

EFFECT OF NANOSTRUCTURED ZnO ON THE PHOTOVOLTAIC PERFORMANCE OF TiO₂ DYE SENSITIZED SOLAR CELLS

M.Balasubramanian¹, K.R.Murali²

¹ School of Information and technology, Vivekananda Institute of Professional Studies, (India)

² Department of theoretical Physics, University of Madras, (India)

ABSTRACT

In the present study, the effect of sol gel dip coated ZnO nanostructure on TiO₂ film was investigated. To achieve the optimum deposition procedure, ZnO films were deposited at various precursor concentrations and deposition times. Dye sensitized solar cells(DSSCs) were fabricated using N719 ruthenium dye and all photovoltaic parameters such as short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and conversion efficiency (η) were measured as well. Field emission-scanning electron microscopy (FE-SEM) was performed to study the structure and morphology of nanostructured TiO₂ /ZnO layers. The results demonstrated the significant enhancement of the short circuit current density and efficiency due to ZnO charge trapping effect.

Keywords DSSC, Tio₂ Film, Solar Cells, Zno, Nanostructure.

I INTRODUCTION

Dye-sensitized solar cells (DSSCs) are one of the most promising alternative renewable energy sources, which have attracted much attention due to their high conversion efficiency, simple manufacturing process, low production cost, and non-toxicity [1–4]. TiO₂ nanostructures have been mostly used in DSSCs because of their unique photovoltaic and photochemical properties. Mainly, they can provide high surface area for efficient dye adsorption and diffusion pathway for charge transfer processes [5]. Recently, many efforts have been done to improve the conversion efficiency of nanostructured TiO₂ photoanodes. One of the promising approaches to enhance the performance of TiO₂ -based DSSCs is the suppression of recombination reactions at the TiO₂ /dye/electrolyte interfaces. Due to a wide direct band gap (3.37 eV) and the large excitation binding energy (60 meV) of ZnO nanostructures, they have been supposed to be an appropriate inherent barrier layer between the photoelectrode and electrolyte in TiO₂ -based DSSCs. Several theories have been proposed to describe the function of ZnO barrier layer on the performance of TiO₂ based photoanodes. It was explained that ZnO can enhances the physical separation between the injected electrons and the oxidized dye redox couples to decline the electron recombination reactions [6]. ZnO has also been



explained to function as a trap to capture the holes where a large number of electrons merge in the conduction band of the TiO₂ nanostructures [7, 8].

Various methods have been investigated to create ZnO layer on TiO₂ photoelectrodes in order to suppress the charge recombination process [9, 10]. RF magnetron sputtering technique was used to fabricate TiO₂ /ZnO photoelectrodes for DSSC with 26% increase in the cell efficiency [9]. Thermal chemical vapor deposition method was used to deposit ZnO nanowires on the surface of TiO₂ NPs with significant enhancement of the V_{OC} and FF values, about 10–15% [10]. Hydrothermal methods also were utilized to prepare hybrid TiO₂ /ZnO nanostructures [11,12]. Although the above mentioned methods represented the proper results, some of their disadvantages such as large deposition time and difficulties have attracted more attention to find the more convenient and feasible deposition methods.

In the present work, the sol gel dip coating method was adopted for the deposition of ZnO films on TiO₂ NPs. This is a very versatile and simple technique, which does not need any vacuum system of sophisticated instrumentation.

II. EXPERIMENTAL METHODS

F-doped SnO₂ conducting glass (FTO) was used as substrates. They were cleaned under ultrasonic treatment (5 min in acetone, 5 min in alcohol), rinsed with double distilled water, and finally treated for 2 min in a 45% nitric acid solution prior to drying in nitrogen atmosphere [13], and used to make both the working and counter electrodes. A 2M aqueous TiCl₄ solution was obtained by dilution of concentrated TiCl₄ (Across chemicals) with pre-cooled distilled water solvent in an ice bath and kept in refrigerator. Then 50 mM aqueous TiCl₄ solution was prepared by dilution of 2 M aqueous TiCl₄. For pretreating the FTO substrates with TiCl₄, the FTO layers were immersed in 50 mM aqueous TiCl₄ solution at 75 °C for 30 min, and dried at room temperature. P-25 TiO₂ paste was prepared from TiO₂ NPs according to the reported method [14]. Doctor Blade technique was acquired to deposit TiO₂ paste on FTO layers. The coated electrodes were annealed gradually under airflow in programmed heating steps. The temperature was raised to 325 °C with heating rate of 10 °C/min and was held at this temperature for 15 min. The temperature was raised to 375 °C with heating rate of 10 °C/min and held at this temperature for 15 min. Next, the temperature was raised to 450 °C with heating rate of 20 °C/min and maintained at this temperature for 15 min. In the final step, the temperature was increased to 500 °C with heating rate of 10 °C/min and kept at this temperature for 30 min, and cooled down to room temperature with rate of 5 °C/min.

