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Preparation of point-line Bi_2WO_6@TiO_2 nanowires composite photocatalysts with enhanced UV/visible-light-driven photocatalytic activity

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ABSTRACT

Bi_2WO_6@TiO_2 nanowires composite photocatalysts (BWO-TNWS) with point-line structures have been successfully fabricated by hydrothermalsynthesis method, and characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), ultraviolet-visible diffuse reflectance spectra (UV–vis DRS), photoluminescence (PL) and electrochemical impedance spectroscopy (EIS). The effects of coupling narrow-band-gap semiconductor Bi_2WO_6 (BWO) to photocatalytic activity for degrading Rhodamine B (RhB) and Phenol under UV–vis light irradiation were investigated. The results demonstrate that the photocatalytic activities of the prepared photocatalysts are associated with the content of Bi_2WO_6 (BWO). 20% BWO-TNWS (containing 20 wt% BWO) composite exhibits the highest degradation rate for RhB and Phenol up to 78% and 33%, respectively. It can be concluded that the improved photocatalytic performance of the BWO-TNWS composite is mainly ascribed to its high photoinduced charge separation rate resulting from the effective heterojunction structure of BWO and TNWS, as well as the enlarged optical response range owing to coupling narrow-band-gap semiconductor BWO.

1. Introduction

Since the discovery of carbon nanotubes in 1991 [1], one-dimensional (1D) nanostructured materials including nanotubes [2], nonorods [3] and nanowires [4] have been attracted significant attention due to their unique structures, excellent properties [5], and wide applications in various aspects such as light-emitting diodes [6], chemical sensors [7], solar cells [8], lithium battery [9] and photocatalysis [10]. Among the various 1D nanostructured materials, one-dimensional TiO_2 is the most widely studied photocatalysts due to the high chemical and photoelectron chemical durability [11]. In particular, TNWS are a kind of excellent semiconductor materials with advantages of high electron transfer rate, short electron transport path and large specific surface area, which can greatly reduce the recombination of photoelectrons and holes, offering abundant active sites on the surface of catalyst [12,13].

However, the photocatalytic activity of the naked TiO_2 is comparatively low, because TiO_2 with the band gap of 3.2 eV, only can response to the ultraviolet light which just accounts for no more than 4% of the solar radiation energy [14]. Therefore, the application of TNWS is also limited to a certain extent. With the aim of obtaining enhanced photocatalytic performance, many studies on different modifications of TiO_2 have been performed [15,16]. For the poor performance of metal and nonmetal doping, researchers pay their attention to the modified compound semiconductors which can effectively reduce the recombination rate of photogenerated electron-hole and broaden the range of their spectral response [17–19]. Therefore, the development of more efficient visible-light-active composite photocatalysts based on TNWS is urgent and indispensable.

BWO, as the simplest member and the most studied example in Aurivillius family, is an important photosensitizer with a direct band gap of 2.8 eV, also used as visible light-responsive photocatalyst [20–25]. However, its application remains limited because of its high electron-hole recombination rate in photocatalytic process. To resolve this problem, the best way may be the fabrication of heterojunction photocatalysts by coupling of another semiconductor with appropriate band edges [26]. Up to now, extensive studies about coupling BWO with TiO_2 have been reported. Huang et al. [23] synthesized anatase TiO_2-modified flower-like Bi_2WO_6 nanostructures by a simple hydrothermal reaction followed by layer-by-layer deposition and calcination. Wang et al. [27] successfully prepared Bi_2WO_6/TiO_2 possessed enhanced visible-light-induced activity in photocatalytic degradation of

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contaminants in aqueous/gaseous phases. Thatt Yang Tan et al. [28] demonstrated the preparation of porous Bi_2WO_6/TiO_2 heterojunction bilayer films on glass substrates using a super hydrophilicity-assisted dip-coating process. Li et al. [29] fabricated a three-dimensional TiO_2/Bi_2WO_6 hierarchical heterostructure by a simple and practical liquid phase method. Attributed to the coupling effects of TiO_2, these composites have exhibited enhanced activities in photocatalytic degradation. As a result, photosensitization of TNWS with narrow-band-gap BWO and design of the composite photocatalysts with point-line structures are promising ways to achieve high photocatalytic activity.

Inspired by the work above, we report a successful attempt at the fabrication of point-line BWO-TNWS composite photocatalysts via the facile hydrothermal synthesis method. TNWS were selected as the matrixes and soaked in the precursor solution containing Bi^{3+}. Thus, the Bi^{3+} ions attached to the carrier by immersion. By the introduction of WO_4^{2-} ions, nano-particles BWO can grow in-situ on TNWS. To evaluate the photocatalytic activity of the as-synthesized composites, RhB is chosen as representative organic substance. Besides, in order to avoid the photosensitization [30], colorless organic pollutant Phenol is also chosen as model reaction to further illustrate composite catalyst present higher photocatalytic degradation efficiency, compared with un-modified ones.

