Performance for Methylene Blue under Visible Light Irradiation

I. INTRODUCTION

Numerous efforts had been made to develop highly effective photocatalysts for the photodecomposition of environmental contaminants like pesticides, dyes and heavy metal in water [1]. Monoclinic scheelite-type BiVO$_4$, one kind of visible light photocatalyst with the energy band gap of 2.4 eV, also attracted a great deal of attention or pollutant elimination under visible light [2, 3]. However, unavoidably, the photocatalytic activity of pure BiVO$_4$ need to be further improved owing to the rapid recombination rate of photogenerated carriers [4]. Therefore, it was necessary to develop effective solution to improve the charge separation efficiency and enhance visible-light photocactivity. Forming a heterojunction between BiVO$_4$ and another semiconductor such as V$_2$O$_5$ [5], Bi$_2$O$_3$ [6], Cu$_2$O [7, 8], and InVO$_4$ [9], was an effective way to address the above two issues [10, 11].

As is known, TiO$_2$, as a wide band-gap semiconductor, has been applied widely because of its high stability, low cost, nontoxity and efficient photocatalytic activities under UV light irradiation [12]. Although it could not be excited under visible light, it had suitable energy band that could effectively transfer the photo-generated charges from BiVO$_4$ [13, 14]. Hu et al. [15] reported that heterojunctions exhibited higher photocatalytic activity than the individual components, which confirmed that the combination of BiVO$_4$ and TiO$_2$ was an effective way to enhance the photocatalytic activity of BiVO$_4$ under visible light irradiation. Zhang et al. [14] prepared TiO$_2$/BiVO$_4$ spherical composite photocatalysts by the one-step microwave hydrothermal method. They investigated the photocatalytic degradation of RhB under UV light and Xe lamp irradiation, results indicated that the degradation efficiency can reach over 94% after 330 min UV irradiation, but only about 83% after 360 min Xe lamp irradiation. Considering the fact that the morphological diversity of inorganic materials had a significant impact on functional diversification and potential applications [16, 17], it was expected that the TiO$_2$/BiVO$_4$ composite with a special morphological diversity would have a good photocatalytic activity under visible light irradiation.

Microfibers possessed high specific surface area and small thickness. These characteristics assured microfibers potential to be exposed to more light and contact with more dye molecules; meanwhile, its separation and migration efficiency of photogenerated electron-hole pairs was effectively improved. In addition, the micro-pores could serve as transport paths for small molecules, benefitting the reactant molecules to get to the reactive sites on the framework walls of photocatalysts [18], which further accelerate the chemical reactions and result in the excellent photocatalytic activity.

ARTICLE

TiO$_2$/BiVO$_4$, a Heterojuncted Microfiber with Enhanced Photocatalytic Performance for Methylene Blue under Visible Light Irradiation

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Novel TiO$_2$/BiVO$_4$ microfiber heterojunctions were constructed using cotton as biomorphic templates. The as-synthesized samples were characterized by scanning electron microscope, X-ray diffraction, X-ray photoelectron spectroscopy, UV-Vis diffuse reflectance spectra and photocatalytic experiment. The morphology of the as-synthesized TiO$_2$/BiVO$_4$ composites was consisted of a large quantity of microfiber structures with diameter from 2.5 μm to 5 μm, and the surface of samples became more coarse and compact with the increase of weight ratio of TiO$_2$. The TiO$_2$/BiVO$_4$ samples with proper content (10.00wt%) showed the highest photocatalytic degradation activity for methylene blue (MB) degradation among all the samples under visible light, and 88.58%MB could be degraded within 150 min. The enhancement of photocatalytic activity was mainly attributed to the formation of n-n heterojunction at the contact interface of TiO$_2$ and BiVO$_4$, which not only narrowed the band gap of BiVO$_4$ for extending the absorption range of visible light, but also promoted the transfer of charge carriers across interface. A possible photodegradation mechanism of MB in the presence of TiO$_2$/BiVO$_4$ microfibrous photocatalyst was proposed.

