

# Preparation of BiVO<sub>4</sub>@Fiber Composites and the Photocatalytic Property for Degradation of Organic Dyes under Visible-Light

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## Abstract

In this article, a novel BiVO<sub>4</sub>@fibers composite photocatalyst was prepared by a process that monoclinic scheelite BiVO<sub>4</sub> 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 BiVO<sub>4</sub> 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 BiVO<sub>4</sub> with fibers didn't decrease the photocatalytic activity with comparison to that of pure BiVO<sub>4</sub>. 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:** BiVO<sub>4</sub>@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 H<sub>2</sub> and O<sub>2</sub> 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 TiO<sub>2</sub> 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 Bi<sup>3+</sup>, In<sup>3+</sup>, Sn<sup>2+</sup> (s<sup>2</sup> configuration) or Ag<sup>+</sup> (d<sup>10</sup> 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 O<sub>2p</sub> orbital, and also narrowing the band gap of the semiconductor [4].

Of various visible-light responsive metal-oxide photocatalysts studied thus far, BiVO<sub>4</sub> 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, BiVO<sub>4</sub> 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  $\text{BiVO}_4$ , 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  $\text{BiVO}_4$  particles on fiber materials to form  $\text{BiVO}_4$ @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 $\text{BiVO}_4$ @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.  $\text{BiVO}_4$ @fibers composite photocatalyst was synthesized by an in-situ co-precipitation process. First, the required amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{NH}_4\text{VO}_3$  were separately dissolved in 2.0 mol/L of nitric acid solution. 5 g of urea was added into the solution of  $\text{Bi}(\text{NO}_3)_3$  and  $\text{NH}_4\text{VO}_3$ , 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  $\text{BiVO}_4$ @fibers photocatalyst was received. As comparison, pure  $\text{BiVO}_4$  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  $2\theta$  (5 - 75) with CuK radiation ( $\lambda = 0.1541$  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  $\text{BaSO}_4$  (IS19-1) as a reference.

### 2.3. Photocatalytic Performances

Photocatalytic activities of the  $\text{BiVO}_4$ @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 Long-nike, UNIC7200) at the absorbance at 490 nm. We also observed the photocatalytic effects under different pH.

## 3. Results and Discussions

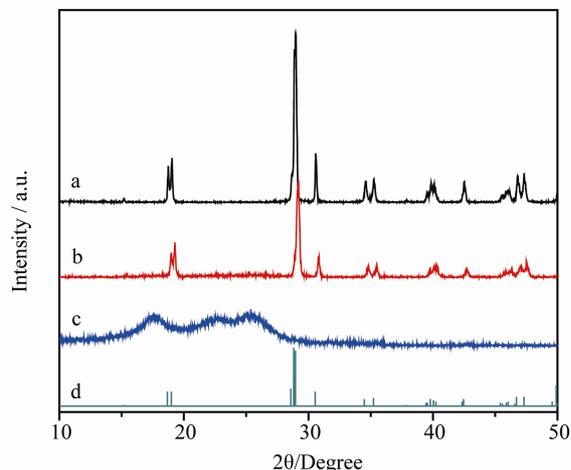
### 3.1. The Crystalline Structure of $\text{BiVO}_4$

**Figure 1** shows the X-ray diffraction patterns of the nonwoven fibers, pure  $\text{BiVO}_4$  and the synthesized composite material. It is observed that all the peaks of  $\text{BiVO}_4$  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  $\text{BiVO}_4$  with high crystallinity. At  $\text{BiVO}_4$ @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  $\text{BiVO}_4$ .

