Preparation of BiVO₄@Fiber Composites and the Photocatalytic Property for Degradation of Organic Dyes under Visible-Light

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Abstract

In this article, a novel BiVO₄@fibers composite photocatalyst was prepared by a process that monoclinic scheelite BiVO₄ nano/micro particles were in situ formed onto fiber materials. The structure, morphology and photophysical properties of the composite materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-Vis diffuse reflectance spectroscopy, respectively. The immobilization of BiVO₄ photocatalyst on fibers reduced the particle size of the photoactive phase, and a few visible-light absorption abilities. The decomposition of a non-biodegradable dye Red FN-3G was selected to examine the photocatalytic activity of the composite photocatalyst. It was found that the formation of composite materials of BiVO₄ with fibers didn’t decrease the photocatalytic activity with comparison to that of pure BiVO₄. Moreover, it demonstrated that when adjusting the dye solution into about pH = 3, the highest efficiency of dye degradation over the fiber composite material can be obtained.

Keywords: BiVO₄@Fibers Composite Photocatalyst, Red FN-3G Decomposition, Photocatalysis

1. Introduction

It is a dream for mankind to convert sustainable solar energy to electric and chemical energies. People has been pursuing this dream for hundreds of years until the photoelectrochemical splitting of water to produce H₂ and O₂ under light irradiation (the Honda-Fujishima effect) was discovered in 1972 [1]. At present, great progresses had been made on this area, and to date, the design and development of visible-light responsive photocatalysts as well as the improvement of photocatalytic reactivity and efficiency became the major goals that most of the researches focused on [2,3].

For the first goal, it is utmost important to develop photocatalyst with narrow band-gap provide that we could know how to engineer smaller band-gap materials with more suitable band edge positions. One of the efforts consists of creating an electron donor level between the valence band and conduction band of TiO₂ by doping with metallic or nonmetallic elements such as V and Cr or N, S, and C. However, although the doping of foreign elements extends the absorption to visible-light ranges, it increases the defects of semiconductor photocatalysts, which therefore, a part of the ultraviolet light-responsive performance that the titanium oxide originally possessed was occasionally ruined. This situation led to fewer breakthroughs for direct utilization of solar energy. Another effort is the exploring of complex compounds that containing Bi³⁺, In³⁺, Sn²⁺ (s² configuration) or Ag⁺ (d¹⁰ configuration) ions in an oxide system. Thus it is able to elevate the valence band by means of the hybridization of their respective orbitals with the O₂p orbital, and also narrowing the band gap of the semiconductor [4].

Of various visible-light responsive metal-oxide photocatalysts studied thus far, BiVO₄ is one of the typical complex oxides with narrow band-gap that showed not only excellent visible-light photocatalytic properties but also high photo-to-current conversion efficiency [5-9]. However, at the present stage, BiVO₄ is still far away the practical applications due to a number of devices and material parameters have yet to be optimized, e.g. the morphology, particle size, et al., which leading to the efficient dissociation of all generated excitons, and subsequent transport of charge carriers out of the particles. Moreover, because the semiconductor particles are slight and hard to settle down, powder photocatalyst can be
easily drained away in waste water treatment and is therefore go against to the regeneration and recycle, causing waste and secondary pollution [10]. However, this problem might be solved by dispersing the photocatalysts onto a support. Nonwoven fiber material is a green material. It provided with flexile, soft, easy to be decomposed, nontoxic, nonirritating, inexpensive and recyclable characters, which could be used not only as absorbing material, but also be functionalized to new material by means of physics, chemistry methods. These nonwoven could be used as the material of loading catalyst.

Several approaches have been reported for the preparation of BiVO₄, such as solid-state reaction, coprecipitation, hydrothermal treatment and metalorganic decomposition [11-14]. However, there is almost no report about catalyst loading on nonwoven fibers. In this article, the loading of BiVO₄ particles on fiber materials to form BiVO₄@fibers photocatalyst by coprecipitation process were reported. An active and nonbiodegradable dye Red FN-3G was used to estimate the photocatalytic properties. The pH condition was also adjusted to get a better activity.

