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Enhanced photovoltaic performance of dye sensitized solar cell with ZnO nanohoneycombs decorated TiO_2 photoanode

Qing-lan Ma [a], Shuqing Ma [b], Yuan Ming Huang [c,*]

[a] School of Electronics and Information, Nantong University, Jiangsu 226019, China
[b] Watang Central School, Xingxian Education Bureau of Science and Technology, Shanxi 033600, China
[c] School of Mathematics and Physics, Changzhou University, Jiangsu 213164, China

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ABSTRACT

Zinc oxide (ZnO) nanohoneycombs were grown on the titanium dioxide (TiO_2) layers of the photoanodes for dye sensitized solar cells (DSSC) via hydrothermal method at 93 °C for 5 h and then at 50 °C for 16 h. The photovoltaic performance of TiO_2 based DSSCs with ZnO nanohoneycombs decorated photoanodes was investigated. Under the illumination of an air mass 1.5 solar simulator, the short-circuit current density of TiO_2 based DSSCs with the decoration of ZnO nanohoneycombs was 21.48 mA/cm^2, which was higher than that of TiO_2 based DSSCs without the decoration of nanohoneycombs (7.65 mA/cm^2). The high specific surface area in ZnO nanohoneycombs enhances the power conversion efficiency (η) of the DSSCs. It is found that the η of the TiO_2 based DSSCs is 5.85% in the presence of ZnO nanohoneycomb decoration but only 4.12% in the absence of ZnO nanohoneycomb decoration. The enhanced photovoltaic performance of DSSCs with ZnO nanohoneycombs decorated TiO_2 photoanodes can be ascribed to the high specific surface area of ZnO nanohoneycombs and more efficient pathways for electron transportation from the electrolyte to the electrode.

1. Introduction

Dye sensitized solar cells (DSSCs) have been intensively investigated as alternative candidates for the next generation photovoltaic cells due to their low cost and low environmental impact competed with conventional silicon based solar cells since they were first introduced by O'Regan and Grätzel in 1991 [1]. The structure of a typical DSSC consists of a photoanode containing with the wide bandgap semiconducting material TiO_2, a liquid electrolyte containing with I^-/I_3^- redox couple and a platinum counter electrode. A photosensitizing dye, anchored to the surface of the wide bandgap semiconductor in the photoanode, absorbs light [2,3]. Under illumination, the excited dye molecule releases photoelectrons and injects the electrons into the wide bandgap semiconductor. Therefore, an effective light harvest and a good electron transport in photoanode are necessary for obtaining high conversion efficiency of DSSCs [4–7]. It is well known that a high recombination rate of electron with oxidized dye or I_3^- often occurs at the interface between photoanode and electrolyte [8–10]. An energy barrier layer between the electrolyte and TiO_2 film can help suppress such kind of electron recombination, and a variety of metal oxides such as ZnO [11–14], MgO [15] and Nb_2O_5 [16] have been utilized to decorate the TiO_2 based photoanodes. The nanostructures (including nanorods, nanotubes, nanowires and so on) of these metal oxides are widely applied to DSSCs since they can provide large surface area for dye adsorption as well as direct pathways for electron transportation from the electrolyte to the TiO_2 based photoanodes [17–20]. Because the electron mobility is much higher in ZnO than in TiO_2 and bandgap is similar to TiO_2 [21], ZnO nanostructures such as nanorods, nanowires and nanohoneycombs become a promising candidate for the photoanode decoration. Recently, Huang *et al.* reported the enhanced photovoltaic performance of DSSCs with ZnO nanorods decorated TiO_2 photoanode [12,13,22]. Yang *et al.* reported that the incorporation of ZnO nanowires scaffolds in the TiO_2 photoanode can significantly improve the photovoltaic performance due to the enhanced electron transport and improved light-scattering [6]. However, no research work of TiO_2 based DSSCs with ZnO nanohoneycomb decorated photoanode has been investigated.

A high-performance ZnO nanohoneycomb photoanode must have a large surface area for dye adsorption and efficient light absorption in order to enhance conversion efficiency. In this work, we used ZnO nanohoneycombs to decorate on the TiO_2 layers in the photoanodes. It is found that the power conversion efficiency of the ZnO nanohoneycomb decorated DSSCs was as 1.42 times

* Corresponding author.
E-mail address: dongshanisland@126.com (Y.M. Huang).

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as that of the ZnO nanohoneycombs decorated DSSCs. The enhanced photovoltaic performance can be attributed to the high specific surface area of the ZnO nanohoneycombs decorated layer in DSSCs.

2. Experiment details

2.1. Preparation of TiO_2 coated FTO substrates

Fluorine-doped tin oxide (FTO, sheet resistance ~14 Ω/cm^2, thickness 2.2 mm) conductive glass was purchased from Wuhan Geao Co., Ltd and used as electrode substrates for our DSSCs. A compact TiO_2 layer of around 40 nm thickness was deposited on the cleaned FTO substrate by immersing the FTO substrate into the aqueous solution of $TiCl_4$ (40 mM) at 70 °C for 30 min and then drying in air. After having been sintered in a furnace at 450 °C for 30 min, the FTO substrate was coated with a 14-μm-thick layer of porous TiO_2 nanoparticles (P25, Degussa) via the doctor blade technique. Plastic spacers were utilized to control the thichkness of the porous TiO_2 layer on the FTO substrate. The TiO_2 coated anodes were annealed at 450 °C for 30 min followed by another 40 mM $TiCl_4$ treatment. This treatment is crucial to cell performance as a TiO_2 sol gel is formed and fills gaps in the mesoporous TiO_2 nanoparticle layer preventing recombination of e−/h+ pairs. A scattering layer composed of 300 nm TiO_2 nanoparticles (Dyesol Inc., MS002260) was added on top of the active layer and then annealed at 450 °C for 30 min.

