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Constructing hierarchical porous titania microspheres from titania nanosheets with exposed (001) facets for dye-sensitized solar cells

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ABSTRACT

In this paper, a facile approach for constructing hierarchical porous TiO_2 microspheres from TiO_2 nanosheets with exposed (001) facets has been demonstrated, which are synthesized using HF generated in situ by reaction of $(NH_4)_2TiF_6$ and H_3BO_3 as a capping and stabilizing agent without introducing any additional HF or HCl under hydrothermal condition. The photoanode constructed with hierarchical porous TiO_2 microspheres as top layer exhibits an improved photoelectric conversion efficiency (7.44%), which is about 1.2 times larger as than that of the commercial TiO_2 nanoparticles as a benchmark photoanode (6.29%). This result is attributed to the superior light-scattering effect of microspheres, excellent light-reflecting ability of the mirror-like plane (001) facets and effective suppression of the back reaction. Therefore, TiO_2 microspheres with exposed (001) facets have the potential applications in the construction of dye-sensitized solar cells.

1. Introduction

Since the pioneering work done by O'Regan and Grätzel in the early 1990s, dye-sensitized solar cell (DSSC) has been of interest to the scientific community and the industrial community due to its high efficiency, low fabrication cost and ease of fabrication [1]. A traditional photoanode of DSSC is composed of nanometer-sized oxide particles, such as TiO_2, ZnO and SnO_2 with large surface area. The anatase TiO_2 nanoparticles have remained the highest performance photoanode material, which has reached a power conversion efficiency of 13% [2]. However, TiO_2 nanoparticles used as the photoanode are very weak for visible light scattering effect, which results in high transmittance of visible light through the semi-transparent TiO_2 film [3,4]. Moreover, the transport of the electrolyte is not efficient due to the irregularity of the pores [4]. Also, the electron transport in nanoparticle photoanode is slower than that in bulk single crystal counterparts due to the random transport of electrons and the trapping/detrapping events along the electron transport path, which facilitates electron loss by recombination [5]. In order to make up for these shortcomings, many methods have been developed for preparing TiO_2 spheres, TiO_2 hollow spheres, mesoporous TiO_2 aggregates or other structures, which can act as light-scattering layer or directly as the light-absorption layer [6–11].

Both theoretical and experimental studies indicated that the (001) surface of anatase TiO_2 is much more reactive than that of the thermodynamically stable (101) counterpart, which would be favorable for photovoltaic cells, photodegradation of organic molecules, and photocatalytic water splitting applications [12,13]. TiO_2 spheres with exposed (001) facets have attracted more attention due to their superior performance in DSSCs. It had been reported that TiO_2 spheres with exposed (001) facets show an effective light-scattering ability of the mirror-like plane (001) facets. At the same time, the (001) surface of anatase TiO_2 have a strong ability to absorb the COOH group, which can increase the dye loading of DSSCs [14–22]. Moreover, the (001) surface of anatase TiO_2 can effectively retard the charge recombination process in DSSCs, which is confirmed by dark current potential and open-circuit voltage decay scans [19]. Therefore, the (001) surface of anatase TiO_2 is a promising candidate in the field of DSSCs application.

Since the first successful preparation of single-crystal anatase TiO_2 sheets with (001) facets by using TiF_4 as the raw material and HF as a shape controlling agent, the synthesis of TiO_2 with (001) facets has received increasing research attention [23]. Up until now, many efforts have focused on the synthesis of anatase TiO_2 with (001) facets. Yang et al. improved their work by adding a synergistic capping agent (HCl and HF) to increase the percentage

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of (001) facets [24]. Han et al. demonstrated that the hydrothermal reaction of $Ti(OBu)_4$ and HF could yield nanosized sheet-like anatase TiO_2 with (001) facets [25]. DSSC by using mirror-like plane (001) TiO_2 microsphere photoanode DSSC could possess an overall efficiency of 7.91% that was 17.5% higher when compared with the commercial TiO_2 photoanode of similar thickness [26]. Yu et al. prepared a doped flower-like anatase TiO_2 with (001) facets, and applied as electrode material in DSSC, which achieved a 52% increase in photocurrent and 22% improvement in conversion efficiency as compared to the commercial TiO_2 photoanode-based DSSC [27]. However, most of these reported synthesis methods were carried out in a HF environment, which was highly toxic, corrosive and dangerous. Therefore, it is expected to explore safe and environmentally friendly capping agents to replace the highly toxic and corrosive HF.

In this study, the hierarchical porous TiO_2 microspheres with exposed mirror-like plane (001) facets have been prepared by a simple and facile hydrothermal method without usage of any additional HF. The as-prepared hierarchical porous TiO_2 microspheres exhibit excellent light-scattering property, which was applied to fabricate a novel hierarchically structured photoanode as the light-scattering top layer and commercial TiO_2 nanoparticles as the bottom layer. The DSSC possesses an overall efficiency of 7.44%, which is 18.3% higher than that of the commercial TiO_2 nanoparticle based DSSC.

2. Experimental

2.1. Chemicals and materials

Ammonium hexafluorotitanate ($(NH_4)_2TiF_6$, CP, 98%) was purchased from Aladdin Chemical Reagent Co. Ltd.. Boric acid (H_3BO_3, AR) was obtained from Guangdong Guanghua Chemical Factory Co. Ltd.. All of the chemicals were used without further purification. N719 dye ($[(C_4H_9)_4N]_2[Ru(II)L_2(NCS)_2]$, where L = 2, 2′-bipyridyl-4, 4′-dicarboxylic acid) was purchased from Solaronix. The substrates were commercial FTO (fluorine-doped tin oxide glass, 14 $\Omega/\square$) from Nippon Sheet Glass Co. Ltd..

