

Structural and photoelectrochemical characteristics of nanocrystalline ZnO electrode with Eosin-Y

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Abstract

Structural and photoelectrochemical characteristics of nanocrystalline ZnO solar cell have been studied in relation to sintering temperature and thickness of ZnO electrode. Photoelectrochemical properties depend strongly on fabrication conditions. Short circuit current and open circuit voltage were dependent on the sintering temperature of ZnO electrodes. This suggests ZnO nanoparticles network to act not only as a large surface area substrate for the dye molecules but also as a transport medium for electrons injected from the dye molecules. The incident monochromatic photon-to-current conversion efficiency was improved by increasing the thickness of the ZnO electrode. The best conversion efficiency was 2.4% for a 1 cm² cell.

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1. Introduction

Dye sensitization of wide-band-gap semiconductor is a rapidly emerging useful method for solar cell applications, recent significant advancement being primarily made by Hagfeldt and Grätzel [1]. They reported a highly efficient dye-sensitized solar cell based on *cis*-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) [Ru(dcbpy)₂(NCS)₂], nanoporous TiO₂ thin film electrodes and an I[−]/I₃[−] redox electrolyte [1–3]. Although most of the recent works investigating new sensitizers in such cells have focused on metal complex dyes, little attention has been paid to organic dyes because they have been considered to be less stable and efficient than metal complexes. Some Grätzel-type cells using organic dyes have been reported lately, such as B(RhB)/ZnO, Rh6G/SnO₂, perylene/SnO₂, natural dye/TiO₂, and coumarin/TiO₂ [4–9]. Compared with metal complex dyes, organic dyes have several advantages such as a wider variety similar to that of natural dyes, higher

absorption coefficient, lower cost, greater preservation of limited precious metal resources, easier handling for cell recycling without removing metal, and so on. In addition, several organic dyes, for example, Eosin-Y, xanthein dye which is a water-soluble yellow dye, is approximately thousand times cheaper than ruthenium bipyridyl complex dyes. Moreover, Eosin-Y presents a promising result when compared with other acid dyes in a ZnO/organic dye system. Also, the IPCE of the dye-sensitized solar cell equipped with an Eosin-Y-sensitized ZnO electrode was larger than that of the cell equipped with a TiO₂ electrode. Dye-sensitized nanocrystalline solar cell contains components such as photosensitizers, nanocrystalline semiconductor thin film electrodes, electrolytes and counter electrodes. We must optimally tune conditions involving these factors to attain maximum cell performance.

In this study, we fabricated a highly efficient solar cell equipped with a nanostructured ZnO electrode sensitized using an organic dye (Eosin-Y) and investigated the structural and photoelectrochemical characteristics of nanocrystalline ZnO solar cell under various conditions to obtain an optimum model of organic dye sensitized ZnO solar cells.

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2. Experimental procedure

A ZnO film electrode was prepared on indium tin oxide-coated glass (ITO glass) by spreading viscous slurry of ZnO powder and sintering. The surface area of the ZnO film was measured using a surface area analyzer (Brunnaner-Emmett-Teller; BET, Micromeritics Co., USA, ASAP 2010). Adsorption of the dye on the ZnO surface was carried out by refluxing the ZnO electrode in a 3.2×10^{-4} mol/L dry ethanol solution of Eosin-Y ($C_{20}H_6O_5Br_4Na_2$) at 80 °C for 30 min, resulting in a photo electrode. The apparent surface area of the dye-adsorbed ZnO electrode was $1.0 \text{ cm} \times 1.0 \text{ cm}$. A pure platinum plate ($0.5 \text{ mm} \times 20 \text{ mm} \times 20 \text{ mm}$) was used as a counter electrode. The dye-sensitized ZnO electrode was incorporated into a thin-layer sandwich-type solar cell with a 50 μm -thick Teflon sheet as a spacer. The electrolyte solution, i.e. a mixture of 0.5 mol/L tetra-*n*-propylammonium iodide ($(CH_3CH_2CH_2)_4NI$) and 0.05 mol/L iodine (I_2) in an ethylene carbonate and dry acetonitrile mixed solvent (60:40 by volume), was introduced between the ZnO and counter electrodes. A Xe lamp was used as a light source in conjunction with a 390 nm cutoff filter to prevent ultraviolet radiation. The light intensity was 100 mW/cm^2 .

