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Composite Photoelectrode Made from Oxides of Tin and Zinc with Zinc Stannate Buffer Layer for Dye-Sensitized Solar Cells

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ABSTRACT

Dye-sensitized solar cells (DSSC) of nanocrystalline TiO_2 offer an alternative to low cost thin film solar cells. These solar cells consist of a dye adsorbed porous nanocrystalline TiO_2 matrix deposited on conducting tin oxide (CTO) glass interpenetrated by I_3^-/I^- redox electrolyte. Recently researchers have focused on other semiconductor materials such as ZnO and SnO_2 in the place of TiO_2. These semiconductor materials as composites have also shown promising results. In this paper we report a composite consisting of Zn_2SnO_4, SnO_2 and ZnO made for photo electrode of a DSSC. This composite was synthesized by grinding $ZnCl_2$ and $SnCl_4$ in 2:1 mass ratio and adding $(CH_3)_4NOH$ dissolved in deionized water. The white precipitate of the above mixture diluted with alcohol was sprayed onto CTO glass plate at 250 ^{0}C and sintered in a furnace to make the composite electrode consisting of Zn_2SnO_4, SnO_2 and ZnO. The formation of Zn_2SnO_4 in above reaction was confirmed with X-ray diffractometry. A composite electrode only with SnO_2 and ZnO was also made dissolving $ZnCl_2$ and $SnCl_4$ in alcohol by 2:1 mass ratio and spraying onto CTO glass plate at 250 ^{0}C followed by sintering. Due to the joint effect of Zn_2SnO_4 with SnO_2 and ZnO, photocurrent and Photovoltage of the former cell increased comparably with the DSSC only with SnO_2 and ZnO. Therefore it seems that Zn_2SnO_4 acts as a buffer layer to increase the current, voltage and efficiency of this DSSC.

1. INTRODUCTION

Solar cells based on dye-sensitized mesoporous films of TiO_2 are low-cost alternative to conventional solid-state devices. Dye-sensitized nanocrystalline solar cells (DSC) provide an economical credibility to conventional inorganic photovoltaic devices. Owing to their high-energy conversion efficiency and low production cost, they have received considerable attention over the past decades. The mesoscopic texture of the TiO_2 film in these cells significantly increases the cross-section of light absorption by surface-anchored charge-transfer sensitizers, while maintaining a good contact with the electrolyte. In these photovoltaic devices, ultrafast electron injection from a photo excited dye into the conduction band of an oxide semiconductor, and subsequently dye regeneration and hole transportation to the counter electrode, are responsible for the efficient generation of electricity. Light-to-electricity conversion efficiency of 10 % at air mass (AM) 1.5 solar irradiance has been obtained for photovoltaic devices based on TiO_2 with Ruthenium bipyridyle dye and a liquid electrolyte containing the I^-/I_3^- redox couple [1]. Researchers have focused on DSSC systems that use nonporous films other than Titanium Dioxide as the electron collector, although semiconductor composite films made from ZnO and SnO_2 have also shown promising results [2]. The improvement in I-V characteristics was mainly due to large open circuit voltages. Hence, it seems interesting to study a composite made of Zn_2SnO_4, SnO_2 and ZnO as working electrode of DSSC. Zinc stannate films have a high bandgap (~3.6 eV), high transmittance and low absorptance. In addition, these films are chemically stable and

cannot be etched by dilute acids [3]. It has been used in polycrystalline thin film solar cells of CdS/CdTe as a buffer layer between CdS and the conducting substrate [4]. Due to these attractive properties it is interesting to use Zn_2SnO_4 as a buffer material in DSSCs. In this report, we present the results of DSSC based on SnO_2 and ZnO with Zn_2SnO_4 as a buffer material where film has been prepared by spray pyrolysis method.

2. EXPERIMENTAL

2.1 Synthesis of Zn_2SnO_4, SnO_2 and ZnO Composite Film

1 g of $ZnCl_2$ and 0.5 g of $SnCl_4$ were weighed (2:1 mass ratio). Then $ZnCl_2$ and $SnCl_4$ were ground in an agate mortar by adding 2 ml of tetra methyl ammonium hydroxide dissolve in 50 ml of deionized water. It was stirred for 10 minutes until a white precipitate was formed. The precipitate diluted with alcohol was sprayed onto CTO glass plate heated up to 250 ^{0}C and sintered at 550 ^{0}C in a furnace for 30 minutes.

2.2 Synthesis of SnO_2 and ZnO Composite Film

1 g of $ZnCl_2$ and 0.5 g of $SnCl_4$ were weighed (2:1 molar ratio). Then $ZnCl_2$ and $SnCl_4$ were ground in an agate mortar by adding only 2 ml of deionized water. The solution diluted with alcohol was sprayed onto CTO glass plate heated up to 250 ^{0}C and sintered at 550 ^{0}C in a furnace for 30 minutes.

