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TiO_2 nanorod arrays/ZnO nanosheets heterostructured photoanode for quantum-dot-sensitized solar cells

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ABSTRACT

The three-dimensional heterostructured photoanode is considered to be an effective way to solve the problems of insufficient specific surface area and high electron recombination rate from one-dimensional nanomaterials. By combining the advantages of nanorods and nanosheets, we construct a novel TiO_2 nanorod arrays/ZnO nanosheets (TNRAs/ZNSs) heterostructure as the photoanode in quantum-dot-sensitied solar cells (QDSSCs) by a controllable chemical bath deposition method at an appropriate temperature. The photoelectrochemical properties are measured by UV–Vis absorption spectra, current density–voltage (*J-V*), open-circuit voltage attenuation test (*V-t*) and electrochemical impedance spectroscopy (EIS). The results reveal that the TNRAs/ZNSs photoanode has larger specific surface area and slower electronic recombination rate, and its power conversion efficiency increases by 260% compared with TNRAs-based QDSSCs. This three-dimensional heterostructure exhibits distinct advantages and we believe that it can be used in other photoelectronic devices.

1. Introduction

In recent years, quantum-dot-sensitized solar cells (QDSSCs) have increasingly become as well-known photovoltaic devices due to their unique characteristics (An et al., 2017; Im et al., 2011; Lee and Lo, 2009; Rühle et al., 2010; Santra and Kamat, 2012). In the QDSSCs, the photoanode plays an essential role, since it not only supplies a sufficient surface area for loading quantum-dots (QDs) but also provides a path for electron transport (Ge et al., 2016; Lv et al., 2013; Tian et al., 2013a, 2013b; Wu et al., 2014a, 2014b). Hence larger surface area and favourable electron pathway are required to enhance the performance of QDSSCs.

To date, TiO_2 as the most commonly used photoanode material for QDSSCs, has garnered much attention owning to its high chemical stability, nontoxicity, low cost and unique physical and chemical properties (Sharma et al., 2016). Diverse efforts on structures and morphologies of TiO_2 photoanodes have demonstrated that one-dimensional (1D) TiO_2 nanostructure, such as nanowires (Wu et al., 2013), nanotubes (Sun et al., 2008) and nanorods (Liu and Aydil, 2009; Li et al., 2016) can provide a direct path for electron transport, which can effectively improve the power conversion efficiency (PCE) of QDSSCs. However, the PCE of QDSSCs based on TiO_2 nanorod arrays (TNRAs) is still unsatisfactory, because of the limited QDs loading on the small specific surface area, which causes the insufficient utilization of sunlight in turn. To improve the specific surface area, various branched structures including tree-like (Liao et al., 2012; Sauvage et al., 2010; Sheng et al., 2014), cactus-like (Wu et al., 2014a, 2014b) and nanorod/nanosheet (Xu et al., 2015) composite films were used as the photoanodes of QDSSCs.

In addition to the enlarged surface area of photoanodes, superior efficiency in QDSSCs is also determined by charge separation and interfacial recombination rate (Ji et al., 2012; Song et al., 2014). To facilitate charge separation and reduce the electron recombination, a core shell three-dimensional (3D) heterostructure, where TiO_2 is coated by a higher conduction band metal oxide semiconductor (ZnO, Nb_2O_5, Al_2O_3, MgO, etc.) to form an energy barrier, has been introduced in QDSSCs (Ji et al., 2012). Among the numerous semiconductors oxide, ZnO has an energy band structure similar to TiO_2, and exhibits a significant advantage in terms of higher carrier mobility (205–1000 $cm^2 V^{-1} s^{-1}$ for ZnO and 0.1–4 $cm^2 V^{-1} s^{-1}$ for TiO_2) and lower photo inactivation compared with TiO_2 (Tian et al., 2013a, 2013b, 2014). As a result, many 3D heterostructures, including TiO_2

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nanorods arrays/branched ZnO (Liu et al., 2014), urchin-like order hollow TiO_2/ZnO nanorods (Cheng et al., 2013), TiO_2/ZnO core shell rice grain (Song et al., 2014), TiO_2 nanofiber/ZnO nanosheet (Cao et al., 2016), etc., have been designed and used in photovoltaic devices. Due to the largely suppressed of charge recombination, the PCE has been significantly improved. Furthermore, the introduction of ZnO on the TiO_2 nanorod arrays can not only promote the separation of photogenerated charge, but also improve the specific surface area. Compared with the same mole of ZnO nanorods and ZnO nanosheets, the latter has a higher density than the former grown in the trunk, and the studies have shown that the nanosheets have a higher light harvesting efficiency and light-scattering capability than nanorods. In order to make full use of the advantages of TiO_2 and ZnO, a TiO_2 nanorod arrays/ZnO nanosheets (TNRAs/ZNSs) composite structure would be profitable. Currently, the methods for preparing ZnO nanomaterials mainly include chemical vapor deposition, electrochemical deposition, hydrothermal method, etc (Zhang et al., 2009). Among these methods, the chemical bath deposition method (CBD) does not require high temperature, and the synthesis route is easy to achieve industrialization, which is advantageous in preparing nanomaterials.

In this paper, by combining the advantages of nanorods providing a direct electron path and nanosheets with large specific surfaces, we construct a novel TNRAs/ZNSs three-dimensional heterostructure by CBD method as the photoanode in QDSSCs. This photoanode shows an excellent light absorption capacity and charge separation ability. The shot-circuit current density (J_{sc}), open-circuit voltage (V_{oc}) and fill factor (*FF*) of the TNRAs/ZNSs-based QDSSCs are higher than those of the bare TNRAs-based QDSSCs. Meanwhile, the light absorption effects, the electron transfer and recombination effects of the TNRAs/ZNSs composite structure were investigated.