Key words: TiO$_2$/BiVO$_4$, Microfiber, Visible-light-response, Photocatalysis
Therefore, instead of the corresponding nanoparticles, microfibers being an important subclass of microstructural materials are deemed as potential good candidates for practical applications [19].

Template procedures were an ideal way to control material structure including the outer morphology and size and the inner pore size and distribution [20]. In recent years, biomorphic mineralization has been noteworthy as a new fabrication technique for functional materials, which is a technique that produces materials with morphologies and structures resembling those of nature living things [21]. Biomorphic mineralization was of low-cost, environmentally benign, and easily removed with heating procedures. Natural cotton had been selected as templates to produce various advanced biomorphic materials, such as MgO [22], NiO [23] and In2O3 [24].

In the present work, we synthesized pure BiVO4 and a series of biomorphic TiO2/BiVO4 microfibers by using cotton fibers as biomorphic templates, and demonstrated their physical properties. The photocatalytic properties of the as-synthesized TiO2/BiVO4 heterojunctions were tested by the photodegradation of methylene blue (MB) aqueous solution under visible light irradiation. The mechanism of enhanced photocatalytic activity of TiO2/BiVO4 heterojunction photocatalysts was also discussed.

II. EXPERIMENTS

A. Materials and Reagents

Bi(NO3)3·5H2O, NH4VO3, citric acid, nitric acid, ammonia, n-tetrabutyltitanate (C16H36O4Ti), methylene blue (MB), and other chemicals were obtained from Shanghai Chemical Reagents Company (China). All chemicals were of analytical reagent grade and used as received without further purification. Ultrapure deionized water was used throughout the experiments.

B. Preparation of TiO2/BiVO4 heterojunction microfibers

In a typical procedure, 0.485 g of Bi(NO3)3·5H2O and the same molar of citric acid were dissolved in 30 mL of 2 mol/L nitric acid aqueous solution, adjusting the pH value to 7.0 by dropwise titration of 1 mol/L ammonia solution under stirring, and transparent solution A was formed. Meanwhile, 0.117 g of NH4VO3 was dissolved in deionized water at 70 °C and the same molar of citric acid was added to obtain dark green solution B. After mixing of solution A and B, uniform dark green solution C was obtained. Different dosage of n-tetrabutyltitanate (C16H36O4Ti) was dissolved in ethanol at room temperature, thus pale-yellow solution D was formed. The dried and loose cotton fibers were immersed into the mixture of solution C and D. After immersing for 24 h, the cotton fibers were taken out, dried at 50 °C for 12 h, which were then placed in an alundum crucible and calcined in air at 500 °C for 1 h. Finally, pale-yellow TiO2/BiVO4 heterojunction were obtained. The weight ratio of C16H36O4Ti/(C16H36O4Ti+Bi(NO3)3·5H2O) was controlled from 12% to 48%, and the final TiO2/BiVO4 were labelled as 4.58%, 10.00%, 16.54% and 24.53%, respectively.

For reference, pure BiVO4 microfibers were synthesized under the same conditions without adding n-C16H36O4Ti.

C. Characterization

The phase identification of the as-prepared powders were obtained on a Rigaku D/max-3C X-ray powder X-ray diffractometry using Cu Kα radiation (λ=1.5405 nm, 40 kV, 40 mA). Scanning electron microscopy (SEM) images were observed by Hitachi S-4800 scanning electron microscopy. UV-visible diffuse reflectance spectra (UV-Vis DRS) of the samples were recorded on Lambda 950 spectrophotometer using BaSO4 as reference.

D. Measurement of photocatalytic activity

The photocatalytic activity of TiO2/BiVO4 heterojunctions was evaluated by measuring the degradation of MB under visible light at room temperature. In a typical process, 100 mg of TiO2/BiVO4 samples were added to 100 mL of 10 mg/L MB solution and then stirred in the dark for 30 min, which allowed it to reach adsorption equilibrium and uniform dispersity. The solution was then exposed to visible light irradiation from a 500 W Xe lamp at room temperature. UV radiation was cut off by using a 400-nm filter, prior to irradiation of the sample. During the irradiation, 5 mL of the suspension was sequentially taken from the reactor every 30 min, and filtered immediately through 0.22 μm membrane filters for UV-Vis analysis. The decolorization efficiency was monitored by determining the absorbance around 664 nm in the UV-Vis spectra.

