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Synergism of 3D g-C_3N_4 decorated Bi_2WO_6 microspheres with efficient visible light catalytic activity

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ABSTRACT

g-C_3N_4 decorated Bi_2WO_6 microspheres with scales of 2.0 ~ 3.0 μm were prepared via a hydrothermal method. The matching of energy band between g-C_3N_4 and Bi_2WO_6 facilitate the absorption visible light and the separation of electron-carrier. The morphology, constitute and optical properties of the as-prepared samples is confirmed by different characterization techniques, such as, XRD, XPS, EDS, SEM, UV–vis, and N_2 adsorption-desorption. The photocatalytic activities were assessed by the photodegradation of Methyl orange (MO) and phenol under visible light irradiation. The results indicated that the decoration of g-C_3N_4 evidently improves the photocatalytic activity of Bi_2WO_6, and the content of g-C_3N_4 has significantly effect on the catalytic activity of Bi_2WO_6. By comparison of other samples, 3 wt% g-C_3N_4/Bi_2WO_6 composites present an extraordinary enhanced photocatalytic activity for the photodegradation of MO and phenol under visible light. On the basis of the result and discussion, the possible mechanism of enhanced photocatalytic activity of g-C_3N_4/Bi_2WO_6 composites is proposed. It implies that the combination of g-C_3N_4 and Bi_2WO_6 provided synergistic photocatalytic activity via an efficient electron transfer process. Furthermore, the photocatalytic degradation of MO over g-C_3N_4/Bi_2WO_6 is promoted mainly by h^+, and the same time •OH also plays a positive role in this degradation process.

1. Introduction

In recent years, semiconductor material has attracted comprehensive interest due to the photo-degradation of environmental pollutants and production of hydrogen from water under light irradiation [1–4]. However, many semiconductors can be excited only under ultraviolet light irradiation because of its relatively wide band gap and inefficient quantum yield, which hinders its further application in industrial process [5–8]. Up to date, a variety of strategies have been employed to improve the photocatalytic efficiencies of photocatalysts in the visible range by different modified methods, such as doped with nonmetal/metal element [9,10]. Unfortunately, the methods used are not completely controlled. Moreover, these dopants may become recombination centers between photogenerated electrons and holes. Evidently, the expected methods are somewhat limited [11,12]. Therefore, to explore more efficient photocatalyst with visible light responsiveness and thermal stability is urgent and indispensable. In order to decrease the recombination of photogenerated electrons and holes, and promote the photocatalytical ability, some novel photocatalyst have been designed and fabricated by coupling a narrow band gap semiconductor with metal and/or other semiconductors [13–15]. Composites catalyts for the oxidative degradation of environmental pollutants or chemical conversions are well known for their efficiency where the photo-generated electron and holes photo-generated are driven effectively apart before recombination [16,17]. Therefore, the construction of semiconductor composites has proved to be an effective approach. Understanding the catalysis mechanism is vital for the design of new functional materials to be a part of an environmentally friendly technology. During the past few years, many important findings have been reported on the fabrication of semiconductor heterojunctions such as, AgBr-Ag-Bi_2WO_6 three component composites [18], Bi_2WO_6-TiO_2 hierarchical composites [19], SnO_2-TiO_2 photocatalysts [20], CuO|-$CuBi_2O_4$ composites [21], and so on. Despite a large number of encouraging versatile composite photocatalysts being available, there are still a few promising developments to designing and fabricating the semiconductor composite photocatalysts, while providing some stimulating perspectives on the future developments.

As an important simplest aurivillius oxide, Bi_2WO_6 has attracted increasing interest because of the photodecomposition of environmental pollutants and generation of hydrogen from water under light irradiation. However, there are three main drawbacks, which limit the photocatalytical ability of Bi_2WO_6. Firstly, Bi_2WO_6 only exhibits photoabsorption properties from UV to visible light with wavelength shorter than about 450 nm. Secondly, the rapid recombination of

