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One-dimensional Fe_2O_3/TiO_2 photoelectrode and investigation of its photoelectric properties in photoelectrochemical cell

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ABSTRACT

We reported a novel Fe_2O_3/rutile TiO_2 nanorod (NR) arrays with the heterogeneous structure for photoelectrochemical (PEC) cells, which were fabricated on fluorine-doped tin oxide glass (FTO) substrates that serve as model architecture via a hydrothermal method. Fe_2O_3 was revealed as an inexpensive and eco-friendly semiconductor sensitizer to make TiO_2 respond to visible light. By using this photoanode, the photoelectric conversion and water splitting properties of PEC cells based on the one-dimensional (1D) Fe_2O_3/TiO_2 heterostructures were investigated in detail under simulated sunlight. Meanwhile, the optimization of photovoltaic performance was also achieved by regulating the amount of Fe_2O_3. The open circuit voltage and short circuit current of the Fe_2O_3/TiO_2 solar cell can reach 0.435 V and 1.840 mA/cm^2, respectively. In addition, theoretical analysis of the photoelectric effect is preliminarily explored on the basis of the flat band potential results.

1. Introduction

Photoelectrochemical (PEC) cells have attracted increasing attention due to their promising applications for solar cells and water splitting [1–3]. The conventional PEC cell consists of a semiconductor photoanode, a redox electrolyte, and a counter electrode. The semiconductors such as TiO_2, $SrTiO_3$ and ZnO usually serve as charge transport materials in photoanodes [4–6], due to their long lifetime and large diffusion coefficient of the photogenerated charge carriers, nevertheless, the visible light can not be used sufficiently in the photoanodes because of their wide band gap. Therefore, materials with narrow band gap such as organic dye [7,8], chalcogenide quantum dots (CdS [9–11], $CuInS_2$ [12], Ag_2S [13] etc) have been used to sensitize these wide-band gap materials. However, their poor stability and high costs greatly limit their further application. One method to solve these problems is directly using narrow-band gap material. For example, Bian and co-workers have used graphitic carbon nitride as visible-light-driven photoelectrode materials for PEC cells [14–17].

α-Fe_2O_3, a common semiconductor with a narrow-band gap of 2.1 eV, has demonstrated promising industrial applications because of its easy fabrication, good chemical resistance under caustic operating conditions, low cost and nontoxic nature [18–21]. But single α-Fe_2O_3 photoanode has been limited due to the short lifetime of photogenerated charge carriers, poor oxygen evolution reaction (OER) kinetics and short hole diffusion length [22–25]. Thus, semiconductor nanocomposites of α-Fe_2O_3 have been intensively investigated due to their good charge separation based on the interfacial heterogeneous structure. Wang et al. demonstrated mesoporous Fe_2O_3/TiO_2 heterostructured photocatalyst with strong optical absorption and enhanced catalytic activity. Fe_2O_3/TiO_2 heterostructured microsphere demonstrates highly visible light photoactivity because of their high electron-hole separation efficiency and mesoporous microsphere structure [26]. Zhang et al. prepared one-dimensional (1D) mesoporous Fe_2O_3@TiO_2 core-shell photocatalyst, which possesses the combined advantages, thus delivering clearly enhanced photocatalytic activity for Rhodamine B under visible light irradiation and the degradation of methyl orange under UV light irradiation [27]. Yao et al. prepared Fe_2O_3-TiO_2 core-shell nanorod arrays by using the glancing angle deposition technique and post-deposition annealing, and showed higher catalytic efficiency for the degradation of methylene blue (MB) and greater efficiency for solar CO_2 conver-

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sion under visible light illumination when compared with pure anatase TiO_2 or α-Fe_2O_3 nanorod arrays [28]. Recently, Jing and co-workers confirmed that the promoted charge separation results from the uncommon transfers of visible-excited high-energy electrons of Fe_2O_3 to rutile TiO_2. Moreover, it is more favorable for the uncommon electron transfers of α-Fe_2O_3 to rutile than to anatase, depending on the conduction band bottom level of TiO_2 [29]. Therefore, the high photocatalytic activities indicate strong photogenerated charges separation exist in the Fe_2O_3-TiO_2 heterostructure. It is easily expected that Fe_2O_3 is a promising material for sensitizer to form heterostructures with TiO_2. However, previous studies have mainly focused on the photocatalytic activities of Fe_2O_3/TiO_2 composites for the degradation of organic dyes. As far as we know, there are few reports on Fe_2O_3 as an effective sensitizers on PEC cells for photoelectric conversion and water splitting.

In the present study, we designed a novel one-dimensional Fe_2O_3/TiO_2 photoanode for solar cells and PEC water splitting, which was fabricated with Fe_2O_3 grown onto 1D TiO_2 nanorods via a hydrothermal method. The photoanode presents some favorable characteristics, which are easy fabrication, excellent light scatter effect, environmental friendliness and low cost [30]. The growth of Fe_2O_3 nanorods can be controlled by increasing the concentrations of $FeCl_3$ and $NaNO_3$. By hydrothermal method, Fe_2O_3 and TiO_2 can be combined to form a heterogeneous structure, endowed with the advantages of its specific structural features, which can better utilize visible light and improve the photoelectric conversion performance of single TiO_2 and Fe_2O_3.

