Synthesis and Photoelectrochemical Properties of ZnO and ZnO-SnO_2 Nanocomposite film

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Abstract. The chemical bath deposition (CBD) method was used for preparation of ZnO and ZnO-SnO_2 nanocomposite films. Characterizations were made on their structural, microstructural and optical properties by X-ray diffraction (XRD), scanning electron microscopy(SEM) and ultraviolet-visible (UV-VIS) spectroscopy. The photoelectrochemical properties such as open circuit voltage(V_{oc}), short circuit current density(J_{sc}), conversion efficiency(η) and fill factor(FF) of ZnO and ZnO-SnO_2 nanocomposite films based DSSC were studied. Onion skin natural dye sensitized solar cell fabricated from ZnO and ZnO-SnO_2 nano-composite generated conversion efficiencies of 0.66 % and 0.81 % respectively.

Keywords: CBD, nanocomposite, photoelectrochemical properties, SEM, XRD
PACS: 70

INTRODUCTION

Nowadays the global growing demand for energy and for protecting our environment can potentially be met by solar cell technology[1-3]. Although the solar cells technology has not yet been in large-scale utilization because of its high cost and insufficient conversion efficiencies in the past, recent advances in nanomaterial and device technologies have offered new opportunities [3-5]. Among the diverse photovoltaic devices, the dye-sensitized solar cells (DSSCs) technology has made enormous progresses and is highly competitive for large-scale commercial fabrication [6]. The critical component in DSSCs is the photoanode, which is typically composed of porous materials with dye molecules adsorbed onto its surface[2-5]. To achieve high performance, the photoanode needs to possess a large surface area and good electron transport capability. A nanoparticle film provides a large enough surface area; however, electron transport is difficult because of the need for electrons to hop across neighboring nanoparticles. By altering the morphology of the photoanode, electron transport pathways may be designed to improve electron collection[7-9].

To further improve the performance of DSSCs, one dimensional nanostructure such as nanotube, nanofiber, nanorods, nanoflower and their composites have attracted considerable research interest in DSSC because of to achieve fast electron transport while maintaining a large surface area for dye coating[9-12]. However, the photoelectro-chemical properties of nanorods(NRs)/ nano-particles(NPs) composite-based electrodes are not straightforward since the decrease of NPs contents leads to smaller surface area for dye adsorption, while the incorporation of NRs can enhance the electron transport rate and light scattering effect [13-18]. Present work focused on the synthesis of ZnO and ZnO-SnO_2 nanocomposite electrodes for DSSC using chemical bath deposition(CBD) method. These nanocomposite films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and ultraviolet visible (UV-VIS) spectroscopy. Photoelectrochemical properties of ZnO and ZnO-SnO_2 nanocomposite photoelectrodes on DSSC's performance were also discussed.

EXPERIMENTAL DETAIL

Materials System

Hexamethyltetramine(HMT) ($C_6H_{12}N_4$, 99.9% purity), zinc nitrate ($Zn(NO_3)_2.6H_2O$, 99.9% purity), tin chloride dihydrate ($SnCl_2{\cdot}2H_2O$, 98% purity) and deionized water were used as the precursor sources to synthesize the nominal stoichiometry of (1−x)ZnO-(x)SnO_2 (x= 0.00 and 0.30) ZnO-SnO_2 nanocomposite films.

