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Original Research Paper

A hierarchical homogeneous core–shell structure of TiO_2 hollow microspheres for high efficiency dye-sensitized solar cells

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ABSTRACT

Core–shell TiO_2 (cs-TiO_2) hollow microspheres are prepared via a facile hydrothermal method, by using titanium potassium oxalate precursor in dilute sulfuric acid. The characterization shows that the as-prepared TiO_2 microspheres have core–shell structure. The diameters of cs-TiO_2 microspheres are in the range of 2–5 μm. The optical investigation evidences that the cs-TiO_2 microsphere film exhibits a prominent light-scattering effect at a wavelength range of 600–800 nm. The cs-TiO_2 microspheres are applied as a scattering layer on top of a nanocrystalline P25 film, serving as the photoanode of dye-sensitized solar cells (DSSCs). A high efficiency of 7.7% is achieved after introducing the cs-TiO_2 hollow microsphere scattering layer, compared with 6.21% for the photoanode with commercial P25. Based on the optical investigation and electrochemical impedance measurement, the improved efficiency can be ascribed to the enhanced light-scattering ability and the reduced interface recombination rate.

1. Introduction

Since the Grätzel and O'Regan reported the groundbreaking research by using nanocrystalline TiO_2 porous film and bipyridine ruthenium (II) complexes to construct dye-sensitized solar cells (DSSCs) [1], many researches on DSSCs have been received widely attention. Compared with traditional silicon solar cells, DSSCs have lots of advantages such as low production cost, simple manufacturing technology and easy to mass production [2]. In traditional DSSCs, the photoanode has been widely constructed with TiO_2 nanocrystals with high specific surface area. However, the nanocrystals can produce the large amount of grain boundaries between nanocrystals, leading to the presence of many electron-hole recombination centers. In addition, the poor absorption of long-range wavelength light is also a key factor restricting the power conversion efficiency of DSSCs [3,4]. To attain higher efficiency DSSCs, many works have been performed, which mainly have included the improvement of specific surface area, electron transport and light-scattering effects. In recent years, many researchers have focused attention on improving light-scattering ability [5–11]. Scattering layers of various structures, such as mesoporous spheres [6,7], microplates [5], hollow spheres [8–10] and multi-hollow spheres [11], involving upper scattering layers and scattering centers, have been effectively utilized to enhance light-harvesting efficiency, thus improving the performance of DSSCs.

Because of their similarly excellent performance as mesoporous spheres, the core–shell structure is an alternative candidate for the light-scattering layers [12–16]. The unique core–shell structure can enhance light-harvesting efficiency, attributed to the multiple reflections of the incident light within the interior cavity of the multi-shelled hollow structure and the light-scattering at out surface of microspheres. Furthermore, it can facilitate the infiltration of the electrolyte and reduce the interface recombination by decreasing the surface charge trap-site density. Wang et al. prepared the hollow shell-in-shell TiO_2 microspheres and gained a high efficiency of 9.10% [11]. Zhu et al. introduced the core–shell TiO_2 as the light-scattering layer and got an efficiency of 8.22% [13]. Jiang et al. introduced spherical multi-hollow TiO_2 nanostructures and achieved a high efficiency of 8.25% [17]. As a result, the core–shell structure has good performance in solar energy conversion, so it may be used as a photoanode to replace the traditional materials.

A general approach to fabricate core–shell TiO_2 hollow spheres accompanies the use of removable or sacrificial templates [13,18–22]. They suffer from many disadvantages such as high cost, tedious procedure and collapse of the hollow structure when removing the templates, which can hinder the large-scale industrial applications. Therefore, it is highly desirable to develop a novel approach for the

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fabrication of core–shell TiO_2 hollow spheres with template-free, surfactant-free, simple manipulation, low cost and large scale production.

In this paper, we reported a novel core–shell TiO_2 hollow microspheres (labeled as cs-TiO_2) prepared by a sample one-step hydrothermal method. The cs-TiO_2 hollow microspheres were used as a light-scattering layer and got a higher conversion efficiency (7.70%) than that of Degussa P25 nanoparticles (6.21%) under AM-1.5G one sun light intensity.

2. Experimental section

2.1. Materials

Titanium potassium oxalate (analytical reagent grade) was purchased from Aladdin Reagent Co., Ltd. Concentrated sulfuric acid (95–98% by weight) was purchased from the Sinopharm Chemical reagent Co., Ltd. Ruthenium dye (N719) was purchased from Everlight Chemical Industrial Co., Taiwan. Transparent conductive fluorine-doped tin oxide (FTO) conducting glass substrates (14 Ω/□, 2.3 mm thick) were purchased from Nippon Sheet Glass Co., Ltd.

2.2. Preparation of cs-TiO_2 microspheres

The typical approach for the preparation of cs-TiO_2 microspheres was as follows: titanium potassium oxalate (0.53 g) was dissolved into 30.0 mL sulfuric acid (2.0 M). The mixture was stirred for about 30 min at room temperature, and then transferred into a Teflon-lined stainless-steel autoclave (50 mL) and maintained at 180 °C for 12 h. After the reaction, the autoclave was cooled to room temperature. The products were collected and washed with deionized water and ethanol for three times, and dried in oven at 70 °C for 6 h.

