Journal of Power Sources 253 (2014) 269–275

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Sugar apple-shaped TiO_2 hierarchical spheres for highly efficient dye-sensitized solar cells

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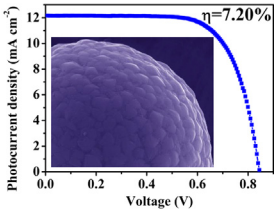
HIGHLIGHTS

- The sugar apple-shaped TiO_2 hierarchical spheres were prepared by a facile hydrothermal method.
- The TiO_2 hierarchical spheres had a prominent light scattering effect.
- DSSCs based on TiO_2 double-layer film had the maximum conversion efficiency.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 October 2013
Received in revised form
8 December 2013
Accepted 10 December 2013
Available online 18 December 2013

Keywords:
Titania
Microspheres
Light scattering
Hierarchical nanostructure
Dye-sensitized solar cells

ABSTRACT

The sugar apple-shaped TiO_2 hierarchical spheres are prepared by a facile hydrothermal method using polyethylene glycol 600 as stabilized reagent, $(NH_4)_2TiF_6$ and urea as starting materials at 180 °C. The characterizations show that the TiO_2 hierarchical sphere has well-defined pyramid-shaped crystal facets. The as-prepared TiO_2 hierarchical spheres are crystalline of the anatase phase, with a diameter of about 2 −4 μm and a surface area of 36.846 $m^2\ g^{-1}$. The optical investigation evidences that the sugar apple-shaped TiO_2 hierarchical sphere film exhibits a prominent light scattering effect at a wavelength range of 600−800 nm due to the unique hierarchical morphology. Furthermore, the sugar apple-shaped TiO_2 hierarchical spheres are deposited as the scattering layer to balance the dye adsorption and light scattering effect in DSSCs and a 7.20% solar energy conversion efficiency is demonstrated, indicating an improvement compared with the P25 cell (6.68%). Based on the optical and electrochemical investigations, the high conversion efficiency is mainly due to the effective suppression of the back reaction of the injected electron with the I_3^- in the electrolyte and excellent light scattering ability.

1. Introduction

Since the first report on a low-cost dye-sensitized solar cell (DSSC) in early-1990s by O'Regan and Grätzel [1], it has been received considerable interest as a promising candidate to replace conventional inorganic photovoltaic cell. Until lately, the highest power conversion efficiency of 12.3% has been achieved [2], but this value is still lower than that of bulk silicon solar cells. However, further improvement in DSSC power conversion efficiency still remains a challenge. In recent years, more researchers have focused attention on improving the efficiency of TiO_2-based DSSC using nanostructured TiO_2 materials, especially one-dimensional TiO_2 materials (nanowires [3–6], nanorods [7,8] and nanotubes [9,10]), which are believed to gain the enhancement of efficiency because of their rapid electron transfer, reduction of charge recombination degree and enhancement of carrier collection through direct transport pathway. Although one-dimensional TiO_2 materials have been regarded as ideal photoanodes for direct electron transport, the performances of the corresponding DSSCs still lag behind those made of mesoporous nanoparticle photoanodes, due to low specific surface area ascribed to larger diameter and/or free space among the neighboring 1D materials (nanotubes, nanorods or nanowires). As a result, the mesoporous particle-based photoanodes are still the workhorse in DSSC research and the closest to practical application.

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0378-7753/$ – see front matter
http://dx.doi.org/10.1016/j.jpowsour.2013.12.035

The overall performance of nanoparticle-based DSSC is still lower than theoretical value due to severe photo-generated electron recombination and poor utilization of near infrared photons. There has been a general consensus that the performance of DSSCs can be further improved by maximizing light harvesting efficiency. To this end, much effort has been dedicated to explore new means to improve light harvesting efficiency [11–22]. The earliest exploited constructions are to incorporate large particles with spherical shape or flat surface into the nanocrystalline TiO_2 matrix or on top of the nanocrystalline TiO_2 layer, which can confine the incident light within the photoanode and increase the optical path of light [15–17]. However, large spherical or flat particles inevitably reduce the surface area of the photoanode and decrease the dye loading. Therefore, it is useful to increase light absorption by scattering effects while maintaining a high surface area of the photoanode for efficient dye adsorption. In recent years, many researchers have made attempts to develop TiO_2 hierarchical microspheres composed of nanoparticles, aiming to provide both high surface area and/or excellent light scattering ability [18–22]. Such TiO_2 microspheres have sub-micrometer or micrometer sizes and thus enhance light scattering ability, while the nanometer-sized building units provide more available surface for dye loading. In spite of the reasonable power conversion efficiency achieved with these TiO_2 hierarchical microspheres, there is still plenty of room for improvements, such as crystallinity, charge transport and dye adsorption capacity.

