One dimensional SnO_2/ZnO nanofiber composite for dye sensitized solar cell

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Abstract: One-dimensional nano-morphology SnO_2 and composite of ZnO/SnO_2 nanofibers were synthesized, and fabricated by electrospinning technique. The materials were characterized by X-ray diffraction (XRD) and scanning electron microscopy (FESEM) techniques to confirm the crystal structure and morphology. Dye-sensitized solar cells (DSSCs) were fabricated using these nanofibers as photoanodes and their performance were compared with ~~to~~ commercial TiO_2 paste (P25)-based DSSCs. photoconversion efficiency (PCE) of 4.64 % was realized in composite ZnO/SnO_2 nanofibers based DSSCs which comparable to 4.75 % for P25 based DSSCs.

Keywords: Renewable Energy, Photovoltaic, SnO_2 nanofibers, SnO_2 –ZnO composite.

1. INTRODUCTION

The dye-sensitized solar cells (DSSCs) have raised remarkable interest since 1991, after the publication of the pioneering study by O'Regan and Gratzel [1]. These photoelectrochemical cells offer alternative to silicon-based photovoltaics (PVs), thanks to their low cost (materials and fabrication processes) and environmental impact [2, 3]. Although their performances are lower (photoconversion efficiency <14%) than traditional PVs [4] due to intrinsic limitation in charge transport, efforts devoted to improve the devices have not been reduced.

The most studied system exploits a thick film (12–18 μm) of TiO_2 nanoparticles (NPs) as photoanode, but a certain interest is being focused also on other potentially suitable semiconducting metal oxides such as ZnO, SnO_2, Nb_2O_5 and WO_3 [5-8]. Among them, ZnO and SnO_2 are the most appealing candidates, due to their higher electron mobility, as compared with TiO_2.

Despite the high electron mobility in SnO_2, the progress with this material has been hindered due to its low-energy level of conduction band (3.6 eV), which facilitates the recombination of photoexcited electrons by the holes in the redox electrolyte (e.g. 4.8 eV of redox potential of iodide/triiodide electrolyte). A strategy to overcome the inherent disadvantages of SnO_2 is to employ composite nanostructures which have shown to increase significantly the photovoltaic performance compared to their pure analogues with J_{SC} and V_{OC} values closer to that of TiO_2 [9, 10].

We report a composite photoanode of SnO_2/ZnO based DSSC employing one-dimensional (1D) NFs (diameter 450–470 nm) synthesized via electrospinning; which later TiO_2 NPs (<10 nm) were grown via a simple solution post treatment. An optimized SnO_2/ ZnO composite photoanode yielded a record PCE of 4.64% (V_{OC} ~730 mV and J_{SC} ~ 10 mA·cm^{-2}), which is significantly higher than a pure SnO_2 photoanode-based DSSC with PCE 1.17 % (J_{SC} ~ 7 mA· cm^{-2} and V_{OC} ~450 mV) at similar experimental conditions and is comparable to P25-based device (4.75%).

2. EXPERIMENTAL DETAILS

2.1 PURE SnO_2 NANOFIBER

8.5 mM tin chloride pentahydrate ($SnCl_4.5H_2O$), 3g of polyvinylpyrrolidone (PVP) were dissolved in an equal volume ratio (1:1) of ethanol and dimethylformamide (DMF). The solution was then transferred to a plastic syringe with steel needles for electrospinning, and the operating parameters were as reported before [11]. Solid nanofibers were then collected from the collector and annealed at temperature 500 ^oC for 3 hours at heating rate 1 ^oC min^{-1}.

2.2 COMPOSITE SnO_2/ZnO NANOFIBRES

Equimolar of $SnCl_4.5H_2O$ and Zinc acetate dihydrate $Zn(O_2CCH_3)_2(H_2O)_2$ following the same procedure for pure SnO_2 to get composite SnO_2/ZnO fibers.

2.3 PASTE PREPARATION

A standard procedure is adopted to prepare a printable paste of SnO_2 and composite SnO_2/ZnO synthesized nanostructure [12]. In brief, sufficient amount of the nanofiber was dispersed in absolute ethanol followed by stirring in ultrasonic bath to obtain a homogenous solution. To this mixture, α-terpinol (α-T, 18 wt.%) and ethyl cellulose (E.C, 10 wt.%) were added and the final paste has a ratio of nanofiber: α-T: E.C, 1:4.05:0.5, respectively, measured in mg unit. The paste was sonicated for an hour and finally heated at 70 ^oC on a hot plate to evaporate ethanol until thick slurry was formed.