III. RESULTS AND DISCUSSION

A. SEM analysis

Figure 1 shows SEM images of pure BiVO4 and TiO2/BiVO4 heterojunctions via cotton biomorphic template. From Fig.1, it is clearly shown that all these samples are consisted of a large quantity of microfibers with diameter from 2.5 μm to 5 μm, indicating the formation of biomorphic TiO2/BiVO4 via cotton template. These microfibers may present as straight or twisted shapes, which are well consistent with the...
straight or twisted shapes of cotton template. Compared with pure BiVO$_4$ microfibers (Fig.1(a)), the surfaces of TiO$_2$/BiVO$_4$ heterojunctions (Fig.1 (b), (c), (d), and (e)) are coarse and have many microstructures on them. In addition, the framework of TiO$_2$/BiVO$_4$ becomes more compact with the increase of weight ratio of TiO$_2$. Therefore, the amount of n-tetrabutyllitanate in the impregnation step has an important influence on the microstructure of TiO$_2$/BiVO$_4$ surface.

B. XRD analysis

The phases and crystallinity of the as-prepared pure BiVO$_4$ and TiO$_2$/BiVO$_4$ heterojunctions were characterized by XRD, as shown in Fig.2. From Fig.2(a), the crystal form of the BiVO$_4$ can be identified to the monoclinic scheelite type with characteristic $2\theta$ values of 18.85° (110), 28.85° (011), 30.54° (121), 34.38° (040), 35.19° (200), 39.91° (002), 42.40° (141), 46.00° (211), 46.82° (150), 47.25° (132), 50.00° (240), 50.26° (222), 53.21° (161), 58.28° (123) and 59.38° (321) respectively (JCPDS card No.14-0688). The main characteristic peaks appearing in the TiO$_2$/BiVO$_4$ composites were similar to those of pure BiVO$_4$. However, a careful comparison shows a small peak at $2\theta=25.4^\circ$ in XRD patterns of TiO$_2$/BiVO$_4$ heterojunctions, but not in XRD patterns of pure BiVO$_4$ sample. This small peak was ascribed to the characteristic peak (101) of anatase TiO$_2$ (JCPDS card No.21-1272), indicating the existence of TiO$_2$. With increasing the contents of TiO$_2$ in the composites, the peak intensities of the anatase TiO$_2$ increased. No extra peaks except for BiVO$_4$ and TiO$_2$ crystal phase were detected in TiO$_2$/BiVO$_4$ heterojunctions. It was also found that after the introduction of TiO$_2$ into BiVO$_4$, the intensities of the diffraction peaks (011) increased, in XRD patterns of 4.58%TiO$_2$/BiVO$_4$ and 10.00%TiO$_2$/BiVO$_4$ samples, indicating that they...
displayed higher crystallinity than others. Furthermore, from the (011) peak, there was a slight shift to high diffraction angle in 10.00%TiO$_2$/BiVO$_4$ XRD pattern, compared with pure BiVO$_4$ (Fig.2(b)), indicating that the appropriate introduction of TiO$_2$ into BiVO$_4$ altered the crystalline structure of BiVO$_4$. All these results confirmed that the heterojunction structure was formed between TiO$_2$ and BiVO$_4$.

