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Dye-sensitized solar cells using network structure of electrospun ZnO nanofiber mats

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Nanostructured semiconducting metal oxides and particularly nanofiber-based photoelectrodes can provide enhanced energy conversion efficiencies in dye-sensitized solar cells (DSSCs). In this study ZnO/poly(vinyl acetate) composite nanofiber mats were directly electrospun onto a glass substrate coated with F:SnO₂, then hot pressed at 120 °C and calcined at 450 °C. This resulted in multiple nanofiber networks composed of a twisted structure of 200–500 nm diameter cores with ~30 nm single grains. The DSSCs using ZnO nanofiber mats exhibited a conversion efficiency of 1.34% under 100 mW/cm² (AM-1.5G) illumination. © 2007 American Institute of Physics.

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Recently, significant progress had been made in developing dye-sensitized solar cell (DSSC) architectures mainly based on thick (~10 μm) TiO₂ or, less often, wide band-gap semiconducting oxides such as SnO₂ or ZnO.¹ These anode films are typically composed of high-surface-area nanoparticles in order to achieve sufficient dye absorption and high solar-power efficiencies. However, in nanoparticle-based DSSCs, high efficiencies are often limited due to their disordered geometrical structures and interfacial interference in electron transport, thus resulting in an enhanced scattering of free electrons and reduced electron mobility due to the recombination of electrons with either oxidized species in the electrolyte or oxidized dye molecules before reaching the collecting electrode. Among the strategies for achieving fast and effective electron transport, i.e., single crystalline ZnO nanowires,² quasiordered arrays of TiO₂ nanotubes,³ and core-shell structures,⁴ the use of nanowires in DSSCs could present unique structural features to create enhanced surface activities that would promote dye adsorption as well as enable the fast and effective transport of electrons to the collection electrode with recombinations suppressed, leading to improved conversion efficiencies. Although the use of nanowire photoanodes is a very promising route for highly efficient DSSCs, most of nanowire synthetic methods involve multiple steps: for example, the fabrication/removal of templates, preparation of catalyst, and additional postsynthesis treatments. The different process conditions in each step often limit the practical device quality. Among the methods for generating fibular mesostructure, electrospinning is one of the most simple, versatile, and cost-effective approaches offering the ability to produce long continuous semiconducting metal-oxide nanofibers.^{5,6} Electrospinning has been explored recently as a means for preparing a wide variety of nanofiber

materials for potential applications, for example, in tissue engineering and drug delivery,⁷ membranes and filters,⁸ solar cells,⁹ and chemical and biological sensors.¹⁰ There are several reports related to the preparation of ZnO semiconducting oxide nanofibers by electrospinning.^{11–13} However, to date, no reports exist regarding DSSCs using electrospun ZnO nanofiber. The poor adhesion of electrospun nanofibers to the substrate is a major problem for practical characterization of the photoanode. Therefore, good electrical contact between the nanofibers and electrodes should be properly addressed to enable practical and reproducible devices. In this regard, a process modification providing means for the fabrication of DSSCs using electrospun ZnO fiber mats is introduced in this study, and results for electrospun ZnO fiber mats exhibiting high solar conversion efficiency are discussed.

ZnO fibers were electrospun from a solution of dimethyl formamide (DMF) (30 ml) of 2.4 g of poly(vinyl acetate) (PVAc, $M_w=1,000,000$ g/mol), which was synthesized using bulk radical polymerization, 6 g of zinc acetate (Aldrich), and 2 g of acetic acid as a catalyst. As in typical electrospinning procedures, the precursor solution was loaded into a syringe and connected to a high-voltage power supply. The flow rate was 15 μl/min. An electric field of 15 kV was applied between the orifice and the ground at a distance of 10 cm. ZnO/PVAc composite nanofibers were directly electrospun on F-doped SnO₂ (F:SnO₂) glass substrates (10 × 10 cm², TEC-15, Pilkington). The as-spun ZnO/PVAc composite fibers were then pressed for 10 min using plates preheated to 120 °C. A 2-mm-thick Teflon plate was inserted between the ZnO/PVAc fiber mats and the plate to apply uniform pressure and to prevent sticking of the fibers to the plate. Subsequently, the samples were calcined at 450 °C for 30 min in air to remove the organic constituents of the PVAc.

