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Tunable synthesis of single-crystalline-like TiO_2 mesocrystals and their application as effective scattering layer in dye-sensitized solar cells

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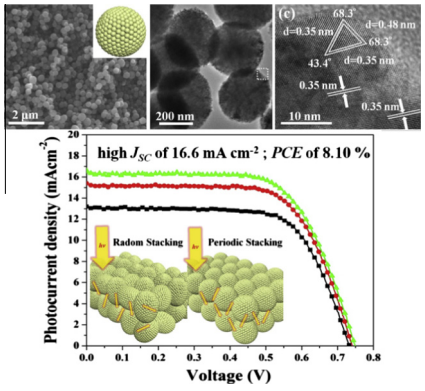
GRAPHICAL ABSTRACT



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ABSTRACT

Single-crystalline-like TiO_2 mesocrystals (TMCs) with spherical and spindle-like shapes were selectively prepared in acetic acid system using benzoic acid as structural directing regent. It was found that the intermediate butyl-benzoic acid could interval the oriented assembly of the primary nanoparticles as porogen and shape regulator, which results in spherical TMCs with greater pore size distribution compared with the spindle-like TMCs. When used as scattering layer in dye sensitized solar cells (DSSCs), the spherical TMCs with long-range ordered stacking pattern results in characteristic photonic reflection, which enhances the scattering effect of the photoanode and leads to a high short circuit current density of 16.6 mA cm^{-2}. Therefore, Cell-spherical TMCs demonstrated a high power conversion efficiencies of 8.10%, indicating substantial improvements compared with Cell-spindle-like TMCs (7.58%) and Cell-nanoparticle (6.59%).

1. Introduction

Recently, many research have been devoted to achieve the self-assembly of primary nanoparticles into superstructures with controllable architectures [1–4]. Mesocrystals, which are assembled from oriented primary nanocrystals exhibiting highly ordered

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pore structures, received increasing research attentions [5,6]. Different from the super-crystals or nanocrystal super-lattices, which consist of periodic nanocrystals irrespective of the orientation of primary building blocks, mesocrystals are characterized by the high crystal quality, high porosity and oriented aligned primary nanoparticles [7,8]. Therefore, they demonstrate many structural advantages compared with the single-crystalline and porous polycrystalline materials because of their potential applications such as drug delivery, catalysis, adsorption catalysis, sensing, and energy storage and conversion [9–12].

Dye-sensitized solar cells (DSSCs) have been considered as a promising alternative to silica based solar cells to convert green and inexhaustible solar energy into electricity due to their low-cost and high power conversion efficiency (PCE) [13,14]. Photoanode is one of the key components of DSSC, the mesoporous photoanode films play two important roles as scaffold for dye molecules and conducting matrix for the injected electrons. Heretofore, TiO_2 nanoparticles received intensive research interests as photoanode materials for DSSCs because of their large surface areas for dye loading amount to utilize solar light efficiently. However, the electron transport in the nanoparticle based film is described as "random walk" with a series of trapping and detrapping processes, which seriously limits the electron diffusion coefficient and the electron collection efficiency at the conductive substrate [15–18]. In addition, the nano-sized particles show lower light scattering ability which results in poorer light-harvesting efficiency of the photoanode. Although polycrystalline materials with high surface area, mesoporous structures and submicron-sized diameters have been proposed to make a comprise between the dye loading amount and light scattering effect, most of these polycrystalline microspheres composed of randomly aggregated primary nanocrystals and the grain boundaries brought forth numerous recombination opportunities between the photoelectrons and the electron acceptors [19–25]. Therefore, they still confronted with electron transportation problems because of the large number of grain boundaries in the photoanode film. In order to enhance the charge transport in the film structure, TiO_2 polycrystalline hierarchical materials assembled by oriented attached nanocrystals or comprised of one dimensional primary structures have been deliberately prepared to improve the connectivity of the film structure [26–32]. Based on these considerations, a photoanode with high surface area, good scattering effect and fast transport pathway are highly desirable to improve the performance of DSSCs.

