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Invited feature article

Facile synthesis of double cone-shaped $Ag_4V_2O_7/BiVO_4$ nanocomposites with enhanced visible light photocatalytic activity for environmental purification

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ABSTRACT

$Ag_4V_2O_7/BiVO_4$ photocatalysts with double cone-shaped nanostructure were successfully synthesized by a facile sodium polyphosphate-assisted hydrothermal method. The results demonstrate that coupling $Ag_4V_2O_7$ with $BiVO_4$ can promote the separation of photoinduced charge carriers and enhance the photon absorption efficiency. Experimental results indicate that $Ag_4V_2O_7/BiVO_4$ composites exhibit the enhanced photocatalystic activity for degradation of methylene blue (MB) and oxidation of NO in high concentrate (1600 ppb) compared to the pure $BiVO_4$ under visible light irradiation ($\lambda > 420$ nm). The composite with 0.08 mol% $Ag_4V_2O_7$ has the highest photocatalytic activity. MB degradation rate can reach 98.48% in 1 h and NO oxidation rate can reach 52.83% in 0.5 h on 0.08-$Ag_4V_2O_7/BiVO_4$, which are about 2.90 and 3.11 times higher than that of pure $BiVO_4$ respectively. The excellent activity can be attributed to the efficient charge transfer between $Ag_4V_2O_7$ and $BiVO_4$, and active species h^+ and $^{\bullet}O_2^-$ play important roles during MB degradation and NO oxidation. In addition, this composite exhibits favorable stability during the cycling experiment, suggesting it may be a promising visible light active photocatalyst for environmental applications.

1. Introduction

During the past decades, the application of semiconductor-based photocatalysis in hydrogen production from water splitting [1–4], degradation of organic pollutants in wastewater, removal of NO_x in air [5–10], and CO_2 reduction to obtain high valuable hydrocarbon fuels [11–15] has attracted considerable attention. Among various semiconductors investigated, TiO_2 has received far more attention in the photocatalysis field due to its low cost, low toxicity and high chemical stability [16–19]. However, the relatively wide band gap (3.2 eV for anatase, 3.0 eV for rutile) of TiO_2 limits its practical applications, which makes TiO_2 only respond to the ultraviolet (UV) light (about 4% of the solar energy) [20,21]. Therefore, great efforts have been devoted to develop the novel photocatalyst with highly visible light activity.

Bismuth vanadate ($BiVO_4$) has garnered considerable attention as a promising photocatalyst due to its excellent properties, such as non-toxic, narrow band gap, good dispersibility, resistance to corrosion, and higher sunlight utilization [22–27]. There are three crystal structures of $BiVO_4$ according to the previous study, including monoclinic scheelite structure (ms-$BiVO_4$), tetragonal scheelite structure (ts-$BiVO_4$), and tetragonal zircon structure (tz-$BiVO_4$) [28,29]. Among these crystalline phases, ms-$BiVO_4$ exhibits much higher catalytic activity under visible light irradiation compared to ts-$BiVO_4$ and tz-$BiVO_4$ due to the effective hybridization of Bi 6s with O 2p to form the valence band with a narrower band gap (Eg = 2.4 eV) [30]. Recently, photocatalytic properties of $BiVO_4$-based materials have been extensively explored.

It is well-known that the photocatalytic performance of $BiVO_4$ is strongly related to its morphology. For instance, Tan et al. prepared hierarchical structures of $BiVO_4$ via the microwave hydrothermal method. It is found that the $BiVO_4$ with different crystal phases and morphologies can be prepared by varying the pH values of the precursors, and the irregular rodlike ms-$BiVO_4$ obtained at pH 7.81 exhibited the best visible-light photocatalytic activity [31]. Ma et al. investigated ms-$BiVO_4$ samples prepared by a hydrothermal method. The results indicated that the morphology of the $BiVO_4$ greatly changed with the increase of ethylenediamine

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tetraacetic acid (EDTA) amount. The obtained $BiVO_4$ with hollow polygon morphology showed higher discoloration rate of MB under simulated sunlight, 90.84% of MB could be degraded within 5 h [32]. Liu et al. discovered that the sheet-like $BiVO_4$ sample with highly exposed (010) facets could be obtained with assistance of glycerol, which exhibited the best photocatalytic performance for MB degradation [33]. Based on the above discussion, it can be concluded that morphology and microstructure have great effects on photocatalytic activity of $BiVO_4$. Nevertheless, the reported $BiVO_4$ with rod-like [31], fusiform-like [32] and sheet-like [33] morphology showed low degradation rate under visible light irradiation, which usually takes about 3–5 h to completely discolor dyestuff. Therefore, the investigation on morphology of $BiVO_4$ would be beneficial to exploration of highly active $BiVO_4$-based photocatalysts.

