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Short communication

Enhanced photovoltaic performance of dye-sensitized solar cells using TiO_2-decorated ZnO nanorod arrays grown on zinc foil

Taibo Guo, Yiqing Chen*, Lizhu Liu, Yinfen Cheng, Xinhua Zhang, Qiang Li, Meiqin Wei, Baojiao Ma

School of Materials Science and Engineering, Hefei University of Technology, Hefei, Anhui 23009, PR China

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ABSTRACT

TiO_2-decorated ZnO nanorod arrays directly grown on zinc foil are fabricated by a two-step approach combining hydrothermal oxidation and a sol–gel process for dye-sensitized solar cells (DSSCs) applications. Its dye absorption and light harvesting are increased by decoration with a TiO_2 particle layer, resulting in enhancement of the photocurrent density. In addition, the open-circuit voltage (V_{OC}) of the DSSCs is improved by suppressing interfacial carrier recombination. As a result, the conversion efficiency (η) of the TiO_2-decorated ZnO photoanode is increased by a factor of 1.78 compared with that of the bare ZnO. The electrochemical impedance spectroscopy (EIS) analysis shows that depositing TiO_2 particles on the surface of the ZnO nanorod arrays can effectively extend electron lifetime and decrease electron recombination rate.

1. Introduction

Dye-sensitized solar cells (DSSCs), as a potential, cost-effective alternative to silicon solar cells, based on a dye-sensitized wide-band-gap nanocrystalline semiconductor (typically TiO_2 and ZnO) films have attracted widespread attention since they were first introduced by O'Regan and Grätzel in 1991 [1]. ZnO is a promising candidate for an alternative anode material, since it possesses an energy-band structure and physical properties similar to those of TiO_2, while it has higher electron mobility, lower combination rate, and better crystallization compared with TiO_2 [2,3]. Recently, DSSCs based on one-dimensional (1D) ZnO nanostructures, including nanowires and nanotubes, have begun to attract wide attention because of better electron mobility in 1D structures [4–6]. However, as photoanode materials, the poor adhesion between ZnO nanostructures and the *F*-doped SnO_2 (FTO) substrate is a key problem, which has limited the application of ZnO nanostructure in DSSCs. Although the adhesion can be improved by the annealing of the seed layer, it seems difficult to avoid peeling of the substrates in large-scale production [7]. In addition, ZnO-based DSCCs have disadvantages of the relative instability of ZnO when exposed to dye-loading solutions as ZnO readily reacts with dye molecules to form insulating complexes (Zn^{2+}/dye agglomerates), which may hinder electron injection from the dye molecules to the semiconductor [8]. One way to improve stability of ZnO-based DSCCs is to modify the surface chemistry via a coating layer. Moreover, the decorating layer is also believed to play a role in suppressing the recombination rate by passivating the recombination sites on the ZnO surface and by forming an energy barrier that prevents the injected electrons from approaching the nanowire surface [9,10].

To overcome the above limitations, a novel ZnO-based photoanode has been fabricated using zinc foil as a substrate instead of fluorine-doped SnO_2 (FTO) transparent conducting glass, and further modified by TiO_2 particles deposited on the surface of the ZnO nanorods for DSSC applications. The TiO_2-decorated ZnO (TiO_2/ZnO) nanorod arrays on flexible zinc foils have been fabricated by a two-step process, first giving a vertical ZnO nanorod arrays grown on zinc foil under hydrothermal condition, then followed by depositing TiO_2 particles on the surface of the ZnO nanorods using a sol–gel method. These cells have the advantages of low cost, simple preparation procedure, and naturally good adhesion between the ZnO nanorod arrays and the zinc foils. Furthermore, ohmic contact between the ZnO nanostructures and the zinc substrate facilitates electron transport and collection [11]. In addition, TiO_2 particles dispersed between ZnO nanorods can offer a high surface area for dye loading. The morphology, structures, and photoelectrochemical properties are characterized and studied in detail. The current–voltage results indicate that the solar conversion efficiency of DSSCs made using TiO_2 decoration is increased by a factor of 1.78, compared with those without TiO_2.

2. Experimental

2.1. Synthesis of TiO_2-decorated ZnO nanorod array electrodes

In a typical procedure [12], the clean zinc foils, as both the zinc source and the substrates, were immersed in a solution of

* Corresponding author. Tel.: +86 551 290 4636; fax: +86 551 290 1362.
E-mail address: chenyq63@126.com (Y. Chen).