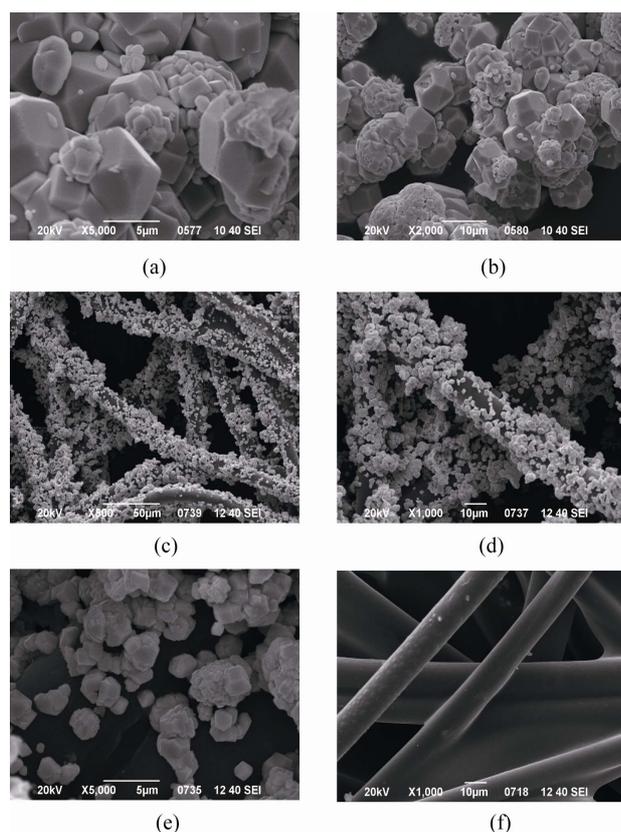
As we have known,  $\text{BiVO}_4$  exists naturally in three different phases, monoclinic scheelite, tetragonal zircon and tetragonal scheelite. The photocatalytic properties of  $\text{BiVO}_4$  are strongly related to its crystal phase, and only monoclinic scheelite structure showed high photocatalytic activity under visible-light irradiation [15,16]. So the target for synthesis of  $\text{BiVO}_4$  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  $\text{BiVO}_4$ .

### 3.2. The Morphologies of $\text{BiVO}_4$

The SEM images of different catalysts are shown in **Figure 2**. The primary particles of pure  $\text{BiVO}_4$  presented a



**Figure 1.** XRD patterns of (a)  $\text{BiVO}_4$  powder, (b)  $\text{BiVO}_4$ @fibers composite, (c) Blank fiber, (d) JCPDS No.14-0688 standard card.



**Figure 2.** SEM micrographs of (a) (b)  $\text{BiVO}_4$  powders, (c) (d)  $\text{BiVO}_4$ @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  $\text{BiVO}_4$  particles are attached tightly on the surface of the fiber materials, by which the  $\text{BiVO}_4$

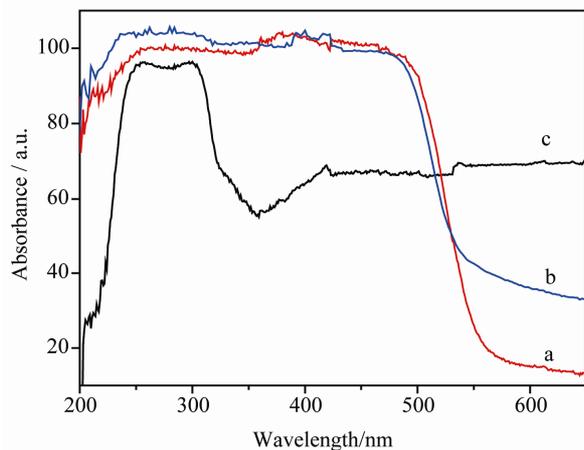
particles cannot be removed during the practical applications. Moreover, it can be observed clearly from **Figures 2(a)** and **(e)** that when  $\text{BiVO}_4$  was loaded on the surface of nonwoven fiber, the particle size appeared to be much smaller than that of  $\text{BiVO}_4$  powder. This result suggested that the confine effect of fibers is beneficial for the formation of nano/micro particles of  $\text{BiVO}_4$ .

