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Enhanced photoelectrochemical performance of CdSe/Mn-CdS/TiO_2 nanorod arrays solar cell

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ABSTRACT

Vertically oriented single-crystalline one-dimensional TiO_2 nanorod arrays was synthesized directly on transparent fluorine-doped tin oxide (FTO) conducting glass substrate by a facile hydrothermal method and was applied as photoanode in CdSe/Mn-doped CdS quantum dots sensitized solar cells (QDSSCs). The effect of coating cycles of QDs on the photovoltaic performance was investigated to find the optimal combination is 10 cycles of Mn-doped CdS and 9 cycles of CdSe, the CdSe(9)/Mn-CdS(10)/TiO_2 solar cell exhibited the best performance due to the complementary effect in the light absorption of Mn-doped CdS and CdSe QDs. The power conversion efficiency of CdSe(9)/Mn-CdS(10)/TiO_2 solar cell reached to 2.40% under one sun illumination (AM 1.5 G, 100 mW/cm^2), which was 46.34% higher than that of CdSe(9)/CdS(10)/TiO_2 solar cell without doping of Mn (1.64%).

1. Introduction

TiO_2 has attracted much attention in recent years due to its wide application in photocatalysis, gas sensing, water photoelectrolysis, and photoelectrochemical cells [1–4]. Nanostructured TiO_2 was usually used as photoanode substrate for quantum dots sensitized solar cells (QDSSCs) because of its several advantages, such as suitable conduction band position, stable chemical and physical properties, strong optical absorption, and inexpensive cost. The one-dimensional (1D) TiO_2 nanostructures including nanorods, nanowires, and nanotubes have shown excellent photoelectrochemical performance due to their efficient charge separation and transport properties [5–7]. The typical approaches to prepare ordered 1D TiO_2 nanostructures for solar cell application include the template-assisted process [8], anodic oxidation [9] and hydrothermal synthesis [10]. An electrochemical anodization is well-known way to synthesize ordered nanotubes on any shape of Ti substrate such as foil or wire. However, the TiO_2 nanotube arrays solar cells have to be constructed in a back illuminated system [11] because of the metal titanium foils are opaque, which cannot make full use of light. In order to overcome this problem, front-side illumination is a better way for QDSSC applications. 1D TiO_2 nanorod arrays directly grown on FTO glass has recently been a focus of investigation for QDSSCs, and its advantages can be explained as follows: first, 1D TiO_2 nanorod arrays directly fabricated on FTO glass can be used as front-side illuminated photoanode in QDSSCs, enhancing the light harvesting efficiency. Second, 1D TiO_2 nanorod arrays synthesized by hydrothermal method is in single-crystalline rutile TiO_2 phase, which possess less boundaries for electron to pass, reducing the possibilities of recombination during the diffusion of electrons. Therefore, 1D single-crystalline TiO_2 nanorod arrays grown directly on a transparent conductive FTO glass was fabricated by a modified hydrothermal approach in this study, and was used as substrate for sensitization with quantum dots (QDs).

Recently, various narrow-band gap semiconductors including CdS, CdSe, CdTe, and PbS have been studied as sensitizers for QDSSCs [12–16]. Among these semiconductor materials, CdS and CdSe have shown much promising as impressive sensitizers due to their appropriate band gap of 2.25 eV and 1.70 eV in bulk, respectively, which can allow the extension of absorption band to the visible region of the solar spectrum [17,18]. Generally, single CdS or CdSe QDs sensitized solar cells presents low power conversion efficiency [19], thus cosensitized structure was proposed to improve the power conversion efficiency of QDSSCs. The cosensitized structure has been proved to be advantageous over single CdS or CdSe; this can be ascribed to the complementary effect [20] of the two kinds of QDs in light absorption and the improvement of light harvesting efficiency. Moreover, it is reported that doping of Mn^{2+} into QDs can modify intrinsic property of semiconductor QDs [21] and alter the charge separation and recombination dynamics in QDSSCs, which is in favor of the improvement of power conversion efficiency.

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In this work, 1D single-crystalline TiO_2 nanorod arrays directly grown on FTO glass was synthesized via a modified hydrothermal method. Mn-doped CdS QDs and CdSe QDs were cosensitized onto TiO_2 nanorod arrays by in situ successive ionic layer adsorption and reaction (SILAR) to form a front-side illuminated photoanode. Our CdSe/Mn-CdS/TiO_2 solar cell exhibited much better photoelectrochemical performance than the CdSe/CdS/TiO_2 solar cell, which verified the potential value of CdSe/Mn-doped CdS solar cell based on 1D single-crystalline TiO_2 nanorod arrays in designing enhanced efficiency QDSSCs.

2. Experimental

2.1. Materials

Titanium butoxide ($Ti(OC_4H_9)_4$), cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$), sodium sulfide ($Na_2S{\cdot}9H_2O$), sodium chloride (NaCl), sodium hydroxide (NaOH), sulfur powder (S), manganese acetate ($Mn(CH_3COO)_2{\cdot}4H_2O$), concentrated hydrochloric acid (HCl, 36.5–38 wt%), selenium powder (Se), sodium sulfite (Na_2SO_3), copper sulfate ($CuSO_4{\cdot}5H_2O$) and thiourea (H_2NCSNH_2) were purchased from Tianjin Chemical Reagents Co. Ltd. All chemicals were used directly in experiments without further purification. Deionized water (DI water, resistivity of 18.2 MΩ cm) was obtained from MilliQ ultra-pure water system (Millipore, USA).