2.3 Fabrication of the cells

The dye was coated by immersing the composite films in a solution of Ruthenium bipyridyle dye in ethanol for 12 hours. The photo electrochemical solar cells were made by placing the dye coated films on Pt coated CTO glass plate and filling the capillaries of the mesoporous film with an electrolyte containing I_3^-/I^- redox couple in acetonitrile.

The cell was illuminated with a 1.5 AM and 1000 Wm^{-2} solar simulator lamp. I-V characteristics of the cells were recorded using a Keithley 240-3A source meter couple to a computer. The X-ray diffractogram was taken with Cu-K_α radiation (1.54 Å) to identify the materials in the composite.

3. RESULTS AND DISCUSSION

Zn_2SnO_4 is a transparent material with a band gap of 3.6 eV and electron mobility of 10–15 $cm^2V^{-1}s^{-1}$ (figure 1). Application of Zn_2SnO_4 in DSSC shows promising results due to particle size in the range of tens of nanometers that ensure high surface area for dye adsorption. In addition, these films are chemically and thermally stable. Therefore Zn_2SnO_4 material could serve as buffer layer in DSSCs. This would increase photocurrent, Photovoltage, fill factor and efficiency of DSSCs.

Figure 2(a) shows I-V curve of DSSC with Zn_2SnO_4 buffer layer around the SnO_2 nanoparticles. This has higher photocurrent and photovoltage than DSSC only with the film of SnO_2 and ZnO composite (figure 2b).

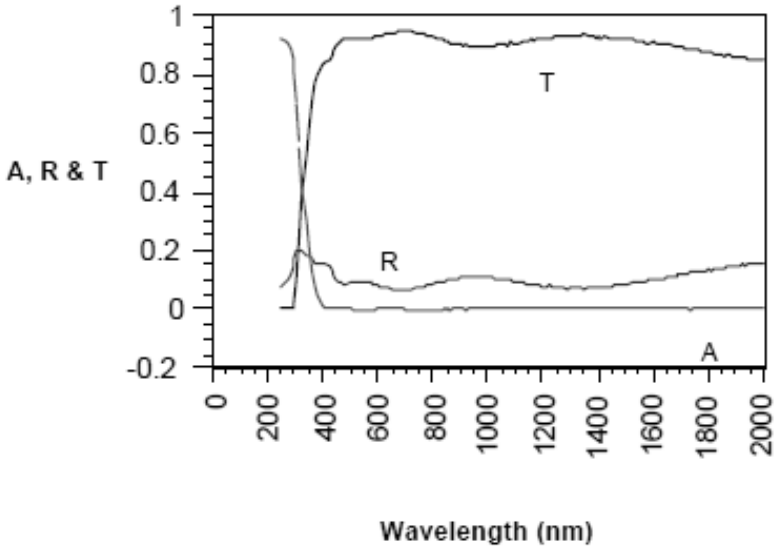

Figure 1: The T-transmittance, R-reflectance, and A-absorptance of a Zn_2SnO_4 film.

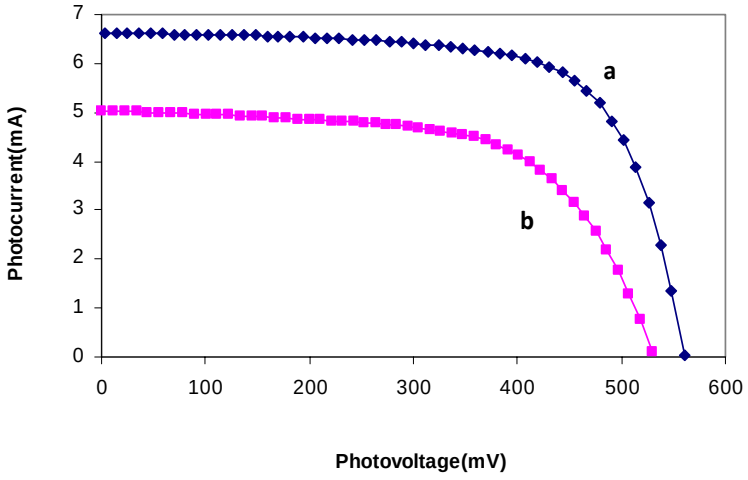

Figure 2: I-V curves of DSSC made of (a) Zn_2SnO_4, SnO_2 and ZnO (b) SnO_2 and ZnO composite semiconductor working electrodes.

The X-ray diffractogram given in figure 3 convinces that Zn_2SnO_4 material has been formed, but peaks are also due to present of SnO_2 and ZnO. The particle size of Zn_2SnO_4 calculated from the broadening of diffraction lines using the Debye and Sherr's equation ($B_{sherr} = 0.9\lambda/B\cos\theta$) is about 25 nm. The film that made without the

addition of tetra methyl ammonium hydroxide has no peaks for Zn_2SnO_4 indicating the film consists only of SnO_2 and ZnO.