2. Experiments

2.1. Preparation of BiVO₄@Fibers Photocatalyst

All chemicals (Shanghai Chemical Reagents Company, China) were of analytic grade and used directly without any further purification, and solutions were prepared using deionized water. BiVO₄@fibers composite photocatalyst was synthesized by an in-situ co-precipitation process. First, the required amount of Bi(NO₃)₃·5H₂O and NH₄VO₃ were separately dissolved in 2.0 mol/L of nitric acid solution. 5 g of urea was added into the solution of Bi(NO₃)₃ and NH₄VO₃, then pretreated fibers were added. The solution was then stirred at 353 - 363 K for 12 h. At last, the mixture was washed, and dried. The BiVO₄@fibers photocatalyst was received. As comparison, pure BiVO₄ was also prepared in the same procedure except without fibers were added.

2.2. Characterizations

X-ray powder diffraction (XRD) patterns were recorded in the range of 2θ (5 - 75) with CuK radiation (λ = 0.1541 nm) using a Bruker AXS, D8 Advance X-ray diffractometer. The morphologies and microstructures were determined by a scanning electron microscopy (SEM, JEOL JSM-6390LV). Diffuse reflectance UV-vis spectrophotometer (DRS, Peking Puxi TU-1901) was used to obtain the absorption spectra of samples in the region of 200 - 800 nm using BaSO₄ (IS19-1) as a reference.

2.3. Photocatalytic Performances

Photocatalytic activities of the BiVO₄@fibers were evaluated by the degradation of red FN-3G dye in a glass reactor with a circulating water system. The light source was a 300 W Xe illuminator (Peking Changtuo, PLS-3XE300) and about 7 cm apart from the liquid level. The 420 nm cutoff filter was placed between the Xe-illuminator and the reactor to ensure the reaction occurred under visible-light condition. About 0.2 g catalyst laden fiber composite was added into 150 ml of 15 mg/l red FN-3G solution. Before illumination, the dye solution were stirred in the dark for 30 minutes to reach a adsorption/desorption equilibrium for the dye and fiber composite, then the light was switched on, and the solution were kept stirring in the process of illumination. At a certain intervals, a few amount of solution were collected, measured by UV-vis spectrophotometer (Shanghai Longnike, UNIC7200) at the absorbance at 490 nm. We also observed the photocatalytic effects under different pH.

3. Results and Discussions

3.1. The Crystalline Structure of BiVO₄

Figure 1 shows the X-ray diffraction patterns of the nonwoven fibers, pure BiVO₄ and the synthesized composite material. It is observed that all the peaks of BiVO₄ and the composite material are match well to the JCPDS No.14-0688 standard card, confirming that the crystal formatted on the fibers is similar to pure phased powder and showed a monoclinic scheelite BiVO₄ with high crystallinity. At BiVO₄@fibers composite, there is no peaks of any other phases or impurities can be detected in the composite sample, but have a little lower diffraction intensities than the pure BiVO₄.

As we have known, BiVO₄ exists naturally in three different phases, monoclinic scheelite, tetragonal zircon and tetragonal scheelite. The photocatalytic properties of BiVO₄ are strongly related to its crystal phase, and only monoclinic scheelite structure showed high photocatalytic activity under visible-light irradiation [15,16]. So the target for synthesis of BiVO₄ is to form more amount of monoclinic scheelite structured material. The above XRD results suggested that the fibers gave a tiny effect on the crystalline structure of BiVO₄.

3.2. The Morphologies of BiVO₄

The SEM images of different catalysts are shown in Figure 2. The primary particles of pure BiVO₄ presented a
Figure 1. XRD patterns of (a) BiVO₄ powder, (b) BiVO₄@fibers composite, (c) Blank fiber, (d) JCPDS No.14-0688 standard card.

Figure 2. SEM micrographs of (a) (b) BiVO₄ powders, (c) (d) (e) BiVO₄@fibers composite, (f) Blank fiber.

little large size and aggregated with each other strongly to be a cluster as shown in Figures 2(a) and (b). From Figures 2(c)-(e), with comparison to Figure 2(f), it could be seen that the BiVO₄ particles are attached tightly on the surface of the fiber materials, by which the BiVO₄ particles cannot be removed during the practical applications. Moreover, it can be observed clearly from Figures 2(a) and (e) that when BiVO₄ was loaded on the surface of nonwoven fiber, the particle size appeared to be much smaller than that of BiVO₄ powder. This result suggested that the confine effect of fibers is beneficial for the formation of nano/micro particles of BiVO₄.