Herein, we have successfully prepared the sugar apple-shaped TiO_2 hierarchical spheres by a facile hydrothermal method. The hierarchical TiO_2 spheres are around 2–4 μm in size, and possess a surface area of 36.846 $m^2\ g^{-1}$. The optical investigation evidences that the sugar apple-shaped TiO_2 hierarchical sphere film has a prominent light scattering effect at a wavelength range of 600–800 nm. Furthermore, we use these sugar apple-shaped TiO_2 hierarchical spheres as the scattering layer to balance the dye adsorption and light scattering effect in DSSCs and a 7.20% solar energy conversion efficiency is demonstrated.

2. Experimental section

2.1. Preparation of the sugar apple-shaped TiO_2 hierarchical spheres

All chemicals were analytical-grade reagents and were used without further purification. In a typical experimental procedure for the preparation of the sugar apple-shaped TiO_2 spheres, 5.0 mmol $(NH_4)_2TiF_6$ was dissolved into 40.0 mL H_2O, adding 1.0 mL polyethylene glycol 600 (PEG-600) drop by drop. Subsequently, 45.0 mmol urea was added slowly under stirring. The mixture was kept on stirring for about 30 min to obtain a clear solution, and transferred in a Teflon-lined stainless-steel autoclave (50 mL). Then the autoclave was sealed and maintained at 180 °C for 12 h in an oven. After the reaction, the autoclave was cooled naturally to room temperature. The products were collected and washed with deionized water and ethanol for several times, and finally dried in oven at 50 °C for 6 h.

2.2. Characterizations of the sugar apple-shaped TiO_2 hierarchical spheres

The phase purity of the products was characterized by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ=1.5418 Å). The field emission scanning electron microscopy (FE-SEM, JSM-7100F) was performed to characterize the morphology and size. 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 samples, the N_2 sorption measurements were 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.

2.3. Preparation of TiO_2 working electrode

Both pastes of P25 particles (Degussa) and TiO_2 hierarchical spheres were prepared according to Ref. [23]. Briefly, the TiO_2 powder (1.0 g P25 or the as-prepared TiO_2 hierarchical spheres) was 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, and then the slurry was sonicated for 20 min in an ultrasonic bath and finally to form a viscous white TiO_2 paste. The TiO_2 photoanodes were prepared via screen-printing of the above TiO_2 paste on the FTO glass substrate (Nippon Sheet Glass, SnO_2 with sheet resistance of 14 $\Omega\ \square^{-1}$). The TiO_2 film thickness could be controlled by repeating the printing number and changing the concentration of the paste. The TiO_2 films 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 then at 500 °C for 15 min) to remove the organic compounds.

2.4. Fabrication and photovoltaic measurement of DSSCs

The TiO_2 films were immersed in 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 films 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′-dicarboxylic acid, Solaronix SA, Switzerland) in acetonitrile/tert-butanol (volume ratio 1:1) for 16 h at room temperature. Afterward, these films were rinsed with acetonitrile in order to remove physisorbed N719 dye molecules. To evaluate their photovoltaic performances, the dye-sensitized TiO_2/FTO glass films 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 glass. The electrolyte, 0.03 M I_2, 0.6 M 1-methyl-3-propylimidazolium iodide (PMII), 0.10 M guanidinium thiocyanate, and 0.5 M tert-butylpyridine in acetonitrile and valeronitrile (volume ratio 85:15), 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: 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 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. 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 (CIMPS-PCS) with tunable light source (TLS03).