2.3. Preparation of photoanode

Viscous pastes (Degussa P25 nanoparticles and cs-TiO_2 microspheres) were as-prepared according to the procedures described in our previous work [23]. In brief, 1.0 g of the as-prepared cs-TiO_2 was dispersed into the mixture of ethanol (8.0 mL) and acetic acid (0.2 mL). Then 3.0 g terpineol and 0.4 g ethyl cellulose were added to the above solution. The solution was ground for 40 min and sonicated for 20 min to obtain a viscous paste. The P25 paste was prepared by the same method. The TiO_2 pastes were then deposited on FTO glass substrates to form a photoanode film by using the screen-printing technique. The thickness of photoanode film could be controlled by repeating the printing times and changing the concentration of the TiO_2 paste. The electrodes coated with TiO_2 pastes were gradually heated at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min, respectively.

2.4. Fabrication and photovoltaic measurement of DSSCs

The resulting TiO_2 photoanodes were immersed into 40.0 mM $TiCl_4$ solution at 70 °C for 30 min, and then calcined at 520 °C for 30 min. After cooling to room temperature, the photoanodes were immersed into 0.5 mM N719 dye ($[(C_4H_9)_4N]_2[Ru(II)L_2(NCS)_2]$, where L = 2,2′-bipyridyl-4,4′-dicarboxylicacid) in acetonitrile and tert-butanol (v/v = 1:1) for 16 h at room temperature. Afterward, these photoanodes were rinsed with acetonitrile in order to remove physisorbed N719 molecules. In order to evaluate their photovoltaic performances, the dye-sensitized photoanodes were sandwiched together with Pt coated FTO glass which was used as the counter electrode. Platinized counter electrodes were fabricated by thermal-deposition of H_2PtCl_6 solution (5.0 mM in isopropanol) onto FTO glasses. The electrolyte containing 0.03 M I_2, 0.05 M LiI, 0.6 M 1-methyl-3-propylimidazolium iodide (PMII), 0.10 M guanidinium thiocyanate and 0.5 M tert-butylpyridine in acetonitrile and valeronitrile (v/v = 1:1) was finally introduced from a hole made on the counter electrode into the space between the sandwiched cells.

The photocurrent–voltage curves 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: 94041A). A 450 W Xenon lamp served as a light source and its incident light intensity was calibrated with an NREL-calibrated Si solar cell (S/N 10510-0661) to approximate AM 1.5 G one sun light intensity before each measurement. The thickness of photoanode film was measured by using a D-100 profilometer of KLA-Tencor. The active area of photoanode was 0.16 cm^2. The electrochemical impedance spectroscopy (EIS) measurements were performed with a Zennium electrochemical workstation (ZAHNER) with the frequency range from 10 mHz to 1000 kHz. The magnitude of the alternative signal was 10 mV. The impedance measurements were carried out under forward bias of -0.83 V in the dark. Incident photon to current conversion efficiency (IPCE) was measured on photo current spectra system of CIMPS (Zahner, PP211, CIMPS-PCS, Germany) with tunable light source (TLS03).

2.5. Characterizations

The compositions and crystal structures of the products were analyzed by X-ray Powder Diffraction (XRD) on a Rigaku Ultima IV X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15418 nm) at a scan rate of 10° min^{-1} in the 2θ from 20° to 80°. The morphology and size of the sample was characterized by the field emission scanning electron microscopy (FE-SEM, JSM-7100F). The transmission electron microscopy (TEM) was performed on a JEOL-2010 HR transmission electron microscope. The specific surface area and pore size distribution of TiO_2 powder were measured at the N_2 adsorption-desorption isotherm by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods using an Autosorb-iQ surface area analyzer (Quantachrome Instruments US). The diffuse reflectance of TiO_2 films and desorption of dyes were measured by UV–Vis-NIR spectrophotometer (UV-1901, Beijing Purkinje General Instrument Co., Ltd).

3. Results and discussion

The phase purity and structure of the as-prepared products were characterized by XRD measurement. As shown in Fig. 1, the XRD pattern reveals all diffraction peaks agree well with pure anatase phase TiO_2 (JCPDS card No. 78-2486). Four main diffraction peaks at 2θ values of 25.3°, 37.8°, 48.0° and 55.0° can be assigned to the (101), (004), (200) and (211) lattice planes of anatase TiO_2. The sharp (101) peak indicates that the as-prepared TiO_2 sample is highly crystalline. By using the Scherrer equation, the crystallite size is about 33.9 nm as estimated from the full width at half maximum of the (101) peak. No characteristic peaks of other phases or impurities are detected, revealing that the as-prepared products are of high purity.

The morphologies of the products were characterized by FE-SEM technique. Fig. 2a shows a panoramic FE-SEM image of the as-prepared core–shell TiO_2 microspheres. The diameters of TiO_2 microspheres are in the range of 2–5 μm. A high-magnification FE-SEM image reveals that the TiO_2 microspheres are produced from