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Improving photoelectrochemical performance by building Fe_2O_3 heterostructure on TiO_2 nanorod arrays

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ABSTRACT

Fe_2O_3@TiO_2 heterostructure nanorod arrays were synthesized on a fluorine-doped tin oxide conductive (FTO) glass substrate via two-step method for improving photoelectrochemical activity of TiO_2. The TiO_2 nanorod arrays on FTO substrate were first prepared by hydrothermal method and then Fe_2O_3 nanoparticles were coated onto the surface of TiO_2 nanorod arrays through chemical bath deposition. The heterojunction yielded a photocurrent density of 39.75 $\mu A\,cm^{-2}$ at a bias potential of 0 V (vs. Ag/AgCl) under visible light irradiation, which is 2.2 times as much as that produced by the pure TiO_2 nanorod arrays. The enhanced photoelectrochemical activity is attributed to the extension of the light response range and efficient separation of photogenerated carriers. Our results have demonstrated the advantage of the novel Fe_2O_3@TiO_2 heterojunction and will provide a new path to the fabrication of heterostructural materials.

1. Introduction

One-dimensional (1D) nanostructure materials have attracted much interest during the last decade due to their unique physical and chemical properties as well as their utilization in solar cells [1–3], sensors [4,5]. Semiconductor TiO_2 nanostructures [6–8], with wide band gap (E_g = 3.0–3.2 eV), have potential applications in photoelectrochemical solar cells and catalytic supports because of their low cost, high specific surface area. However, a major factor affecting the photoelectrochemical properties of TiO_2 is its narrow absorption spectral range, which can only absorb the ultraviolet energy in solar light. Another limitation is the fast recombination of photo-induced electron–hole pairs in TiO_2. To overcome these problems, some methods have been proposed, including noble metal deposition [9], doping of metal or nonmetal ions [10], semiconductor heterostructure [11] and photosensitized with dye [12]. In particular, heterojunction has been considered as an effective alternate for solving the charge separation, transport, and enhancement of light absorption problems [13–16]. Many heterojunctions have been successfully built in recent years, such as CdS/TiO_2 [17], Co_3O_4/TiO_2 [18], CdS/ZnO [19], Ag_2O/TiO_2 [20], In_2O_3/TiO_2 [21], etc. Ferric oxide (Fe_2O_3), a conventional *n*-type semiconductor with a band gap of 2.2 eV, is a promising material for solar energy conversion due to its unique properties [22,23]. But low conductivity and short length of holes diffusion in Fe_2O_3 impede its practical applications [24]. Heterojunction constructed by Fe_2O_3 and TiO_2 with their suitable valence band and conduction band positions is a promising strategy for promoting photon-excited carriers separating and transporting, and thus enhancing light absorption activity.

In this work, we successfully prepared a novel Fe_2O_3@TiO_2 heterojunction nanorod arrays (NRs) in an attempt to improve the photoelectrochemical response of the TiO_2 NRs in the visible light region. The Fe_2O_3@TiO_2 heterostructure NRs exhibit excellent photoelectrochemical performance due to the synergistic effect of the heterojunction, making it promising as a high performance photoelectrode in photoelectrochemical cells.

2. Experimental

2.1. Preparation of Fe_2O_3@TiO_2 heterostructure NRs

The Fe_2O_3@TiO_2 heterostructure NRs were fabricated via a three-step process: (1) The TiO_2 NRs were fabricated on FTO substrate using a hydrothermal method [4]. (2) The Fe_2O_3@TiO_2 heterostructure NRs were synthesized by an ordinary chemical bath deposition. Typically, the TiO_2 NRs were immersed in a $Fe(NO_3)_3$ solution with different concentrations (0.05, 0.1, 0.2 and

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0.4 mol L^{-1}) for 2 days, and then carefully washed with distilled water and dried in air for 1 h. (3) Finally, the prepared samples were annealed at 450°C for 2 h in air atmosphere with a heating rate of 10 °C min^{-1}. Then, the Fe_2O_3@TiO_2 heterostructure NRs was formed. The amount of Fe_2O_3 nanoparticles was controlled by changing the $Fe(NO_3)_3 \cdot 9H_2O$ concentration and is listed in Table 1.

2.2. Characterization

The structure, morphology, compositions and chemical valences of the as-prepared products were characterized with X-ray diffraction (XRD-6000, Shimadzu, with Cu Kα radiation), filed emission scanning electron microscopy (FESEM, FEI Nova 400), transmission electron microscope (TEM, JEOL-4000EX), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS, VG ESCALAB 210). Room temperature ultraviolet–visible (UV–vis) reflection spectrum was recorded by UV–VIS–NIR Spectrophotometer (Shimadzu UV-3600) in the wavelength range of 240–800 nm.

2.3. Photoelectrochemical measurement

The photoelectrochemical measurement was performed in a conventional three-electrode system linked with the electrochemical workstation (CH Instruments, model CHI 660D). The prepared samples served as the working electrodes with an exposed area of 1 × 1 cm^2, a Pt foil and a saturated Ag/AgCl served as the counter electrode and a reference electrode, respectively. An aqueous solution containing 0.1 M Na_2S was used as an electrolyte. The simulated sunlight (CHF-XM-500W) was used for the photoelectrochemical measurement and the light intensity, equivalent to AM 1.5 light at 100 mW cm^{-2}, was calibrated by using a laser power meter (BG26M92C, Midwest Group). Electrochemical impedance spectroscopy (EIS) measurement was carried out to understand the charge transport properties of the photoelectrodes. The measurement was done in 0.1 M Na_2SO_4 aqueous solution at 0.25 V (vs. Ag/AgCl) under the same conditions as described above for photoelectrochemical tests. The amplitude of the sinusoidal wave is 10 mV and the frequency range is 10^5 Hz–0.1 Hz. All the experiments were carried out under ambient conditions.

