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Multi-dimensional titanium dioxide with desirable structural qualities for enhanced performance in quantum-dot sensitized solar cells

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HIGHLIGHTS

- A bridge-linking mechanism was proposed to illustrate the formation of MD-THS.
- The wide pore size distribution facilitates the anchoring process of quantum dots.
- The oriented aligned primary nanocrystals inhibit undesired charge recombination.
- Cell-MD-THS demonstrates much higher PCE of 4.15% than Cell-Nanocrystal (3.03%).

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ABSTRACT

Multi-dimensional TiO_2 hierarchal structures (MD-THS) assembled by mesoporous nanoribbons consisted of oriented aligned nanocrystals are prepared *via* thermal decomposing Ti-contained gelatin-like precursor. A unique bridge linking mechanism is proposed to illustrate the formation process of the precursor. Moreover, the as-prepared MD-THS possesses high surface area of ~106 $cm^2\ g^{-1}$, broad pore size distribution from several nanometers to ~100 nm and oriented assembled primary nanocrystals, which gives rise to high CdS/CdSe quantum dots loading amount and inhibits the carries recombination in the photoanode. Thanks to these structural advantages, the cell derived from MD-THS demonstrates a power conversion efficiency (*PCE*) of 4.15%, representing ~36% improvement compared with that of the nanocrystal based cell, which permits the promising application of MD-THS as photoanode material in quantum-dot sensitized solar cells.

1. Introduction

Quantum-dot sensitized solar cell (QDSSC) represents a group of new solar energy conversion devices. Although it shares many design configuration and working principle with dye-sensitized solar cell (DSSC), the Quantum dots (QDs) sensitizers, generally the metal chalcogenides, have many inherit advantages compared with the costly Ru based dyes, such as the flexible solar spectrum matching capability, high extinction ratio and the unique multiple excitation generation (MEG) resulting from the impact ionization effect [1–4]. Because of the MEG effect, a high theoretical *PCE* of ~44% could be achieved, which is much higher than the traditional Shockley and Queisser limit of ~31% [5]. CdS/CdSe co-sensitized strategy is commonly used to achieve high *PCE* in QDSSC [6–9]. In addition, other sensitizers such as CdTe, PbS and PbSe were also developed to enhance the *PCE* by broadening the absorption spectrum or improving the injection efficiency of the photoelectrons [10–12]. Most recently, QDSSCs based on low toxicity sensitizers (Ag_2S, Sb_2S_3 or $CuInS_2$), solid-state or flexible configurations were also designed and prepared [13–16]. However, the highest *PCE* of these devices merely reaches to ~7%, which still lags far behind compared with DSSC (~13%) [17–20]. The low *PCE* generally results from the massive recombination in the unsophisticated cell configurations, indicating the photoanode, electrolyte and the counter electrode are not satisfactorily optimized. [21–24].

Photoanode is one of the key components in QDSSCs, which

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serves as both the scaffold to anchor QDs and diffusing matrix for the injected photoelectrons, many groups have made various efforts to optimize the TiO_2 structures so as to enhance the light harvesting capability and electron transport performance [25–29]. Several design rules should be considered as priorities. First of all, the QDs have much greater size than the monolayer adsorbed dye molecules, thus a photoanode film with large pore size distribution is favorable for the QDs loading. Especially in the pre-synthesis strategies, in which the QDs are prepared before loaded on the photoanode, the small pore size inevitably jeopardizes the QDs penetration and results in QDs aggregation inside the film structures [30,31]. Secondly, the high surface area could increase the initial nucleation population of the QDs on the photoanode structures, which can improve the QDs coverage and retard undesired interface recombination [27,32–34]. Particularly, for the *in situ* growth strategies, in which the QDs were loaded on the photoanode film by means of successive ionic layer adsorption and reaction (SILAR) or chemical bath deposition (CBD), photoanode film with high surface area is of same significance as the pore size distribution. Thirdly, although the continuous QDs coating layer may serve as additional electron transport path, the majority of the generated photoelectrons are collected through the TiO_2 matrix. Therefore, just like the DSSC cases, hierarchical structures consisted of one-dimensional subunits or orderly aligned primary units can greatly improve the electron collection efficiency by minimizing the population of the grain boundaries [35]. However, the previously reported hierarchical structures can hardly balance the required structural qualities of high surface area, broad pore size distribution and oriented aligned subunits. Especially for the TiO_2 hierarchical structures with small pore size distribution, the QDs aggregation inevitably takes place in the pore channels, which results in increased charge recombination and leads to *PCE* plummet. Therefore, the TiO_2 hierarchical structures should be further optimized for the particular demands in QDSSCs.