2.2. Materials synthesis

Hierarchical porous TiO_2 microspheres with (001) facets were prepared by a one-step hydrothermal method. In a typical synthesis procedure, 3.0 mmol of $(NH_4)_2TiF_6$ (0.5938 g) and 4.0 mmol of H_3BO_3 (0.2473 g) were dissolved in 40.0 mL of deionized water. After stirred for about 30 min to obtain a homogeneous solution, the reaction solution was transferred to a Teflon-lined stainless-steel autoclave (50 mL capacity). Afterwards, the sealed autoclave was heated at 150 °C for 12 h in an electric oven, and then cooled to room temperature. The final products were centrifuged, washed with deionized water and absolute ethanol for several times. Finally, they were dried at 70 °C for 3 h in air.

2.3. Materials characterizations

The compositions and crystal structures of the products were analyzed by X-ray diffraction (XRD, D8 ADVANCE X-ray diffractometer, Cu Kα radiation λ=0.15418 nm) with a scanning rate of $10^{\circ}\ min^{-1}$ in the 2θ from 20 to 80°. The surface morphology and size of samples were investigated by field emission scanning electron microscopy (FE-SEM, JSM-7100F). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEOL-2010 HR transmission electron microscope. To determine the Brunauer-Emmett-Teller (BET) surface area and pore size distribution of the sample, the N_2 sorption measurement was performed by using an Autosorb-iQ surface area analyzer (Quantachrome Instruments US). UV-vis diffuse reflectance spectra and absorption spectra were measured on a UV-Vis-NIR spectrophotometer (UV-1901, Beijing Purkinje General Instrument Co. Ltd., China) to measure the diffuse reflectance of films and dye amounts detached from films, respectively.

2.4. Preparation of TiO_2 photoanode

Viscous pastes (commercial TiO_2 nanoparticles and hierarchical porous TiO_2 microspheres) were prepared according to the procedures described in our previous work [28]. In brief, hierarchical porous TiO_2 microspheres (1.0 g) were ground for 40 min in the mixture of ethanol (8.0 mL), acetic acid (0.2 mL), terpineol (3.0 g) and ethyl cellulose (0.4 g) to form the slurry, which was sonicated for 20 min in an ultrasonic bath and finally to form a viscous white TiO_2 paste. These pastes were then deposited on FTO glass substrate to form a photoanode by using the screen-printing technique, which were kept in a clean box for 3 min and dried for 6 min at 125 °C. The thickness of TiO_2 film could be controlled by repeating the printing number and changing the concentration of the paste. The photoanodes were annealed by a calcination process in the furnace through a programmed temperature process at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and finally at 500 °C for 15 min to remove the organic compounds.

2.5. Fabrication and photovoltaic measurements of DSSCs

The as-prepared TiO_2 photoanodes were immersed in a 40.0 mM $TiCl_4$ solution at 70 °C for 30 min, then calcined at 520 °C for 30 min. After cooling down to ~80 °C, the TiO_2 photoanodes were immersed into 0.5 mM N719 dye solution (acetonitrile and tert-butyl alcohol with a volume ratio of 1: 1) for 16 h at room temperature. Afterwards, the dye-sensitized TiO_2 photoanodes were rinsed with acetonitrile to remove physisorbed N719 dye molecules. To evaluate their photovoltaic performances, the dye-sensitized TiO_2 photoanodes were sandwiched together with Pt coated FTO glass, which was used as the counter electrode and were fabricated by thermal-deposition of H_2PtCl_6 solution (5.0 mM in isopropanol) onto FTO glass. The electrolyte is a solution composed of 0.03 M I_2, 0.05 M LiI, 0.6 M 1-methyl-3-propylimidazolium iodide (PMII), 0.10 M guanidinium thiocyanate (GuSCN), and 0.5 M tert-butylpyridine (TBP) in a mixture of acetonitrile and valeronitrile (volume ratio 85: 15), which was introduced from a hole made on the counter electrode into the space between the sandwiched cells.

The photocurrent-voltage characteristics of DSSCs were recorded using a Keithley model 2400 digital source meter under one sun AM 1.5 G ($100\ mW\ cm^{-2}$) illumination with a solar light simulator (Oriel, Model: 94,041A). A 450 W Xenon lamp was served as a light source and its incident light intensity was calibrated with a NREL-calibrated Si solar cell to approximate AM 1.5 G one sun light intensity before each measurement. The thickness of TiO_2 films was measured by using a D-100 profilometer of KLA-Tencor. The active area of photoanode was 0.16 cm^2. Electrochemical impedance spectroscopy (EIS) measurements were performed with a Zennium electrochemical workstation (ZAHNER) with the frequency range from 10 mHz to 1000 kHz and the magnitude of the alternative signal as 10 mV, which were carried out under forward bias of −0.84 V in the dark.

3. Results and discussion

XRD analysis was used to examine the crystal structure of the obtained TiO_2 sample. A typical XRD pattern of the as-prepared (001) TiO_2 porous microspheres is shown in Fig. 1. It can be seen