Fabrication, Characterization Of Photo-Electrode And Counter Electrode

The depositing solutions were prepared as follows. First of all, $C_6H_{12}N_4$ and Zn $(NO_3)_2.6H_2O$ was dissolved in deionized water with desired composition by stirring for 3 h. Next, desired amounts of $SnCl_2 \cdot 2H_2O$ were added to the solution while stirring for 3 h at 70 °C. In this study, we prepared two precursor solutions for ZnO and ZnO-SnO_2 nanocomposite films. Before films deposition, ITO /glass (2cm×2cm) were thoroughly cleaned by ultrasonic cleaning method. The synthesis process of ZnO and ZnO-SnO_2 nanocomposite films contained two steps, i.e seed layer formation and nanorod growth. In the first step the glass substrates were immersed into the aqueous solution for 1h at a required temperature 80 °C to form seed layer. In the second step seed layer coated glass was tilted against the wall of the aqueous solution beaker. Then the beaker was heat treated for 5 h at a constant temperature of 80 °C. After growth, the substrate was removed from the solution, rinsed with deionized water and then dried at room temperature. After annealed at 500 °C for 1h, ZnO and ZnO-SnO_2 nanocomposite films were obtained. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM, JSM-5610) were used to characterize the crystalline state and morphology of the films. UV-VIS spectra were measured on a UV-1800 Spectrophotometer to study the optical properties.

Onion skin extract solution was used as natural dye sensitizer. It was adsorbed in to the ZnO and ZnO-SnO_2 composite films by immersing in natural dye sensitizer for 20 h. And then it was heated at 80 °C for 30 min, ZnO and ZnO-SnO_2 nanocomposite films based DSSC were obtained which served as photoelectrodes. The counter electrode, the same dimension of photoelectrode area was made by TCO glass coated with carbon layer.

Measurement of Cell Efficiency

Sandwiched cells were prepared by using ZnO and ZnO-SnO_2 nanocomposite soaked with onion skin extract dye as photoelectrode and carbon coated glass as counter electrode with an exposed area of (0.8cm×0.8cm). The iodide electrolyte was injected inside the cell utilizing a capillary action through predefined channels. Photoelectrochemical cell (PEC) measurement was performed using Na-lamp and Fluke Scopemeter.

RESULTS AND DISCUSSION

XRD Analysis

The diffraction patterns of ZnO and ZnO-SnO_2 nanocomposite films were identified using JCPDS (Joint Committee of Powder Diffraction Standards) data file. XRD profile of ZnO and ZnO-SnO_2 nanocomposite films were described in figure 1(a-b). In figure 1(a) all of reflection planes were well-match with ZnO standard JCPDS data library. In all reflection planes, (101) peak was one of the most intense peaks in all XRD spectra. In figure 1(b) ZnO and SnO_2 were examined to be composite form ZnO-SnO_2 nanocomposite. All diffraction peaks can be indexed as the tetragonal structure for SnO_2 and a hexagonal wurtzite structure for ZnO.