The activity of pristine ms-$BiVO_4$ is still low owing to the rapid recombination rate of electron-hole pairs and weak surface adsorption properties, which significantly limit its practical application. Previous studies had shown that composite photocatalysts could enlarge the spectral responsive range and promote the separation of photoinduced charge carriers, and thus could remarkably improve the photocatalytic activity of an individual semiconductor [34–38]. As a result, several $BiVO_4$-based composites have been fabricated by coupling $BiVO_4$ with other semiconductors. For instance, Chang et al. described that the *p*-Co_3O_4/n-$BiVO_4$ heterojunction can effectively suppress the excessive formation of recombination centers at interface and improve the surface reaction kinetics simultaneously. This composite achieved the highest photocurrent for water oxidation [39]. Wetchakun et al. prepared $BiVO_4/CeO_2$ nanocomposites by using precipitation method and hydrothermal techniques. The results clearly show that $BiVO_4/CeO_2$ nanocomposite with mol ratio of 0.6:0.4 exhibited the highest photocatalytic activity in dye wastewater treatment [40]. Li et al. synthesized the novel $BiVO_4/FeVO_4$ heterojunction photocatalysts by one-step hydrothermal method. The composites showed higher photocatalytic efficiency for the photodegradation activity of MNZ (metronidazole) under visible light irradiation, which was much higher than individual $BiVO_4$ or $FeVO_4$ [41]. In addition, other $BiVO_4$-based composites such as $BiVO_4/TiO_2$ [42], $V_2O_5/BiVO_4$ [43], $SnO_2/BiVO_4$ [44], $CuO/BiVO_4$ [45], $WO_3/BiVO_4$ [46] and $SiO_2/BiVO_4$ [47] have also been reported. These studies show that the enhanced photoactivity results from a coupling effect between the two components in the composites, which can increase the electron transfer and inhibits the recombination of photo-generated charge carriers [44,48]. However, to the best of our knowledge, $Ag_4V_2O_7/BiVO_4$ photocatalyst has not been reported, and photocatalytic removal of high concentration NO in air using $Ag_4V_2O_7/BiVO_4$ composites under visible light irradiation has never been investigated.

In this work, we have successfully prepared a series of double cone-shaped $Ag_4V_2O_7/BiVO_4$ composites by a sodium polyphosphate-assisted hydrothermal method with an expectation to obtain a promising visible light driven catalyst. The as-obtained composite has been explored for the degradation of MB and oxidation of NO in high concentrate under visible light irradiation ($\lambda > 420$ nm). The composite shows superior photocatalytic activity as compared with pure material. Moreover, the possible photocatalytic mechanism of the double cone-shaped $Ag_4V_2O_7/BiVO_4$ composites was also discussed.

2. Experimental section

All chemicals were of analytical reagent grade and used without further purification. Distilled water was used throughout.

2.1. The preparation of $Ag_4V_2O_7/BiVO_4$

The double cone-shaped $Ag_4V_2O_7/BiVO_4$ samples were prepared via hydrothermal process, the details of which are as follows: $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 20 mL of HNO_3 (solution A) and NH_4VO_3 was dissolved in 20 mL of NaOH (solution B) respectively, the molar ratio of $Bi(NO_3)_3 \cdot 5H_2O$ and NH_4VO_3 is 1:1. Then a certain amount of surfactant sodium polyphosphate was added to solution B under stirring. The two solutions were magnetically stirred for 30 min at room temperature to obtain transparent solutions, then solution B was added dropwise into solution A under magnetic stirring to obtain a yellow homogeneous suspension. Subsequently, certain amount of $AgNO_3$ was added into the mixture. After further stirring for 2 h, the pH of the solution was adjusted to 7 by adding of NaOH solution, which was transferred into a 100 mL Teflon-lined stainless steel vessel, followed by heating at 180 °C for 4 h. After cooled to room temperature naturally, the yellow precipitate was centrifuged, washed three times separately with distilled water and ethanol to remove the impurities. Finally, the obtained samples were dried in an oven at 60 °C for 24 h. Briefly, the sample was denoted as 0.02-$Ag_4V_2O_7/BiVO_4$, 0.04-$Ag_4V_2O_7/BiVO_4$, 0.06-$Ag_4V_2O_7/BiVO_4$, 0.08-$Ag_4V_2O_7/BiVO_4$, 0.10-$Ag_4V_2O_7/BiVO_4$, 0.02, 0.04, 0.06, 0.08 and 0.10 represent the molar ration of $AgNO_3$ to $Bi(NO_3)_3 \cdot 5H_2O$ in the starting materials, respectively. For comparison, pure double cone-shaped $BiVO_4$ was prepared without using $AgNO_3$, and bulk-shaped $BiVO_4$ (BS-$BiVO_4$) was prepared in the absence of sodium polyphosphate and $AgNO_3$. The synthesis process is illustrated in Fig. S1 of Supplementary material.

2.2. Characterization techniques

The morphologies were observed by a scanning electron microscopy (SEM, JSM-6390A) equipped with an energy-dispersive x-ray (EDS) analysis. The crystalline phases of the samples were identified by X-ray diffractometer (Shimadzu, XRD-6000, Cu Kα radiation). UV–vis diffuse reflectance spectra were recorded on a Shimadzu UV-3600 spectrophotometer with an integrating sphere, and $BaSO_4$ was used as a reference. X-ray photoelectron spectroscope was performed to examine the surface properties and composition (XPS, Kratos AXIS NOVA spectrometer). Photoluminescence (PL) spectra were obtained using a florescence spectrophotometer (Hitachi F-7000). The products of the photocatalytic oxidation of NO were analyzed by ion chromatography with ECD detector (DIONEX ICS-2100, AS18 as chromatographic column, 23 mmol L^{-1} of KOH solution as mobile phase).

2.3. Photocurrent-time measurement

Photocurrent-time measurements were performed on an electro-chemical analyzer (CHI660E, CHI Shanghai, Inc.) with a standard three electrode cell at room temperature. The prepared sample, saturated calomel electrode (SCE), and a Pt electrode were used as the working electrode, the reference electrode and the counter electrode, respectively. A 300 W Xe-lamp served as a light source, 0.1 M Na_2SO_4 aqueous solution was used as the electrolyte. The working electrodes were prepared as follows: Fluorine doped tin oxide (FTO) glass pieces (2 cm × 3 cm) were cleaned successively by acetone and deionized water, and then dried in air. 5 mg of prepared sample was mixed with N-methyl-2-pyrrolidone to make slurry. Then the mixture was ultrasonicated for 1 h to obtain a suspension, which was coated onto the FTO glass substrate. The electrolyte was dried at 50 °C for 6 h to obtain working electrode with a similar film thickness [49].