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Mesoporous Hierarchical Anatase for Dye-sensitized Solar Cells Achieving Over 10% Conversion Efficiency

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ABSTRACT

Interest in both one-dimensional and hierarchical architectures of metal oxide semiconductors has intensified within the field of materials science over recent years. Herein, a new mesoporous anatase TiO_2 architecture that combines these two concepts, as it is composed of individual, high-aspect-ratio, nanoribbon-like components, was synthesized via a facile hydrothermal method without any surfactant or template. An 8.3% solar-to-electric conversion efficiency was obtained when these structures were used in photoanodes for dye-sensitized solar cells, which are superior to commercial state-of-the-art TiO_2 (6.6%), due to enhanced dye loading and efficient light scattering. To further improve the light scattering effect, a bi-layer structure was rationally designed (with this architecture as a scattering layer on top of a transparent, 12-μm-thick layer of nanocrystalline TiO_2). A high efficiency of 10.3% was achieved, compared with an efficiency of 8.2% for the control electrode (optimized transparent/reflective commercial titania paste) with a scattering layer of similar thickness.

1. Introduction

Since Dye-sensitized Solar Cells (DSCs) were first reported by O'Regan and Grätzel in the early 1990s, they have captured a great deal of both scientific and popular attention due to their reduced energy input, projected low cost, and ease of fabrication in manufacture [1,2]. Considerable efforts have been made to improve the energy conversion efficiency by developing or modifying DSC components, such as sensitizers [3–5], photoanodes [6,7], electrolytes [8,9], and counter electrodes [10–12]. As the key element of the DSC device, the TiO_2 photoanode, sensitized by a chromophore (whether it be a quantum dot, polypyridil Ru-containing complex, or organic donor-acceptor unit), acts as both a physical support for the sensitizer and a means of charge transport. Photoinjected electrons travel from the TiO_2 network to the fluorine doped tin oxide (FTO) substrate by diffusion, but are strongly limited by trapping and detrapping, both within particles and at grain boundaries. This process facilitates carrier recombination within the electrolyte at the surface. Electron transport is limited due to the mesoporous structure, which can hinder higher conversion efficiencies.

One method of improving DSC efficiency is to ensure that the electron diffusion length is greater than the TiO_2 film thickness. Highly crystalline (less internal traps) one-dimensional (1D) or 2D nanostructures, such as wires [13,14], tubes [15,16], rods [17,18], belts [19,20], fibers [21–23], and sheets [24,25], have attracted much attention because of their faster electron transport. The probability of charge recombination is reduced in 1D crystalline nanostructures, as compared to polycrystalline structures which have many grain boundaries. Enhanced electron diffusion length of low-dimensional TiO_2 has been demonstrated with vertically aligned TiO_2 nanowires and nanotubes synthesized by electrochemical anodization using Ti metal [26–32]. When 1D nanostructures were employed as photoanodes, the recombination rate was 10 times slower than for the conventional nanoparticle film [33]. It is, however, more difficult for the liquid electrolyte to

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penetrate into the 1D nanostructure than into the nanoparticle network. In addition, many 1D nanostructures suffer from having a lower surface area, which leads to reduced dye loading and light harvesting, and hence lower energy conversion efficiency, η.

The synthesis of hierarchical architectures with high surface area and efficient light trapping is another route to higher η [34–36]. In this work, we present a novel architecture combining these two concepts (one-dimensional and hierarchical structuring) via a facile hydrothermal method, without any surfactant or template. This architecture consists of hierarchical assemblies of high-aspect-ratio nanocrystalline ribbons of anatase TiO_2, morphologically resembling a spheres and giving rise to a sea-urchin-like structure. When sensitized by N719 and used as a photoanode in a DSC, along with a I_3^-/I^- redox mediator-based electrolyte, this system can provide an η of 8.3% under simulated air mass (AM) 1.5 sunlight irradiation, a 26% improvement compared to commercial state-of-the-art TiO_2 (6.6%). The higher η for this morphology is due to the higher specific surface area, leading to higher dye loading and efficient light scattering. To further improve the light scattering effect, a bi-layer structure was produced (with this architecture as a scattering layer on top of a layer of transparent, 12-μm-thick, nanocrystalline TiO_2). An even higher η of 10.3% was achieved, compared with 8.2% for the Dyesol electrode (optimized transparent/reflective titania paste) with a scattering layer of 400 nm TiO_2 of similar thickness.

2. Experimental

2.1. Synthesis of Mesoporous Hierarchical Anatase TiO_2 (MHAT)

Acetic acid (AA, ACS reagent, ≥ 99.7%, Sigma–Aldrich) and titanium butoxide (TB, Ti $(OCH_2CH_2CH_2CH_3)_4$, 97%, analytical reagent, Sigma–Aldrich) were used without further purification. MHAT was prepared via a very simple acid thermal process. Briefly, 1.0 mL of TB, was added at room temperature to 30 mL AA solution whilst under stirring (with stirring maintained for 24 h). This solution was then transferred to a Teflon lined reactor (Parr Instrument Company, 45 mL) and heated to 150 °C for 12 h. Afterwards, the sample was cooled before being centrifuged and washed with distilled water and ethanol sequentially (3 cycles). Following this, the samples were dried at 90 °C overnight and calcined at 500 °C for 3 h.