2.2. Decoration of the TiO_2 with ZnO nanohoneycombs

Both the ZnO nanoparticles and the ZnO nanohoneycombs were grown on the TiO_2 layer by the hydrothermal route. At first, a ZnO seed layer was grown on the TiO_2 layer using the method reported by Yang *et al.* [12,13]. Next, ZnO nanohoneycombs were grown onto the ZnO-seeded TiO_2 layers. 40 mL of equal molar aqueous solution of zinc nitrate hexahydrate (0.15 M) and hexamethylenetetramine (0.15 M) was prepared and filled in a 50 mL Teflon-lined stainless steel autoclave. ZnO-seeded TiO_2 films were put face down at the top of the aqueous solution surface in the Teflon-lined stainless steel autoclave. The reaction vessel was heated to 93 °C and kept at 93 °C for 5 h and then heated to 50 °C and kept at 50 °C for 16 h, and finally was let cool down naturally. The current synthesis route has manifested unique advantage of being without any post-treatment or any surfactant.

2.3. Assembling of DSSCs

The photoanodes were prepared by dropping the ethanol solution of the N719 dye (0.4 mM) onto the ZnO nanohoneycomb decorated TiO_2 films. The platinum counter electrode was formed by immersing a cleaned FTO substrate into the ethanol solution of H_2PtCl_6 (4 mM) for 1 min, drying the substrate in air and then sintering the substrate at 450 °C for 2 h. The photoanode and platinum counter electrode were assembled into a sandwiched structure with a sealing spacer between them. The free space in the sandwiched structure was filled with a redox liquid electrolyte. The electrolyte was prepared by dissolving KI (1.712 g), I_2 (0.272 g) and water (1 mL) into acetonitrile (20 mL).

2.4. Characterization

A field-emission scanning electron microscope (FE-SEM, SUPPRA 55, Zeiss, Germany) was utilized to characterize the surface morphologies of the ZnO films. The crystalline structures of samples were analyzed by X-ray diffractometer (XRD, D/max 2500 PC, Rigaku, Japan) with a copper target radiation. The photoluminescence (PL) spectra of samples were recorded with a spectrophotometer. The 325 nm laser line from a helium–cadmium laser was employed as the excitation source for the PL measurement. The output power of the ultraviolet laser was about 12 mW. For the photocurrent-voltage (*J-V*) measurement of the DSSCs, an AM 1.5 solar simulator with a 500 W xenon lamp was employed to illuminate the DSSC, the incident light power was calibrated to 100 mW/cm^2. A Keithley model 2400 digital source meter was used to measure the open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) of the DSSCs.

3. Results and discussion

Fig. 1 shows the top-view and cross-sectional SEM images of ZnO nanohoneycomb structures that were grown on the TiO_2 coated FTO substrates at 93 °C for 5 h and then at 50 °C for 16 h. The left panel of Fig. 1 shows the ZnO honeycomb structure grown on TiO_2 layer. As can be seen in the right panel of Fig. 1, the typical ZnO nanohoneycombs possess randomly stacked and bending sheets having a relatively rough surface. The thickness of the nanohoneycomb structure grown on 16 μm-thickness TiO_2 layer was about 600 nm. The ZnO nanohoneycombs can provide high specific surface area for the photoanode in DSSCs.

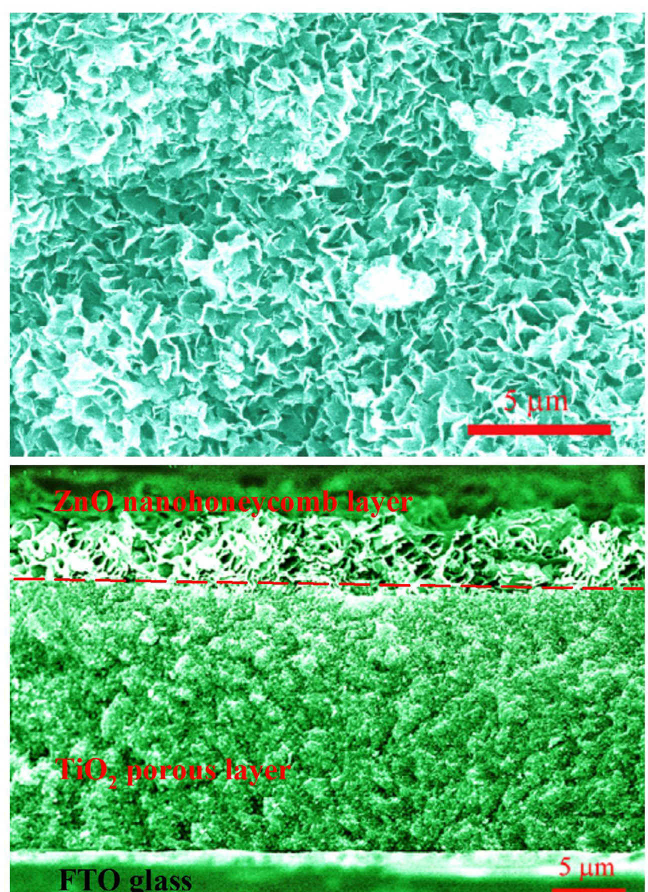

Fig. 1. Top-view and cross-sectional FESEM micrographs of ZnO nanohoneycombs grown on the TiO_2 coated FTO substrates at 93 °C for 5 h and then at 50 °C for 16 h.