Novel micro-ring structured ZnO photoelectrode for dye-sensitized solar cell

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The micro-ring like structured zinc oxide (ZnO) film was deposited on SnO_2: F coated glass substrate by sol-gel dip-coating technique with 1.0 g polyethylene glycol (PEG) content. The surface morphology of micro-ring structured ZnO film has been confirmed by the scanning electron microscope. This ZnO film is used to fabricate the solar cell with the help of ruthenium based dye and carbon counter electrode. The photoelectric and incident photon-to-current conversion efficiency was 1.17% and 48.4%, respectively. The DSC results have been compared with ZnO films prepared without PEG contents.

Dye-sensitized solar cell (DSC) is considered as an attraction for energy conversion applications due to low cost and high efficiency (11%) [1,2]. In general, DSC consists of porous TiO_2 photoanode sensitized by dyes and platinum cathode with ethylene glycol containing I_3^- /I^- as an electrolyte [3]. Recently, considerable research advances and studies on DSC have focused on the improvement of electron transport and reducing the recombination rate by the alternative semiconductor materials or core-shell structures [4]. Compared to TiO_2, Zinc oxide (ZnO) is an alternative material [5] due to its wide band gap (~ 3.2 eV) [6], large exciton binding energy (60 meV) at room temperature, as well as high thermal and mechanical stability [7,8], but they (TiO_2 and ZnO) have very different surface chemistry [6]. Electron mobility of ZnO at room temperature (115~155 cm^2 V^{-1} s^{-1}) is higher than that of anatase TiO_2 ($<10^{-5}$ cm^2 V^{-1} s^{-1}) [9-11]. In addition, the surface structures of ZnO can be easily controlled by synthesis method, and have simple tailorability of nanostructure as compared to TiO_2 [12]. The fabrication of novel nano/microstructures with special size and well-defined shape may open new opportunities for exploring unique physical and chemical properties and their potential applications [13]. Therefore, development of morphologically controllable synthesis of ZnO nano/ microstructures is urgently important to answer the demand for exploring the potentials of ZnO [14].

This work is continuation of our previous work [15], where the DSC with ZnO films was optimized with respect to zinc acetate concentrations and film thickness. In previous works, the upper surface of the optimized ZnO electrode has some crack/cannel and wall like structure, but maximum surface remains smooth. To overcome these limitations, the polyethylene glycol (PEG) was used [16] as surface modified. The present paper reports on the synthesis of micro-ring structured ZnO electrode by the same sol-gel method but with 1.0 g PEG content. The structural, optical, and surface morphological properties of the resulting ZnO photoelectrode and the photovoltaic performance of the DSC have been investigated and discussed. Moreover, performance of this DSC device has been compared with DSC without PEG based ZnO film.

The micro-ring like ZnO film was prepared by the simple sol-gel dip-coating technique according to the reference [15]. The precursor solution was prepared by using zinc acetate [$Zn(CH_3COO)_2.2H_2O$], absolute ethanol, diethanolamine [$NH(CH_2CH_2OH)_2$: DEA], and deionized water. In addition, the 1.0 g of PEG content was added in the above solution. When the precursor solution became clear then the clean SnO_2:F (FTO) coated glass substrate was dipping and withdrawing (2 mm/min). After every withdrawing, the coated film was dried at 60°C in air for 10 min. The above process was repeated, so as to obtain desired film thickness (~2.3 μm). Finally the obtained film was annealed at 500°C. The DSC was fabricated by soaking the ZnO film with dye: cis-di (thiocyanate) bis (2,2′-bipyridyl-4, 4′-di-carboxylate) ruthenium (II), the

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electrolyte: 0.5 M KI, 0.05 M I$_2$ and 0.05 M 4-tert-butylpridine and carbon counter electrode [17]. The active cell area was 0.3 cm^2. The photovoltaic data of DSC were measured using a Keithley Model-2400 source measure unit and monochromator (SG-80, Yokogawa).