2.4 CHARACTERIZATIONS AND MEASUREMENTS

The crystal structure of the material was studied by XRD technique using Rigaku Minifex II X-ray diffractometer employing Cu Kα radiation (λ= 1.5406 °A). The morphology and microstructure of the materials were studied by scanning electron microscopy technique (7800F, FESEM, JEOL, USA). The photocurrents of the DSSCs were measured at AM 1.5 G (intensity 100 mW.cm^{-2}) via a solar simulator (SOLAR LIGHT, Model 16-S 150) with power supply (XPS 400). The I–V curves were obtained using a potentiostat (Autolab PGSTAT30, Eco Chemie B.V., The Netherlands) employing NOVA software. The level of standard irradiance (100 mW.cm^{-2}) was set with a calibrated c-Si reference solar cell.

3. RESULT AND DISCUSSION

Fig.1.a shown the Thermogravimetric analysis (TGA),curve for SnO_2 and Composite SnO_2/ZnO nanofiber recorded in air indicates a three-step pattern for weight loss of the precursor. From room temperature to 110 ^oC, the weight loss of 5% corresponds to desorption of physically adsorbed water molecules. The second and third weight loss of 40% and 60% from 110 to 400 ^oC is associated with the removal of polymers units and the degradation of organic groups contained in the precursor fibers. The crystal structures of the samples were verified using XRD, and the

observed peaks of SnO_2 from XRD pattern Fig.1.b are (110), (101), (200), (211), (220) and (200) planes at 26.5°, 34°, 38°, 52°, 54° and 59° indicate pure SnO_2 nanostructures [13], which is in close agreement with the standard data (JCPDS Card no. 41-1445). It is clear from the Figure 1.b that composite SnO_2/ZnO (black curve) was formed from the dictated peaks,(100), (101), (102) and (110) at 31.7°, 34°, 47.5° and 56.5 for ZnO oxide which is in close agreement with the (standard 071-0652). No remarkable shift in diffraction peak was detected. This observation indicates that no obvious interface reaction of zinc oxide and tin oxide.

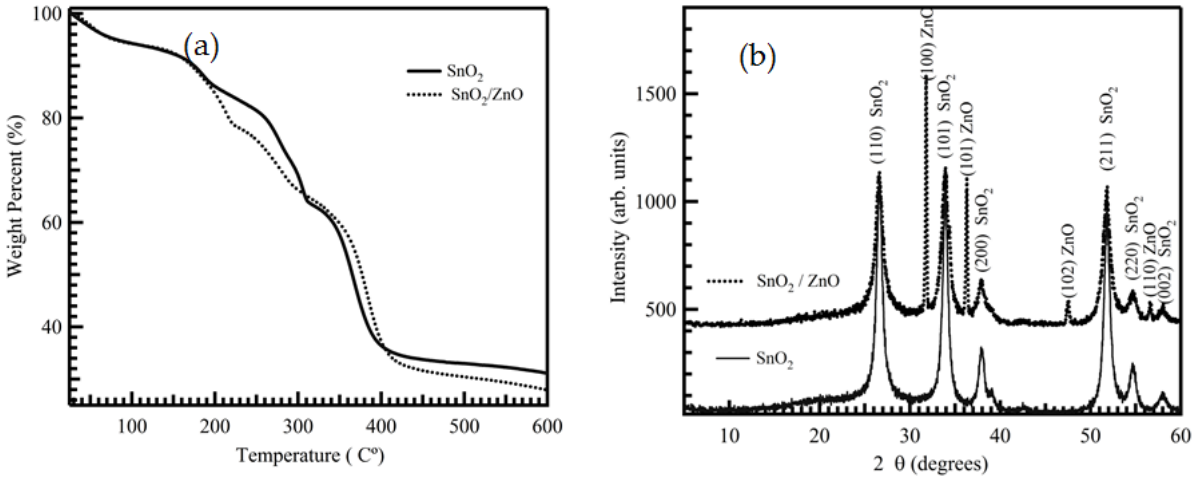


Figure 1: (a) TGA of and SnO_2 and SnO_2/ZnO Composite nanofiber (b) XRD diffraction patterns of SnO_2 and SnO_2/ZnO Composite nanofiber.

Fig. 2 shows FESEM images of annealed nanofibers for samples SnO_2 (a and b) and composite SnO_2/ZnO (c and d). For the pure SnO_2 nanofibre, diameters ranging from 150–160 nm, while adding zinc acetate precursor resulted in larger diameter (450–470 nm) for the ZnO/SnO_2 composite fibers.

