

One dimensional SnO₂/ZnO nanofiber composite for dye sensitized solar cell

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Abstract: One-dimensional nano-morphology SnO₂ and composite of ZnO/SnO₂ 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 the commercial TiO₂ paste (P25)-based DSSCs. photoconversion efficiency (PCE) of 4.64 % was realized in composite ZnO/SnO₂ nanofibers based DSSCs which comparable to 4.75 % for P25 based DSSCs.

Keywords: Renewable Energy, Photovoltaic, SnO₂ nanofibers, SnO₂-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 TiO₂ nanoparticles (NPs) as photoanode, but a certain interest is being focused also on other potentially suitable semiconducting metal oxides such as ZnO, SnO₂, Nb₂O₅ and WO₃ [5-8]. Among them, ZnO and SnO₂ are the most appealing candidates, due to their higher electron mobility, as compared with TiO₂.

Despite the high electron mobility in SnO₂, 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 SnO₂ 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 TiO₂ [9, 10].

We report a composite photoanode of SnO₂/ZnO based DSSC employing one-dimensional (1D) NFs (diameter 450–470 nm) synthesized via electrospinning; which later TiO₂ NPs (<10 nm) were grown via a simple solution post treatment. An optimized SnO₂/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 SnO₂ 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 SnO₂ NANOFIBER

8.5 mM tin chloride pentahydrate (SnCl₄·5H₂O), 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 °C for 3 hours at heating rate 1 °C min⁻¹.

2.2 COMPOSITE SnO₂/ZnO NANOFIBRES

Equimolar of SnCl₄·5H₂O and Zinc acetate dihydrate Zn(O₂CCH₃)₂(H₂O)₂ following the same procedure for pure SnO₂ to get composite SnO₂/ZnO fibers.

2.3 PASTE PREPARATION

A standard procedure is adopted to prepare a printable paste of SnO₂ and composite SnO₂/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 °C 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 K α radiation (λ = 1.5406 Å). 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 SnO₂ and Composite SnO₂/ZnO nanofiber recorded in air indicates a three-step pattern for weight loss of the precursor. From room temperature to 110 °C, 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 °C 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 SnO₂ 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 SnO₂ 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 SnO₂/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.

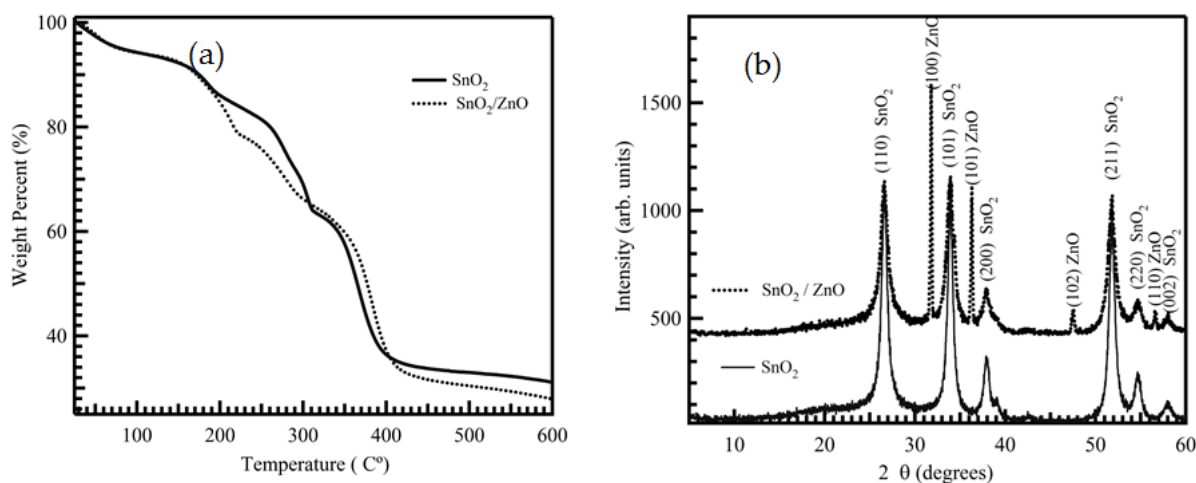


Figure 1: (a) TGA of and SnO₂ and SnO₂/ZnO Composite nanofiber (b) XRD diffraction patterns of SnO₂ and SnO₂/ZnO Composite nanofiber.