3. Results and discussion

3.1. XRD analysis

Fig. 1 presents XRD patterns of the TiO_2 NRs and Fe_2O_3@TiO_2 heterostructure NRs. The diffraction peaks at $2\theta = 36.28°$ and 63.13° can be labeled as (1 0 1) and (0 0 2) planes of the rutile phase TiO_2 (JCPSD, No. 87-0920). After Fe_2O_3 nanoparticles being coated onto the TiO_2 nanorods, additional peaks appear at $2\theta = 33.14°$ and 54.24°, which are assigned to the (1 0 4) and (1 1 6) planes of Fe_2O_3 (patterns b–e). The intensity of the peak at $2\theta = 33.14°$ increases gradually with the increase in concentration of ferric nitrate solution. The average crystallite size of the Fe_2O_3 nanoparticles was calculated to be about 25 nm from the main diffraction peak at 33.14° using Scherrer's equation [25]. A possible fundamental reaction involved can be simplified as follows:

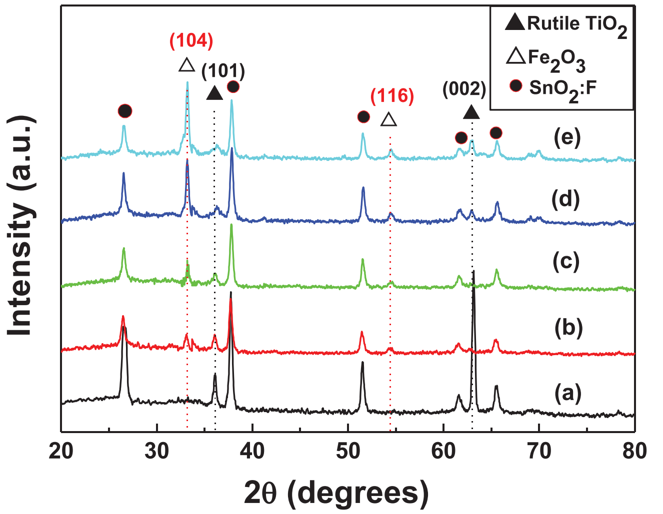

Fig. 1. XRD of (a) pure TiO_2 NRs, (b) S-a, (c) S-b, (d) S-c and (e) S-d, respectively.

$$4Fe(NO_3)_3 = 2Fe_2O_3 + 12NO_2\uparrow + 3O_2\uparrow \qquad (1)$$

In addition, other iron oxides or Fe_xTiO_y phases are not found in the patterns of XRD, which is in accord with the results reported by Refs. [26,27]. The XRD results confirm that Fe_2O_3 nanoparticles were coated onto the surface of TiO_2 NRs.

3.2. Thin film structure

Fig. 2(a) and (b) shows typical FESEM images of the TiO_2 nanorod film. It can be clearly observed from Fig. 2(a) and (b) that highly dense TiO_2 NRs with smooth surface are nearly perpendicular to the FTO substrate. The nanorods are tetragonal in shape with a square facet on the top, 120–140 nm in diameter and 2.0 μm in length. After chemical bath deposition, the TiO_2 NRs retain their tetragonal morphology, as is shown in Fig. 2(c) and (d). Compared with TiO_2 nanorods, the TiO_2 nanorods exhibit an increase approximately 20 nm in diameter and the surface of nanorods becomes rough, indicating that the Fe_2O_3@TiO_2 heterojunction NRs are formed by being coated with Fe_2O_3. Fig. 3 shows the morphologies of the Fe_2O_3@TiO_2 heterojunction NRs obtained from different concentration of ferric nitrate solutions. With an increase in the ferric nitrate concentration, more Fe_2O_3 nanoparticles are distributed uniformly onto the surface of TiO_2 NRs. The corresponding EDS analyses in Fig. 3(e) and (f) reveal the existence of the elements O and Ti for the TiO_2 NRs and Ti, O and Fe elements for the Fe_2O_3@TiO_2 heterojunction NRs (S-b) (note that the Sn and Si signals from the substrate).

The more detailed microstructure characteristics of the pure TiO_2 and Fe_2O_3@TiO_2 heterostructure NRs are further studied by TEM, as is shown in Fig. 4. The TEM image (Fig. 4(a)) shows that the as-prepared TiO_2 sample is rod-shaped with smooth walls and a diameter of 300 nm for 4 h growth. The corresponding SAED pattern (Fig. 4(b)) shows that the nanorods are single-crystalline growing in the (0 0 1) direction. A low magnification TEM image of Fe_2O_3@TiO_2 heterostructure NRs (S-b) is illustrated in Fig. 4(c). It is evident that the surface of TiO_2 nanorods is coated with Fe_2O_3 layer with a thickness of about 25 nm. Fig. 4(d) shows high crystalline nature of the Fe_2O_3 with more than 20 nm grain size deposited onto the single crystalline TiO_2 nanorods. This unique structural feature provides an intimate interface between the Fe_2O_3 nanoparticles and TiO_2 nanorods, which might contribute to the

Table 1
Experimental conditions for the preparation of the Fe_2O_3@TiO_2 heterostructure and their corresponding physicochemical properties.

Sample	$Fe(NO_3)_3$ (M)	Anneal	Composition	Photocurrent	Activity
TiO_2 NRs	0	450 °C	TiO_2	Low	Low
S-a	0.05	450 °C	TiO_2@Fe_3O_2	Medium	Medium
S-b	0.1	450 °C	TiO_2@Fe_3O_2	Medium	Medium
S-c	0.2	450 °C	TiO_2@Fe_3O_2	High	High
S-d	0.4	450 °C	TiO_2@Fe_3O_2	Medium	Medium