Figure 1 (a) shows the grazing incidence X-ray (GIXRD, SHIMADZU XRD-6000 with Cu-Kα line) pattern (α = 0.48°). The ZnO film shows good crystallinity and wurtzite hexagonal structure. The crystallite size, having been estimated by using Debye-Scherer's equation [18] with (101) crystalline peak, is 12.2 nm. Inset of Fig. 1 (a) shows the chemical (atomic wt%) composition spectrum of ZnO films obtained by energy dispersive spectroscopy (EDS, JEOL 6700F and JED2200). The tin (Sn) and fluorine (F) exhibit due to FTO glass substrate. The wt% of Zn and O are 54.3 and 27.7, respectively, which demonstrate the existence of ZnO film and its excellent chemical purity. In Fig. 1 (b), the ZnO film has very small visible emission photoluminescence (PL, RF-5301) peak intensity, so that the oxygen vacancies of this film are very few [19]. Figure 1 (b) (inset) shows the Raman shift of ZnO film using Micro-Raman, JASSCO NRS-1000. The E$_2$ (high) = 437.3 cm^{-1} mode corresponds to characteristics band of hexagonal wurtzite phase. In addition, the A$_1$ (LO) = 580.1 cm^{-1} peak is associated with the formation of defects such as oxygen vacancy, zinc interstice, or their complexes [20]. This A$_1$ (LO) peak of micro-ring structured ZnO films is weaker than that of the ZnO films with compact surface [15], which indicates that the micro-ring structured ZnO film has less structural defects [20].

Figure 2 (a)-(c) shows the field emission scanning electron microscopy (FE-SEM, JEOL 6700F) images of ZnO film in different magnifications (2,000, 20,000, and 80,000). The ZnO film has shown uniform micro-ring structure and crack [9] free
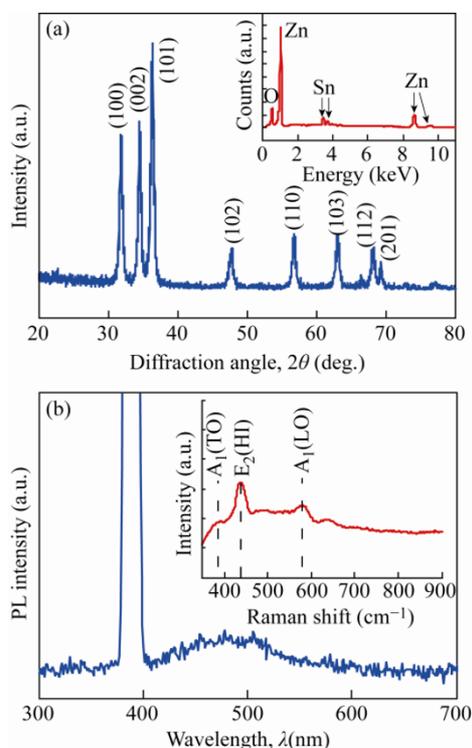
structure. The smaller and larger micro-rings have 5 and 13 μm diameter respectively. Moreover, compared to ZnO films grown without using PEG content [15,21,22], the complete surface of ZnO film has porous structure. The grain cluster size is around 23 nm, which is smaller than the ZnO films reported in literatures [21,22]. The micro-ring structures have also been found in atomic force microscope (AFM, SHIMDZU SPM-9500J2) image shown in Fig. 2 (d). The *rms* roughness value is 126 nm.
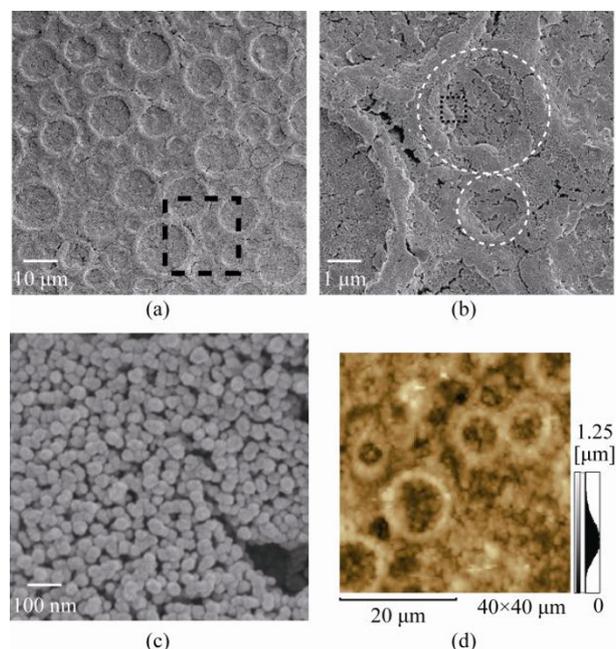

FIG. 2. ZnO films with 1.0 g of PEG (a)-(c) FE-SEM images in different magnifications, and (d) AFM image.