2. Experimental section

2.1. Synthesis of α-Fe_2O_3 film

Fe_2O_3 photoanode was fabricated via a hydrothermal method. A fluorine-doped tin oxide glass (FTO, Nippon Sheet Glass) of 2.0 × 2.5 cm was fully cleaned with deionized water, ethanol, acetone and ethyl acetate. The FTO was put into a fresh aqueous solution of 0.03 M $FeCl_3$ (99%, Aladdin) and 0.2 M $NaNO_3$ (99%, Sinopharm Chemical Reagent Co., Ltd) in an autoclave with the single conductive side facing the wall of the liner, then the autoclave was placed in a regular laboratory oven and heated to 100 °C for 12 h. After the reaction, the film formed on the FTO substrates was thoroughly rinsed with deionized water and annealed in air at 550 °C for 2 h at a ramp rate of 2 °C·min^{-1}.

2.2. Synthesis of pure TiO_2 NR arrays

Pure TiO_2 NR arrays were directly grown on FTO substrates (20 ohm per square) via a hydrothermal method reported previously. 15 mL of deionized water was mixed with 15 mL of concentrated hydrochloric acid (36–38%, Beijing Chemical Works). The mixture was stirred under ambient condition for 5 min. Then, 0.5 mL of tetrabutyl titanate (98+%, Aladdin) was added to the mixture and further stirred for 5 min. Then, 8 mL of the solution was transferred to a Teflon-lined stainless steel autoclave (15 mL volume), where a cleaned FTO glass was placed in the Teflon reactor with the conductive side facing down. The hydrothermal synthesis was maintained at 150 °C for 20 h in a regular laboratory oven. After the autoclave was cooled to room temperature, the FTO substrate with the TiO_2 NR arrays were taken out, rinsed extensively with deionized water and allowed to dry in ambient air.

2.3. Synthesis of Fe_2O_3/TiO_2 nanocomposites

For the preparation of Fe_2O_3/TiO_2 nanocomposites, an aqueous solution (10 mL) containing 0.03 M $FeCl_3$ (99%, Aladdin) and 0.2 M $NaNO_3$ (99%, Sinopharm Chemical Reagent Co., Ltd) was sealed in a 15 mL Teflon-lined stainless steel autoclave. A FTO grown with TiO_2 was placed in the liner with the FTO side facing the wall of the liner. The liner was put into a self-sealing autoclave and heated at 100 °C for 12 h. After the reaction, the films formed on the FTO substrates were thoroughly rinsed with deionized water and annealed in air at 550 °C for 2 h at a ramp rate of 2 °C · min^{-1}. The amount of Fe_2O_3 was regulated by increasing the concentrations of $FeCl_3$ and $NaNO_3$. $2Fe_2O_3$/TiO_2 and $5Fe_2O_3$/TiO_2 mean 2 times and 5 times of initial concentration of raw material, respectively.

2.4. Characterization

X-ray diffraction (XRD) patterns were characterized on a Bruker (Germany) D8 Advance diffractometer with Cu Kα radiation in the range of 20°–80° (2θ). Field emission scanning electron microscopy (FESEM) images were determined by using a FESEM JSM-6700F microscope. UV–vis diffuse reflectance spectroscopy (DRS) measurements were obtained on an UV–vis spectrometer (Shimadzu UV-2550) using $BaSO_4$ as a reference standard. In photovoltaic measurements, the Fe_2O_3/TiO_2 working electrodes together with platinized conducting glasses serve as a prototype solar cell device. The current density-voltage (I–V) curves were recorded by an electrochemistry workgroup (CHI660E, Shanghai). A 500 W xenon lamp (CHFXQ500W, Beijing Trusttech Co. Ltd.) was used as the light source and a filter plate (simulated AM 1.5 sunlight, Beijing Trusttech Co. Ltd.) was used to control the wavelength of light. The output light intensity was about 100 mW/cm^2, which was measured with a radiometer (Photoelectronic Instrument Co., attached to Beijing Normal University, China). The effective area of the solar cell is 0.25 cm^2. The photocurrent density-time (I–t) curves were also carried out using this photovoltaic measurement. The solar cells were directly tested in chopping mode, light on-off repeatedly. The photovoltage generated by the solar cells can result in strong photocurrent and no applied bias was used. The flat band (FB) potentials of TiO_2 and Fe_2O_3 were determined from Mott-Schottky plots recorded by electrochemistry workgroup (CHI660E, Shanghai). A three-electrode single compartment immersed in 0.5 M Na_2SO_4 solution was used for capacitance analysis. The as-prepared film on FTO was used as a working electrode while Ag/AgCl electrodes and platinum electrodes were used as reference electrodes and counter electrodes, respectively. The PEC water splitting measurements were recorded by electrochemistry workstation system (CHI660E, Shanghai) with a Xe lamp (CHFXM500, Beijing Trusttech Co. Ltd.) as light source under AM 1.5 optical filter (Beijing Trusttech Co. Ltd.). A three-electrode configuration was used with the samples on FTO as working electrode, Ag/AgCl reference electrode and platinum counter electrode. The light intensity was calibrated to 100 mW/cm^2.

3. Results and discussion

3.1. Structural studies

The XRD patterns of TiO_2 NR arrays film, Fe_2O_3 film and Fe_2O_3/TiO_2 heterogeneous structure are depicted in Fig. 1. The crystal phase of the TiO_2 NR arrays was a rutile phase with a tetragonal structure (JCPDS 21–1276). The relatively high intensity of the (002) peak implies that the nanorods are well crystallized and oriented with respect to the FTO substrate [31,32]. The data of Fe_2O_3 film can be indexed to the characteristic peaks of α-Fe_2O_3 (JPCDS 86–0550), after subtracting the diffraction peaks originating from FTO. The peak intensities of TiO_2 in the composites are weak. This should be caused by the surface coating of the Fe_2O_3. Therefore α-Fe_2O_3 and TiO_2 were successfully combined together, and the heterogeneous structure was formed.