



Synergistic combination of electronic and electrical properties of SnO₂ and TiO₂ in a single SnO₂-TiO₂ composite nanofiber for dye-sensitized solar cells

Zinab H. Bakr^{a, b}, Qamar Wali^{a, c}, Jamil Ismail^a, Naveen Kumar Elumalai^d, Ashraf Uddin^d, Rajan Jose^{a, *}

^a Nanostructured Renewable Energy Materials Laboratory, Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, Gambang, 26300, Kuantan, Malaysia

^b Physics Department, Faculty of Science, Assiut University, Assiut, 71516, Egypt

^c Materials Research Laboratory, Department of Physics, University of Peshawar, Peshawar, 25120, Pakistan

^d School of Photovoltaics and Renewable Energy Engineering, University of New South Wales, Sydney, 2052, Australia

ARTICLE INFO

Article history:

Received 18 June 2017

Received in revised form

27 December 2017

Accepted 11 January 2018

Available online 31 January 2018

Keywords:

Renewable energy

Energy conversion materials

Photovoltaics

Hybrid nanofibers

Electrospinning

ABSTRACT

Tin dioxide (SnO₂) and titanium dioxide (TiO₂) are popular metal oxide semiconductors; they are explored for many applications because of their unique properties. This paper details that electronic and electrical properties of SnO₂ and TiO₂ can be synergistically combined in an one-dimensional nanostructure, such as electrospun nanofibers. The resulting composite nanofibers (CNFs) showed beneficial properties when used as a photoanode in dye-sensitized solar cells (DSSCs). In particular, the CNFs showed higher conduction band energy than SnO₂ and higher electrical conductivity than TiO₂. The SnO₂-TiO₂ CNFs are synthesized by electrospinning a polymeric solution containing equimolar concentration of tin chloride and titanium alkoxide precursors and subsequent annealing. The composite formation is demonstrated by X-ray diffraction and energy dispersive X-ray measurements and morphology by scanning electron microscopy. Synergy in electronic and electrical properties are demonstrated by cyclic voltammetry, absorption spectroscopy, and electrochemical impedance spectroscopy. Dye-sensitized solar cells fabricated using the CNFs as photoanode showed higher open circuit voltage and short circuit current density than those achieved using pure SnO₂ and pure TiO₂, respectively.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

One-dimensional (1D) metal oxide semiconducting (MOS) nanostructures such as nanowires (NWs), nanotubes (NTs), nanorods (NRs), and nanofibers (NFs), as a medium for absorber (dye) hosting and charge transport in dye-sensitized solar cells (DSSCs), which medium is called photoelectrode, is a well researched topic [1–4]. The 1D nanostructures offer several advantages over the spherical nanoparticles as a photoelectrode: (i) larger surface area for similar volume [5,6]; (ii) guided charge transport [7]; and (iii) possibility of band edge type conduction in nanomaterials [8,9]. Most desirable 1D photoelectrodes are the ones vertically aligned on a conducting glass substrate; however, their scalability to

develop large area panels is a crucial issue. Towards this end, random NFs by scalable nanofabrication technique such as electrospinning is the best compromise between upholding 1D properties and scalability of materials production [10–12].

Many MOS nanostructures have been investigated as photoanodes in DSSCs; among them TiO₂ and SnO₂ offer complementary properties [13,14]. To visualize the above argument, consider the one-dimensional current density (J) of an electronic device, $J = n\mu\nabla E_F$, where n is the electron density, μ is the charge mobility, and ∇E_F is the gradient in Fermi levels of a materials interface across which the photocurrent flows. In the case of DSSCs, n is contributed by the amount of the dye-anchored onto the photoelectrode and hence depend on the surface area, μ is controlled by the conduction band effective mass of the photoelectrode, and the $\nabla E_F \sim E_F(\text{photoanode}) - E_F(\text{electrolyte}) \propto V_{OC}$ [15], where V_{OC} is the open circuit voltage. The TiO₂ offers high surface area and higher Fermi energy compared to that of the SnO₂; on the other

* Corresponding author.

