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CTAB assisted hydrothermal preparation of Bi_2WO_6—WO_3 nanosheets on TiO_2 nanotube arrays for photoelectrocatalytic applications

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ABSTRACT

Bi_2WO_6—WO_3 nanosheets were deposited on the surface of TiO_2 nanotube arrays (TiO_2 NTs/Bi_2WO_6) via the one-pot hydrothermal method by adjusting the addition of cetyltrimethyl ammonium bromide (CTAB), and the morphology, composition and visible light response were investigated. The as-prepared TiO_2 NTs/Bi_2WO_6 showed significantly enhanced visible light absorption, visible light photocurrent and photoelectrocatalytic removal of MO, RhB, MB and Cr(VI). The results indicated that when the addition of CTAB was 0.1 g, the Bi_2WO_6—WO_3 nanosheets with a thickness of 10 nm on TiO_2 NTs showed the visible light photocurrent density of 104.89 mA/cm^2, photoelectrocatalytic removal efficiencies of 75.65%, 66.07%, 95.21% and 74.18% for the removal of MO, RhB, MB and Cr(VI), respectively. The excellent photoelectrochemical performances of TiO_2 NTs/Bi_2WO_6 were ascribed to the high visible light absorption and rapid transportation of photogenerated electrons on Bi_2WO_6—WO_3 nanosheets, and the corresponding mechanism was tentatively proposed.

1. Introduction

In recent years, TiO_2 nanotube arrays have been recently drawing great attention as a star material for solar energy application because of their superior photocatalytic and photoelectronic performance [1–3]. The high specific surface area and unique highly ordered array structure prepared on a Ti substrate provide the excellent carrier for quantum dot adsorption and effective photogenerated electron transportation. Because of the inherent narrow band gap, many efforts especial serious semiconductor sensitizations have been attempted to harvest visible light which contributes about 45% of the whole solar spectrum. Various semiconductors including sulfide semiconductors [4], oxide semiconductors [5] and even complex semiconductor compounds [6] were deposited on the surface of TiO_2 NTs to improve the visible light harvesting. However, the microstructures of these semiconductors were not paid special attention, and the influences of semiconductor structures on the photoelectrochemical performance especial the electron separation and transportation of hybrid materials should be investigated in detail. It is well known that graphene is the marvellous transportation materials due to its ultrathin sheet structures, and TiO_2 NTs/graphene hybrid photoelectrodes are prepared to reduce the recombination chance of electron-hole pairs, which achieve the perfect results [7]. However, graphene only could be used to accelerate the transportation of photogenerated electrons, but the solar absorption efficiency is too low as TiO_2 NTs sensitizers. Therefore, it is exciting to explore the high visible light active sensitizers with 2 D nanosheet structures, which would synchronously overcome the restrictions on the poor visible light response and high recombination rate of TiO_2 NTs.

Compared with $BiVO_4$ and other bismuth based semiconductor [8–10], the Bi_2WO_6 photocatalyst with a bandgap of ~2.8 eV has attracted intensive interest due to its excellent intrinsic physical and chemical properties for decomposition of organic dyes in recent years [11]. Investigation researches indicate the morphology of Bi_2WO_6 significantly influences the photocatalytic degradation of dye molecules, and the regulation synthesis of Bi_2WO_6 with uniform microstructures could be achieved by addition of morphological controlling agents [12]. Zheng and his co-workers [13] prepared flower-like Bi_2WO_6 by the hydrothermal method using CTAB as the morphological controlling agent. Zhang [14] prepared a series of Bi_2WO_6 photocatalysts by a surfactant-assisted hydrothermal method, and the influences of surfactant on the photocatalytic activity of Bi_2WO_6 nanoparticles were studied in detail. Kong et al. [15] reported the ultrathin Bi_2WO_6 nanosheets with high harvesting ability of ultraviolet or/and visible light, whereas the near-infrared, and the nanosheet structures greatly improved the photoelectrochemical properties. Therefore, Bi_2WO_6 nanoparticles, especial Bi_2WO_6 nanosheets, would be the excellent sensitizer to enhance the solar absorption and photoelectrochemical properties. To the best of our knowledge, little work has been reported so far concentrating on the deposition of Bi_2WO_6 nanosheets on the surface of

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TiO_2 NTs to improve the visible light photocurrent and photocatalytic removal of pollutants. In this paper, the cationic surfactant CTAB was used to adjust the morphology of Bi_2WO_6 nanoparticles on the surface of TiO_2 NTs by the one-pot hydrothermal method, and Bi_2WO_6-WO_3 nanosheets with thicknesses of 10 nm were prepared by addition of 0.1 g CTAB. The prepared TiO_2 NTs/Bi_2WO_6—WO_3 showed the high visible light response, photocurrent and photoelectrocatalytic properties.