Fig. 2 shows FESEM images of annealed nanofibers for samples SnO₂ (a and b) and composite SnO₂/ZnO (c and d). For the pure SnO₂ nanofibre, diameters ranging from 150–160 nm, while adding zinc acetate precursor resulted in larger diameter (450–470 nm) for the ZnO/SnO₂ 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 $V_{OC} \sim 450$ mV and $FF \sim 0.37$ in SnO₂ 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 SnO₂/ZnO which improve the PV parameters to $V_{OC} \sim 580$ mV and $FF \sim 0.59$ while decreasing the short circuit current density, J_{SC} , from 7 to 5 mA·cm⁻². A strategy to overcome the inherent disadvantages of this composite is to introduce a thin layer of TiO₂ onto the composite SnO₂/ZnO by TiCl₄ treatment (the treated samples were named as 0.2 TiCl₄ SnO₂/ZnO). The TiCl₄ treated photoelectrode showed remarkable increase in photovoltaic parameters ($J_{SC} \sim 10.6$ mA·cm⁻², $V_{OC} \sim 730$ mV and $FF \sim 0.60$) which comparable with commercial paste P25 ($J_{SC} \sim 10.1$ mA·cm⁻², $V_{OC} \sim 700$ mV and $FF \sim 0.67$). 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 SnO₂ 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

SnO₂ and composite SnO₂/ZnO nanofiber have fabricated via electrospinning technique. Composite electrode showing higher PCE~ 4.64 % when treated with thin layer of TiCl₄ compared to the conventional devices employed commercial TiO₂ paste, PCE~ 4.75%.

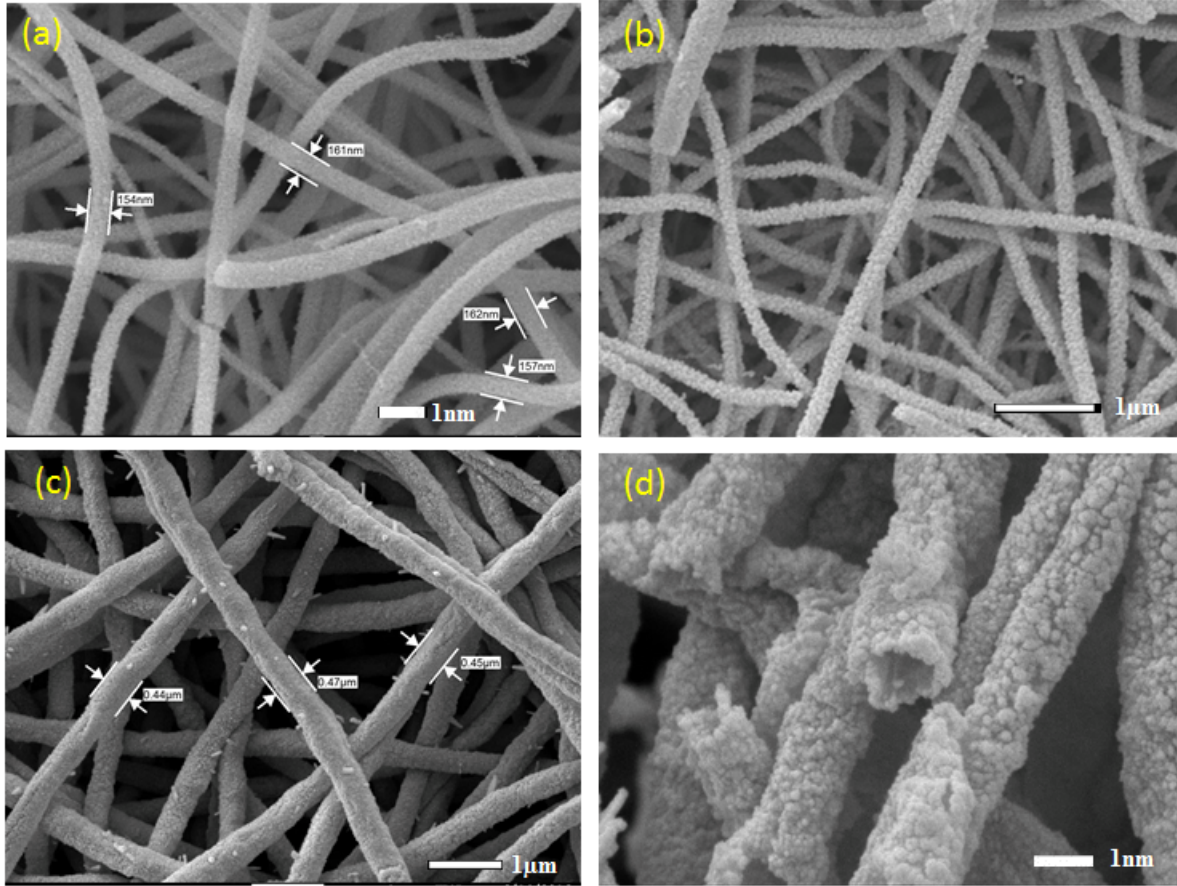


Figure 2: FESEM images of the (a and b) pure SnO₂ and (c and d) composite SnO₂/ZnO at low and high magnifications, respectively.