C. XPS analysis

To contrast the electronic environment and surface composition of 10.00%TiO$_2$/BiVO$_4$ heterojunctions with that of pure BiVO$_4$, survey XPS and high-resolution XPS analysis of both pure BiVO$_4$ and 10.00%TiO$_2$/BiVO$_4$ were performed and the results are shown in Fig.3. From Fig.3(A), Ti, V, O and C (the carbon contamination is often ubiquitous in the XPS measurements [25]) were observed in the samples of both pure BiVO$_4$ and 10.00%TiO$_2$/BiVO$_4$ where they were expected to be. In the 10.00%TiO$_2$/BiVO$_4$ sample, two peaks with binding energies of 464.1 and 458.2 eV, corresponding to Ti2p$_{3/2}$ and Ti2p$_{1/2}$ were detected (Fig.3(B)), which was in excellent agreement with the literature data for TiO$_2$ [26] in 10.00%TiO$_2$/BiVO$_4$ composites. From the high-resolution XPS spectra of the Bi4f region in Fig.3(C), it could be seen that the peaks of Bi4f$_{7/2}$ and Bi4f$_{5/2}$ in pure BiVO$_4$ were observed at 158.7 and 164.1 eV, respectively, which was in agreement with the literature data [27]. While the peaks of Bi4f$_{7/2}$ and Bi4f$_{5/2}$ for 10.00%TiO$_2$/BiVO$_4$ shifted to 159.0 and 164.3 eV, respectively. From Fig.3(D), V2p peaks in the XPS spectra located at 524.0 and 516.5 eV for pure BiVO$_4$ shifted to 524.4 and 516.9 eV for 10.00%TiO$_2$/BiVO$_4$. A similar shift was also found in the XPS spectra of O1s (529.5 eV for pure BiVO$_4$ shifted to 529.8 eV) (Fig.3(E)). Such inner shift of the Bi4f, V2p, and V1s orbits originated from the interaction of BiVO$_4$ and TiO$_2$. The analysis distinctly revealed that the interaction between BiVO$_4$ and TiO$_2$ was chemical bonding rather than a simple physical mixing.

D. UV-Vis DRS analysis

The energy band structure feature of a semiconductor was a key factor in determining its photocatalytic activity. Figure 4(a) presented UV-Vis diffuse reflectance analysis of the pure BiVO$_4$, pure TiO$_2$ and 10.00%TiO$_2$/BiVO$_4$ samples. It was shown that pure TiO$_2$ displayed no absorption of visible-light and the spectrum of pure BiVO$_4$ showed absorption from UV light to 600 nm, while the 10.00%TiO$_2$/BiVO$_4$ showed drastic and stronger photoabsorption in the 400–600 nm wavelength range due to the band gap transition. For a crystalline semiconductor, the opti-
appropriate amount of TiO$_2$ prepared with pure BiVO$_4$ in aqueous solution under visible light, and com-
erojunctions was evaluated for degradation of dye MB. Photocatalytic properties driven photocatalyst.

composite will be a potential candidate as visible-light performance of BiVO$_4$.

Therefore, based on these characterization results, it can be deduced that the photoabsorption performance of BiVO$_4$ was greatly improved by coupling the appropriate amount of TiO$_2$, and 10.00%TiO$_2$/BiVO$_4$ composite will be a potential candidate as visible-light driven photocatalyst.

E. Photocatalytic properties

The photocatalytic activity of the TiO$_2$/BiVO$_4$ heterojunctions was evaluated for degradation of dye MB in aqueous solution under visible light, and compared with pure BiVO$_4$ under the same condition.

Figure 5 shows the photodegradation efficiency of MB under visible light in the presence of pure BiVO$_4$ and TiO$_2$/BiVO$_4$ heterojunctions. It was observed that the pure BiVO$_4$ degraded about 33.22% of MB in 150 min while 4.58%TiO$_2$/BiVO$_4$, 10.00%TiO$_2$/BiVO$_4$, 16.54%TiO$_2$/BiVO$_4$, and 24.53%TiO$_2$/BiVO$_4$ degraded about 64%, 88.58%, 71.07%, and 74.28%, respectively. It was clear that the coupling of TiO$_2$ with BiVO$_4$ increased the photodegradation efficiency of MB under the visible light. It also showed that the photocatalytic activity of TiO$_2$/BiVO$_4$ was strongly dependent on the coupling amount of TiO$_2$. Optimum TiO$_2$ coupling amount in this study was 10.00%. This was possibly due to the enhanced light absorption intensity of the TiO$_2$/BiVO$_4$ heterojunction as emphasized by UV-Vis DRS spectra in Fig.4. An excess of TiO$_2$ amount (16.54% and 24.53%) might block the incident visible light irradiation on BiVO$_4$, due to the fact that TiO$_2$ displays no absorption of visible-light.

