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Photovoltaic performance of dye-sensitized ZnO solar cell based on Eosin-Y photosensitizer

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The paper reports on the fabrication and characterization of dye sensitized solar cells using ZnO due to its stability against photo-corrosion and photochemical properties similar to TiO_2. Thin films of nanocrystalline ZnO and Al-doped ZnO (AZO) were deposited on transparent conducting oxide glass using glass rod spreading method. Both doped and undoped ZnO films were found to be polycrystalline in nature. The ZnO electrode was dye sensitized by using an organic dye, Eosin-Y. The maximum quantum efficiency appears at the wavelength of 550 nm in both cases. However, the maximum quantum efficiency is higher (12%) in the case of ZnO cell electrode than AZO (7%) cell. The electric energy conversion efficiency was found to be 1.43% and 0.6% for undoped ZnO and Al-doped ZnO electrodes respectively. The lower conversion efficiency of the Al-doped ZnO solar cell could be attributed to lower injection efficiency due to less porosity in dye sensitized Al-doped ZnO electrode.

Key words: *ZnO electrode; dye sensitized solar cells; Eosin-Y*

1. Introduction

Since the pioneering work of Regan and Gratzel [1], a great attention has been paid to dye sensitized solar cells (DSSC) as cheap, effective and environmentally benign candidates for a new generation solar power devices [2]. DSSC is a photo-electrochemical device which effectively utilizes a property of nanocrystalline wide bandgap metal oxide semiconductor porous electrode. Generally, a DSSC consists of an indium-tin oxide (ITO), dye modified electrode, electrolyte and a counter electrode. When the DSSC is illuminated with sunlight, the dye absorbs the light and becomes excited. The absorption of light by the dye is followed by the injection of an electron from the excited state of the dye to the conduction band of the semiconductor. Simultaneously the oxidized dye is reduced by the electron donor in the electrolyte and returns to the ground state. The electrons in the conduction band of the semiconductor are collected at the counter electrode and flow through the external circuit.

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Through these processes, radiant energy is converted into electricity [3, 4]. It is understood [1] that cations influence the electron injection yield at the electrode. Optimization of DSSC is still a challenging task as it is a highly complex interacting molecular system. Surface-adsorbed cations exert a profound influence on the efficiency of DSSC. Further, the interfacial cations concentration also affects the stability of sensitizer surface attachment.

Nanoparticle TiO_2 is typically used as the photoanode material, made into a porous thick film (ca. 10 μm) by coating its colloidal paste onto a conductive glass substrate and sintering it at around 450 °C [5–11]. Alternative wide band gap metal oxide semiconductor such as ZnO [12] and Nb_2O_5 [13] have also exhibited decent performance when prepared into porous electrodes in the same manner. Although various dye molecules have been investigated as photo-sensitizers in the last decade, Ru complexes with carboxylated polypyridine ligand such as $Ru(dcbpy)_2(NCS)_2$ remains as one of the best sensitizers for TiO_2 [5]. Recently Keis et al. [14, 15] achieved the conversion efficiency of ~5% with a porous ZnO electrode prepared by the high-pressure compression method and sensitized with $Ru(dcbpy)_2(NCS)_2$. Nonomura et al. [16] have indicated that thinner films of ZnO and $Ru(dcbpy)_2(NCS)_2$ performed considerably better than thicker films synthesized by one step cathodic electrodeposition from oxygen-saturated aqueous solutions containing zinc chloride and the Ru complex. Particle size and shape, porosity, necking structure, film thickness, distance between electrodes, electrolyte composition and illumination direction are significant factors in DSSC. Thus it is also essential to compare various materials for fundamental understanding of nanostructured systems. Most of the research concerning nanostructured systems is based on particles around 10–40 nm in size. Rensmo et al. [17] reported that sensitized films consisting of 150 nm large Al-doped ZnO crystallites yield a solar energy conversion efficiency of 0.5%. Lee et al. [18] showed the variation of efficiency and fill factor with ZnO thin film thickness. The conversion efficiency of the solar cell was 2.4%. Law et al. [19] fabricated DSSCs with nanowires of ZnO and TiO_2 sensitized with $Ru(dcbpyH)_2(NCS)_2$. At a full sun intensity of $100 mW/cm^2$ the cell exhibited photo-conversion efficiency $\eta \sim 1.5\%$.