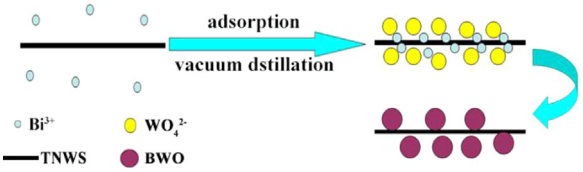
2. Experimental method

2.1. Catalysts preparation

A typical synthesis of point-line 20% BWO-TNWS by the hydrothermal synthesis method is shown in the following way: firstly, $Bi(NO_3)_3 \cdot 5H_2O$ (0.349 g) was dissolved in EG, to which TNWS (1.0 g) was added under vigorous magnetic stirring at room temperature. After stirring for 2 h, EG was removed by vacuum distillation. $Na_2WO_4 \cdot 2H_2O$ (0.119 g) dissolved in EG was added into the above product. After vigorous magnetic stirring for 3 h, the suspension was transferred into a 50 mL Teflon-lined autoclave with a stainless steel tank. The autoclave was heated at 160 °C for 10 h. Finally the sample was separated by centrifugation and washed with ethanol and water several times, followed by drying under vacuum at 50 °C to obtain the 20% BWO-TNWS composite. The weight contents of 10%, 15%, 20%, 25% and 30% BWO in the composite photocatalysts were synthesized and expressed as 10% BWO-TNWS, 15% BWO-TNWS, 20% BWO-TNWS, 25% BWO-TNWS and 30% BWO-TNWS, respectively. The detail synthetic route is shown in Scheme 1.

For comparison, BWO nano-particles were prepared according to the above-mentioned methods without TNWS.

TNWS were prepared according to the literature [31]. TiO_2 sol (15 g) was added into NaOH solution (10 mol/L, 60 mL), with magnetic stirring for 2 h. Then the mixture was transferred into a 100 mL Teflon-lined autoclave with a stainless steel tank. The autoclave was heated at 180 °C for 48 h. After washed with HCl (1 mol/L), the sample was then immersed in HCl (1 mol/L) for 12 h. Finally, the sample was dried and calcined after washed with water.



Scheme 1. Synthesis path diagram of BWO-TNWS composite.

2.2. Characterization of the catalysts

X-ray powder diffraction (XRD) analysis was carried out on a D/Max-rB rotating anode X-ray diffractometer with monochromatized Cu-Kα radiation ($\lambda = 0.15406$ nm) at a setting of 45 kV and 40 mA. The scanning rate was 0.02° (2θ)/s, and the scanning range was 20–75°. The general morphology of the composite photocatalysts was examined using scanning electron microscopy (SEM) on a FEI.SIRION instrument operated at 20 kV. Transmission electron microscope (TEM) was carried out on a JEOL H-7650 microscope at 100 kV. Energy dispersive X-ray spectroscopy (EDS) was used to determine elemental composition of the particles, using an Oxford 7200 IncaPentaFET-x3 Energy Dispersive X-ray Spectrometer. For the TEM observation, the catalysts were dispersed in ethanol by ultrasonic treatment and dropped on the support film with carbon coating copper grids. The UV–vis diffuse reflectance spectra (DRS) of samples were recorded over a UV–vis spectrophotometer (UV-3010) using $BaSO_4$ as reference. Scans range was 200–800 nm. Photoluminescence (PL) spectra of the photocatalysts were detected using a fluorescence spectrophotometer RF-5301PC made in Japan. The electrochemical impedance spectra (EIS) were on the CHI760D by using three-electrode cells. The samples were fabricated into thin film electrodes via the uniformly dispersed by mixing catalyst with methanol solutions for 30 min on the FTO glass substrate. Then the working electrodes were dried at 80 °C for 48 h in air. The frequency range covers from 10000.0 kHz to 0.01 Hz with modulation amplitude of 5 mV.

2.3. Photocatalytic activity

RhB and Phenol solution, acting as colored and colorless organic pollutants, respectively, are chosen as representative organic substances to evaluate the photocatalytic activity of the as-prepared BWO-TNWS composite catalyst. The photocatalytic activity of the samples was determined in a photochemical glass reactor equipped with a 500 W high-pressure xenon lamp, which was placed at about 15 cm from the reactor. For the decolorization of RhB, photocatalyst (0.1 g) was added into RhB solution (20 mg/L, 100 mL) and stirred in the dark for 1 h, maintaining the temperature at 25 ± 1 °C, in order to make the reactive system uniform and the adsorption equilibrium, then begin to illuminate. About 5 mL of the suspension continually was taken from the reaction cell at given time intervals. The catalyst in the mixture was removed by centrifugation, and the residual dyes in the solution were determined over a UV–vis spectrophotometer at the wavelength of 553 nm. The formula of removal rate is $(1-C/C_0)\times 100\% = (1-A/A_0)\times 100$, C_0, C, A_0, A are concentrations and absorbance values of RhB before and after light irradiation, respectively. For photodegradation of Phenol, similar to that of RhB, the photocatalysts (0.1 g) and Phenol solution (20 mg/L, 80 mL) were used, and the Phenol concentration was measured by the colorimetric method of 4-aminoantipyrine at the wavelength of 505 nm.

3. Results and discussion

3.1. XRD analysis

Fig. 1 showed the XRD patterns of the samples. The XRD patterns of sole TNWS and BWO were offered. All the peaks for the sample are readily indexed to the anatase TNWS (JCPDS card no. 89-4921) and mix orthorhombic phase of BWO (JCPDS card no. 73-1126). No other characteristic peaks were observed, indicting the high purity of the as-prepared samples. Moreover, the narrow and sharp peaks indicate high crystallinity. It is observed that, with