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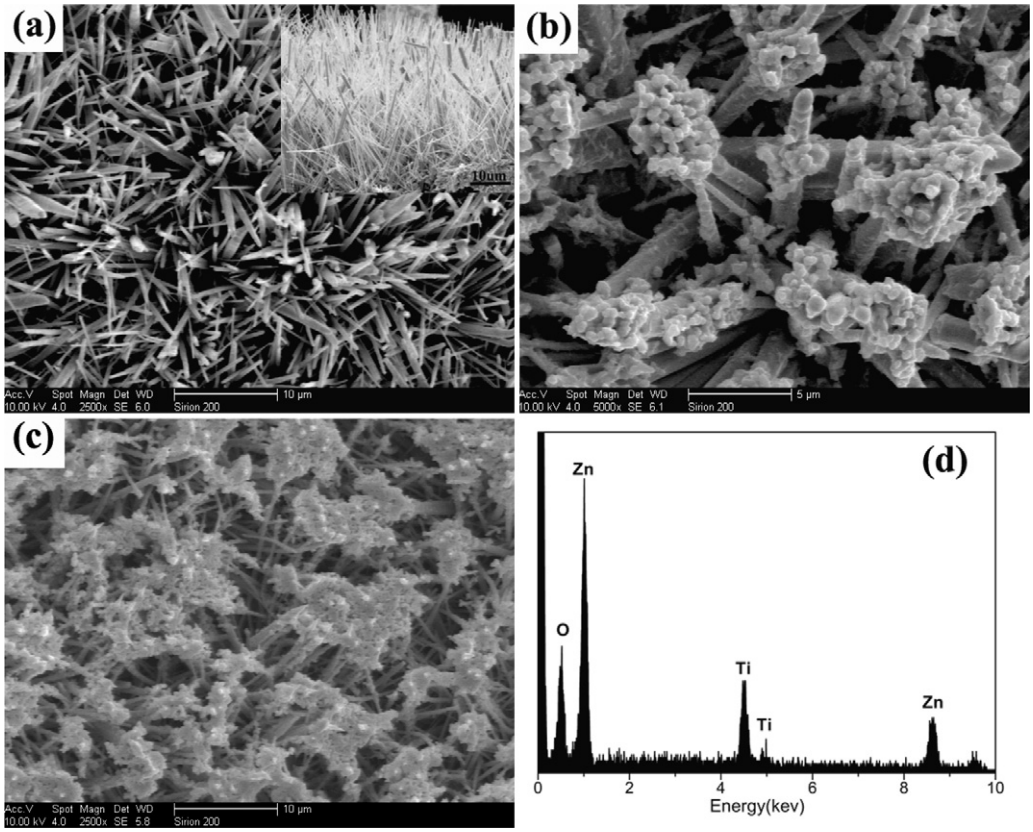

Fig. 1. (a) Top-view SEM image of the as-prepared ZnO nanorod arrays grown on a zinc foil. The inset is a side-view SEM image. (b) and (c) SEM images of TiO_2/ZnO nanostructures with dip-coating times of 10 cycles and 30 cycles, respectively. (d) Corresponding EDS pattern of the ZnO nanorods arrays after dip-coating times of 10 cycles.

ethylenediamine (12 mL), ethanol (10 mL) and water (13 mL). The solution was placed in a Teflon-lined stainless steel autoclave (50 mL), and was heated to, then maintained at a temperature of 170 °C for 20 h. The resulting zinc foils carrying ZnO nanorods were taken out and thoroughly rinsed with ethanol and dried in air. Subsequently, the surface of the ZnO nanorod arrays was decorated with TiO_2 particles by dipping in a well-dispersed TiO_2 sol (tetrabutyltitanate (0.2 M) in ethanol, modified with acetylacetone), water, and ethanol. Each dip-coating cycle took 10 s and each sample was given different number of cycles. The as-synthesized films were dried at 100 °C for 10 min, and heated to 450 °C for 2 h in air to obtain the TiO_2-decorated ZnO nanorod arrays.

2.2. Fabrication of DSSC

For DSSC fabrication, TiO_2-decorated ZnO nanorod array electrodes were immersed in a 0.3×10^{-3} mol L^{-1} ethanol solution of N719 (cis-diisothiocyanato-bis(2,20-bipyridyl-4,40-dicarboxylato) ruthenium(II) bis(tetrabutylammonium), Dalian HeptaChroma SolarTech, China) for 2 h for dye loading. The DSSCs were assembled by sandwiching the (Zn foils)/(dye-sensitized TiO_2/ZnO nanorod array anodes)/(Pt-coated FTO cathodes) using a frame of thermoplastic films (Surlyn™ 1702, Dalian HeptaChroma SolarTech, 25 μm thick) and were laminated for about 1 min at 125 °C. The internal space of the cell was filled with an electrolyte (0.5 M LiI, 50 mM I_2, 0.5 M 4-tertbutylpyridine in 3-methoxypropionitrile, Dalian HeptaChroma SolarTech) by capillary action through a small predrilled hole in the counter electrode. The total active electrode area was 0.20 cm^2.

2.3. Characterization and photoelectrochemical measurement

The morphology and the structure of the hybrid electrodes were characterized by field emission scanning electron microscopy (FESEM: FEI Sirion 200, USA) and X-ray diffraction (XRD: X'Pert PRO, PHILIPS). To study the composition, the sample was subjected to energy dispersive X-ray spectrum (EDS, Oxford INCA). The optical absorption spectra of the dye coated electrodes were measured by a UV–Vis-NIR spectrophotometer (DUV-3700, SHIMADZU, Japan). The photovoltaic performance of the DSCCs was measured by a Keithley 4200 under a solar simulator (XES-301S, NIPPON SOKKI, Xenon lamp, AM 1.5, 100 mW cm^{-2}), and the incident light intensity was calibrated with a standard crystalline silicon solar cell. Electrochemical impedance spectra (EIS) were measured using an electrochemical work station (CHI660D, CH Instruments, Shanghai) at V_{OC} with a bias alternating current (AC) signal of 5 mV in the frequency range of 1–10^5 Hz.

3. Results and discussion

The morphology of the ZnO nanorod arrays grown on a zinc foil substrate is shown in Fig. 1a. The nanorod arrays are of diameters ranging from 200 to 500 nm and lengths of about 15 um (from the side view of inset). The surface of the nanorods is smooth, and aligned ZnO nanorods directly grow on the Zn substrate. It can be observed that a large number of particles are coated on the surfaces of ZnO nanorods after 10 cycles of dip-coating, as shown in Fig. 1b. With 30 cycles of dip-coating many more particles penetrated and were dispersed between the ZnO nanorods, with the larger fraction coating the top surface of the arrays (Fig. 1c). The EDS spectrum (Fig. 1d) indicates that the nanorod arrays are composed of the elements Zn, Ti, and O after 10 cycles of dip-coating.