In this paper, we report on the photo-conversion properties of undoped and Al-doped ZnO (AZO) films. The particle size of the ZnO particles was ~30 nm. The dye sensitized solar cell is fabricated using an organic dye, namely, Eosin-Y which is water soluble and approximately 1000 times cheaper than ruthenium bipyridyl complex dyes. The DSSCs are characterised for their quantum efficiency and other solar cell parameters. The efficiency of solar cells was found to depend on the porosity of the ZnO layer.

2. Experimental details

Electrode preparation. For the present work nanosize (~30 nm) ZnO powder (Finex 30, Sakai Chemical Industry, Japan) was used. The nanoporous semiconductor electrode was prepared by the glass rod spreading method. In order to break the ag-

gregates into separate particles, the ZnO powder was ground in a porcelain mortar with a small amount of deionised water containing poly(ethylene glycol) to prevent re-aggregation of the particles. The ITO glass substrates were covered on two parallel edges with adhesive tape to control the thickness of the ZnO film and to provide non-coated areas for electrical contact. Before deposition, the substrates were cleaned in acetone and methanol using an ultrasonic cleaner and etched with 10% aqueous HF solution for 10 sec. The colloid was applied to one of the edges of the conducting glass and distributed with a glass rod sliding over the tape-covered edges. After air drying, the electrode was sintered for 30 min. at 400 °C in air. Al_2O_3 (2 wt. %) was used as the dopant material to prepare aluminium doped ZnO. [20]

Dye sensitization. The dye (Eosin-Y) was used as received. The dye was dissolved in ethanol at the concentration of 3.2×10^{-4} M. Colouring of the ZnO surface with dye was carried out by soaking the film for 1 hr in a solution of the Eosin-Y in ethanol. The electrode was dipped into the dye solution while it was still hot at 80 °C. This process helps in the prevention of rehydration of the ZnO surface or capillary condensation of water vapours from ambient air inside the nanopores of the film. The presence of water in the pores decreases the injection efficiency of the dye. After dye adsorption, dye-coated films were rinsed in ethanol, dried by blowing N_2 stream and were kept in dark in an air tight case till the assembly of the cell.

Characterization of electrode. Thickness of ZnO layer was measured with a SF220 surface profiler. The thickness of the ZnO electrode was 6–9 μm. Absorption spectrum of Eosin-Y in ethanol adsorbed on ZnO and AZO thin films were recorded using a UV-spectrophotometer 1601. Surface morphology of the films was observed by a high resolution scanning electron microscope (SEM) JEOL JSM-6300. Incident photon conversion efficiency (IPCE) was also recorded using monochromatic light for various wavelengths. X-ray diffraction (XRD) patterns of the deposited films were taken by X'pert PRO Philips using CuK_α radiation.

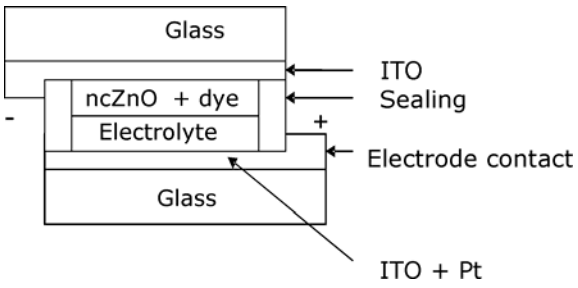

Fig. 1. Schematic diagram of DSSC

Fabrication of DSSC. The dye sensitized ZnO electrode was incorporated into a thin-layer sandwich-type solar cell with a spacer. The counter electrode was thin platinum sheet. The electrolyte solution was a mixture of 0.5 mol/dm^3 tetrapropyl-ammonium iodide and 0.05 mol/dm^3 iodine in ethylene carbonate and acetonitrile

mixed solvent (60:40 by volume). *I–V* characteristics were recorded with a computerized Keithley source meter (Model 2400). The active electrode area was typically 1 cm^2. The schematic diagram of DSSC is shown in Fig. 1.