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photogenerated electrons - holes pairs and inefficient quantum yield seriously limits the light energy-conversion efficiency. Lastly, Bi_2WO_6 exhibits high dispersion in the solid-liquid system, which results in a difficult for its recovery [22–25]. Therefore, to improve these drawbacks, especially, to broaden the range of visible light responsiveness and enhance the separation of photogenerated carriers are important in enlarging the efficiency photocatalytic application. Graphitic C_3N_4 (g-C_3N_4) is another attractive and promising semiconductor with a small band gap of approximately 2.7 eV [26–28]. It is reported that g-C_3N_4 is suitable for photocatalytic reduction with conduction band(CB) position and photocatalytic oxidation with valence band(VB) position. Moreover, g-C_3N_4 could cause red shift of the photoabsorption wavelength, produce nonlinear optical responsiveness and enhance the oxidation and reduction capacity of other semiconductor, thus it has been used as coating on other semiconductor for visible light absorption and to improve the photochemical stability of the semiconductor, respectively [29–31]. Especially, the CB of g-C_3N_4 possesses smaller electropositive than the corresponding Bi_2WO_6, and the VB have more electronegative than that of Bi_2WO_6. In the g-C_3N_4/Bi_2WO_6 composites system, the photoinduced electrons tend to pass from the CB of g-C_3N_4 to the CB of Bi_2WO_6, meanwhile the photoinduced holes tend to pass from the VB of Bi_2WO_6 to the VB of g-C_3N_4 [32,33]. Thus, the formation of g-C_3N_4/Bi_2WO_6 composites with the efficiency separation and transfer of photogenerated carriers is more possible, and well-fabricated g-C_3N_4/Bi_2WO_6 composites could availably restrict the recombination of photogenerated carriers and effectively enhance the visible-light photocatalytic activity.

Although, the research of g-C_3N_4/Bi_2WO_6 is carried out, however, the research did not clearly present the influence of the synthesis conditions on the microstructure, crystallinity and activity of the catalysts [34,35]. Therefore, we intend to explore comprehensive correlation among the processing, structure and property of the g-C_3N_4/Bi_2WO_6. Therefore, to further favor versatile photocatalytic material with visible light catalytic efficiency, we design and fabricate 3D hierarchical spherical g-C_3N_4/Bi_2WO_6 composites with basement on semiconductor band manipulation theory of p-n heterojunction. 3D spherical g-C_3N_4/Bi_2WO_6 composites were subsequently characterized by XRD, SEM, TEM, EDS and XPS. Methyl orange (MO) and phenol were available to evaluate the photocatalytic activity of the 3D spherical g-C_3N_4/Bi_2WO_6 composites under visible light irradiation. The experimental results demonstrated that g-C_3N_4 coated hierarchical Bi_2WO_6 represented remarkable enhanced photocatalytic activity for the degradation of MO and phenol. In addition, 3D spherical g-C_3N_4/Bi_2WO_6 composites were high-stability and easy-recycle. Afterwards, the mechanism of photocatalytic activity of 3D spherical g-C_3N_4/Bi_2WO_6 composites was also discussed based on the calculated energy positions of g-C_3N_4 and Bi_2WO_6.

2. Experimental section

2.1. Preparation

All the reagents were analytical grade. The typical preparation process of g-C_3N_4/Bi_2WO_6 composites is showed in the following way.

The melamine was calcined at 250 °C for 1 h, and then at 550 °C for 2 h. After cooling naturally to room temperature, the sample was filtered off, washed with 0.1 M nitric acid solution and distilled water. Afterwards, the sample was dried at 80 °C for 8 h. Thus, g-C_3N_4 samples were obtained.

0.02 mol $Bi(NO_3)_3{\cdot}5H_2O$ were dissolved in 2.5 mL nitric acid (4 mol L^{-1}) and 7.5 mL distilled water, and then 10 mL Na_2WO_4 solution at a concentration of 0.002 mol L^{-1} was added drop-wise to the solution under vigorous magnetic stirring at room temperature. In a typical preparation process, an amount of g-C_3N_4 samples was added to a mixture solution. The resulting solution was continuously stirred for 30 min in air, then transferred and sealed in a 100 mL Teflon liner stainless vessel, which was maintained at 180 °C for 12 h. After naturally cooling to room temperature, the precipitate was filtered off, washed with distilled water and absolute ethyl alcohol. Afterwards, the precipitate was dried under vacuum at 80 °C in air for 8 h. Thus, the aimed samples were obtained, and the samples were named as 0.5 wt% g-C_3N_4/Bi_2WO_6, 1 wt% g-C_3N_4/Bi_2WO_6, 2 wt% g-C_3N_4/Bi_2WO_6, 3 wt% g-C_3N_4/Bi_2WO_6, 4 wt% g-C_3N_4/Bi_2WO_6, respectively.