ZnO films were deposited on the TiO₂ NPs by the following procedure: 1 mM of zinc nitrate (AR, Emerck) was dissolved in ethanol (solution A). 1 ml of this solution A was diluted 10 times to obtain 1x 10⁻⁴ M solution (solution B), 1 ml of this solution B was further diluted ten times to obtain 1 x 10⁻⁵ M solution (solution C), 1 ml of solution C was diluted ten times to obtain 1 x 10⁻⁶ M solution. (solution D). 30 ml of above solutions were separately taken in a 50 ml beaker kept at 75°C, prior to dipping the TiO₂ NPs, the pH of the four solutions was adjusted to 9 by NH₄OH.



Four separate coated TiO₂ NPs were dipped individually in the above four Zn²⁺ solutions. The dipping time was kept constant at 30s. For Dynamic light scattering experiments (DLS), ZnO films were coated under identical conditions on clean glass substrates with the above solutions. The films were withdrawn from the solutions after 30 min and washed with ethanol and dried at room temperature. These four films were further heated in air at 350°C for ZnO formation.

The bare and ZnO coated TiO₂ photoelectrodes of active area 0.30 cm² were immersed in ethanolic dye solution of 0.25 M N719 for about 15 hours. The dye absorbed photoelectrodes were washed with ethanol and dried at room temperature. The counter electrodes were prepared by drop coating of 0.5 mM H₂ PtCl₆ solution on the FTO surface and then heated at 400 °C for 15 min [17,28]. The photoanodes and Pt counter electrode were assembled into a DSSC structure. A thermal adhesive Surlyn (Dyesol) was used as spacer. The structure was kept in a hot press at 120°C for 10 min and the redox electrolyte composed of 0.1M1-propyl-3-methylimidazoliumiodide(PMII),0.05M LiI, 0.1M GNCS, 0.03M I₂ , 0.5M 4-tert-butylpyridine (TBP) in mixed solvent of acetonitrile and propylene carbonate (PC) (volume ratio:1/1) was injected through a hole drilled in the back side of the counter electrode. The hole was sealed by a glass piece.

III. RESULTS AND DISCUSSION

Quantitative analysis of energy-dispersive X-ray spectroscopy (EDX) was performed to identify chemical composition of the TiO₂ /ZnO layer which is shown in Fig. 1. The presence of tin, zinc and titanium elements has been indicated. Inductively coupled plasma (ICP) technique was used to determine the quantity of Zn deposited on TiO₂ layer. The results indicate that 1.8 % of Zn was obtained for the films deposited with 10⁻⁵ M Zn⁺, which increased to 2.9 % for the films deposited with 10⁻³ M Zn⁺.

A 500W Xenon light source (Oriel, USA) was used to illuminate the cells with an irradiance of 100mWcm⁻² (AM 1.5) which was calibrated by a Si photodiode. The current-voltage characteristics of the cells are shown in Fig.2 for the cells with and without ZnO coating. The degradation of fill factors compared to bareTiO₂ caused by ZnO film is related to the increase in photoanode resistance, due to either extra thermal treatment performed for ZnO annealing or resistance of thick deposited ZnO layer, which leads to decline in the cell efficiency [15], the lowest value was achieved for the bare TiO₂ photoanode. The slight improvement of V_{OC} and J_{sc} values obtained after ZnO coating indicates the effect of ZnO. The effect of ZnO NPs shifts the Fermi level of TiO₂ NPs [16] provides extra traps on TiO₂ nanoporous structure to capture the carriers and reduce the rate of recombination reactions. In fact, the deposition of the appropriate amount of ZnO NPs could act as charge trapping to capture the carriers, which resulted in suppressing the recombination reactions and subsequently enhancing the J_{sc} values. The values of the photovoltaic parameters are presented in Table -1.

For further characterization of TiO₂/ZnO DSSC, the incident photo-to-current conversion efficiency (IPCE) or external quantum efficiency (EQE) test was performed. Before starting the experiment, a calibrated Si photodiode

was used as the reference device for the counting of incident photons. The results indicate that the DSSC based on the TiO_2/ZnO photoanode has a slightly better photo response compared with pure TiO_2 -based DSSC (Fig. 3). A slight improvement in all wavelength regions can be seen. IPCE can be expressed by the following equation:

$$\text{IPCE} = \text{LHC}(\lambda) \phi_{\text{inj}} \eta_{\text{col}} \dots\dots\dots(1)$$

$\text{LHE}(\lambda)$ is the photon harvesting efficiency; ϕ_{inj} is the quantum yield in electron injection from dye excited molecules and η_{col} is the charge collecting efficiency of the charge transfer in the photoanode layer. $\text{LHE}(\lambda)$ can be defined as the ratio of the excited charge carrier numbers to the incident photon numbers associated with the amount of dye loading into the photoanode. ϕ_{inj} depends on energy-level difference between the excited energy level of dye (E_{ex}) and the photoanode conduction band edge (E_{cb}). According to Eq. (2), η_{col} is associated with K_t , and $K_t + K_r$ parameters which are defined as transport rate and recombination rate constants, respectively.

$$\eta_{\text{col}} = K_t / (K_t + K_r) \dots\dots\dots(2)$$

Deposition of ZnO on TiO_2 decreases the K_r value, resulting in increased η_{col} and hence an increase in IPCE value [17].