Regular 10.00%TiO$_2$/BiVO$_4$ particles (10.00%TiO$_2$/BiVO$_4$-R) were synthesized by a similar procedure to that of 10.00%TiO$_2$/BiVO$_4$ microfiber, except that no cotton template was used. Figure 6 shows the photocatalytic performance of 10.00%TiO$_2$/BiVO$_4$-R and 10.00%TiO$_2$/BiVO$_4$ for the degradation of MB. The inset described SEM images of 10.00%TiO$_2$/BiVO$_4$-R and 10.00%TiO$_2$/BiVO$_4$. As shown, 10.00%TiO$_2$/BiVO$_4$-R showed the lowest activity of 54.11% after 150 min irradiation, while microfiber 10.00%TiO$_2$/BiVO$_4$ showed a significant activity as high as 88.58%. Such dramatic activity enhancement should be due to the large surface area [29]. With a larger surface area, the number of active surface sites increases and so does the surface charge carrier transfer rate in photocatalysis, which can contribute to the higher photocatalytic activity [30]. Furthermore, the microfiber structure can facilitate mass transfer and increase the accessibility of active sites on 10.00%TiO$_2$/BiVO$_4$ surface to methylene blue.

\[
(\alpha h\nu)^2 = A(h\nu - E_g)^{n/2}
\]

where $\alpha$, $\nu$, $E_g$, and $A$ are the absorption coefficient, the light frequency, the band gap, and a constant, respectively. Therefore, plot $(\alpha h\nu)^2$ versus $h\nu$ and the band gap energies ($E_g$) can be estimated by extrapolating the linear region straight line to the $h\nu$ axis intercept as shown in Fig.4(b). In this work, the band gaps ($E_g$) were estimated to be 2.80, 3.20, and 2.16 eV from the absorption edge, corresponding to the pure BiVO$_4$, pure TiO$_2$ and 10.00%TiO$_2$/BiVO$_4$. Thus, 10.00%TiO$_2$/BiVO$_4$ has a wider photoabsorption range and more suitable band gap for photocatalytic applications.

Moreover, the microfiber structure can contribute to the higher photocatalytic activity [30]. Furthermore, the microfiber structure can facilitate mass transfer and increase the accessibility of active sites on 10.00%TiO$_2$/BiVO$_4$ surface to methylene blue.

\[
E_g = \frac{h^2}{2m^*}\frac{1}{A'}
\]

where $h$ is Planck’s constant, $m^*$ is the effective mass, and $A'$ is the effective dielectric constant.
FIG. 6 Photodecomposition of MB under visible light irradiation in the presence of 10%TiO$_2$/BiVO$_4$-R and 10%TiO$_2$/BiVO$_4$ microfiber heterojunctions.

molecules. The result was in agreement with the idea that photocatalytic activity is structure dependent [16, 17].

Figure 7 shows the time-dependent UV-Vis absorption spectra of MB during photoirradiation with pure BiVO$_4$ and 10.00%TiO$_2$/BiVO$_4$ heterojunction. As shown, the characteristic absorption band around 664 nm could be attributed to a chromophore containing a long conjugated $\pi$ system, while the absorption peaks at 245 and 292 nm were related to aromatic rings [31]. From Fig. 7, it could be seen that the 10.00%TiO$_2$/BiVO$_4$ (Fig. 7(b)) decolorized MB faster than pure BiVO$_4$ (Fig. 7(a)), and the characteristic absorption peaks at 292 and 664 nm diminished gradually with no detection of any new peak. According to Fig. 7(b), the decrease of the 664 nm absorption band suggested the conjugated $\pi$ bond of the molecule structure of MB was broken [31]. The decrease of the absorption bands around 245 and 292 nm in the UV region was due to the breaking of the aromatic rings in the MB molecules which confirms the destruction of degradation intermediates including aminobenzothiazole and aniline [31, 32]. These results indicated that the MB molecules were photocatalytically decomposed by 10.00%TiO$_2$/BiVO$_4$ under visible light irradiation. The exact intermediate and the final products were currently unclear, and will be elucidated in future work.

