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Hydrothermal synthesis of graphitic carbon nitride–$BiVO_4$ composites with enhanced visible light photocatalytic activities and the mechanism study

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ABSTRACT

Novel graphitic carbon nitride (C_3N_4) and bismuth vanadate ($BiVO_4$) composite photocatalysts were successfully synthesized by a facile hydrothermal method. The scanning electron microscopy (SEM) revealed that an intimate interface between C_3N_4 and $BiVO_4$ formed in the composites. Compared with the pure C_3N_4 and $BiVO_4$, the C_3N_4–$BiVO_4$ photocatalysts showed remarkably the higher photocatalytic activities in degrading rhodamine B (Rh B). The best active heterojunction proportion was $0.5C_3N_4$–$0.5BiVO_4$. Over this catalyst, the 100% degradation of Rh B (0.002 mmol L^{-1}) was obtained under visible light irradiation ($\lambda > 420$ nm) for 40 min. The active species in Rh B degradation were examined by adding a series of scavengers. The study on photocatalytic mechanism revealed that the electrons injected directly from the conduction band of C_3N_4 to that of $BiVO_4$, resulting in the production of superoxide radical ($O_2^{\bullet -}$) and hydroxyl radical ($OH^{\bullet}$) in the conduction band of $BiVO_4$. Simultaneously, the rich holes in the valence band of g-C_3N_4 oxidized Rh B directly to promote the photocatalytic degradation reaction.

1. Introduction

Water pollution has been one of the most serious problems in modern society. While green chemistry has also become a necessary requirement for sustainable development of society. In all kinds of green chemical technology, semiconductor photocatalysis is in constant rise [1–3]. Among them, bismuth vanadate ($BiVO_4$) is an ideal photocatalytic material for degradation of organic pollutants under visible light irradiation [4–6]. $BiVO_4$ shows a strong absorption in the visible region, and its response wavelength ranges up to 500 nm. At the same time, the photocatalytic activity of $BiVO_4$ depends on its structure, synthesis methods, grain size and grain morphology [7–8]. According to previous reports, $BiVO_4$ [6] has three main crystal phases: a zircon structure with a tetragonal (z–t) system and a scheelite structure with a monoclinic (s–m) and a tetragonal (s–t) system, However, among the above three crystal phases, $BiVO_4$ (s–m) is the best visible-light-driven photodegradation of organic pollutants [4]. However, similar to other photocatalysts, poor quantum yield and poor visible light absorption efficiency are still challenges to enhancing the photocatalytic efficiency of m-$BiVO_4$ to meet the practical application requirements [5]. To solve this problem, the formation of composite by coupling of two semiconductors has attracted special attention as a novel strategy for overcoming the defect above the traditional phototalysts and improving the photocatalytic activity of phototalysts [9,10]. The composite system with two semiconductors can effectively suppress with the recombination rate of photogenerated electron–hole pairs, such as Fe_2O_3/ZnO [11], Ag/SiO_2 [12] and Ag/$BiPO_4$ [13].

To the best of our knowledge, graphitic carbon nitride (C_3N_4) exhibits high photocatalytic performance for degradation of organic dyes under visible light irradiation. The photocatalytic efficiency of C_3N_4 is strongly dependent on its porosity and high degree of condensation. This organic semiconductor possesses a narrow band gap of 2.7 eV. Because of the extraordinary properties of C_3N_4, it has been developed, including coupling with heterogeneous semiconductors, element doping, introduction of mesoporous structure, these all can improve photocatalytic activity of C_3N_4 [14]. Up to now, there are several kinds of C_3N_4 based composites have been developed, C_3N_4–Bi_2WO_6 [15], C_3N_4–TaON [16], C_3N_4–TiO_2 [17], C_3N_4–ZnO [18], C_3N_4–$SrTiO_3$ [19], C_3N_4–CdS [20], etc.

By comparing the energy levels of C_3N_4 with $BiVO_4$, it is very lucky that overlapping band-structure well match the energy

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levels of between C_3N_4 and $BiVO_4$, suiting to construct a semiconductor with a high visible light catalyst activity. Most recently, Ji et al. have successfully prepared a C_3N_4–$BiVO_4$ heterojunction by mixing and heating methods of C_3N_4 and $BiVO_4$ [21]. Nevertheless, the obtained insufficient contact interface by mechanical mixing would limit the transfer of photogenerated charges. Motivated by the above efforts, we further research the synthesis of the coupling of $BiVO_4$ with C_3N_4 for improving photocatalytic efficiency by a facile hydrothermal method, which is a commercial and widely used process in preparing many kinds of functional materials [22]. The advantages of hydrothermal synthesis are that the experimental parameters such as the concentrations of reactants, the pH values, the temperature, and the reaction medium can be easily tuned to control the microstructures, and thus the properties and property dependent applications, of the target materials. Furthermore, to the best of our knowledge, the hydrothermal synthesis of C_3N_4–$BiVO_4$ composites has not been reported previously.

Herein, we report the hydrothermal synthesis of the composites between $BiVO_4$ and C_3N_4. At the same time, we study the photocatalytic activities of C_3N_4–$BiVO_4$ composites by degrading the Rh B under visible light irradiation. The possible photodegradation mechanism of the C_3N_4–$BiVO_4$ composite was discussed in detail.

2. Experimental

2.1. Preparation of photocatalysts

All chemicals used in the present experiments were obtained from commercial sources as analytical reagents. A typical synthesis process was as follows: At first, C_3N_4 was synthesized by polycondensation of melamine. Typically, 2 g of dicyandiamide powder was put into an alumina crucible with a cover, then heated at a rate of 2.3 °C/min to reach a temperature of 550 °C, and then tempered at this temperature for another 2 h. All the experiments were performed under air conditions. The yellow product was collected and milled into a powder for further use.