In this study, we demonstrated a one-step solvothermal method to construct size-tailored and single-crystalline-like TiO_2 mesocrystals (TMCs) which demonstrate tunable light scattering over a wide visible-light range. Inspired by the effect of light scattering, we introduced the spherical and spindle-like TMCs as scattering layer in DSSCs. The periodic stacking patterns of the spherical TMCs in the scattering layer induces scattering reinforcement at the particular range, which increases the light harvesting efficiency and short circuit current (J_{SC}) of the device. Therefore, a notable ~22% power conversion efficacy (*PCE*) improvements was achieved compared with the semitransparent nanoparticles based devices, which indicates that the as-prepared TMCs are potential candidates in photovoltaic devices.

2. Experimental details

2.1. Preparation of the TMCs

The TMCs were prepared in solvothermal method using acetic acid as reaction medium and tetrabutyl titanate (TBT) as Ti precursor. For the spherical TMCs, 1 g benzoic acid was dissolved in 25 mL acetic Acid (HAC, 98%). After being stirred for 15 min at room temperatures, 0.5 mL TBT was added in the mixture solution with continuous stirring for another 15 min (the TBT dosage was also adjusted to 0.25 and 1 mL for the control experiment). The white precursor was transferred into a 50 mL Teflon autoclaves and maintained at 200 °C for 24 h. The final precipitate was centrifuged and washed with water and ethanol. Finally, the as-prepared sample was calcined at 400 °C for 30 min later use. The spindle-like TMCs was prepared in a similar procedure but without using benzoic acid.

2.2. Preparation of TiO_2 nanocrystals

Typically, 7.5 mL of titanium isopropoxide (Sigma) was added into 45 mL of 0.1 M HNO_3 aqueous solution. The suspension was placed in an 80 °C water bath and stirred for 8 h. The concentrated suspension was then transferred into a 50 mL autoclave and heated at 230 °C for 12 h. The as-prepared TiO_2 nanocrystals with an average diameter of 15–20 nm were collected by centrifugation and stocked for later use.

2.3. Material characterization

The morphologies and structures of the products were characterized by scanning electron microscopy (SEM, JEOL, JSM-6400-LV), transmission electron microscopy (TEM, JEOL, JSM-2100), X-ray powder diffraction (XRD, Rigaku D/max-2500 diffractometer with Cu Ka radiation, l¼0.1542 nm, 40 kV, 100 mA) and Brunauer–Emmett–Teller (BET, Micrometrics ASAP 2010).

2.4. Preparations of the DSSCs

Hydroxypropyl cellulose (Aldrich) was added to diethylene glycol (with a concentration of ~10 wt%) under vigorous stirring to prepare the paste. The paste was added into the stock TiO_2 colloids in a proportion of 40% of TiO_2 weight. The mixture was vigorously stirred to obtain the slurry for the semi-transparent adsorption layer. The slurry for the scattering layer was also prepared with similar method using spherical or spindle-like TMCs. The bilayer film was constructed by the doctor-blade method through two-step calcination. Nanocrystals were spread onto fluorine-doped tin oxide (FTO) glass substrate (TEC-8, LOF) with adhesive tape to control the film thickness. After drying in air, the film was heated up to 450 °C at a rate of 5 °C min^{-1} and maintained for 30 min. After calcination, another layer of the TMCs were deposited on the semi-transparent layer and annealed with the same heating profile. After cooling to 80 °C, the films were sensitized in a solution of cis-bis(isothiocyanato) bis(2,20-bipyridyl-4,4-dicarboxylate) ruthenium(II)bis-tetrabutyla mmonium(N719, Solaronix SA, Switzerland) in ethanol (3×10^{-4} M) for 24 h. The dyed films were then sandwiched together with platinized FTO counter electrodes and the electrolyte was then injected into the cell from the edges by capillarity. The content of the electrolyte is 0.05 M LiI, 0.05 M I_2, 0.5 M 4-tert-butylpyridine and 0.6 M 1-propyl-3-methy-limidazolium iodide (PMII) in 3-methoxypropionitrile.

2.5. Photovoltage measurements

Photocurrent–voltage (*I–V*) measurements were performed on a Keithley 2400 semiconductor characterization system using simulated AM 1 sunlight with an output power of 100 mW cm^{-2} produced by a solar simulator (Newport 69920). The incident monochromatic photon-to-electron conversion efficiency (IPCE) was recorded on a Keithley 2000 sourcemeter under the irradiation