IV. FIGURES AND TABLE

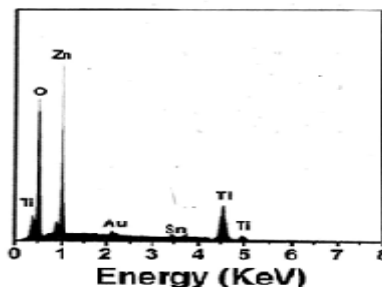


Fig.1 – EDAX spectrum of ZnO coated TiO_2 coated DSSC(10^{-5}Zn^{2+})

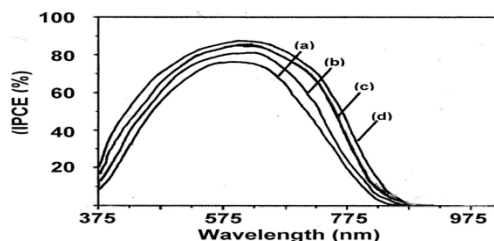


Fig.2 – IPCE versus wavelength of bare TiO_2 and ZnO coated TiO_2 DSSC (b) bare TiO_2

(a) 10^{-3}M Zn^{2+} (c) 10^{-6}Zn^{2+} (d) 10^{-5}Zn^{2+}

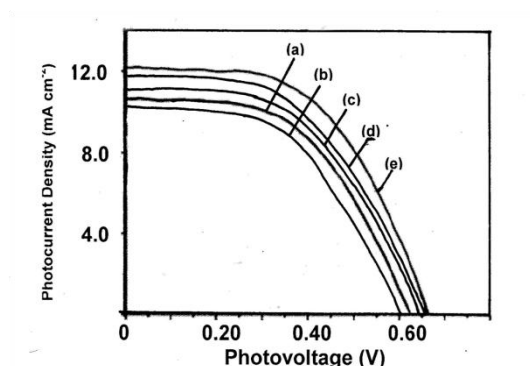


Fig.3 – Photocurrent – photovoltage characteristics of bare TiO_2 and ZnO coated TiO_2

DSSC (a) bare TiO_2 (b) $10^{-3} \text{ M Zn}^{2+}$ (c) 10^{-4} Zn^{2+} (d) 10^{-6} Zn^{2+} (e) 10^{-5} Zn^{2+}

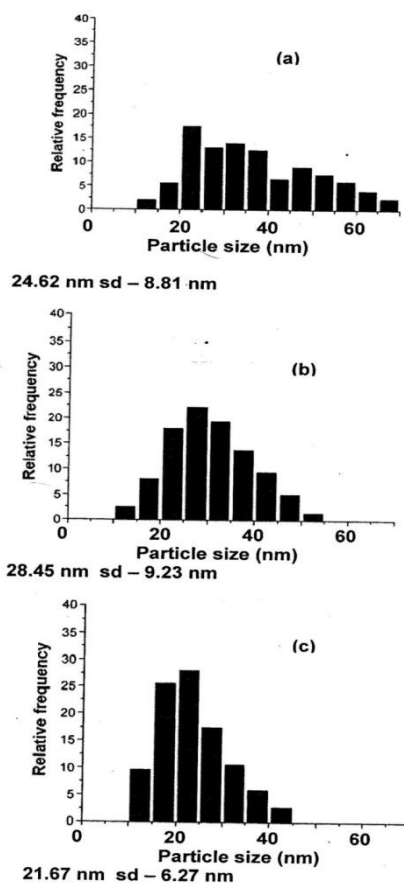


Fig.4 – Particle size distribution of coated ZnO NPs (a) $10^{-4} \text{ M Zn}^{2+}$

(b) 10^{-3} Zn^{2+} (c) 10^{-5} Zn^{2+}

TABLE -1
Photovoltaic parameters of bare and doped TiO₂ photoanodes
Intensity: 100 mW cm⁻²

conc. (M)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	ff	η (%)
0	0.62	11.1	0.58	4.0
10 ⁻³	0.60	10.6	0.56	3.6
10 ⁻⁴	0.64	11.5	0.54	4.0
10 ⁻⁵	0.66	12.1	0.65	5.2
10 ⁻⁶	0.65	11.8	0.60	4.6

V. CONCLUSIONS

To decrease recombination and improve the performance of TiO₂ NPs, an effective way is to coat ZnO NPs on the TiO₂ layer. These ZnO NPs provide charge trapping to suppress the recombination reactions. Herein, the amount of trapping centers must be optimized to provide enough quantity to either prevent the recombination reactions or transfer electrons from the excited dye without deteriorating the TiO₂ NPs performance. Therefore, by optimizing the concentration of Zn⁺ as the main parameter in ZnO coating, an applicable procedure was provided to reveal the function of ZnO NPs as charge traps for reducing the recombination reactions. Consequently, the short circuit current density, and overall efficiency were enhanced.

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