The current–voltage analysis of the DSSCs is given in Fig. 3.a and the corresponding photovoltaic parameters are listed in the Table 1. It is clear that the lower V_{OC} ~ 450 mv and FF~ 0.37 in SnO_2 based DSCs due to its lower conduction band edge which results in high electron recombination with the electrolyte species. In order to suppress the charge recombination, we introduce composite SnO_2/ZnO which improve the PV parameters to V_{OC} ~ 580 mv and FF~ 0.59 while decreasing the short circuitcurrent density, $J_{SC,}$ from 7 to 5 mA· cm^{-2}. A strategy to overcome the inherent disadvantages of of this composite is to introduce a thin layer of TiO_2 onto the composite SnO_2/ZnO by $TiCl_4$ treatment (the treated samples were named as 0.2 $TiCL_4$ SnO_2/ZnO. The $TiCl_4$ treated photoelectrode showed remarkable increase in photovoltaic parameters (J_{SC} ~10.6 mA. cm^{-2}, V_{OC} ~ 730 mv and *FF*~ 0.60) which comparable with commercial paste P25 (J_{SC} ~10.1 mA. cm^{-2}, V_{OC}~ 700 mv and FF~ 0.67). Fig. 3.b shown the open circuit voltage decay (OCVD) measurements which performed in the dark.

It can be seen from Fig. 3.b that V_{OC} decays slowly for all passivated devices, while there was an abrupt drop in pure SnO_2 NFs. This slower decay observed in the passivated DSCs not only assures that electron could last longer and consequently yielded longer electron life time but also open a new concept that a built in potential is formed between the two metal oxide semiconductor having different conduction band and other physiochemical properties.

4. CONCLUSIONS

SnO_2 and composite SnO_2/ZnO nanofiber have fabricated via electrospinning technique. Composite electrode showing higher PCE~ 4.64 % when treated with thin layer of $TiCl_4$ compared to the conventional devices employed commercial TiO_2 paste, PCE~ 4.75%.