X-ray diffraction (XRD) was used to examine the phase composition of fiber mats. Scanning electron microscopy (JSM-6330F, JEOL) was carried out for an investigation of

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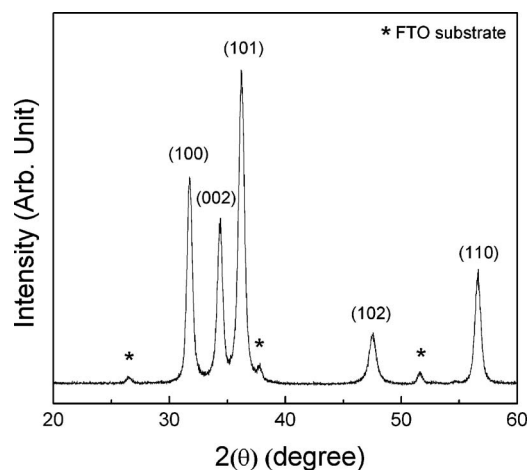


FIG. 1. X-ray diffraction pattern of ZnO nanofiber mats prepared on a F:SnO₂-coated glass substrate.

the development of the microstructure during the process steps. Transmission electron microscopy (TEM) was used to examine the microstructure of the ZnO nanofibers. Ultrasonication was used to disperse the networks of ZnO nanofibers in ethanol followed by mounting on a carbon-coated Cu grid. High-resolution transmission electron microscopy (HRTEM) (JEM-3000F, JEOL) was used to investigate individual ZnO nanocrystal structures. Brunauer-Emmett-Teller (BET) analysis (Sorptomatic 1990, ThermoFinnigan) was performed on ZnO fiber mats to examine specific surface area.

In order to prepare the DSSC, the calcined ZnO nanofiber mats were immersed in the ethanol solution $3 \times 10^{-4} M$ *cis*-di(thiocynato)-*N,N'*-bis(2,2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxylate) ruthenium (II) (N719, Solaronix). Dye sensitization time was only for 3 h to minimize the formation of Zn²⁺/dye aggregation.^{14,15} The dye-adsorbed ZnO electrodes were rinsed with ethanol and dried under a nitrogen flow. The liquid electrolyte was prepared by dissolving 0.6M of 1-butyl-3-methylimidazolium iodide (BMII), 0.03M of iodine (I₂), 0.1M of guanidinium thiocyanate, and 0.5M of 4-*tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (volume ratio is 85:15). The counter electrode was produced by coating F:SnO₂ glass with a thin layer of a 5 mM solution of H₂PtCl₆ in isopropanol. The coated films were heated at 400 °C for 20 min. The two electrodes were sealed together with Surlyn polymer film (24-μm-thick, DuPont). The typical active area of the cell was 0.20 cm². The photovoltaic characteristic was measured using a Keithley 2400 source-measure unit. A Xe lamp (Oriel, 1000 W) served as a light source, and its light intensity (or radiant power) was adjusted with a Si reference solar cell equipped with KG-5 filter (Fraunhofer Institute, Germany) for approximating AM-1.5 radiation. All samples were measured under 100 mW/cm² irradiation.

Structural identification of the electrospun ZnO nanofiber mats calcined at 450 °C was carried out using XRD in the range of 2θ between 20° and 60°, as shown in Fig. 1. The result indicated that the electrospun ZnO nanofiber mats had polycrystalline structures consisting of a wurtzite ZnO phase characterized with primary (100), (002), and (101) peaks. Based on the Scherrer equation ($D = k\lambda_x / \beta \cos \theta$, where D is the mean grain size, 2θ is the diffraction angle, λ_x is the x-ray wavelength, and β is the full width at half maximum of