2.2. Preparation of Photoanodes

Photoanodes were prepared in a manner similar to that reported previously [37]. Briefly, F: SnO_2 glass was cleaned using first soapy water, then acetone and finally ethanol before being dried. A dense TiO_2 layer was applied using spray pyrolysis of a titanium (IV) diisoproxide-*bis*-acetylacetonate (75 wt % in isopropanol, Aldrich) solution (dilution 1:9 in ethanol) at 450 °C. A screen printing paste of the MHAT was prepared using 1.0 g TiO_2 ground in ethanol and water. To this was added 0.167 mL AA, 4 g terpineol, and 0.5 g ethyl cellulose (in the form of a 10 wt % solution in ethanol). Water and ethanol were then removed using rotary evaporation, and the resulting paste was printed using a semiautomatic screen printer and custom patterned 43 T screen to create 4 mm × 4 mm electrodes. These were dried at 125 °C before subsequent layers were deposited in order to realise thicker electrodes. After all the printing steps were complete the electrodes were subjected to an extended sintering process (10 min at 150 °C, 5 min at 325 °C, 5 min at 375 °C, 30 min at 450 °C, then 15 min at 500 °C). Finally, a post-treatment was completed by soaking the electrodes in a 20 mM aqueous solution of $TiCl_4$ (Sigma) for 30 min at 70 °C and then resintering (500 °C, 30 min).

Dyesol-T, 18NR-T transparent titania paste, and Dyesol-S, WER2-O reflective titania paste, were both obtained from Dyesol (Australia).

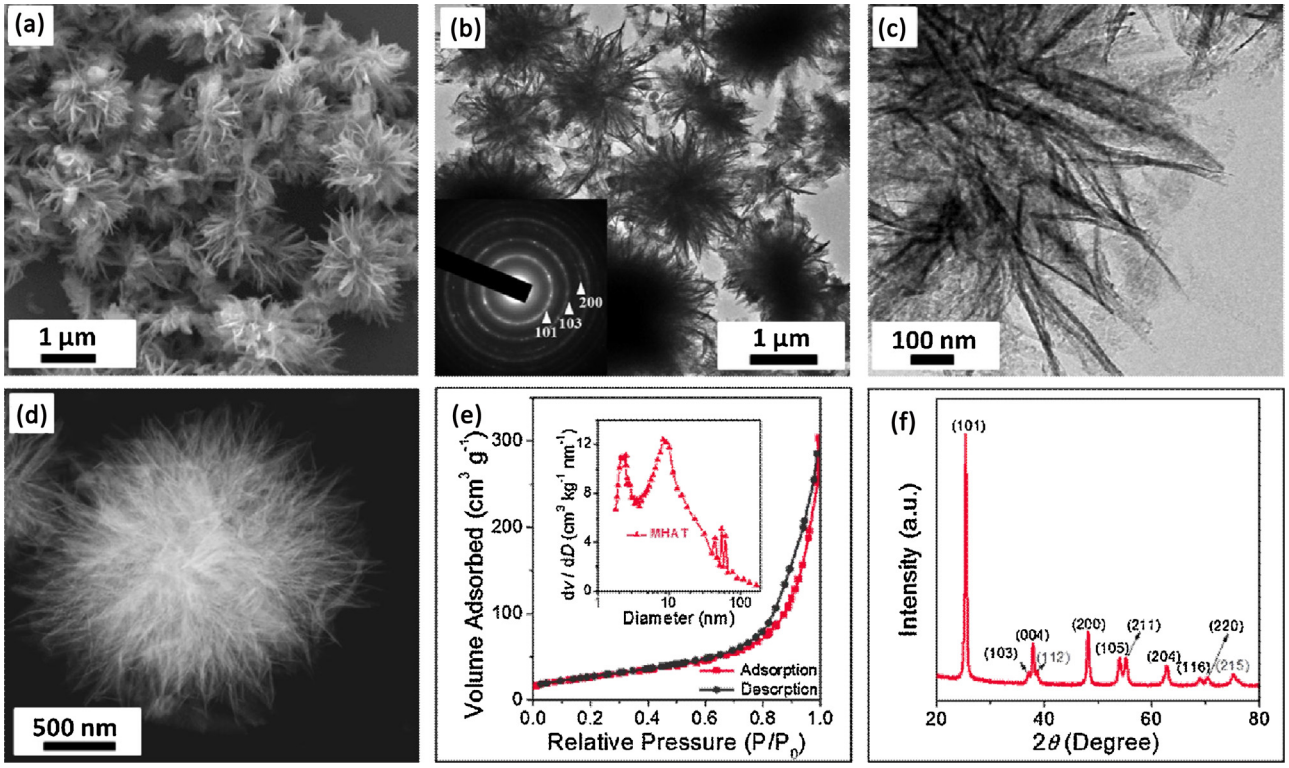

Fig. 1. Characterization of mesoporous hierarchical anatase TiO_2 (MHAT): (a) low magnification SEM image; (b) low magnification bright-field TEM image, with the inset showing the corresponding SAED pattern; (c) enlarged TEM image; (d) ADF-STEM image of a selected sphere; (e) N_2 adsorption-desorption isotherm, with the inset image showing the pore size distribution calculated from the adsorption branch of a nitrogen isotherm by the Barrett-Joyner-Halenda (BJH) method; (f) XRD pattern.