3. Results and discussion

In order to determine the effect of the dye, the photovoltaic characteristics of dye-sensitized ZnO solar cells using Eosin-Y were investigated. We fabricated Grätzel-

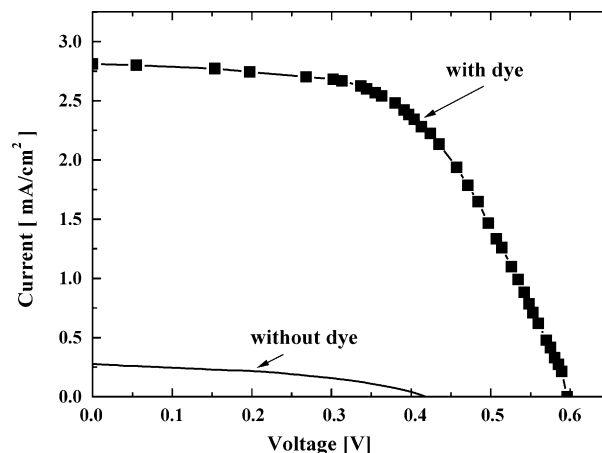


Fig. 1. Current–voltage characteristics of Grätzel type solar cell with and without dye.

type cells with and without the dye. As shown in Fig. 1, the electrical properties were very much improved in a dye-sensitized structure in comparison with a non-sensitized one, and the electric power conversion was much enhanced. Since the lowest unoccupied molecular orbital (LUMO) of Eosin-Y is above the ZnO conduction band (CB), the $E_{LUMO} - E_{CB(ZnO)}$ difference presents an enthalpic driving force for electron injection [10]. Similarly, since the highest occupied molecular orbital (HOMO) of the dye is below the iodide/triiodide E_{redox} , it offers a driving force for hole injection into the electrolyte. This is the major mechanism for charge separation in the dye-sensitized ZnO solar cells.