2. Experimental section

2.1. Preparation of TNRAs

TNRAs were grown onto fluorine-doped tin oxide (FTO) glass substrates using a hydrothermal method reported elsewhere (Ai et al., 2015). Briefly, 0.45 mL titanium n-butoxide and 0.6 g NaCl were added into the 30 mL diluted hydrochloric acid (mass fraction 18.25–19%) and stirred until the mixture became clear. After that, the above precursor was transferred into a 20 mL Teflon-lined stainless steel autoclave in which the FTO substrates were placed with an angle against the in-wall with the conductive side facing down. The hydrothermal process was conducted in an electric oven at 150 °C for 8 h. After cooling, the resultant samples were removed and rinsed with water to get rid of any residual reactants and dried in air at 80 °C.

2.2. Synthesis of hierarchically structured TNRAs/ZNSs

The TNRAs were immersed in an aqueous solution of 0.01 M zinc nitrate, 0.01 M hexamethylenetetramine (HMT) and 0.001 M trisodium citrate at 50–80 °C for 8 h (Tian et al., 2014). The substrate was drained from the reaction solution, washed several times with deionized water, and then calcined at 350 °C for 30 min.

2.3. Deposition of CdS QDs on TNRAs/ZNSs

For the growth of CdS QDs, first, the substrates were immersed in a 0.05 M aqueous solution of cadmium nitrate [$Cd(NO_3)_2$] and an aqueous solution for 2 min, respectively, to allow Cd^{2+} to adsorb onto the surface of TNRAs/ZNSs. Second, the substrates were dipped into a 0.05 M aqueous solution of sodium sulfide (Na_2S) and an aqueous solution for another 2 min, respectively, to allow S^{2-} to react with the pre-adsorbed Cd^{2+}, leading to the formation of CdS. This procedure was denoted as one SILAR cycle. In total, sixteen SILAR cycles were employed to obtain a suitable amount of CdS on the substrates.

2.4. Fabrication of CdS-Sensitized solar cell

The TNRAs/ZNSs films were used as photoanodes for QDSSCs. In order to evaluate the photovoltaic performance, the photoanodes were assembled with a Cu_2S counter electrode in a sandwich type, and the polysulfide electrolyte was injected into the space. The polysulfide electrolyte containing 1 M Na_2S, 1 M sulfur and 0.1 M NaOH in 7:3 (v/v) methanol/water was the same as those in previous report (Feng et al., 2015). The Cu_2S counter electrode was synthesized through facile chemical bath deposition. A total of 0.5 g $CuSO_4$ was dissolved in 100 mL of deionized water. Then, 2 g $Na_2S_2O_3{\cdot}5H_2O$ was added to the system, forming a light-green solution, which was kept in a 70 °C water bath for 3 h. After that, the Cu_2S counter electrode was rinsed with deionized water and dried in ambient air.

2.5. Characterization

The morphology and structure of TNRAs/ZNSs heterostructures were characterized by field-emission scanning electron microscopy (FESEM; JSM-6700F).The reflectance spectra were performed on a UV–visible spectrophotometer (UV-2550). The photovoltaic performance of QDSSCs was characterized by a Agilent B1500A sourcemeter using a solar light simulator (Newport 94023A) to simulate AM 1.5 G illumination (100 mW cm^{-2}). The electrochemical impedance spectroscopy (EIS) spectra were measured by an electrochemical workstation (CHI660E A15182) at a bias potential of V_{oc} in a frequency range from 0.01 Hz to 1 MHz under dark conditions. Impedance parameters were analyzed by fitting of the impedance spectra using Z-view software.

3. Results and discussion

3.1. Microstructure of TNRAs/ZNSs heterostructures

Fig. 1 shows the morphologies of TNRAs measured by FESEM. The

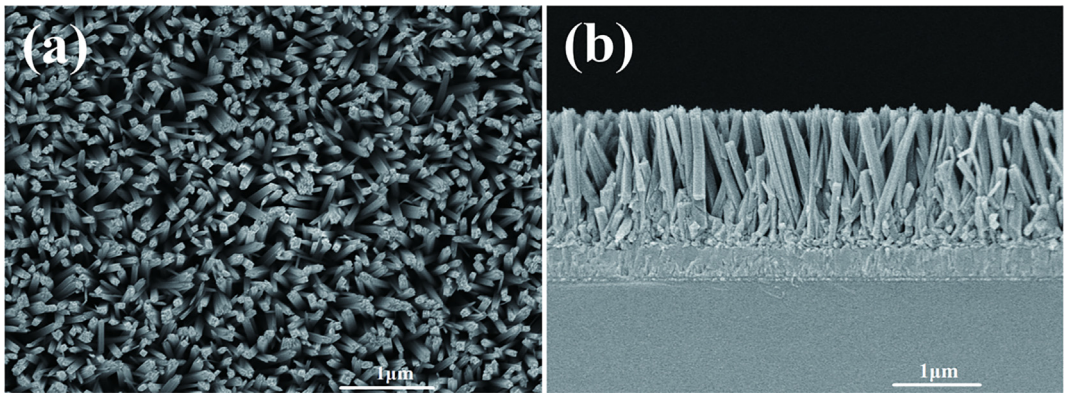

Fig. 1. FESEM micrographs of TNRAs. a, the top of the TNRAs; b, the side view of the TNRAs.