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Ellipsoidal TiO_2 mesocrystals as bi-functional photoanode materials for dye-sensitized solar cells

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ABSTRACT

Ellipsoidal TiO_2 mesocrystals (MCs) with varying particle sizes depending on the amount of titanium precursor are synthesized by solvothermal method using acetic acid and tetrabutyl titanate. The large one (MC-1) is predominant 700 nm in length and 400 nm in width, while the small one (MC-2) is 250 nm in length and 100 nm in width. SEM and TEM images reveal that the mesocrystals exhibit single-crystalline-like structures, which are constructed by the orderly aggregating of tiny primary TiO_2 nanocrystals. The specific surface areas of MC-1 and MC-2 are 119.5 and 132.4 m^2/g respectively. The mesocrystals are potential photoanode materials in DSSCs, which can not only enhance the light scattering and dye adsorption, but also enhance the electron transport. The highest efficiency of 7.16% is achieved for the bi-layer NC-MC-2 DSSCs when the MC-2 is applied as a scattering layer on top of the nanocrystalline underlayer. The improvement of the efficiency is mainly attributed to the high specific surface area as well as the efficient light scattering, both of which result in the increase of light harvesting. Meanwhile, the electron transport of the photoanodes is also investigated. It is found that the electron transport of the single-crystalline-like mesocrystals is superior than nanoparticles, corresponding to the excellent energy conversion efficiency.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted worldwide attentions since the breakthrough research of Prof. Grätzel [1]. Compared with traditional silicon solar cells, DSSCs are featured with advantages of low cost, easy manufacturing process and eco-friendly. The champion energy conversion efficiency of DSSCs has reached over 13% using the cobalt (II/III) redox shuttle [2], and efficiencies would be improved by utilizing co-sensitized methods [3]. In the components that fabricate DSSCs, nanocrystalline oxides based photoanode plays a key role in determining the photovoltaic performance. A variety of semiconductor oxides including TiO_2 [4], ZnO [5,6], SnO_2 [7,8], WO_3 [9] and Nb_2O_5 [10] have been applied for the photoanodes of DSSCs. As the most widely used material, TiO_2 is featured with chemical stability, nontoxicity, appropriate conduction band energy level and controlled morphology [11].

Mesoporous films prepared by tiny anatase TiO_2 nanoparticles (NC) show good performance on dye-adsorption due to the large specific surface area, however, the light harvesting is not satisfied because the high transparency of the film makes the incident light not be fully utilized by the sensitizers [12]. Adding a layer of (sub) micro-sized light-scattering particles atop the nanocrystalline film could extend the paths of incident light in the photoanode, thus increases the light harvesting. Particle size comparable with the wavelength of visible light can facilitate multiple scattering and convert more photons to electrons [13]. One of the popular light scattering particles was TiO_2 particle with different construction, such as hierarchical TiO_2 mesoporous microspheres [14], hierarchical submicrometer TiO_2 hollow spheres [15], cauliflower-like TiO_2 rough spheres [16] and mesoporous TiO_2 beads [17]. For the highly efficient DSSCs, the scattering particles should not only scatter light, but also adsorb

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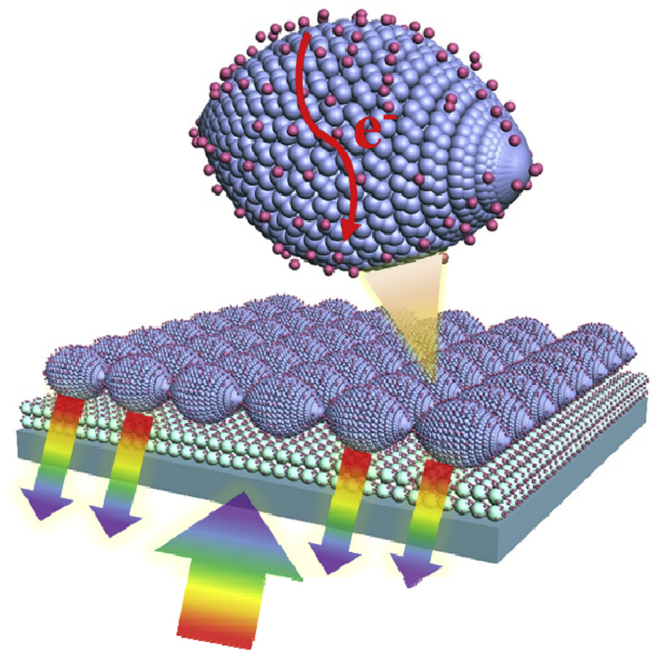
large amounts of dye and have fast charge mobility [18]. So the specific surface area of scattering particles is expected to be high enough. If the scattering layers possess fast electron transport and long electron lifetime, it will also be helpful to improve the cell performance. Snaith et al. firstly designed the mesoporous single-crystalline anatase TiO_2 which showed higher conductivity and electron mobility than conventional TiO_2 particles using a silica-templated method, where the templates are quasi-close-packed array of silica beads, and by seeding this template could make a near-unity yield of single-crystalline TiO_2 [19]. Using a similar silica-templated hydrothermal method, Zheng et al. also synthesized rutile and anatase TiO_2 mesoporous single crystals with diverse morphologies [20]. In addition, Yang et al. synthesized mesoporous SnO_2 single crystals with a silica-templated hydrothermal method and applied them as electron collector of perovskite solar cell. The solar cell had lower transport resistance due to the fast electron transport of SnO_2 single crystal [21]. Although mesoporous single-crystalline anatase TiO_2 performs well on electron transport, the silica-template assisted methods leads to a complicated procedure and the specific surface area of the crystals is relatively small due to the large inner pores. Fu et al. fabricated mesoporous single crystal TiO_2 through a template-free method, and obtained a higher specific capacity in lithium ion battery anodes. The better performance was attributed to the mesoporous structure and the long-range electronic connectivity which could shorten the ionic diffusion paths as well as decrease the contact resistance [22]. Due to the similar advantages of the single crystal TiO_2 mentioned above, mesoporous TiO_2 aggregation with long-range ordered stacking could be used as the scattering particles [23]. Owing to the porous construction and rough surface of this kind of mesoporous TiO_2 aggregates, it could play the multiple roles of efficient light scattering, dye adsorption and electrolyte permeation [24]. Besides, this kind of crystals was formed with the oriented aggregation of small nanocrystals, the local ordering of the nanocrystals construction was beneficial to the diffusion of electron among the particles, leading to the faster electron transport [25].