2. Experimental

2.1. Materials

Cetyltrimethyl ammonium bromide (CTAB), Ti substrate, bismuth nitrate ($Bi(NO_3)_3·5H_2O$) and sodium tungstate ($Na_2WO_4·2H_2O$) are purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), of analytical grade, and used without further purification.

2.2. Preparation of Bi_2WO_6—WO_3 nanosheets sensitized TiO_2 NTs

TiO_2 nanotube arrays were prepared on a Ti substrate by a simple anodization method, which was similar with our previous report [16]. Bi_2WO_6 nanosheets were deposited on the surface of TiO_2 NTs by a hydrothermal method using CTAB as a morphological controlling agent. Firstly, 1 mmol of $Bi(NO_3)_3·5H_2O$ was dissolved into 30 mL of 1 M HNO_3 solution under sustained magnetic stirring, and then 1 mmol of $Na_2WO_4·2H_2O$ was added into the $Bi(NO_3)_3$ solution to prepare Bi_2WO_6 precipitations. To obtain the uniform morphology of Bi_2WO_6 nanoparticles, CTAB with different addition amounts of 0 g, 0.05 g, 0.10 g and 0.15 g, were dissolved into the mixed solution. Secondly, the solution was transferred into a 50 mL autoclave with an inner Teflon lining, maintained at 160 °C for 14 h, and then cooled to room temperature. Lastly, the film was taken out from the autoclave, and ultrasonically washed thoroughly with ethanol and deionized water, and dried at 60 °C in air. To investigate the influence of CTAB on the morphology and photoelectrochemical performances of TiO_2 NTs, the samples prepared with different CTAB additions of 0 g, 0.05 g, 0.10 g and 0.15 g were marked as TiO_2 NTs/Bi_2WO_6 (0), TiO_2 NTs/Bi_2WO_6 (0.05), TiO_2 NTs/Bi_2WO_6 (0.10) and TiO_2 NTs/Bi_2WO_6 (0.15), respectively.

2.3. Characterization

The products were characterized by using XRD (D8 ADVANCE, Germany), SEM (Quanta 200 FEG, Japan), and DRS (UV-2550, Japan). The transient photocurrent responses and electrochemical impedance spectroscopy (EIS) Nyquist plots of the samples were acquired using a (CHI610E, China) electrochemical workstation with a standard three electrode system. The working electrode was the prepared samples with an active area of 1.8 cm^2, and Ag/AgCl and Pt served as the reference and counter electrodes, respectively. The sample electrodes were illuminated with a solar simulator equipped with a 500 W Xe lamp (CEL-S500) with a visible-light filter (> 400 nm).

2.4. Measure of the photoelectrocatalytic activity

The photoelectrocatalytic (PEC) activities of the samples for the degradation of methylene orange (MO), methylene blue (MB), rhodamine B (RhB) solution were measured under solar irradiation simulated using a 500 W Xe lamp (CEL-S500). A 0.1 M Na_2SO_4 solution was used as supporting electrolyte, and the potential was fixed at 1 V versus Ag/AgC. Before photodegradation, adsorption equilibrium for the dye on catalyst surface was established by magnetic stirring in the dark for 30 min. After visible-light irradiation for 20 or 30 min, the remaining dye concentration was determined with a UV–vis spectrophotometer by detecting the maximum absorption wavelength for MO, MB and RhB at 464, 664 and 552 nm, respectively.