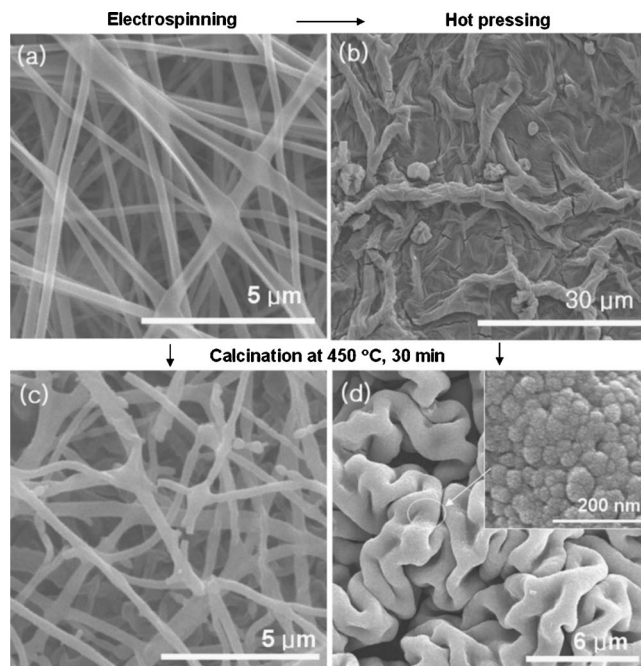


FIG. 2. (a) SEM image of the as-spun ZnO/PVAc composite nanofiber mats fabricated by electrospinning. (b) SEM image of ZnO/PVAc composite nanofiber mats after hot pressing at 120 °C for 10 min. (c) SEM image of unpressed ZnO nanofiber mats after calcinations at 450 °C. (d) SEM image of ZnO nanofiber mats hot pressed at 120 °C and calcined at 450 °C. The inset exhibits the networks of twisted nanofibers composed of individual grains of ~30 nm.

diffraction peak), the ZnO nanofiber mats exhibited a mean grain size of approximately 36 nm. The size distribution is in good agreement with the results measured by scanning electron microscopy (SEM) and HRTEM micrographs.

Figure 2 shows SEM images of ZnO nanofiber mats fabricated by heating at 450 °C for 30 min after electrospinning. The as-spun ZnO/PVAc composite nanofibers [see Fig. 2(a)] exhibit a range of diameters from 200 to 500 nm. With no hot pressing pretreatment, but after calcinations at 450 °C in air for 30 min to remove the PVAc, the ZnO fibers exhibited a typical structure composed of 200–500 nm diameter cores, as shown in Fig. 2(c). However, as spun onto the F:SnO₂ substrate, the ZnO fiber mats exhibited poor adhesion to the substrates. After calcination at 450 °C, the ZnO nanofiber mats were cracked and peeled off from the F:SnO₂ substrates. In order to solve the adhesion problem, a hot pressing process was introduced before the calcination step. The hot pressing was introduced to drive the PVAc above its glass transition temperature (28–30 °C), resulting in a markedly better adhesion. In contrast to untreated fibers, the hot-pressed fibers did not peel off of the substrate during handling and testing. An interconnected morphology of the ZnO/PVAc composite fiber was obtained due to the partial or entire melting of PVAc, as shown in Fig. 2(b). The partial formation of twisted nanofiber networks was observed within hot-pressed ZnO/PVAc composite nanofibers, as shown in Fig. 2(b). Subsequent calcination at 450 °C for 30 min resulted in high surface area structures, i.e., twisted networks of ZnO nanofibers, as shown in Fig. 2(d). The inset of Fig. 2(d) emphasizes that the ZnO networks are composed of single crystalline grains of 20–40 nm in diameter. At this stage, further clarification is needed to investigate the origin of the formation of the twisted structure in the hot-pressed

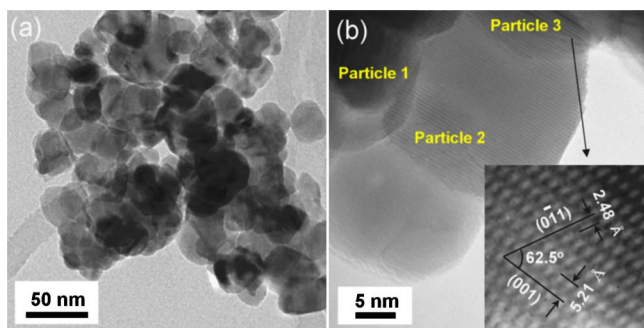


FIG. 3. (Color online) Microstructure of ZnO grains obtained after hot pressing and calcinations of electrospun ZnO nanofibers: (a) bright-field TEM image and (b) HRTEM image. The inset shows a lattice image of a single crystalline ZnO grain.

and calcined ZnO nanofiber mats. The unique structural features may be advantageous, as this morphology provides high porosity for efficient permeability of electrolytes into the inner structure while maintaining a high surface area for enhanced surface activities, as compared to that of the ZnO fiber structure obtained without a hot-pressing step, as shown in Fig. 2(c).