3. Results and discussion

The X-ray diffraction pattern (Fig. 2) shows the polycrystalline nature of undoped and AZO films. Planes corresponding to (100), (002) and (101) are observed in the pattern. The SEM micrographs of undoped ZnO and AZO films are shown in Fig 3. Both undoped ZnO and AZO films exhibited porous structure. It is also revealed from the SEM micrographs that particle size in AZO films decreased and the microstructure of the film became denser. The increase in packing density resulted in the reduction of porosity [21].

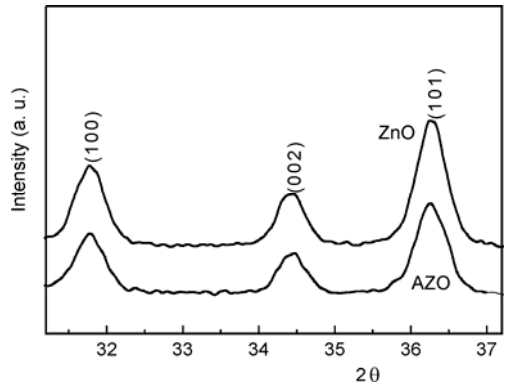

Fig. 2. X-ray diffraction pattern of undoped ZnO and doped ZnO films

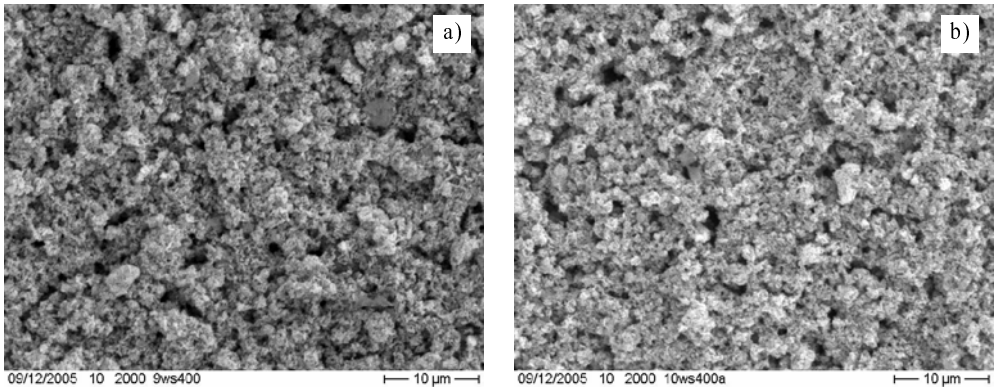

Fig. 3. SEM photographs of ZnO: a) undoped, b) doped

The absorption spectrum of Eosin-Y adsorbed on ZnO electrode and AZO electrode is shown in Fig. 4. The absorption spectra of 10^{-4} M solution of Eosin-Y in ethanol shows that this compound can absorb visible light in the range of 500–550 nm wavelength with

the characteristic absorption peak at 525 nm. Thus this compound absorbs light of appropriate wavelength and can be used as photo sensitizer for wide-band gap semiconductors such as ZnO (E_g = 3.2 eV) which alone cannot absorb visible light. It is seen from the figure that absorption of is lower in the AZO film as compared to the undoped ZnO.