In this work, we prepared two kinds of ellipsoidal mesoporous TiO_2 mesocrystals (MCs) with different particle sizes as the photoanode materials. Compared with the widely reported spherical scattering particles which result in big useless pores within the film due to random loose packing, ellipsoids can randomly pack more densely according to previous research, and thus increase the space utilization [26,27]. The light-scattering property depends on the particle size distribution and shape, optical anisotropy, and interactions between neighboring particles [28], and the particle size of ca. 300 nm exhibits the strongest scattering at wavelength of 560 nm (the center of the visible spectrum). Furthermore, the ellipsoids exhibit different sizes in the long axis and short axis, so the size distribution of scattering centers is wider for ellipsoids than microspheres, which may lead to better light scattering [28,29]. Firstly, when the MC-1 and MC-2 were applied as the dye-adsorbed underlayers of DSSCs, the PCE of 3.27% and 5.98% were obtained respectively, which suggested that the MCs not only own the capability of light scattering, but also they are able to adsorb a certain amount of dye. Secondly, when the MCs were used as the scattering layers, MC-1 and MC-2 can effectively improve the PCE of DSSCs from 6.39% to 6.75% and 7.16%, respectively. The improvement is mainly resulted from the excellent light scattering of MC-1 as well as the good dye adsorption of MC-2. It could be concluded that the scattering layer of MCs is suitable to improve the photovoltaic performance of DSSCs (Scheme 1).



Scheme 1. A schematic diagram of the bi-layer photoanode with MCs scattering layer on top of the nanocrystalline underlayer.

2. Experimental

2.1. Synthesis of ellipsoidal TiO_2 mesocrystals (MCs)

The synthesis of ellipsoidal TiO_2 mesocrystals was according to previous work with modification [23]. The tunable size of TiO_2 mesocrystals was achieved by adjusting the hydrolysis of the precursor. In a typical synthesis, 1 ml of TBT was dropwise added to 50 ml of HAc, under magnetic stirring. The obtained white suspension was transferred to a Teflon-lined stainless-steel autoclave, and subjected to hydrothermal treatment at 200 °C for 24 h. After the autoclave cooled to room temperature, the product was collected by centrifugation, and washed with ethanol three times (thereafter named as MC-1). Similarly, 2 ml of TBT was added to 50 ml of HAc with identical procedure, and the product was named as MC-2.

2.2. Preparation of electrodes and assembly of DSSCs

Before preparing the TiO_2 working electrode, the cleaned FTO glass (14 Ω/□, Nippon Sheet Glass, Japan) was immersed in a 40 mM aqueous $TiCl_4$ for nearly 30 min, then washed with water and ethanol. When the glass was dry, the TiO_2 paste was coated on the FTO glass by doctor blade to form the underlayer. The preparation of TiO_2 paste was according to our previous recipe [30–32]. The as-prepared MC-1 (1.29 g) was added into the ethanolic solution of ethyl cellulose (0.38 g), and then mixed with terpineol (2.61 g) and ethanol to form the suspension, dispersed by ultrasonic and magnet tip. Finally, the suspension was concentrated by rotary evaporation to remove the ethanol. The obtained paste was named as P-MC-1. Similarly, MC-2 (0.76 g) mixed with ethyl cellulose (0.38 g) and terpineol (3.07 g) was also fabricated as the DSSCs paste, named as P-MC-2. The proportions of ethyl cellulose and terpineol mainly depend on the particle sizes, and higher proportions of ethyl cellulose and terpineol are needed for smaller particles according to the literature [33]. When MC-1 and MC-2 were respectively used as the scattering layer, the 20 nm anatase