In addition, the dense networks of twisted nanofibers are beneficial in terms of direct conduction paths for efficient electron collection to the F:SnO₂ electrode. Thus, hot pressing serves two important purposes: that of enhancing the adhesion strength between ZnO fiber mats and substrates, and the creation of a large active area for the DSSC performance.

In order to investigate individual single grains of ZnO nanofiber mats, an HRTEM analysis was carried out. Figure 3(a) shows micrographs of individual ZnO single grains with size distributions of 20–40 nm. The size distribution is well matched with that (36 nm) based on the Scherrer equation from the XRD pattern. Lattice images are clearly observed in Fig. 3(b), indicating that the ZnO single grains are highly crystalline. The lattice distance was measured as 5.21 and 2.48 Å, corresponding to the {011} and {001} planes. The measured angle between the (011) and (001) planes was 62.5°, consistent with the theoretical angle (61.6°) of the ZnO wurtzite structure.

BET analysis was carried out in order to investigate the specific surface area. The measured specific surface area of the hot-pressed and calcined ZnO fiber mats was found to be 24.08 m²/g.

The DSSCs were assembled with electrodes using electrospun ZnO nanofiber mats and characterized at an illumination intensity of 1 sun (AM-1.5). Figure 4 shows the photocurrent density versus the voltage characteristics of a DSSC based on the electrospun ZnO fiber mats with a liquid electrolyte. A light-to-electricity conversion efficiency of solar cells, i.e., η , can be evaluated from the given equation $\eta = (FF \times |J_{sc}| \times V_{oc}) / P_{in}$, where FF is the fill factor, $|J_{sc}|$ is the short circuit current density, V_{oc} is the open circuit voltage, and P_{in} is the incident light power density. The short-circuit current density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (FF), and the overall conversion efficiency (η) of the electrode using ZnO fiber mats were found to be 3.58 mA/cm², 0.60 V, 0.62, and 1.34%, respectively.

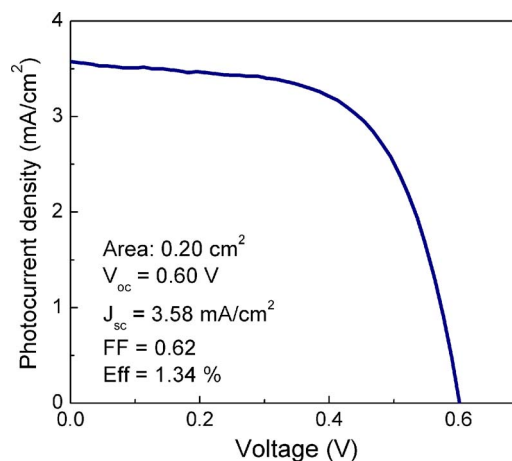


FIG. 4. (Color online) Photocurrent density vs voltage characteristics of a DSSC using electrospun ZnO nanofiber mats.

The use of the ZnO fiber mats in DSSCs indicates that the efficient penetration of the electrolyte into the ZnO electrode occurs through micropores in the twisted nanofiber mats.

In summary, multiple networks of ZnO nanofibers were prepared using an electrospinning method followed by hot pressing and calcinations steps. Unique morphologies composed of a twisted structure of 200–500 nm diameter cores with ~30 nm single grains were achieved. The structural morphologies resulted in enhanced surface activities for dye-sensitized solar cells applications. A DSSC using ZnO nanofiber mats exhibited a conversion efficiency of 1.34% under 100 mW/cm² illumination. The simplicity and versatility of these techniques, it is believed, will establish promising opportunities in the processing of nanostructured materials with enhanced surface activity for various applications, including solar cells.

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