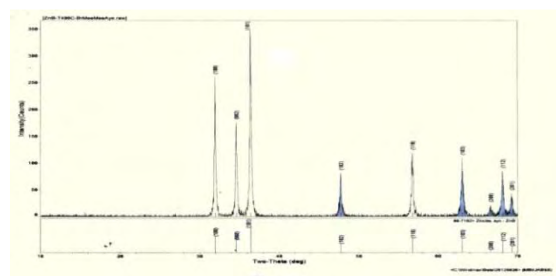

FIGURE 1. (a) XRD profile of ZnO nanorod film

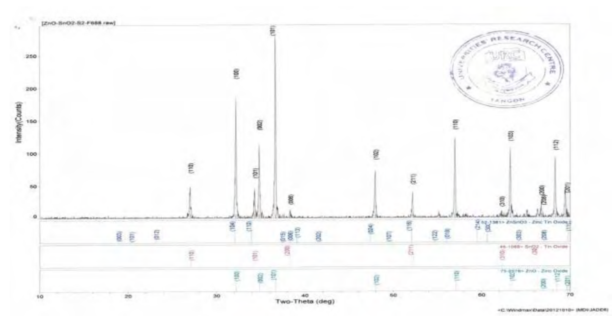

FIGURE 1.(b) XRD profile of ZnO-SnO_2 nanocomposite film

Surface Morphology

The schematic scanning electron images of ZnO and ZnO-SnO_2 nanocomposite films were shown in figure 2(a-b). Figure 2(a) showed the schematic of the solar cell based on ZnO nanorod arrays with hexagon cross section and figure 2(b) observed ZnO nanorod arrays were fully filled with SnO_2 nanoparticles. The ZnO nanorods were disorderly, and exhibited a wide size distribution. It was convinced that some defects were formed in ZnO nanorods due to disengaged growth on the solution. The diameter of SnO_2 nanoparticles have in the range of 50 to 70 nm. ZnO nanorods have a diameter in the range of 100 to 140 nm and 1 to 2 µm in length. Solar cells with the two photoanode morphologies were investigated to illustrate the factors that affect the solar cell performance.

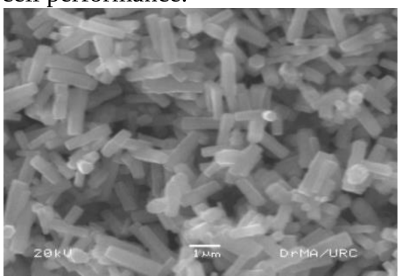

FIGURE 2.(a) Scanning electron image of ZnO nanorod film

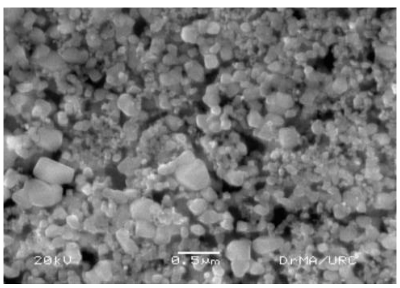

FIGURE 2.(b) Scanning electron image of ZnO-SnO_2 nanocomposite film

OPTICAL PROPERTIES

Figure 3(a-b) showed the optical absorption spectra for ZnO and ZnO-SnO_2 nanocomposite films. In these figures all of optical absorption spectra were well accepted. The absorption bands were observed at 361 nm for ZnO films and near 300 nm for ZnO-SnO_2 nanocomposite. The estimated band gap of ZnO-SnO_2 nanocomposite was larger than ZnO film. It might be attributed to the improvement of the crystalline quality of ZnO-SnO_2 nano-composite. Figure 3(c) showed absorption properties of onion skin dye extract solution. It could absorb near visible region from 200 to 300 nm. The optical band gap values obtained were summarized in Table 1.

TABLE 1. Optical band gap of ZnO, ZnO-SnO_2 nanocomposite film and onion skin dye extract

Specimen	Optical Band Gap (eV)
ZnO	3.32
ZnO-SnO_2	4.08
Onion skin dye extract	4.12