3. Characterization

The phase and composition of the g-C_3N_4/Bi_2WO_6 composites were identified by X-ray diffraction (XRD) using monochromatized Cu K_α radiation under 40 kV and 100 mA and with the 2θ ranging from 10° to 80° (Shimadzu XRD-7000). The morphologies and microstructures of the g-C_3N_4/Bi_2WO_6 composites were analyzed by the scanning electron microscope (SEM) (JEOL JSM-6700 F). The UV–vis diffuse reflectance spectrum (DRS) of the g-C_3N_4/Bi_2WO_6 composites was recorded with an UV–vis spectrophotometer (Shimadzu UV-2550) using an integrating-sphere accessory, $BaSO_4$ was used as a reflectance standard. The chemical state of constituent elements of the g-C_3N_4/Bi_2WO_6 composites was analyzed by EDS (Bulker Q73). X-ray photoelectron spectroscopy (XPS) analysis of the g-C_3N_4/Bi_2WO_6 composites was performed on a VG MultiLab2000 X-ray photoelectron spectrometer with a monochromatic Al K_α source. The specific surface area of the g-C_3N_4/Bi_2WO_6 composites was calculated by the Brunauer - Emmet - Teller (BET) method on the basis of nitrogen uptake measured at −192 °C (Micromeritics ASAP, 2010).

3.1. The visible ligh photocatalytic properties

Photocatalytic property of the g-C_3N_4/Bi_2WO_6 composites was evaluated by degradation of the phenol-containing (MB-containing) model wastewater at ambient temperature. A 400 W metal halide with a 400 nm cut-off filter was used as the visible light source. 250 mL of a phenol-containing solution of a desired concentration (10 mgL^{-1}) was added to a quartz tube that contained 200 mg of the g-C_3N_4/Bi_2WO_6 composites at a constant temperature of 25 °C. The tubes were agitated at 140 rpm continuous magnetically in the dark for 2 h to assure the adsorption-desorption equilibrium between the g-C_3N_4/Bi_2WO_6 composites and the target organic pollutant. After certain contact time, the g-C_3N_4/Bi_2WO_6 composites were separated from the phenol-containing solution by centrifugation. The phenol(MB) content in the supernatant was determined using a UV–Vis spectrophotometer (Shimadzu, UV-2550, Japan) in the spectrophotometric method.

4. Result and discussion

4.1. XRD, EDS and XPS analysis

The XRD patterns of the as-prepared samples are shown in Fig. 1. From Fig. 1, It can be see that the all of the as-prepared composites are well crystallized. The diffraction peaks at 2θ of 28.6°, 33.1°, 47.3°, 56.1°, 58.4°, 68.5°, 76.2°, 78.4°can be indexed to tetragonal Bi_2WO_6 (JCPDS No. 26–1044; a = 5.48 Å,b = 5.48 Å,c = 11.5 Å), corresponding to the indices of (103), (200), (220), (303), (107), (400), (109) and (307) planes, respectively [36]. Moreover, the diffraction peaks of g-C_3N_4 and other impurities are not observed in these Bi_2WO_6, 0.5 wt% g-C_3N_4/Bi_2WO_6, 1 wt% g-g-C_3N_4/Bi_2WO_6 and 2 wt% g-C_3N_4/Bi_2WO_6 samples. The reason can be ascribed to low weight loading of g-C_3N_4 on the surface of the Bi_2WO_6. These phenomena can be found in the preparation of the other kinds of semiconductor composite. For example, it was difficult to find the characterization peaks of g-C_3N_4 with less than 1:1.33 of weight ratio of g-C_3N_4 to Ag_2O in the g-C_3N_4/Ag_2O [37]. The characterization peaks of metallic Ag was not examined in the Ag/g-C_3N_4 heterostructures with low Ag doping amount [38]. However, the diffraction peaks of g-C_3N_4 appear and are identified