Herein, we designed and prepared a unique MD-THS which is assembled by mesoporous nanoribbons consisted of oriented aligned nanocrystals. Time dependent trails reveal an interesting growth and assembling process of the hierarchal gelatin precursor and the formation is driven by the energy minimization on the coordinating modes of carboxyl groups. In addition, when used as photoanode material in CdS/CdSe co-sensitized cells, the MD-THS could integrate the advantages of different dimensional materials: the three dimensional (3D) hierarchical structure provides a suitable outer diameter of ~1 μm and a wide pore size distribution from several nanometers to ~100 nm, which improves the harvesting of incident light. The one dimensional (1D) nanoribbon with oriented assembled primary nanocrystals reduces the grain boundaries and charge recombination. Moreover, the zero dimensional (0D) nanocrystals with diameter of ~15 nm leads to high surface area of ~106 $cm^2\ g^{-1}$, which favorites the loading process of QDs sensitizers. Therefore, the cell derived from MD-THS demonstrates a high *PCE* of 4.15%, which indicates ~36% improvement compared with nanocrystal based cell (3.03%).

2. Experimental section

2.1. Materials synthesis

The MD-THSs were prepared in a solvothermal method. 1 mL of titanium n-butoxide (TBT) was added drop wise to 20 mL of acetic acid with rigorous stirring. Afterwards, the mixture was transferred into 25 mL Teflon-lined stainless steel reactor and heated at 200 °C for 2 h. After cooling, the white product were collected by centrifugation and washed with distilled water and ethanol several times, then dried at 60 °C for 3 h. Finally, the samples were heated to 450 °C at a rate of 5 °C min^{-1} and calcinated for 3 h to obtain the final product.

The nanocrystals were prepared based on M. Gratzel et al.'s work [36]. Briefly, 7.5 mL titanium isopropoxide was added into 45 mL 0.1 M HNO_3 aqueous solution. The suspension was placed in

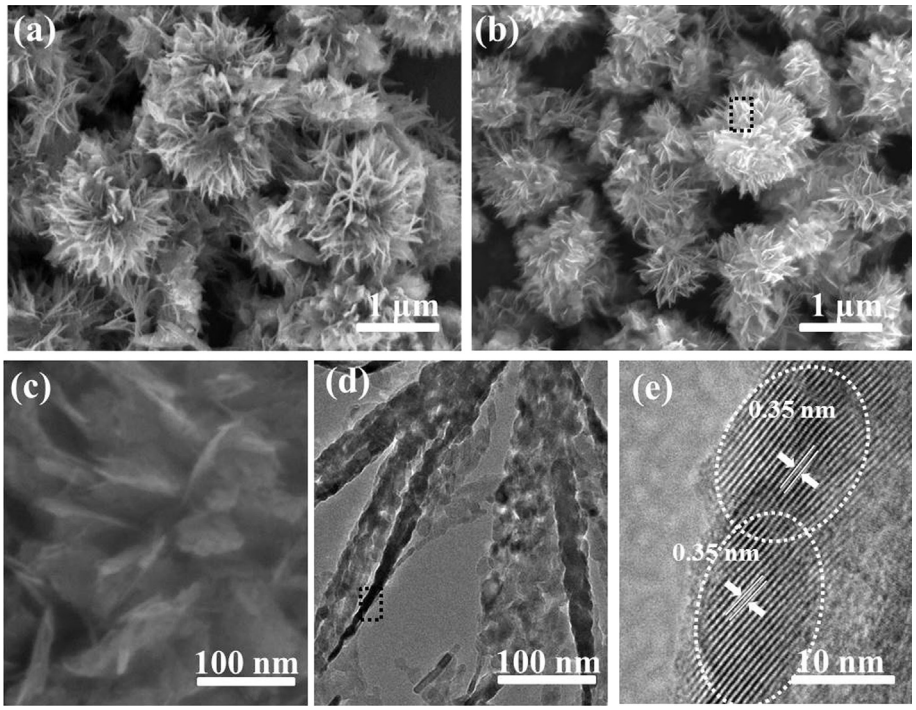

Fig. 1. FESEM images of (a) hierarchical gelatin precursor obtained by solvothermal treatment; (b) MD-THSs after calcination; (c) the magnified image located at the black dot square in (b); (d) and (e) are the corresponding TEM and HRTEM images of the mesoporous ribbons.