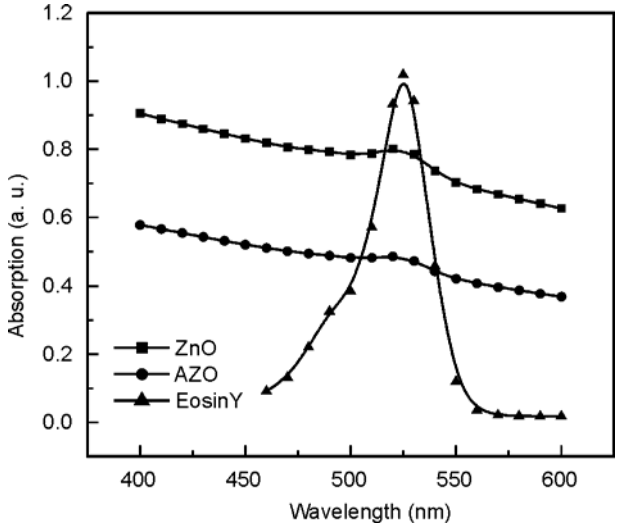

Fig. 4. Absorption spectra of aqueous solution of Eosin Y, ZnO/EosinY, AZO/Eosin Y films

The incident photon-to-current conversion efficiency (IPCE) value is the ratio of the observed photocurrent divided by the incident photon flux, uncorrected for reflective losses for optical excitation through the conducting glass electrode. The IPCE was calculated using the following relation [5]

$$\text{IPCE (\%)} = \frac{1250 \times \text{photocurrent density (A/cm}^2\text{)}}{\text{Wavelength (nm)} \times \text{photon flux (W/cm}^2\text{)}} \times 100$$

and is shown in Fig. 5. The maximum value of 53% at 520 nm for an undoped ZnO film was found to be higher than that for Al-doped film (50%). A low value of IPCE in AZO case may be attributed to high degree of charge carrier recombination. The observed value of maximum IPCE was comparable with the results obtained for TiO_2, [5] showing that ZnO-based electrodes can be considered as candidates for photoelectrochemical devices.

Figure 6 shows the quantum efficiency of the ZnO and AZO solar cell. The maximum quantum efficiency appears at the wavelength of 550 nm in both cases. However, the maximum quantum efficiency is higher (12%) in the case of ZnO cell electrode than AZO (7%) cell. Figure 7 shows the photocurrent–voltage characteristics of the solar cells based on the nano-structured ZnO/Eosin-Y electrode and AZO/Eosin-Y electrodes under white light illumination (100 mW/cm^2).

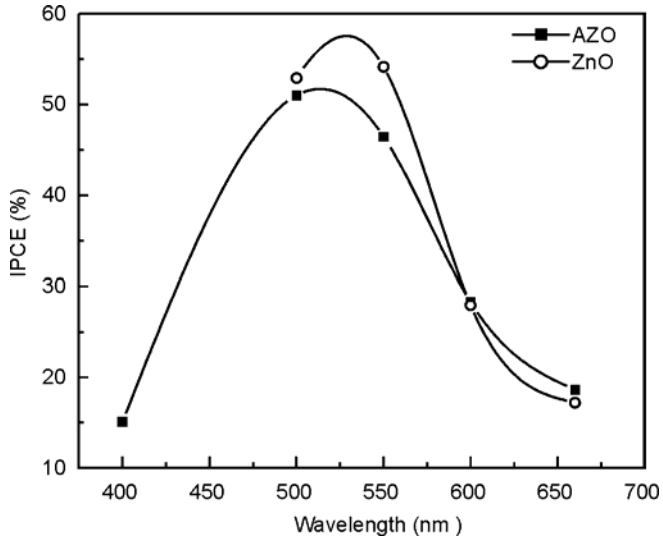

Fig. 5. Photocurrent action spectrum of ZnO/Eosin Y thin film electrode in comparison with Al-doped ZnO/Eosin Y electrode