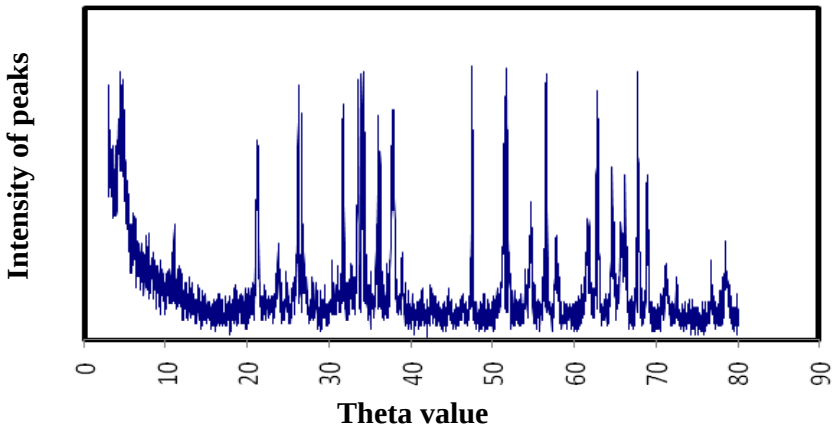

Figure 3: X-ray Diffractogram of Zn_2SnO_4, SnO_2 and ZnO composite film. (Peaks due to Zn_2SnO_4 are denoted by *)

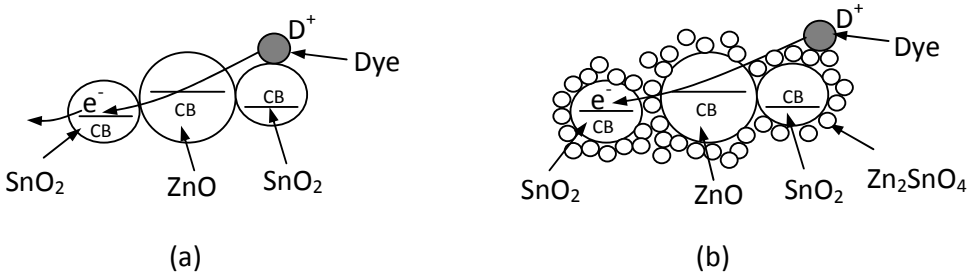

Figure 4: (a) Long distance separation of germinated electron in SnO_2 and ZnO composite (b) Suppression of electron leakage by the ZnO_2SnO_4 buffer layer in Zn_2SnO_2, SnO_2 and ZnO composite in addition to the long distance separation of germinated electron.

The higher photocurrent and photovoltage of the DSSC of ZnO and SnO_2 composite film with the Zn_2SnO_4 buffer layer is attributed to the suppression of recombination of photo electrons injected into SnO_2 particles due to the buffer layer around the SnO_2 particles. In a previous report high efficiency of DSSC made of SnO_2 and ZnO composite cell is explained as the long distance separation of the germinated electrons in the composite film [2]. However even after the relaxation of the electron in the conduction band of SnO_2 particle, it could recombine with dye cation (D^+) or leak into the electrolyte to recombine with the ions (I_3^-) in the electrolyte. But with the addition of Zn_2SnO_4 buffer layer around the SnO_2 particles this could be avoided as shown in figure 4. Therefore recombination of electrons is suppressed in this DSSC made of SnO_2 and

ZnO composite film with Zn_2SnO_4 buffer layer in addition to the long distance separation of germinated electrons.

4. CONCLUSION

DSSC was made with composite electrode of Zn_2SnO_4, SnO_2 and ZnO using $ZnCl_2$ and $SnCl_4$ as the staring material. The X-ray diffractogram clearly showed that Zn_2SnO_4 is formed in the spray pyrolysis of $ZnCl_2$ and $SnCl_4$ in the presence of tetra methyl ammonium hydroxide. The films made without tetra methyl ammonium hydroxide result only a composite of SnO_2 and ZnO. The efficiency of DSSCs made only with SnO_2 and ZnO composite films are less than the DSSCs made of SnO_2 and ZnO composites with the Zn_2SnO_4 buffer layer. The enhancement in the DSSCs with Zn_2SnO_4 buffer layer is explained as suppression of recombination of injected electrons relaxed to conduction band of SnO_2 particles. The efficiencies of the DSSCs made of composite films of SnO_2 and ZnO using the SnO_2 colloid and ZnO powder that reported in the literature are higher than the values reported in this paper [2]. That is due to the high porosity of those films compared to the films made by spray pyrolysis techniques. Application of Zn_2SnO_4 buffer layer for those porous composite films are under investigation.

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