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Short communication

Fabrication of a novel hierarchical flower-like hollow structure Ag_2WO_4/WO_3 photocatalyst and its enhanced visible-light photocatalytic activity

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ABSTRACT

A series of hierarchical flower-like hollow structure Ag_2WO_4/WO_3 photocatalysts was synthesized and characterized by XRD, SEM, Raman spectroscopy, XPS, photoluminescence (PL) spectra, and BET. The obtained results indicated the growth of finely distribution of Ag_2WO_4 on the surface of the WO_3 hollow sphere. UV–vis diffuse reflectance spectroscopy (DRS) was used to investigate the absorption range and band gap of photocatalysts. The photocatalytic activities of the photocatalysts were evaluated by the decolorization of Rhodamine B (RhB) under visible-light irradiation. The results showed that the highest activity could be reached up to 94%. It was also found that the heterojunction structure photocatalyst exhibited excellent stability. The kinetic reaction rate of heterojunction structure photocatalyst was nearly 17.0 and 7.5 times higher than those of pure WO_3 and Ag_2WO_4. A possible photocatalytic mechanism for decolorization of Rhodamine B was proposed.

1. Introduction

During past decades, the semiconductor photocatalysts have attracted much attention originated from their potential applications in environment purification [1,2]. WO_3 is an n-type semiconductor with an indirect band gap of 2.7 eV, which can be activated by visible light, regarded as another potential photocatalytic material [3].

Among the silver based catalysts (SBC), silver tungstate (Ag_2WO_4) is a semiconductor with a wide band gap in the range of 2.9 eV to 3.1 eV [4]. Ag_2WO_4 catalyst was expensive and instability, which restricted its practical application. And therefore, many researchers have attempted to improve the activity and stability of Ag_2WO_4 through surface modification and surface plasmon resonance (SPR) [5]. Vignesh and Kang reported [6] the Ag_2WO_4/C_3N_4 composites and used them as catalysts for the photodecomposition of methylene blue (MB) dyes under visible light irradiation.

In this work, a hierarchical flower-like hollow structure Ag_2WO_4/WO_3 photocatalyst was synthesized by calcining method and photocatalytic activity in the decolorization of Rhodamine B (RhB) under visible-light irradiation was investigated. A detailed possible mechanism for the photo-decolorization process over Ag_2WO_4/WO_3 photocatalyst was also discussed.

2. Experimental

2.1. Preparation

Na_2WO_4 (1.31 g) and $Pb(AC)_2 \cdot H_2O$ (1.51 g) were dissolved in 50 mL of ethylene glycol (EG) solution. The suspension was further stirred for 10 min and then was transferred into a Teflon-lined stainless steel autoclave, which was heated at 160 °C for 12 h. After slow cooling to room temperature, the products were filtered and washed several times with alcohol/water mixture (V/V = 1:1). The $PbWO_4$ precursor was obtained.

The $PbWO_4$ precursors with different morphologies were firstly immersed in a certain amount of HNO_3 solution (4 mol L^{-1}) for 48 h. Then, the precipitate (H_2WO_4) was filtered, washed with distilled water, and dried in air. After then, the products were put into a quartz crucible with a cover and calcined at 500 °C for 2 h. The hollow sphere WO_3 was obtained.

A certain concentration of $AgNO_3$ solution was stirred under vigorous magnetic stirring. Subsequently, a certain amount of $NaHCO_3$ (3 mmol) was added dropwise into above aqueous. The suspension was continuously stirred for 1 h at room temperature to ensure complete reaction. The obtained products were collected by filtering, and washed with distilled water and ethanol several times. Finally, sample was dried in a vacuum at 60 °C for 10 h and Ag_2CO_3 was obtained.

A certain amount of WO_3 and Ag_2CO_3 powder were mixed and ground in an agate pestle for 30 min. Then, the mixture was calcined at 500 °C for 2 h and cooled to room temperature. The heterojunction

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structure Ag_2WO_4/WO_3 photocatalyst was obtained. According to different mass content of Ag_2CO_3 to WO_3, a series of photocatalysts were prepared, and named as A/W-1, A/W-2, A/W-3 and A/W-4, respectively (the mass ratios of Ag_2CO_3 to WO_3, were 10%, 20%, 30% and 40%, respectively). The pure Ag_2WO_4 photocatalyst was prepared using mass content 1:1 of Ag_2CO_3 to WO_3. The synthetic route of hierarchical flower-like hollow structure Ag_2WO_4/WO_3 photocatalyst is shown in Fig. 1A.

2.2. Characterizations

X-ray diffraction (XRD) patterns were measured on the Shimadzu LabX-6000 X-ray Diffractometer (40 kV, 30 mA). The surface morphologies and microstructures were probed by using Hitachi S-4800 scanning electron microscope (SEM). Raman spectroscopy was performed using a DXR Smart Raman spectrometer. The surface elemental compositions and chemical states were analyzed by X-ray photoelectron spectra (XPS) on an ESCALAB250 XPS spectrometer. UV–vis diffuse reflectance spectroscopy (DRS) of the materials was recorded using a Hitachi UV-3010 UV–vis spectrophotometer. The photoluminescence (PL) spectra were measured with a Quanta Master™ 40 instrument. The Brunauer-Emmett-Teller (BET) surface areas were analyzed by nitrogen adsorption and desorption isotherms in an NDVA2000e Quntachrome Corporation analytical system.