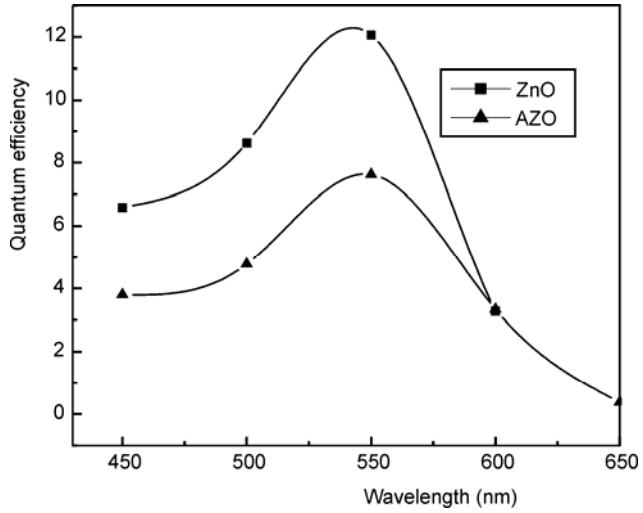

Fig. 6. Quantum efficiency of the ZnO/EosinY and AZO/EosinY solar cell

The energy conversion efficiency (η) and fill factor (FF) were evaluated using the following relations

$$\eta = \frac{I_m V_m}{P_{inc}}; \qquad FF = \frac{I_m V_m}{I_{sc} V_{oc}}$$

The short circuit photocurrent (I_{sc}), the open circuit voltage (V_{oc}), FF and η for the undoped ZnO electrode were found to be 4.0 mA/cm^2, 0.588 V, 61% and 1.43%, re-

spectively. I_{sc}, V_{oc}, FF and η for the AZO electrode were found to be 2.86 mA/cm^2, 0.425V, 50% and 0.6% respectively.

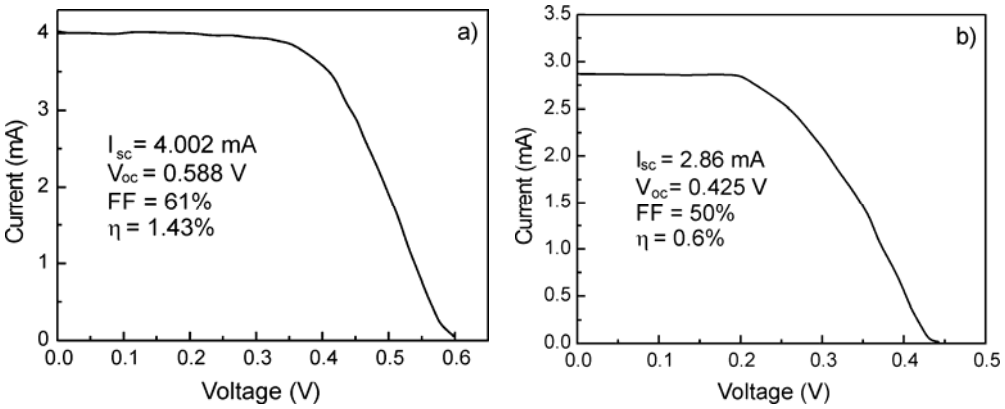

Fig. 7. Output power characteristics of the cell based on Eosin Y sensitized ZnO electrode (a) undoped and (b) doped

The lower energy conversion efficiency in AZO cell could be attributed to the lower porosity of the AZO film. Due to the lower porosity, a lower amount of dye is adsorbed in the film resulting in lower absorption of light as is also clear from Fig.4. The lower adsorption of dye and absorption of light reduces the injection efficiency of carriers and the energy conversion efficiency.

4. Conclusions

Dye sensitized solar cells using ZnO/Eosin-Y and AZO/Eosin-Y electrodes have been successfully fabricated. The maximum value of IPCE = 53% at 520 nm obtained in the present work is higher than the values reported earlier. The quantum efficiency of 12% is achieved in ZnO DSSC at 550 nm. The incident solar light to electric energy conversion efficiency was found to be 1.43% and 0.6% for undoped ZnO and Al-doped ZnO electrode respectively. The efficiency of the cell depends on the porosity of ZnO layer. The reason for lower efficiency of AZO solar cell could be attributed to the injection efficiency due to lower porosity.

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