Different mass ratios C_3N_4–$BiVO_4$ heterojunctions were synthesized by hydrothermal route. As $0.5C_3N_4$–$0.5BiVO_4$ for example, in a typical procedure, 0.3 g C_3N_4 and 0.1083 g NH_4VO_4 were mixed in the 30 mL of deionized water and followed by vigorous stirring 3 h for a uniform suspension. At the same time, 0.449 g $Bi(NO_3)_3 \cdot 5H_2O$ solid was dissolved in 3 mL of HNO_3 (1 mol L^{-1}) to obtain a clear suspension. The solution was added rapidly to the suspension and soon afterwards stirred for additional 3 h at room temperature. After carefully adjusting the pH value of 8 using NaOH solution (1 mol L^{-1}), the mixed solution was transferred into a Teflon-lined steel autoclave, which was heated in an oven at 160 °C for 20 h. At last, the obtained $0.5C_3N_4$–$0.5BiVO_4$ composite was collected and washed with ethanol and distilled water several times, and dried at 100 °C for 2 h. On this basis, different mass ratios of C_3N_4–$BiVO_4$ at 7:3, 6:4, 4:6 and 3:7 were prepared and denoted as $0.7C_3N_4$–$0.3BiVO_4$, $0.6C_3N_4$–$0.4BiVO_4$, $0.4C_3N_4$–$0.6BiVO_4$, and $0.3C_3N_4$–$0.7BiVO_4$, respectively. The pure $BiVO_4$ sample was fabricated under the same conditions in the absence of C_3N_4 powder.

2.2. Characterization of photocatalysts

The crystal structures of the samples were characterized by X-ray diffraction (XRD) on a Rigaku (Japan) D/max 2500 X-ray diffractometer (Cu K_α radiation, $\lambda = 0.154\ 18$ nm). The morphologies of the as-prepared samples were detected by using an emission scanning microscopy (SEM, Hitachi S-4800). Fourier transform infrared (FT-IR) spectra was recorded on FTIR spectrometer (America Perkin Elmer, Spectrum One) using the standard KBr disk method. The UV–vis diffuse reflectance spectra (DRS) were recorded on a scan UV–vis spectrophotometer (UV–vis, UV-2550) equipped with an integrating sphere assembly. The specific surface areas of samples were measured through nitrogen adsorption BET method (3H-2000PS1 BET/BJH Surface Area).

2.3. Photocatalytic activities studies

All the different mass ratios of C_3N_4–$BiVO_4$ composites were evaluated by the photodegradation of Rh B dye solution (0.002 mmol L^{-1}, 100 mL) under visible light irradiation. A 500 W Xe lamp ($\lambda > 420$ nm) was used to provide visible light irradiation. A glass sheet was inserted between the lamp and the sample to filter out UV light ($\lambda < 420$ nm). Rh B was a very stable dye. Its photodegradation has been used widely as a representative reaction for examining the performance of numerous visible light active catalysts. In the experiment, 0.03 g catalyst was suspended in aqueous solution 100 mL of Rh B. Prior to visible light illumination, the suspension was strongly stirred in the dark for 30 min to ensure the establishment of adsorption–desorption equilibrium. Then the solution was exposed to visible light irradiation under magnetic stirring. At given time intervals, 4 mL of the suspension was periodically collected and analyzed after centrifugation. The Rh B concentration was analyzed by a UV-2550 spectrometer to record intensity of the maximum band at 552 nm in the UV–vis absorption spectra.

2.4. Active species trapping experiments

To determine the active species in the photocatalytic process, some sacrificial agents, such as 2-propanol (IPA), disodium ethylenediamine tetraacetic acid (EDTA-2Na), and 1, 4-benzoquinone (BQ) were used as the hydroxyl radical ($OH^\bullet$) scavenger, hole (h^+) scavenger and superoxide radical ($O_2^{\bullet -}$) scavenger, respectively. The method was similar to the former photocatalytic activity test with the addition of 1 mmol of scavenger in the presence of Rh B.

3. Results and discussion

Fig. 1 displays the XRD patterns of the prepared $BiVO_4$, C_3N_4 and C_3N_4–$BiVO_4$ composites. According to interlayer stacking of aromatic segments, the distinct peaks of the pure C_3N_4 can be indexed as the (002) diffraction for graphitic materials. The characteristic peak was 27.47° [22,23]. The pure $BiVO_4$ sample also displays a series of narrow and sharp diffraction peaks, which

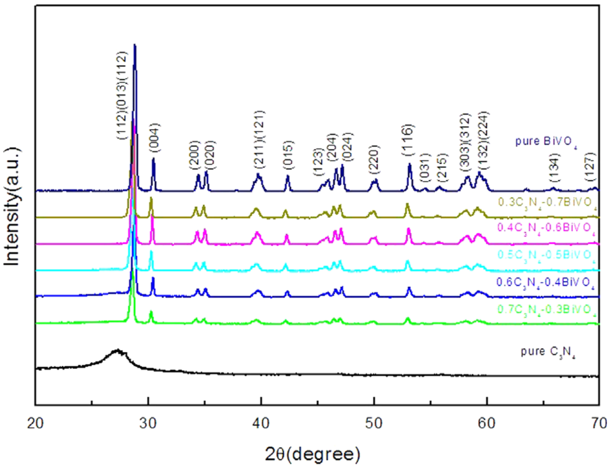

Fig. 1. XRD patterns of pure C_3N_4, pure $BiVO_4$ and C_3N_4–$BiVO_4$ composites.