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Ultralong Rutile TiO_2 Nanorod Arrays with Large Surface Area for CdS/CdSe Quantum Dot-sensitized Solar Cells

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ABSTRACT

By using hydrothermal method and post-etched with hydrochloric acid at high temperature, the ultralong TiO_2 nanorod arrays (TNARs) for CdS/CdSe co-sensitized solar cells (QDSCs) were fabricated on fluorine-doped tin oxide (FTO) glass. Then CdS quantum dots (QDs) and CdSe QDs were deposited respectively on the as-prepared TNARs by successive ionic layer adsorption reaction (SILAR) and chemical bath deposition (CBD). The deposition time of CdSe and the etching time of TNARs were regulated to optimize the properties of energy conversion. The morphologies, crystal structure and optical prosperities of TNARs/CdS/CdS were characterized by SEM, TEM, XRD, EIS and UV-vis spectra. A thickness of 17.6 μm TNARs with large inner surface area was first used for sandwich-type ordered QDSCs, it is found that the J_{sc} reached the maximum value (17.22 mA cm^{-2}) and the cell conversion efficiency obtained with Pt as counter electrode reached 2.66%.

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1. Introduction

Titania nanostructured materials have been widely applied in photovoltaic conversion devices since Michael Grätzel and Brian O'Regan made great breakthrough in dye-sensitized solar cells (DSCs) in 1991.[1] However, the quantum efficiency of pure TiO_2 with a wide band gap (e.g., 3.20 eV for anatase TiO_2 and 3.02 eV for rutile TiO_2) [2,3] is rather low under the irradiation of solar light because TiO_2 can only absorb UV light (< 387 nm), which only possesses 4-5% of the solar spectrum.[4] Various kinds of methods have been developed to extend the light absorption of nanostructured TiO_2 to the visible region, for example, doping non-metal (e.g., N,[5–7] P,[8] S,[6] and etc.) and metal (e.g., Fe,[6,9] Ag,[10] Pd,[11,12] Nb[12] and etc.) atoms into the TiO_2 lattice to minish its band gap. One of the most efficient methods is sensitization, which can extend the absorption of solar spectrum to visible region, and organic dye[13,14] and inorganic quantum dots (QDs) [15–18] are most used sensitizer.

Quantum dot-sensitized solar cells (QDSCs) have received much interest in recent years since inorganic QDs (e.g., CdS,[15] CdSe,[19–21] PbS,[22,23] Sb_2S_3[24] and etc.) exhibit huge advantages over organic dyes, such as easy obtainability, low cost, high molar extinction coefficient and convertibility of band gap.[4,21,25] More importantly, QDs can harvest hot electrons, generate multiple electron-hole pairs and be designed with intermediate band, which offer opportunity to achieve considerable high-performance solar cells.[21] The theoretical conversion efficiency of QDSCs is as high as 44%[20,26] which makes QDs prominent candidates for solar cells. However, in spite of the thrilling advantages, the highest conversion efficiency now only reaches around 5%,[16,21,27] which is considerably lower than that of the dye-sensitized solar cells (DSCs). Numerous efforts have been focused on improving the performance of QDSCs.[16,28–31] Kamat et al. fabricated CdS/CdSe co-sensitized solar cells with CdS QDs doped by Mn^{2+} and obtained an efficiency of 5.4% with a high current density of 20.7 mA cm^{-2}.[16] Meng et al. reported a CdS/CdSe co-sensitized solar cells based on template TiO_2 nanotube arrays which boosted the open circuit voltage to about 0.69 V, obtaining an optimized efficiency of 4.61%.[21] Generally, CdS QDs and CdSe QDs are the most commonly used sensitizers because of their well matched band edges and proper band gaps which facilitate the charge separation and injection into semiconductor (e.g., TiO_2).[21,32–34] As an important role in QDSCs, TiO_2 films act as the support for QD loading and charge transport medium, thus many works have been carried out to exploit efficient TiO_2 nanostructures. Among various nanostructured TiO_2 materials, nanorod arrays have been attracted considerable attention because of their excellent charge transport ability. Li et al. have synthesized TiO_2 nanorod with length of 2.9 μm for solar cells and got a current density of 2.49 mA cm^{-2}. Xia reported solar cells based on CdSe/CdS co-sensitized TiO_2 nanorod array with a current density of 5.78 mA cm^{-2}.[35] Chang reported solar cell based on TiO_2 nanorod arrays of the thickness

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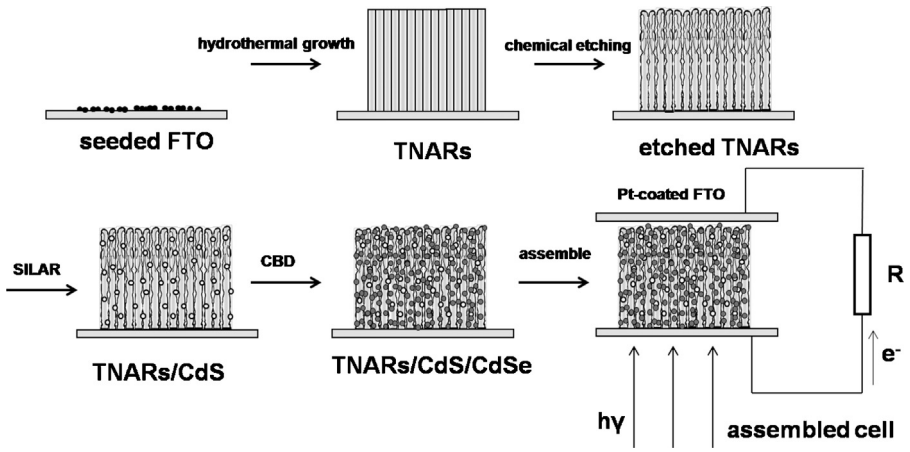

Scheme 1. Schematic processes of preparing etched TNARs on FTO glass, depositing CdS and CdSe on the obtained TNARs, and cell fabrication. TNARs mean TiO_2 nanorod arrays. Yellow and red dots represent CdS and CdSe QDs respectively.

around 3 μm decorated with CdSe/CdS and reached an efficiency of 3.06% with the current density of 13.83 mA cm^{-2}.[36] However, the current density of TiO_2 nanorod-based QDSCs is relatively low comparing to TiO_2 nanoparticle-based DSCs (over 20 mA cm^{-2}),[13] and can be further developed.