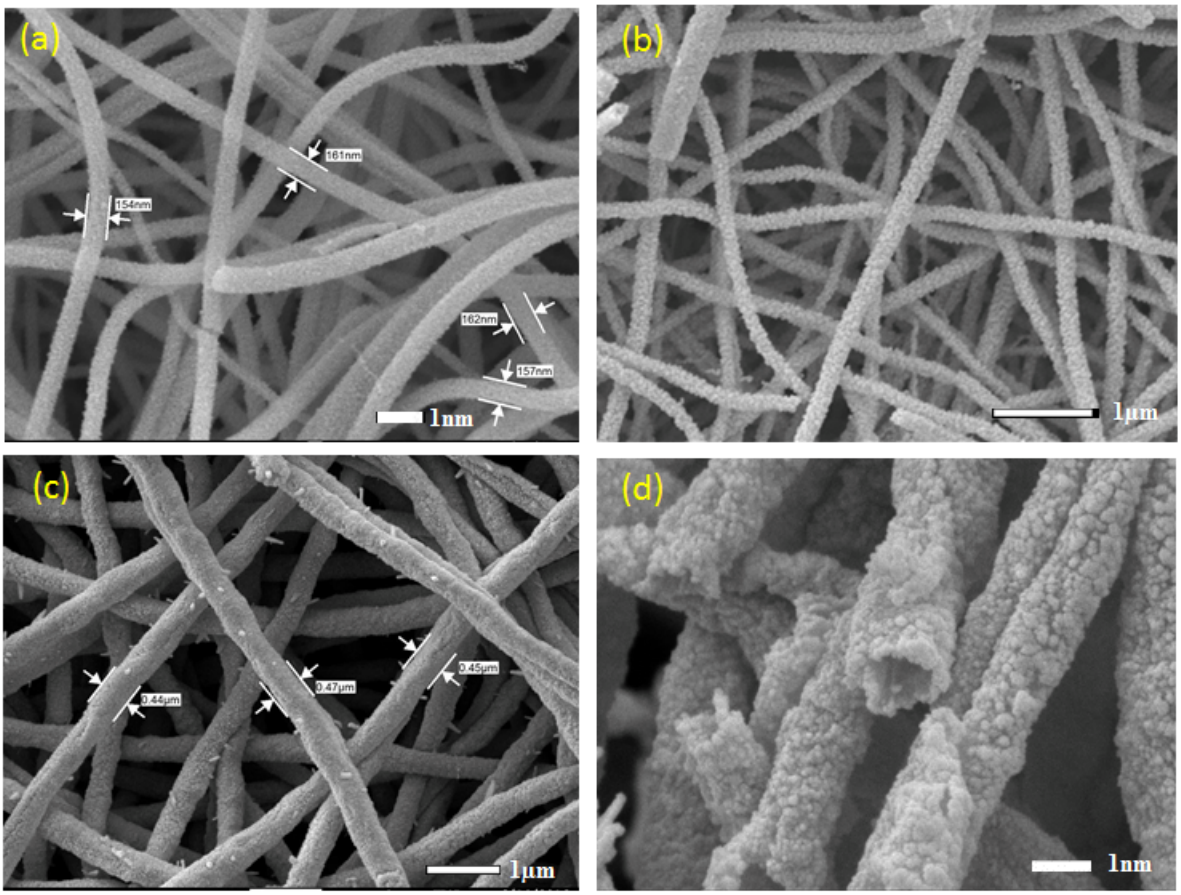
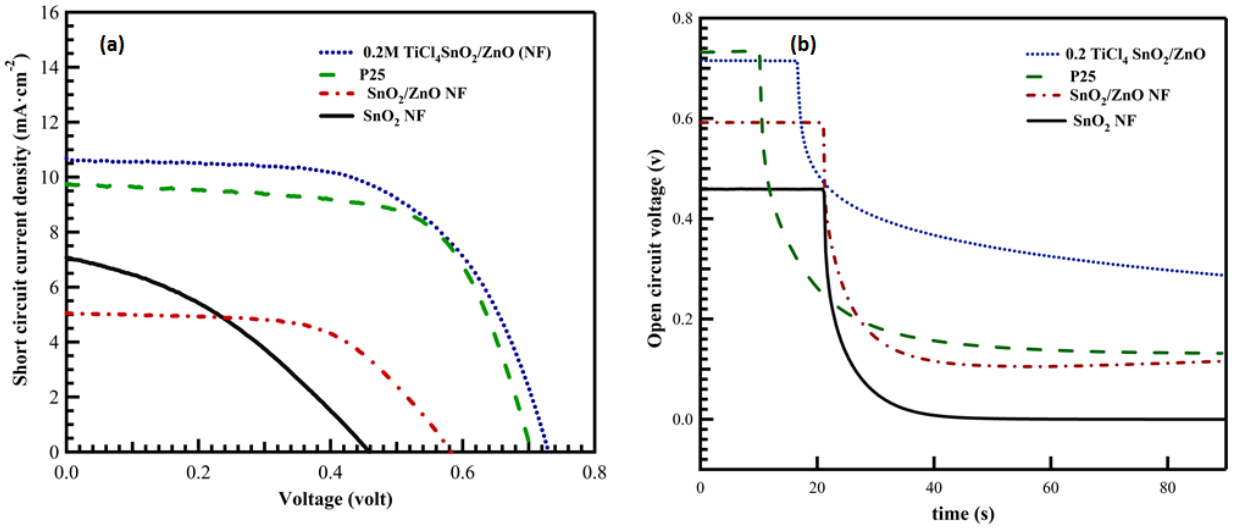


Figure 2: FESEM images of the (a and b) pure $SnO_2$and (c and d) composite SnO_2/ZnO at low and high magnifications, respectively.



(a) (b)

Figure 3: (a) The short circuit current density versus voltage (J–V) curves of DSCs at AM 1.5G conditions and (b) open circuit voltage decay measurements of pure SnO2 NF and composite SnO_2/ZnO NFs based DSCs.

Table.1: Photovoltaic parameters (J_{SC}, V_{OC}, *FF* and *PCE*) of SnO_2, SnO_2/ZnO Nanofiber, 0.2 $TiCl_4$ SnO_2/ZnO and P25 DSCs.

Device	V_{OC} (mV)	J_{SC} (mA·cm^{-2})	FF	PCE %
SnO_2	450	7.0	0.37	1.17
SnO_2/ZnO	580	5.0	0.59	1.72
0.2 $TiCl_4$ SnO_2/ZnO	730	10.6	0.6	4.64
P25	700	10.1	0.67	4.75

ACKNOWLEDGMENT

The authors would like to acknowledge financial support from Ministry of Higher Education Malaysia (MOHE) under grant FRGS 140126.

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