2.3. Photocatalytic decolorization

In the experimental setup, a halogen–tungsten lamp (500 W) was employed as the light source. The visible light ($\lambda = 420$ nm) used in the present study was obtained by the filter with cut-off wavelength of 420 nm. The photocatalyst (10 mg) was dispersed in RhB aqueous solution (1000 mL, 10 mg L^{-1}). And then the mixture was stirred in the dark for 30 min at room temperature (about 25 °C) to reach absorption-desorption equilibrium. After light illumination, suspension (about 5 mL) was then taken out for a certain period and the photocatalyst was removed by centrifugation. The filtrates were analyzed at 553 nm using UV–vis spectrophotometer to calculate the concentration of the RhB. The degradation efficiency was evaluated using the relative concentration (C/C_0) of RhB as a function of degradation time, where C_0 (mg L^{-1}) is the initial concentration of RhB, C (mg L^{-1}) is the RhB concentration at time t (min).

3. Results and discussion

XRD patterns of the pure WO_3 (a), pure Ag_2WO_4 (b), A/W-4 (c), A/W-3 (d), A/W-2 (e) and A/W-1 (f) are shown in Fig. 1B. The as-prepared WO_3 is in good agreement with orthorhombic phase of WO_3 indexed to be the data in the JCPDS card (no. 20-1324) [7]. The diffraction peaks of Ag_2WO_4 are identical to the orthorhombic phase of Ag_2WO_4 in the JCPDS card (no. 34-0061) [8]. The pure Ag_2WO_4 displays sharp diffraction peaks at 2θ values of 16.71, 30.27, 31.63, 33.09, 45.45, 54.65 and 58.16° correspond to the planes of 011, 002, 231, 400, 402, 361 and 333, respectively. It is noteworthy that the peak intensity ($2\theta = 31.63°$) is stronger compared to other diffraction peaks. For Ag_2WO_4/WO_3 heterojunction structure, the diffraction peaks of Ag_2WO_4 and WO_3 are also clearly observed in comparison with bare Ag_2WO_4 and WO_3. Moreover, the diffraction peaks of Ag_2WO_4 strengthen gradually as the silver material concentration increases. In the case of Ag_2WO_4 (Fig. 1C), the sharp peak centered at about 881 cm^{-1} is related to (—W—O—) stretching vibration modes of [WO_6] octahedral. As for bare WO_3, the bands centered at 807 cm^{-1} and 713 cm^{-1} are attributed to —W—O— stretching vibrations mode. In addition, W—O—W bending vibration is revealed at the band centered at about 273 cm^{-1}. For the heterojunction structure A/W-3 photocatalyst, all of the Raman bands for Ag_2WO_4 and WO_3 can be observed, confirming the presence of Ag_2WO_4 and WO_3 in the heterojunction structure photocatalyst, which further suggests the decoration of Ag_2WO_4 on the WO_3 surface.

WO_3 sample (Fig. 2a) consists of a large number of microspheres with a narrow size distribution. The average size of the microspheres is about 4.5 μm. The single WO_3 microsphere exhibits a well-defined 3D morphology (Fig. 2b) which can be resembled a snow-ball flower-like pattern. Their entire flower-like hollow spheres structure WO_3 sample was assembled by numerous nanoplates with an average thickness of about 40 nm. These nanoplates could be stacked together

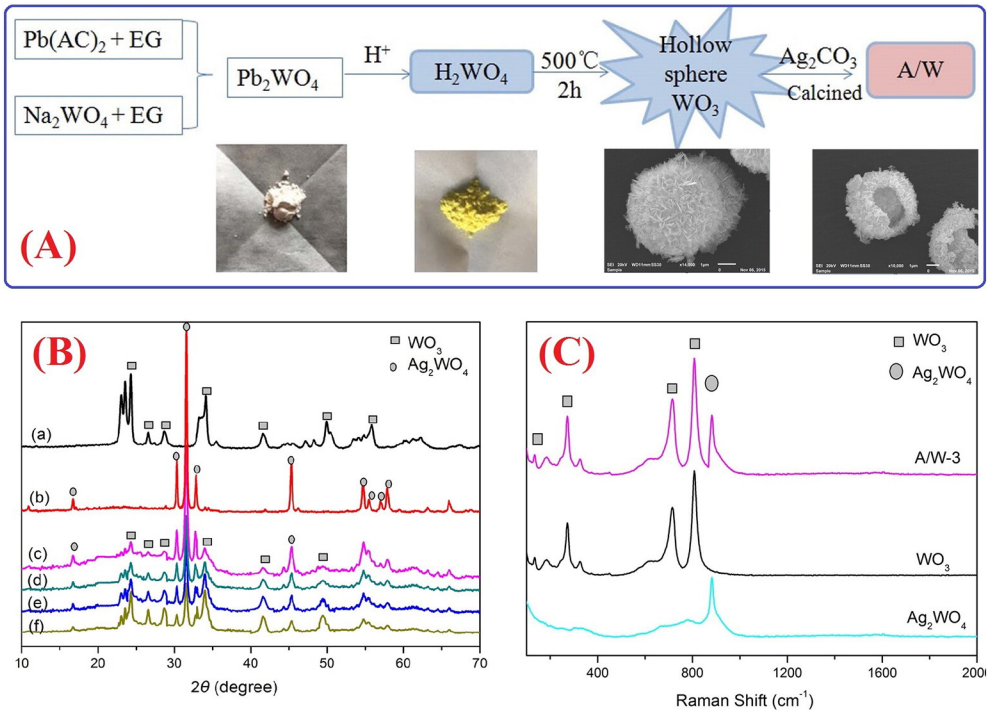

Fig. 1. (A) The synthetic route of hierarchical flower-like hollow structure Ag_2WO_4/WO_3 photocatalyst; (B) XRD patterns of the pure WO_3 (a), pure Ag_2WO_4 (b), A/W-4 (c), A/W-3 (d), A/W-2 (e) and A/W-1(f); (C) Raman spectra of bare Ag_2WO_4, WO_3 and heterojunction structure A/W-3 photocatalyst.