E-mail address: rjose@ump.edu.my (R. Jose).

hand, SnO₂ offers orders of magnitude higher of μ [16] due to its lower conduction band effective mass (0.17 m_e) compared to that of TiO₂ (9 m_e) [17,18]. Many experiments are reported to increase the μ through electrospun TiO₂ NFs using n-type dopants such as Nb and W [19], p-type dopants such as Ni [20], and homovalent substitution using Zr [21]. Similarly, experiments are reported to increase the surface area and uplift the Fermi energy of the electrospun SnO₂ by developing a layer of TiO₂ onto SnO₂ NFs [14,22,23]. However, the above achievements are on an average; and optimizing a dopant concentration [24] or layer thickness [16,25] to achieve a best performance is a tedious task. One may even argue that the best performance has not been achieved using the above protocols.

We show in this article that properties of TiO₂ and SnO₂ can be simply and synergistically combined in a single composite nanofiber (CNF) containing these two materials by electrospinning technique. The CNFs showed lower band gap energy than SnO₂ but higher Fermi energy than TiO₂ and higher electrical conductivity than TiO₂. The photovoltaic conversion efficiency (PCE) of the CNFs based device was increased by ~100% than SnO₂ based device and over ~50% than the TiO₂ based device. The origin of this property has been investigated and reported.

2. Experimental details

Three types of NFs were synthesized by electrospinning for the present study (i) TiO₂, (ii) SnO₂ and (iii) SnO₂-TiO₂ composite. The materials were synthesized using previously reported procedures [14]; the only difference in the synthesis of composite NFs is that 1:1 M mixture of the titanium and tin precursors was used. In a typical synthesis of SnO₂-TiO₂ CNFs, the precursor solution for electrospinning was prepared by simultaneously dissolving polyvinylpyrrolidone (PVP, 3 g, mol. wt. ~1,300,000 g mol⁻¹), tin chloride hydrate (SnCl₄·5H₂O, 7 mM) and titanium isopropoxide (C₁₂H₂₈O₄Ti, 7 mM) in a mixture of ethanol (18 mL) and dimethylformamide (DMF, 18 mL). The mixture was then stirred vigorously for 24 h at room temperature to form a homogeneous solution. The solution was electrospun at 0.5 mL h⁻¹ at ~25 kV with a needle to tip collector distance of ~15 cm using a commercial electrospinning set up (Electroris, NanoLab, Progenelink Sdn Bhd, Malaysia). The as-spun polymeric fibers containing precursors of tin and titanium were then sintered at 500 °C for 3 h in air.

Crystal structures of the materials were studied by X-ray diffraction (XRD) technique using Rigaku Miniflex II X-ray diffractometer employing Ni-filtered CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$). Elemental analyses of the CNFs were carried out by energy dispersive X-ray measurements (EDX-720, Shimadzu, Japan). The surface atomic structures of the materials were identified by the X-ray photoelectron spectroscopy (XPS, Ulvac-Phi/Phi 5000 Versaprobe II). The survey spectra were recorded from 0 to 1200 eV with a pass energy of 1 eV whereas the high-resolution spectra were recorded at a smaller constant pass energy of 0.25 eV. Charge referencing were performed against adventitious carbon C (~284.8 eV). The analysis of the high-resolution spectra was done by fitting into multiple Gaussian curves using Origin software. Morphology and microstructure of the materials were studied by scanning electron microscopy (7800F, FESEM, JEOL, USA). UV-Visible diffuse reflection (DR) spectra of the samples were measured using a UV-Vis-NIR spectrophotometer (UV-2600, Shimadzu, Japan). Samples for the reflectance spectra were films developed on glass substrates. The films were prepared from respective pastes developed as follows: sufficient amount of the nanofibers was dispersed in absolute ethanol followed by stirring in ultrasonic bath to obtain a homogeneous 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 nanofibers: 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. The films for the reflectance measurement were prepared by coating a NFs paste on glass substrate, dried at 100 °C and subsequently sintered at 450 °C for 3 h. The electrochemical properties of the electrodes were investigated using cyclic voltammetry (CV) and Mott-Schottky (MS) measurements using a potentiostat-galvanostat (Autolab PGSTAT30, Eco Chemie B.V., The Netherlands). The electrodes were prepared as explained elsewhere [26]. Briefly, the electrodes were prepared from the active nanofibers materials, carbon black and polyvinylidene fluoride in the weight ratio of 85:10:5, respectively. The tests were performed with a three-electrode system configuration using a platinum plate counter electrode, a Ag/AgCl reference electrode, and the nanofiber photoanode as a working electrode. The CV tests were performed in the potential range between 0 and 0.5 V with scan rate of 10 mV s⁻¹ in 5 M aqueous KOH solution. For MS measurement, the electrodes were acquired in 1 M Na₂SO₄ electrolyte and the impedance spectra were recorded from -0.6 to 0.6 V at step of 0.1 V. The capacitance values were calculated from impedance data at 50 kHz and plotted as a function of the applied voltage. The electrical resistance of the electrode materials were determined using linear sweep voltammetry (LSV) using the Autolab PGSTAT30. For LSV measurements, ~50 mg powder samples were pressed into pellets of thickness ~1 mm and diameter ~8 mm using a hydraulic press at 5 tons for 30 s.