In this paper, we have synthesized well-aligned TiO_2 nanorod arrays with thickness up to ~17 μm by hydrothermal method. $TiCl_4$ was hydrolyzed in hydrochloric acid system to form the initial TiO_2 nanorods on seeded FTO substrate and the obtained TNARs were etched by concentrated hydrochloric acid. To our best knowledge, this kind of ultralong TiO_2 nanorod arrays with high inner surface area has not been applied to QDSCs yet. CdS QDs were deposited on TNARs by SILAR process and CdSe QDs deposited on CdS QDs by CBD method. The overall strategy was presented in Scheme 1. The etching time of TNARs and the time of CdSe deposition were carefully optimized and herein we got a considerably high cell short current density of ~17 mA cm^{-2} and a best cell conversion efficiency of 2.66%.

2. Experimental

2.1. Preparation of etched TNARs

Etched TNARs on seeded FTO substrates were synthesized by the strategy previously developed in our lab.[37] Briefly, the cleaned FTO substrates were immersed in 0.18 M $TiCl_4$ aqueous solution in drying oven at 70°C for 30 min, and then washed with deionized water (DIW), dried under air stream, annealed in muffle at 550°C for 60 min. Thus, the seeded FTO substrates were prepared. The TNARs were grown on the seeded FTO substrates by a hydrothermal method. 30 mL DIW was mixed with 30 mL concentrated hydrochloric acid (36.0-38.0 wt %) and the mixture was stirred for 10 min. 3 mL $TiCl_4$ was added to the mixture slowly and stirred for another 2 hours. The mixture was transferred into a 100 mL sealed Teflon-stainless reactor after the seeded FTO substrates were placed with the conducting side facing down within the reactor. The hydrothermal synthesis was conducted at 150°C in a drying oven for 10 h. After the reaction, the Teflon-stainless reactor was cooled to room temperature and the FTO substrates attached with TNARs on the conducting side were taken out and rinsed with DIW, then the TNARs with a thickness about 17 μm were prepared. Subsequently, the obtained TNARs were processed by another hydrothermal reaction with the solution of 20 mL DIW and 40 mL concentrated hydrochloric acid (36.0%-38.0% wt %) to etch the nanorods at 150°C for 1-9 hour. After cooling to room temperature, the etched TNARs were taken out and rinsed with DIW thoroughly, dried in air and annealed at 450°C for 2 hour. As a comparison, thickness of ~9 μm TNARs were prepared under the same conditions for 4 h and etched in a mixture of 25 mL DIW and 35 mL concentrated hydrochloric acid at 150°C for 7 h.

2.2. Preparation of TNARs/CdS/CdSe photoanodes

CdS and CdSe QDs were successively deposited on the as-prepared TNARs by SILAR process and CBD method respectively according to the literature.[21,38] Firstly, CdS QDs was deposited on TNARs by immersing the samples in an ethanol solution containing $Cd(NO_3)_2$ (50 mM) for 2 min, with ethanol washing and then immersing in a Na_2S methanol solution (50 mM) for 2 min also with ethanol washing. Such a SILAR cycle was repeated 5 times and then the TNARs/CdS QDs were prepared. Secondly, CdSe QDs was deposited on TNARs/CdS QDs by CBD method. Sodium selenosulphate (Na_2SeSO_3) aqueous solution was used as Se source, which was prepared by dissolving Se (0.1 M) in an aqueous solution of Na_2SO_3 (0.18 M) at 70°C for about 7 h and the black Se powder was almost reacted. After cooling to room temperature, the obtained Na_2SeSO_3 aqueous solution was filtered to remove unreacted Se. 0.08 M $Cd(NO_3)_2$ aqueous solution was prepared as Cd source. The CBD process of CdSe QDs was conducted in a mixture of Na_2SeSO_3 solution and $Cd(NO_3)_2$ solution mentioned above with a volume ratio of 1:1 under 5°C for 10-40 hours. Different photoanodes of TNARs/CdS/CdSe were thus prepared.

2.3. Cell fabrication

The TNARs/CdS/CdSe photoanodes were coupled with Pt-deposited FTO glasses as counter electrodes to fabricate the QDSCs. The Pt electrode was prepared by thermal decomposition of 1 drop of 2 mg/mL chloroplatinic acid hexahydrate ethanol solution on 1 cm × 1.5 cm cleaned FTO substrates at 400°C for 10 min. These two electrodes were separated by a 60 μm thick hot-melt glue and sealed by heating at 100°C for 4 min in dry oven and then the polysulfide electrolytes which composing 0.5 M Na_2S, 0.2 M S, and 0.2 M KCl in a mixture of methanol and DIW (3:7 vol/vol) was injected into the sealed cells.

2.4. Characterizations

The morphologies of TNRAs were observed by field-emission scanning electron microscope (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100) operating at

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