### 3.3. UV-Vis Diffusion Reflectance Spectra

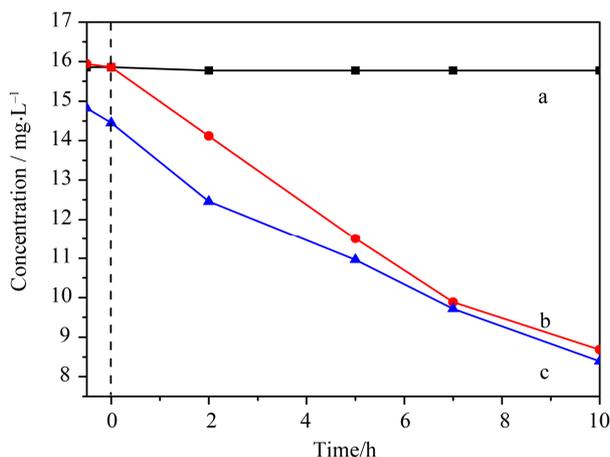
The UV-Vis diffuse reflectance spectra of the pure  $\text{BiVO}_4$ , the synthesized composite material and the nonwoven fibers, are depicted in **Figure 3**. The nonwoven fibers gave a strong absorption in the UV region of 200 - 340 nm. It can also absorb some portion of light with wavelength higher than 350 nm. When the spectra of the synthesized composite material and pure  $\text{BiVO}_4$  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  $\text{BiVO}_4$  has almost no absorption in the region of 550 - 800 nm, but  $\text{BiVO}_4$ @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  $\text{BiVO}_4$ @fibers composites. This absorption might redound to the improvement of photocatalytic activity.

### 3.4. The Photocatalytic Performances

The photocatalytic performance of  $\text{BiVO}_4$ @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  $\text{BiVO}_4$ @fibers and pure  $\text{BiVO}_4$  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  $\text{BiVO}_4$ , and about 50% of dyes can be photodecomposed over  $\text{BiVO}_4$ @fibers composites. The  $\text{BiVO}_4$ @fibers photocatalyst gave a similar activity to pure  $\text{BiVO}_4$ . The particles size of  $\text{BiVO}_4$  formatted on the composite photocatalyst was smaller than that of pure  $\text{BiVO}_4$ , 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  $\text{BiVO}_4$  was much lower than that of pure  $\text{BiVO}_4$  powder. Thereby, these two reverse



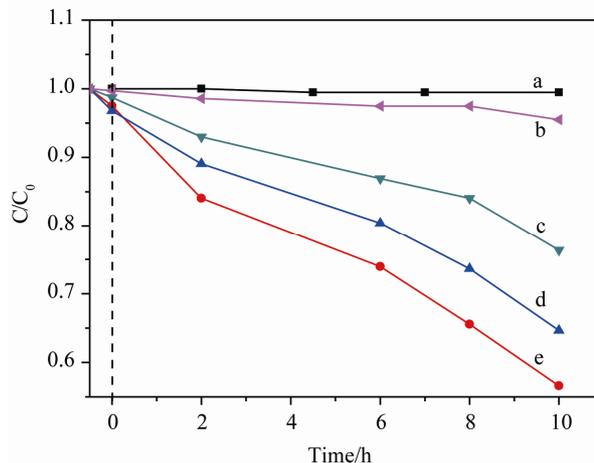
**Figure 3.** Diffuse-reflectance spectra of (a)  $\text{BiVO}_4$  powder, (b)  $\text{BiVO}_4$ @fibers composite, (c) Blank fiber.



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

effects make a similar photocatalytic degradation efficiency over composite photocatalyst with pure  $\text{BiVO}_4$ . Furthermore, the reactor used in our experiment may have influence on the light absorption, which resulted in low fraction of light are irradiated. The  $\text{BiVO}_4$ @fibers is soft and sometimes was folded during the experiment, the received illumination upon the active  $\text{BiVO}_4$  may be decreased, by which the photocatalytic activity was ruined.

In order to improve the activity of  $\text{BiVO}_4$ @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,  $\text{BiVO}_4$  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



**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.

the charge character formed on the surface of  $\text{BiVO}_4$ . Because  $\text{BiVO}_4$  is an n-type semiconductor, the isoelectric point of  $\text{BiVO}_4$  is arrived at alkaline addition. When the pH was adjusted to 9, almost no net charges on the surface of  $\text{BiVO}_4$  are left, the solution will be tend to balance. However, in acidic condition, the  $\text{H}^+$  in the acid solution promote the formation of B acid site on the surface of  $\text{BiVO}_4$ , which is favourable for the photogenerated electrons on  $\text{BiVO}_4$ 's conduction band move to surface, leading to the effective separation of photon-activated electrons and hole, thus enhance the photocatalytic efficiency.

## 4. Conclusions

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

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