Figure 3 (a) shows the difference of absorbance (using JASSCO UV-vis V-550) of ZnO films (where, difference absorbance=(absorbance of dye-sensitized ZnO films)-(absorbance of bare ZnO films) with and without dye-sensitization) and incident photon-to-current efficiency (IPCE) of DSC. It is easily noticeable that ZnO film shows the higher ΔA value i.e. more photoactive around 400~550 nm, near the absorption peak of the ruthenium dye. The maximum IPCE [23] of DSC is about 48.4%. The IPCE spectrum shows two peaks at 405 and 535 nm, which are close to ruthenium based dye (N3-dye). The photoelectric conversion efficiency of the DSC has been calculated by the reference [24]. Figure 3 (b) shows the photocurrent-photovoltage characteristics of DSC with PEG and without PEG ZnO sample. The DSC with PEG sample shows the better photocurrent (6.12 mA/cm^2) than that of DSC without PEG sample, but the photovoltage (418 V) value is lower than without PEG of ZnO based DSC [9]. Comparative photovoltaic data of DSC with PEG and without PEG ZnO films have been shown in Table 1 (inset of Fig. 3 (b)). The DSC with PEG (ZnO) sample shows the higher efficiency, 1.17% compared to the DSC without PEG sample [15]. Still, the results obtained for ZnO-based DSC has shown relatively low overall conversion efficiency, compared to state-of-art TiO$_2$-based DSC. The limited performance in ZnO-based DSC may be explained by low thickness (~2.3 μm), the instability of ZnO in acidic dye (i.e., protons from the dyes cause the dissolution of Zn atoms at ZnO surface, resulting in the formation of excessive Zn^{2+}/dye agglomerates) [25] and the

FIG. 1. (a) The GIXRD patterns of ZnO film with α = 0.48°, (inset) EDS spectrum of ZnO film; (b) Photoluminescence spectrum of ZnO film, (inset) Micro-Raman spectra of ZnO film. Raman shift of ZnO films.
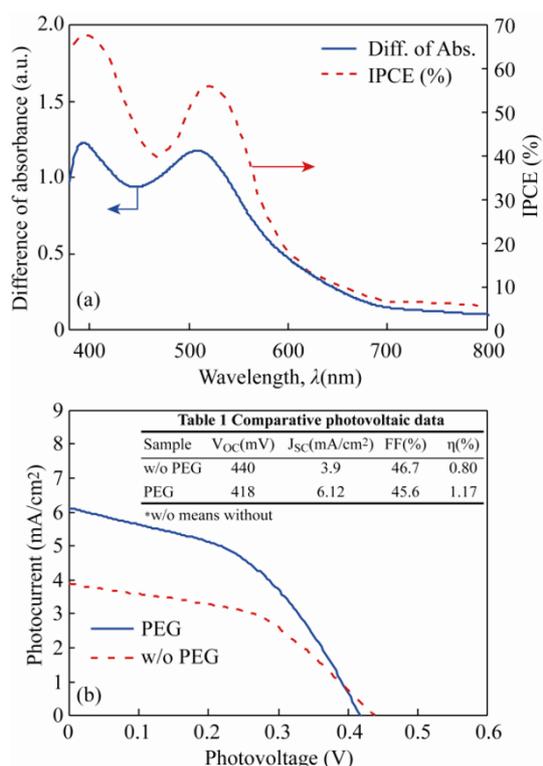
FIG. 3. (a) The difference of absorbance of ZnO film with and without dye-sensitization; and IPCE spectrum of DSC; (b) Photocurrent-photovoltage characteristics of DSC.

slow electron-injection kinetics from dye to ZnO. But we still have chance to get higher efficiency by increasing the thickness of ZnO film.

In summary, the micro-ring structure of ZnO film was successfully prepared by using simple sol-gel technique with 1.0 g of PEG content. The micro-ring structures were confirmed by using the FE-SEM and AFM analysis. The DSC was fabricated with this ZnO film, ruthenium based dye, KI based electrolyte and carbon counter electrode. The efficiency was found 1.17%, which shows better performance compared to DSC with ZnO film without PEG content.

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