3.3. UV-Vis Diffusion Reflectance Spectra

The UV-Vis diffuse reflectance spectra of the pure BiVO₄, the synthesized composite material and the nonwoven fibers, are depicted in Figure 3. The nonwoven fibers gave a strong absorption in the UV region of 200 - 340 nm. It can also absorb some portion of light with wavelength higher than 350 nm. When the spectra of the synthesized composite material and pure BiVO₄ are compared, it can be found that the absorption edges have almost no difference, only a small difference in the absorption of wavelength higher than 550 nm was observed. The pure BiVO₄ has almost no absorption in the region of 550 - 800 nm, but BiVO₄@fibers have some parts of absorption in this region. This result may be attributed to the absorption of fibers, indicating that the fiber materials gave a certain influence on the light absorption of BiVO₄@fibers composites. This absorption might redound to the improvement of photocatalytic activity.

3.4. The Photocatalytic Performances

The photocatalytic performance of BiVO₄@fibers composites were evaluated in terms of the degradation of Red FN-3G in aqueous solution under visible-light irradiation. Red FN-3G is an active dye which is hard to be decomposed by biological process. Figure 4 shows the results of Red FN-3G photodecomposition over BiVO₄@fibers and pure BiVO₄ sample. As a comparison, the photodecomposition of Red FN-3G was also performed without adding photocatalyst. The result without photocatalyst indicates that the decomposition of Red FN-3G could be ignored after 10 h of irradiation. However, in 10 hours irradiation, 45% of Red FN-3G can be decomposed by pure BiVO₄, and about 50% of dyes can be photodecomposed over BiVO₄@fibers composites. The BiVO₄@fibers photocatalyst gave a similar activity to pure BiVO₄. The particles size of BiVO₄ formatted on the composite photocatalyst was smaller than that of pure BiVO₄, which may be beneficial for the improvement of photocatalytic activity. However, the available surface was fewer due to part of the surface was adhered to fiber and the amount of photoactive BiVO₄ was much lower than that of pure BiVO₄ powder. Thereby, these two reverse
Figure 3. Diffuse-reflectance spectra of (a) BiVO$_4$ powder, (b) BiVO$_4$@fibers composite, (c) Blank fiber.

Figure 4. Comparison of degradation red FN-3G efficiency over (a) Blank solution, (b) BiVO$_4$ powder, (c) BiVO$_4$@fibers composite.

Figure 5. Comparison of degradation red FN-3G efficiency at different pH (a) Blank solution (b) PH = 9, (c) PH = 7, (d) PH = 5, (e) PH = 3.

In order to improve the activity of BiVO$_4$@fibers, we tried to change the pH to observe the photocatalytic property. In this experiment, NaOH and HCl were used to adjust the pH. From Figure 5, we could see that the photocatalytic activity is the best when pH is 3. That is to say, BiVO$_4$ get better catalytic effect under acidic condition, and then followed neutral, alkalinity. And with a higher acidity of the dye solution give a better decomposition efficiency. This observation may be attributed to the charge character formed on the surface of BiVO$_4$. Because BiVO$_4$ is an n-type semiconductor, the isoelectric point of BiVO$_4$ is arrived at alkaline addition. When the pH was adjusted to 9, almost no net charges on the surface of BiVO$_4$ are left, the solution will be tend to balance. However, in acidic condition, the H$^+$ in the acid solution promote the formation of B acid site on the surface of BiVO$_4$, which is favourable for the photogenerated electrons on BiVO$_4$’s conduction band move to surface, leading to the effective separation of photon-activated electrons and hole, thus enhance the photocatalytic efficiency.

4. Conclusions

BiVO$_4$ with a small particle-size has been immobilized on the surface of fiber materials. The synthesized fiber composites exhibited the typical monoclinic scheelite BiVO$_4$ structure. The BiVO$_4$@fibers showed the absorption in the visible region between 550 and 800 nm, though presented a little blue shift compared with pure BiVO$_4$. It was also found that a better photocatalytic activity over BiVO$_4$ is in acidic condition. The photocatalytic activity of BiVO$_4$@fibers was similar to that of pure BiVO$_4$. The results improved the industrial applications of this advanced material.

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6. References