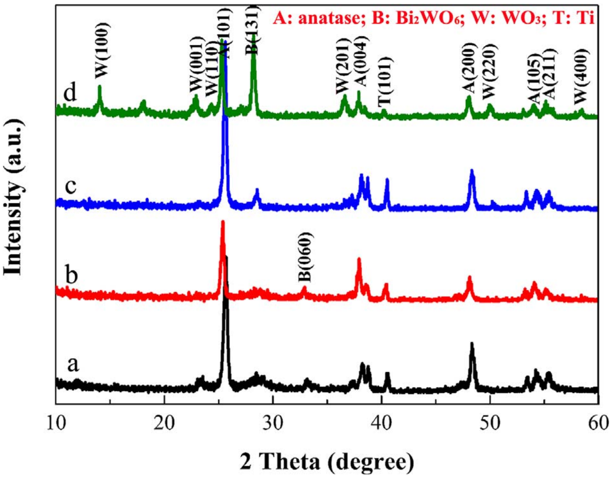

Fig. 1. XRD patterns of the as-prepared samples: (a) TiO_2 NTs/Bi_2WO_6 (0), (b) TiO_2 NTs/Bi_2WO_6 (0.05), (c) TiO_2 NTs/Bi_2WO_6 (0.10) and (d) TiO_2 NTs/Bi_2WO_6 (0.15).

The PEC reduction of Cr(VI) was performed similar with the PEC degradation of dyes. A 0.1 M NaCl solution was used as supporting electrolyte, and the potential was fixed at 0.5 V versus Ag/AgC. The Cr (VI) content in the solution was determined colorimetrically at 540 nm using the diphenylcarbazide method.

3. Results and discussion

The phase compositions of TiO_2 NTs and TiO_2 NTs/Bi_2WO_6—WO_3 were investigated by X-ray diffraction patterns. As shown in Fig. 1a, except for the diffraction peaks of Ti substrates, (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 1 1) crystal faces located at diffraction peaks 25.3°, 37.8°, 48.1°, 53.9° and 55.1° could be observed, which are identical with the standardization anatase TiO_2 (JCPDS12-1272). After the hydrothermal deposition, new diffraction peaks at 28.3° corresponding to the (1 3 1) diffraction face of Bi_2WO_6 (JCPDS 39-0256) is observed. Surprisingly, several distinct peaks at 13.9°, 22.7°, 24.3°, 36.6°, 49.9° and 58.3° could be indexed as (1 0 0), (0 0 1), (1 1 0), (2 0 1), (2 2 0) and (4 0 0) diffraction faces of WO_3 (JCPDS 33-1387), respectively. The WO_3 particles are the byproduct during the formation of Bi_2WO_6, and they could form heterojunction with high electron transportation interfaces, which has been reported by Li and his colleagues [17].

The influence of CTAB addition on the morphology of Bi_2WO_6-WO_3 deposited on the surface of TiO_2 NTs was investigated from SEM images of TiO_2 NTs/Bi_2WO_6—WO_3. As shown in Fig. 2a and b, few Bi_2WO_6—WO_3 nanoparticles are covered on the surface of TiO_2 NTs when no CTAB was added in the hydrothermal progress. When 0.05 g CTAB was added into the solution, the cationic surfactant molecules could rapidly adsorbed on Bi_2WO_6—WO_3 crystal faces with high energy, and the adsorption effect induces the orientated growth of Bi_2WO_6—WO_3 nanoparticles. Therefore, CTAB is an effective morphological controlling agent, which has the key roles in the formation of Bi_2WO_6—WO_3 nanosheets. Further improving the addition of CTAB to 0.1 g, the ultrathin Bi_2WO_6—WO_3 nanosheets with thicknesses of 10 nm are vertically arranged on the surface of TiO_2 NTs, and these uniform Bi_2WO_6—WO_3 flakes intersect with each other to form petalstructures. When the amount of CTAB was improved to 0.15 g, too much CTAB inversely destroyed the uniform morphology of Bi_2WO_6—WO_3 nanosheets, and the thickness of Bi_2WO_6—WO_3 nanosheets becomes too large, which cause the absolute coverage of TiO_2 nanotubes.

The visible light response properties of TiO_2 NTs and TiO_2 NTs/Bi_2WO_6 were evaluated by UV–vis diffuse reflectance spectra (DRS). As shown in Fig. 3a, pure TiO_2 NTs could only absorb the UV light with wavelength shorter than 385 nm, which is ascribed to the inherent band