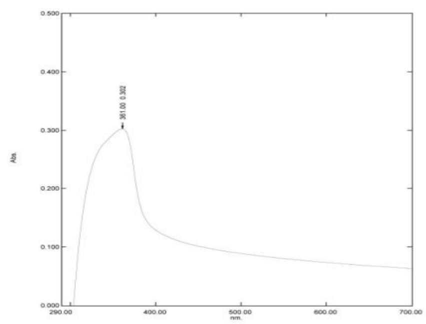

FIGURE 3.(a) The optical absorption spectra of ZnO nanorod film

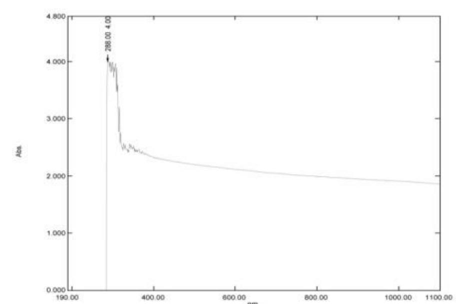

FIGURE. 3.(b) The optical absorption spectra of ZnO-SnO_2 nanocomposite film

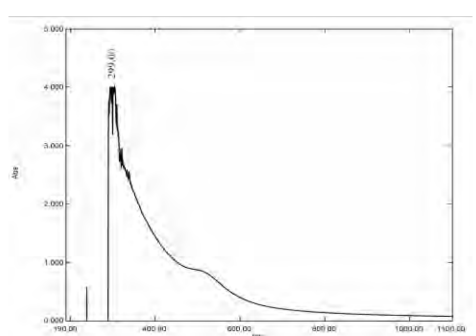

FIGURE. 3.(c) The optical absorption spectra of onion skin natural dye

Photoelectrochemical Properties

The J_{sc}, V_{oc}, FF, and η are well-accepted indicators for solar cell performance; additional information can be obtained by analyzing the entire J-V curve. The J-V performance of the DSSCs enhanced with ZnO and ZnO-SnO_2 nanocomposite electrodes were shown in figure 4. In this figure it was observed that the solar cell parameters depended on photoelectrode morphology. The increase in the V_{oc} and J_{sc} were observed in ZnO-SnO_2 nanocomposite photoelectrode DSSC. This is possibly resulted from differences in electrical properties between ZnO nanoparticles and nanorods. Nanorods provide efficient transport pathways for electrons coming from surrounding nanoparticles and nanoparticles create the large amount of light absorption area by natural dye. The conversion efficiency and FF of the devices based on composite photoanodes were higher than that of the nanorod-based device, which is only 0.81% and 0.51. Solar cell parameters of DSSC with ZnO nanorod and ZnO-SnO_2 nanocomposite film electrode were listed in Table 2.

TABLE 2. Photovoltaic cell parameters for DSSC with ZnO and ZnO-SnO_2 nanocomposite electrode

DSSC	ZnO	ZnO-SnO_2
V_{oc}(V)	0.149	0.161
J_{sc} (mA)	0.404	0.441
V_m(V)	0.103	0.114
J_m(mA)	0.291	0.317
FF	0.50	0.51
η(%)	0.66	0.81

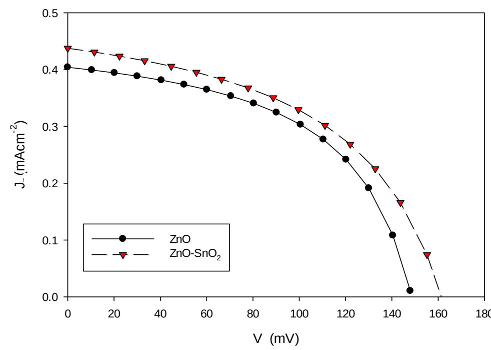

FIGURE. 4. J-V characteristic curve for ZnO and ZnO-SnO_2 nanocomposite electrode DSSC

CONCLUSION

DSSCs based on various morphologies of ZnO and ZnO-SnO_2 photoelectrodes with onion skin natural dye as the light-absorbing material have been fabricated. XRD results demonstrated the ZnO nanorod films with the hexagonal wurtzite structure. The morphologies of nanorod(NRs) and nanoparticle(NPs) were observed in ZnO-SnO_2 composite. The optical band gap increased in nanocomposite film, which could be related to grain variation. The results showed that onion skin natural dye exhibited a promising application in the preparation of dye sensitized solar cell. The photoelectrochemical measurement showed that the conversion efficiency of ZnO-SnO_2 based cell (0.81%) was observed to be larger than that of ZnO based cell(0.66%). Both conversion efficiencies were quite acceptable for low cost DSSC architecture. The conversion efficiency is quite reasonable that band gap of ZnO film is matched with that of onion skin and it will also be almost the same if either SnO_2 is. However, only those combining ZnO and SnO_2 have given better conversion efficiency. In conclusion, the ZnO and ZnO-SnO_2 nanocomposite electrode DSSC with onion skin dye sensitizer exhibits the potential to be a low-cost photovoltaic cell application. Thus the present research allowed more economical coating, easily adoptable and technically simplicity thereby making products that are more compact.

ACKNOWLEDGEMENT

This research was totally supported at Department of Physics, University of Yangon, Myanmar (2012-2013).

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