2.2. Preparation of TiO_2 nanorod arrays on FTO glass

The 1D single-crystalline TiO_2 nanorod arrays on transparent conductive FTO glass electrode was prepared using the hydrothermal method reported by Liu and Aydil [22] with slight modifications. Briefly, 25 ml of DI water and 5 ml of saturated NaCl aqueous solution were mixed with 30 ml of concentrated hydrochloric acid. After stirring 5 min under ambient conditions, 1 ml of titanium butoxide was added dropwise to the mixture to obtain a clear transparent solution, and then was transferred to a Teflon-lined stainless steel autoclave, filling the 80% volume of the autoclave. One piece of FTO substrate (F: SnO_2, 14 Ω/square) ultrasonically cleaned for 30 min in a mixed solution of DI water, acetone, and 2-propanol (volume ratios of 1:1:1), was placed at an angle against the wall of the Teflon liner with the conductive side facing down. The hydrothermal synthesis was conducted at the temperature of 150 °C for 12 h in an electric oven. After synthesis, the autoclave was cooled to room temperature under flowing water. The product was taken out, rinsed thoroughly with DI water and ethanol respectively, and dried in ambient air.

2.3. Sensitization of Mn-doped CdS/CdSe QDs onto TiO_2 nanorod electrodes by SILAR

In situ successive ionic layer adsorption and reaction (SILAR) method [23] is used to assemble Mn-doped CdS and CdSe QDs onto the TiO_2 nanorod photoanode. For Mn-doped CdS QDs, the TiO_2 nanorod arrays electrode was dipped into a mixed solution of ethanol and DI water with volume ratio of 1:1 containing 0.1 M $Cd(NO_3)_2$ and 0.075 M $Mn(CH_3COO)_2$ for 5 min, and then dipped for another 5 min into the same mixed solution containing 0.1 M Na_2S. Following each dipping, the electrode was rinsed with ethanol for 2–3 min to remove excess precursors and dried at 150 °C for 10 min before the next dipping. The two-step dipping procedure is termed as one SILAR cycle and the incorporated amount of Mn-doped CdS can be increased by repeating the SILAR cycles. For CdSe QDs, Na_2SeSO_3 is used as Se source, which is prepared by refluxing Se (0.3 M) in an aqueous solution of Na_2SO_3 (0.6 M) at 70 °C for about 7 h. The SILAR process of CdSe is similar to that of CdS except that a longer time (15 min) is required for dipping the sample in the Na_2SeSO_3 solution. We prepared several different SILAR cycles of CdSe/Mn-CdS/TiO_2 electrodes to investigate the optimal combination of Mn-doped CdS and CdSe. As a control experiment, we also prepared CdSe/CdS/TiO_2 electrode without doping of Mn^{2+}.

2.4. Solar cell fabrication

The QD-sensitized TiO_2 nanorod photoanode and $Cu_{1.8}S$/CuS-coated FTO (the synthesis details can be found in the literature [24]) counter electrode were assembled in sandwich fashion using 60 μm thick Surlyn film as spacer. 0.1 M S, 1 M Na_2S, and 0.1 M NaOH [25] in the co-solvent of water/methanol (3:7 by volume) was used as polysulfide electrolyte. The utilization of the co-solvent is to reduce the surface tension of the electrolyte, which is in favor of electrolyte penetration into TiO_2 nanorod arrays and scavenging holes, thus improve the overall efficiency. The active area of the cell was 0.16 cm^2.

2.5. Characterization

The morphology of the samples was characterized by field-emission scanning electron microscope (FE-SEM) operating at 5.0 kV. Transmission electron microscope (TEM) and high-resolution TEM (HR-TEM) investigations were carried out by JEOL JEM-2100F microscope. To prepare TEM samples, the QDs sensitized TiO_2 nanorods was detached from the FTO substrate and dispersed in ethanol, and then the solution was dropped onto a copper grid. Energy dispersive spectroscopy (EDS) was used to analyze the composition of the samples. The X-ray diffraction (XRD) spectra of the samples were recorded by a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ = 1.5416 Å) from 10° to 90° at a scan rate of 2.4° min^{-1}. Diffuse reflectance absorption spectra of bare TiO_2 nanorod arrays and QD-sensitized TiO_2 nanorod arrays were recorded in the range from 300 to 800 nm using a Hitachi U-3010 spectroscopy.

2.6. Photovoltaic measurements

The photocurrent–voltage (*I–V*) curves were measured by Oriel *I–V* test station under illumination of a solar simulator (Pecell-L, Japan) calibrated by standard silicon cell at one sun (AM 1.5 G, 100 mW/cm^2). The active illuminated area of the QDSSC was fixed to 0.16 cm^2. The incident photon to current conversion efficiency (IPCE) measurements were performed with a monochromator to select the illumination wavelength, a 500 W xenon arc lamp (Oriel) served as a light source.

3. Results and discussion

3.1. Structure and morphology characterization of single-crystalline TiO_2 nanorod arrays

The phase structure of the as-prepared TiO_2 nanorod arrays on FTO glass was characterized by X-ray diffraction patterns. As shown in Fig. 1, only the rutile structure of SnO_2 (JCPDS no. 41-1445) can be indexed in the XRD patterns of bare FTO glass. It is worth noting that as-prepared TiO_2 nanorod arrays show a tetragonal rutile structure (JCPDS no. 21-1276) after the hydrothermal reaction. The successful growth of TiO_2 nanorods can be ascribed to small lattice mismatch between FTO and rutile TiO_2 [26], which promote the epitaxial nucleation of TiO_2 on FTO substrate. Compared with the intensity of (1 0 1) and (1 1 2) diffraction peaks in XRD patterns of as-prepared TiO_2, the enhanced (0 0 2) peak indicates that the nanorods were well crystallized and grew in [0 0 1] direction with the growth axis parallel to the substrate surface.