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Self-assembled Bi_2MoO_6/TiO_2 nanofiber heterojunction film with enhanced photocatalytic activities

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ABSTRACT

TiO_2 nanofiber film (TiO_2 NFF) was successfully fabricated by an ethylene glycol-assisted hydrothermal method, and then self-assembled flake-like Bi_2MoO_6 was grown on the surface of TiO_2 nanofiber under alcohol thermal condition. The investigations indicate that the nanofiber structure of TiO_2 films exhibits excellent visible light scattering property, the scattering light overlaps with the absorption band of Bi_2MoO_6, which can enhance the utility of incident light. The prepared Bi_2MoO_6/TiO_2 composites show obviously enhanced photocatalytic activity for methylene blue (MB) degradation compared with pure TiO_2 nanofiber under visible light irradiation ($\lambda > 420$ nm). The enhanced photocatalytic activity is primarily attributed to the synergistic effect of visible light absorption and effective electron-hole separation at the interfaces of the two semiconductors, which is confirmed by photoluminescence (PL) and electrochemical tests.

1. Introduction

The development of semiconductor photocatalysis has been considered as the most promising method to solve the energy shortages and environmental-related problems [1,2]. Over the past few decades, TiO_2-based semiconductors have attracted a great deal of attention in photocatalysis field, for their strong oxidizing power, nontoxicity, and environmentally friendly feature [3–8]. However, the application of TiO_2 is greatly limited by the fast recombination of electron/hole pairs and narrow light-absorption range [9–15]. Therefore, many efforts have been already employed to overcome the aforementioned problems, such as element doping, surface photosensitization, structural control and so on [16–20].

It has been proved that narrow-band gap semiconductor combination is an effective strategy for restraining the recombination of the electrons and holes and extending light absorption range [21–28]. Among the various photocatalysts, Bi_2MoO_6 semiconductor with a typical band gap of about 2.75 eV, has sparked considerable interest of researchers for their layer structures, excellent intrinsic physical and chemical properties [29]. More importantly, Bi_2MoO_6 have suitable band edges, which can match well with TiO_2 to form a heterojunction photocatalyst. Zhang et al. [30] prepared one-dimensional Bi_2MoO_6/TiO_2 hierarchical heterostructure by a combination of electrospinning and a solvothermal technique, which possessed a much higher degradation rate of Rhodamine B than the unmodified TiO_2 nanofiber and Bi_2MoO_6 under UV and visible light. In addition, Tian et al. [31] prepared 3D Bi_2MoO_6 nanosheet/TiO_2 nanobelt heterostructure by a simple hydrothermal method, which possesses high photocatalytic oxygen production with a rate of 0.668 mmol h^{-1} g^{-1}, and shows an enhanced photoelectochemistry performance under irradiation of solar illumination.

In our previous studies, an overlapped light trapping phenomenon was observed in Au/TiO_2 nanofiber film due to the visible light scattering nanostructures of TiO_2 film and the surface plasmon resonance of Au nanoparticles, the investigations reveal that the overlapped light-trapping nanostructures can greatly improve the photocatalytic activity of a composite system. Jiang et al. [32] demonstrated that dye sensitized solar cells with the TiO_2 nanospindles as light scattering layer show a 27% increment of energy conversion efficiency compared to that of P25 single layer film. Wang et al. [33] introduced the TiO_2 hollow sphere's scattering layer in quantum dot-sensitized solar cells and achieved a notable 10% improvement of solar-to-electric conversion efficiency. Based

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on the above understanding, TiO_2 nanofiber film with remarkable visible light scattering ability can be employed as a proper light harvesting layer to achieve an overlapped light trapping nanostructures, which may provide a strong interaction between Bi_2MoO_6 and TiO_2 photocatalyst.

In this paper, TiO_2 nanofiber films were prepared using a hydrothermal method with ethylene glycol as a morphology-controlling agent. Subsequently, self-assembled flake-like Bi_2MoO_6 was grown on the surface of TiO_2 nanofiber under alcohol thermal condition to obtain the Bi_2MoO_6/TiO_2 heterostructure photocatalysts. The investigations indicate that the nanofiber structure of TiO_2 films exhibit excellent visible light scattering property, the scattering light overlaps with the absorption light of Bi_2MoO_6, which can enhance the utility of incident light. What is more, the photocatalytic performance of samples was evaluated by degradation MB, the results indicated that the composite heterostructure exhibited a much higher degradation rate of MB than the unmodified TiO_2 nanofiber under visible light illumination. In addition, the mechanism of enhanced photocatalytic activity over Bi_2MoO_6/TiO_2 heterojunction was also proposed.

2. Experimental details

2.1. Preparation of TiO_2 nanofiber film (TiO_2 NFF)

TiO_2 nanofiber films were prepared using a hydrothermal method. First, 2 g of NaOH was dissolved in a mixture containing 25 mL of H_2O and 25 mL of $HOCH_2CH_2OH$. The resulting solution and the surface-polished Ti sheet (>99.5% purity, 2.1 mm × 4.2 mm × 0.5 mm) were maintained at 180 °C for 24 h. After cooling down naturally, the product was cleaned with water and immerged in 0.25 wt% HCl aqueous solution for 24 h, then washed with water again. Finally, it was annealed at 400 °C for 2 h with a heating rate of 5 °C/min to obtain the TiO_2 NFF.