For fabrication of DSSCs, a paste of the NFs was prepared as reported before [14] and screen printed at an area of ~0.2 cm² on fluorine-doped tin oxide (FTO) (sheet resistance 15 $\Omega \text{ cm}^{-2}$) coated glass substrates (working electrode). The films were dried at 100 °C and subsequently sintered at 450 °C. The sintered films were immersed for 24 h in 0.3 mM ethanolic solution of *cis-bis*(isothiocyanato)*bis* (2,20-bipyridyl-4,40-dicarboxylato)-ruthenium(II) dye (N719). The dye-sensitized samples were then washed with ethanol to remove unanchored dye and subsequently dried in air. A platinumized FTO glass substrate was used as the counter electrode. DSSCs were obtained by assembling the working and counter electrodes separated by a 50 μm thick plastic spacer (Surlyn); the electrolyte (iodide/triiodide redox couple) was then injected to the spacer region. Photocurrent measurements of the fabricated cells were carried out at AM 1.5G (100 mWcm⁻²) using a solar simulator (SOLAR LIGHT, Model 16-S 150) employing single port simulator with power supply (XPS 400). The current-voltage (I-V) curves of the devices were recorded using a potentiostat (Autolab PGSTAT30, Eco Chemie B.V., The Netherlands). Electrochemical impedance spectra (EIS) of the DSSCs were obtained using the Autolab PGSTAT30 employing the NOVA software by keeping them in dark. The devices were scanned in a frequency range of 100 kHz to 0.5 Hz with an AC signal 10 mV in amplitude. The EIS were fitted to a well-known transmission line [27] model by using Z-view software.

3. Results and discussion

Fig. 1 shows the XRD patterns of the SnO₂-TiO₂ CNFs compared with their single component counterparts. The XRD pattern of TiO₂ NFs showed peaks at 2θ ~25.96, ~36.96, ~37.83, ~38.59, ~48.05, ~53.95, and ~55.08° corresponding to (101), (103), (004), (112), (200), (105), and (211) crystal planes of anatase, respectively. The lattice parameters (a and c) and the cell volume (V) calculated using a least squares refinement program [28] were $a = 3.783 \text{ \AA}$, $c = 9.501 \text{ \AA}$ and $V = 136.045 \text{ \AA}^3$ which closely agree with reported patterns of anatase TiO₂ (JCPDS, # 84-1286). The XRD pattern of SnO₂ NFs showed peaks at 2θ ~26.64, 33.94, 38.01, 51.86 and 54.76° corresponding to (110), (101), (200), (211) and (220) planes of tetragonal cassiterite phase with lattice parameters $a = 4.735 \text{ \AA}$, $c = 3.176 \text{ \AA}$

Download English Version:

<https://daneshyari.com/en/article/6604486>

Download Persian Version:

<https://daneshyari.com/article/6604486>

[Daneshyari.com](https://daneshyari.com)