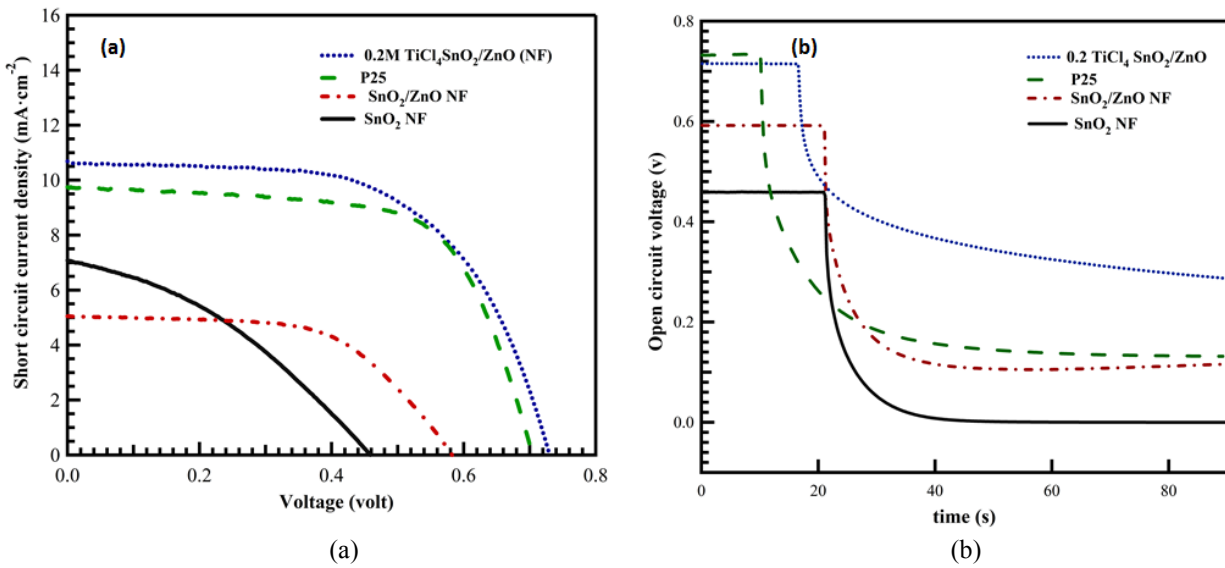


Figure 3: (a) The short circuit current density versus voltage (J-V) curves of DSCs at AM 1.5G conditions and (b) open circuit voltage decay measurements of pure SnO₂ NF and composite SnO₂/ZnO NFs based DSCs.

Table.1: Photovoltaic parameters (J_{SC} , V_{OC} , FF and PCE) of SnO₂, SnO₂/ZnO Nanofiber, 0.2 TiCl₄ SnO₂/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

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REFERENCES

- [1] B. O'regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized, nature, 353 (1991) 737-740.
- [2] M. Grätzel, Solar energy conversion by dye-sensitized photovoltaic cells, Inorganic chemistry, 44 (2005) 6841-6851.
- [3] M. Wu, X. Lin, T. Wang, J. Qiu, T. Ma, Low-cost dye-sensitized solar cell based on nine kinds of carbon counter electrodes, Energy & Environmental Science, 4 (2011) 2308-2315.
- [4] A. Yella, H.-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.-G. Diau, C.-Y. Yeh, S.M. Zakeeruddin, M. Grätzel, Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency, science, 334 (2011) 629-634.
- [5] I. Concina, A. Vomiero, Metal Oxide Semiconductors for Dye-and Quantum-Dot-Sensitized Solar Cells, Small, 11 (2015) 1744-1774.
- [6] L. Li, T. Zhai, Y. Bando, D. Golberg, Recent progress of one-dimensional ZnO nanostructured solar cells, Nano Energy, 1 (2012) 91-106.
- [7] Y. Fukai, Y. Kondo, S. Mori, E. Suzuki, Highly efficient dye-sensitized SnO₂ solar cells having sufficient electron diffusion length, Electrochemistry Communications, 9 (2007) 1439-1443.
- [8] H. Zhang, Y. Wang, D. Yang, Y. Li, H. Liu, P. Liu, B.J. Wood, H. Zhao, Directly Hydrothermal Growth of Single Crystal Nb₃O₇(OH) Nanorod Film for High Performance Dye- Sensitized Solar Cells, Advanced Materials, 24 (2012) 1598-1603.
- [9] D.C. Look, D.C. Reynolds, J. Sizelove, R. Jones, C.W. Litton, G. Cantwell, W. Harsch, Electrical properties of bulk ZnO, Solid state communications, 105 (1998) 399-401.
- [10] C. Seager, S. Myers, Quantitative comparisons of dissolved hydrogen density and the electrical and optical properties of ZnO, Journal of applied physics, 94 (2003) 2888-2894.
- [11] Q. Wali, A. Fakharruddin, I. Ahmed, M.H. Ab Rahim, J. Ismail, R. Jose, Multiporous nanofibers of SnO₂ by electrospinning for high efficiency dye-sensitized solar cells, Journal of Materials Chemistry A, 2 (2014) 17427-17434.
- [12] S. Ito, T.N. Murakami, P. Comte, P. Liska, C. Grätzel, M.K. Nazeeruddin, M. Grätzel, Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%, Thin solid films, 516 (2008) 4613-4619.
- [13] G. Shang, J. Wu, M. Huang, J. Lin, Z. Lan, Y. Huang, L. Fan, Facile synthesis of mesoporous tin oxide spheres and their applications in dye-sensitized solar cells, The Journal of Physical Chemistry C, 116 (2012) 20140-20145.