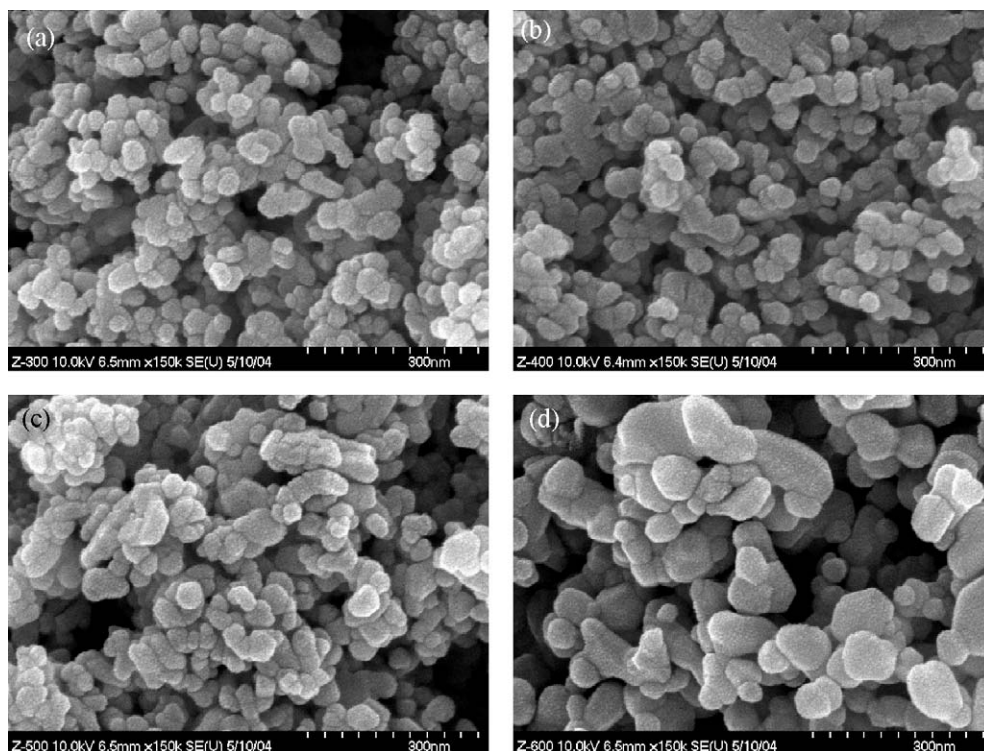


Fig. 2. SEM images of the ZnO electrode at various sintering temperatures: (a) 300 °C, (b) 400 °C, (c) 500 °C and (d) 600 °C, respectively.

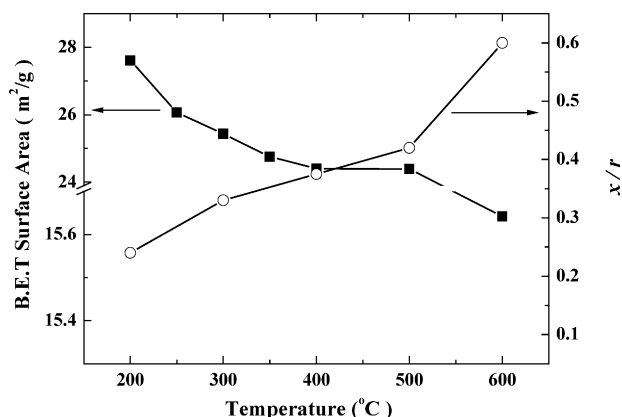


Fig. 3. Surface area and neck growth between spherical particles of ZnO at various sintering temperatures.

Fig. 2 shows scanning electron microscope (SEM) images of the ZnO electrode at various sintering temperatures, up to $\sim 600^\circ\text{C}$. Grain size and neck between particles increased with sintering temperature. The surface area of ZnO was measured using a surface area analyzer. Fig. 3 shows the surface area and neck value (x/r) at various sintering temperatures. As the sintering temperature was increased, x/r value was increased but ZnO surface area became small. Small surface area at high sintering temperature means small amounts of Eosin-Y absorbing. On the contrast, increased bond area (neck) causes transfer of electrons from the dye molecules easily [11]. Fig. 4 shows short circuit current density (J_{SC}) and open circuit voltage (V_{OC}) changes at various sintering temperatures. J_{SC} was dependent on the sintering temperatures of ZnO nanoparticles. J_{SC} increased up to 400°C , and then decreased. This shows the ZnO nanoparticles network to act not only as a large surface area substrate for the dye molecules but also as a transport medium for the electrons injected from the dye molecules [12]. Even though a wide surface area of substrate is essential to absorb more dye molecules when producing

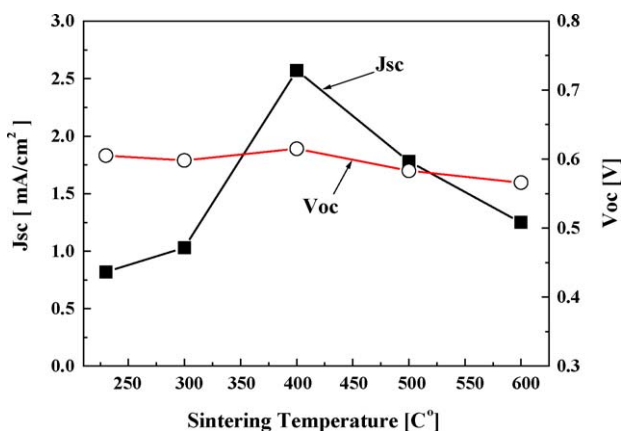


Fig. 4. Short circuit current density (J_{SC}) and open circuit voltage (V_{OC}) vs. sintering temperature.