2.2. Preparation of Bi_2MoO_6/TiO_2 film

Bi_2MoO_6/TiO_2 composite films were prepared through alcohol thermal method.First, $Bi(NO_3)_3$ $5H_2O$ and Na_2MoO_4 $2H_2O$ with molar ratio (Bi/Mo) of 2:1 were dissolved in a mixture containing 20 mL of ethylene glycol and 50 mL of ethanol respectively. Subsequently, the resulting solution and TiO_2 NFF were heated at 160 °C for 5 h. After the reaction, the products were washed with water and ethanol to remove residual. Finally, y Bi_2MoO_6/TiO_2 films were obtained after drying in an oven at 60 °C for 12 h (y representing the apparent Bi_2MoO_6 dosage, y = 0.02, 0.04, 0.06, 0.08, and 0.10 mmol in this work).

2.3. Characterization

The phase structure of the samples was characterized by a Shimadzu XRD-6000 powder diffractometer. The morphologies of the samples were characterized by a scanning electron microscopy (SEM, JEOL JSM-6390A system). X-ray photoelectron spectroscope (XPS, Kratos AXIS NOVA spectrometer) was performed to examine the surface properties and composition of the sample. The UV–vis diffuse reflectance spectra were obtained on a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer. Photoluminescence (PL) spectra were collected on a florescence spectrophotometer (Hitachi F-7000).

2.4. Photocatalytic experiments

Methylene blue (MB, 50 mL, 5 mg/L) was selected as the target pollutant for evaluating the photocatalytic activity of Bi_2MoO_6/TiO_2 film, since it is a typical azo dye and hard to decompose. A 300 W Xe-lamp equipped with a 420 nm cutoff filter was used as light source (Beijing Perfectlight Technology Co. Ltd., China, Microsolar 300UV, visible light: 17.6 W). The sample was added into MB solution. Before illumination, the mixture was kept in darkness with a magnetic stirring for 30 min to establish adsorption-desorption equilibrium of MB. Subsequently, air was continuously bubbled through the system. At regular intervals of 20 min, 2 mL of the mixed suspensions were extracted and centrifuged to remove the photocatalysts. The supernatant solution was analyzed by a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer and the absorption peak at 664 nm was monitored. The degradation efficiency was calculated as follows:

$$\eta = (C_o - C)/C_o \times 100\%$$

where, C_o is the absorbance of original MB solution and C is the absorbance of the MB solution after light irradiation.

The photocatalytic process can be expressed as the following equation:

$$\ln C_o/C = kt$$

where, k is the apparent pseudo-first-order rate constant.

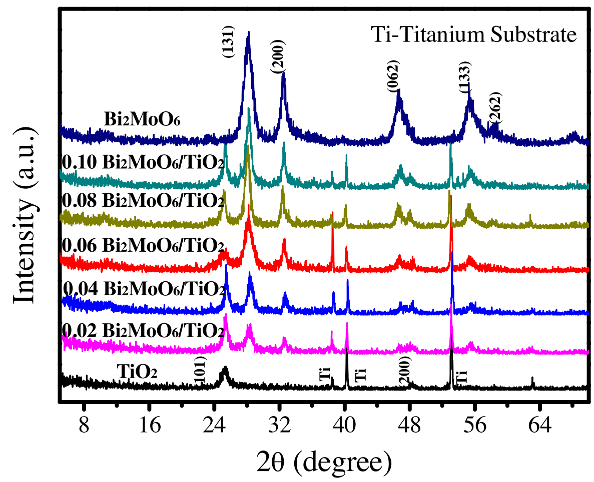

Fig. 1. XRD patterns of pure TiO_2 nanofiber, sample 0.02 Bi_2MoO_6/TiO_2, 0.04 Bi_2MoO_6/TiO_2, 0.06 Bi_2MoO_6/TiO_2, 0.08 Bi_2MoO_6/TiO_2, 0.10 Bi_2MoO_6/TiO_2 and Bi_2MoO_6.

2.5. Photoelectrochemical measurements

Photocurrent density was measured in a standard three electrode system (CHI 660E) with as-prepared samples as the working electrode, in which a platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes. 0.5 M Na_2SO_4 aqueous solution was applied as the electrolyte. The I-t curves were measured under irradiation from a solar stimulation source (Zolix, 150 W, AAA) with light on-off switches of 10 s.

3. Results and discussion

The crystal structure and phase composition of the prepared TiO_2, Bi_2MoO_6/TiO_2 and Bi_2MoO_6 samples are shown in Fig. 1. For the TiO_2 nanofiber, two characteristic peaks at 25.30° and 48.38° well correspond to the (101) and (200) crystal planes of anatase phase TiO_2 (JCPDS 21-1272), respectively. The intense diffraction peaks at 38.89°, 40.59°, and 53.62° belong to the Ti substrate under the TiO_2 nanofiber film. The Bi_2MoO_6 displays several diffraction peaks at 28.29°, 32.53°, 46.65°, 55.29°, and 58.58°, which can be indexed to the characteristic peaks of the orthorhombic structure of Bi_2MoO_6 (JCPDS 76-2388). Besides, the peaks in the composites