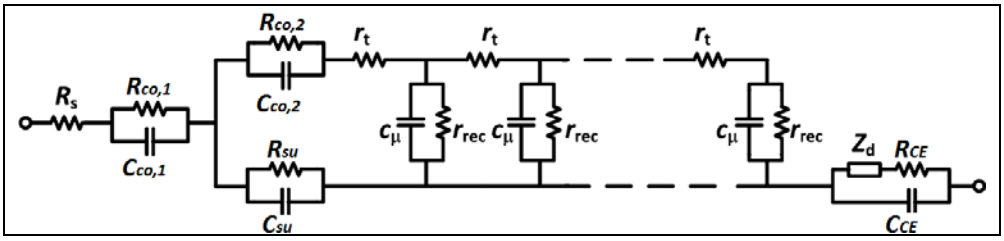

Fig.5. Equivalent circuit model of dye-sensitized solar cell

One component of our photoanode is a ZnO thin layer used as blocking layer. Therefore, we assumed that the contact impedance of the interface blocking layer/nanorods or nanoparticles to be negligible because the materials are similar, thus $R_{co,2}$ was set to zero, also making $C_{co,2}$ redundant. Also, the presence of R_{su} and C_{su} cannot be justified.

At open-circuit conditions the electron Fermi level of ZnO semiconductor approaches the conduction band edge, making it sufficiently conductive so that the electron transport resistance becomes negligible. As a result, the transmission line model reduces to a parallel connection of the charge transfer resistance R_{rec} and C_{μ} the capacitance of ZnO layer. Also, at open-circuit conditions, $R_{co,1}$ was assumed negligible.

The electrochemical impedance spectra were fitted using the Zview software by means of the equivalent circuits shown in Fig.4,b. The equivalent circuit of the solar cell (Fig.4,b) includes the series resistance R_1 which accounts for the sheet resistance of the conducting glass plus any other element that might be considered to be in series with the rest of the circuit, charge transfer resistance R_3 and C_1-double layer capacitance at the platinized FTO, charge transfer resistance R_2 and capacitance C_2 at the photoanode/electrolyte interface and Warburg impedance W_1. The values of the parameters determined by fitting the experimental data to the equivalent circuit shown in Fig.4, b are: $R_1 = 13\Omega$, $R_2 = 8.06\ \Omega$, $R_3 = 2.35\ \Omega$, $C_1 = 12.8\ \mu$ F and $C_2 = 0.65$ mF. This ZnO layer based photoanode shows a low charge transfer resistance associated to recombination of electrons at ZnO/dye/electrolyte interface.

The lifetime of the electron (τ_e) in ZnO layer was evaluated from Bode phase plot, using equation $\tau_e = 1/2\ \pi\ f_{max}$, where f_{max} is the frequency at the maximum of the phase, to be 5.2ms.

Conclusions

In this paper, we presented a new photoanode for DSC based on nanoporous ZnO layer prepared by electrophoretical deposition on the surface of ZnO nanorod array, having the role to improve the mechanical stability and adherence of ZnO layer deposited by electrophoretic technique. A thin layer of ZnO grown by electrodeposition was used as blocking layer for photoanode.

Although there were observed some bad mechanical connections between nanorod array and nanoparticles from ZnO layer, the electron transport resistivity in the photoelectrode was small. Small solar cell efficiency (1.34%) was attributed to low charge transfer resistance associated to recombination of electrons at ZnO/dye/electrolyte interface.

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