In order to investigate the mechanism of the enhanced photocatalytic activity of heterojunction, the band edge positions of conduction band (CB) and valence band (VB) of the two semiconductors at the point of zero charge should be confirmed according to the empirical equation [33, 34]:

$$E_{0}^{\text{CB}} = \chi - E_C - E_g$$  \hspace{1cm} (2)

Where $\chi$ is the absolute electronegativity of the semiconductor, which is defined as the geometric mean of the absolute electronegativity of the constitute atoms.

According to the equation above, the calculated CB and VB of TiO$_2$ are $-0.2$ and $3.00$ eV, and of BiVO$_4$ are $0.11$ and $2.27$ eV, respectively. When the BiVO$_4$ and TiO$_2$ were closely contacted together and visible-light irradiation took place, BiVO$_4$ was excited and the electrons ($e^-$) in the VB were excited to the CB, leaving the holes ($h^+$) behind. Then the excited-state electrons could be easily injected from the CB of BiVO$_4$ into the CB of coupled TiO$_2$ due to the joint of the electric fields between two materials. The electrons and holes transfer between the semiconductors made the Fermi level of TiO$_2$ to move down, while that of BiVO$_4$ move up until pseudo-equilibrium was reached. Thus, TiO$_2$/BiVO$_4$ n-n junction would be formed, which was favorable for the fast separation of electrons and holes due to the effect of inner electric field, analogous to BiOI/TiO$_2$ [35], Bi$_2$O$_2$CO$_3$/BiO$_2$ [36], Bi$_2$WO$_6$/TiO$_2$ [37] and TiO$_2$/Bi$_2$O$_3$ [38] heterojunctions. Thus, based on the above results, a possible photocatalytic mechanism of TiO$_2$/BiVO$_4$ heterostructure was proposed, as shown in Scheme 1.

The photoinduced holes in VB of BiVO$_4$ were powerful oxidative species, they were able to oxidize water (H$_2$O) molecules and hydroxyl (OH$^-$) groups to gener-
ate highly reactive hydroxyl (·OH) radicals. Meanwhile, the electrons injected into the CB of TiO$_2$ would then be captured by O$_2$ to yield ·O$_2$⁻. Highly reactive ·OH and ·O$_2$⁻ radicals had extremely strong oxidative capability to partially or completely mineralize MB molecules. In this way, the recombination of electron-hole pairs generated on BiVO$_4$ could be effectively reduced. The activity enhancement of BiVO$_4$ was ascertained owing to this high efficient separation mode for TiO$_2$/BiVO$_4$ heterostructure. Furthermore, the weak photosensitization effect of dyes on TiO$_2$/BiVO$_4$ could be also favorable for the dyes degradation [39].

IV. CONCLUSION

In this study, TiO$_2$/BiVO$_4$ heterojunctions with microfiber structures were synthesized by using cotton as biotemplates. It was demonstrated that coupling of TiO$_2$ with BiVO$_4$ can result in a high active photocatalyst for degradation of dye MB in aqueous solution under visible light irradiation. The introduction of TiO$_2$ led to the formation of n-n heterojunction at the contact interface of TiO$_2$ and BiVO$_4$, which not only narrowed the band gap of BiVO$_4$ for extending the absorption range of visible light, but also promoted the transfer of charge carriers across interface for suppressing the recombination of photogenerated electron-hole pairs, and thus improved the photocatalytic performance of TiO$_2$/BiVO$_4$ heterojunctions. The results indicated that the photocatalysts with proper coupling weight ratio of TiO$_2$ can efficiently catalyze the degradation of MB relative to pure BiVO$_4$. 10.00%TiO$_2$/BiVO$_4$ photocatalyst showed the highest photocatalytic activity towards the degradation of MB, and 88.58%MB could be degraded within 150 min. This work provides a new insight for developing novel composite catalysts, as well as offering high efficient visible-light-driven photocatalysts for water purification and environmental remediation.

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