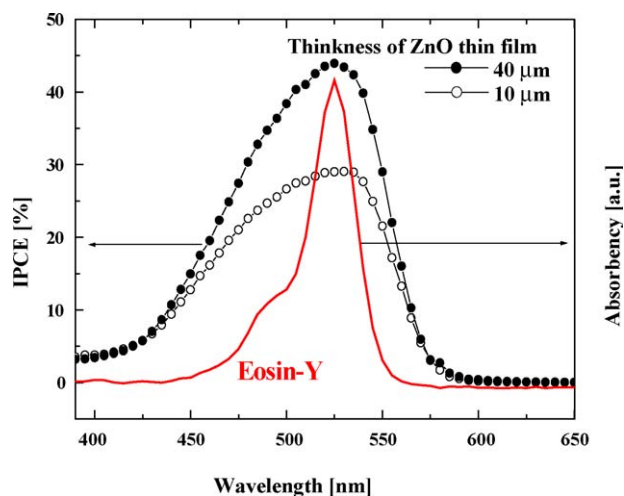


Fig. 5. IPCE of the solar cell and an Eosin-Y absorption spectrum.

dye-sensitized solar cell, the connection between particles is also important for a better transfer of electrons, which comes from dye molecules. In this study, we conclude that a sintering temperature of 400°C is an optimal condition for dye-sensitized ZnO solar cell for both particle connection and a wide substrate surface area.

Fig. 5 indicates the incident monochromatic photon-to-current conversion efficiency (IPCE) and the absorption spectrum of the Eosin-Y in the wavelength range of 400–600 nm. The IPCE was improved by increasing the thickness of the ZnO electrode and reached 45% when the electrode thickness was $40\ \mu\text{m}$. This indicates that amount of absorbed dye was increased. Fig. 6 shows the best performance obtained in the present work. The conversion efficiency of the solar cell was 2.4% under the following conditions: sintering temperature of 400°C , ZnO thin film thickness of $40\ \mu\text{m}$, space between ITO glass and Pt electrodes of $50\ \mu\text{m}$.

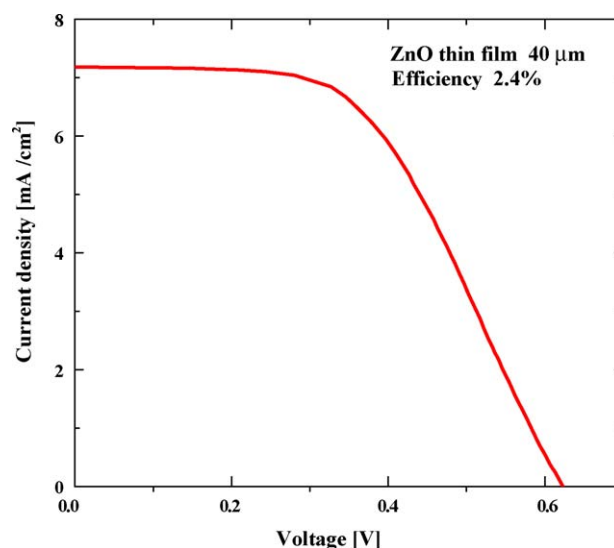


Fig. 6. Current–voltage characteristics of the solar cell.

4. Conclusions

Structural and photoelectrochemical characteristics of nanocrystalline ZnO electrode with Eosin-Y have been studied. The current density was dependent on the sintering temperature. IPCE was improved by increasing the thickness of the ZnO electrode. We fabricated ZnO solar cell based on a nanocrystalline ZnO sensitized using Eosin-Y. The conversion efficiency of the solar cell was 2.4% under the following conditions: sintering temperature of 400 °C, ZnO thin film thickness of 40 μm, space between ITO glass and Pt electrodes of 50 μm.

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