Efficient removal of methylene blue over composite-phase BiVO$_4$ fabricated by hydrothermal control synthesis

Lili Zhang$^{a,b,*}$, Jinxin Long$^a$, Wenwen Pan$^a$, Shouyong Zhou$^a$, Junwu Zhu$^c$, Yijiang Zhao$^a$, Xin Wang$^c$, Guozhong Cao$^{b,**}$

$^a$Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials, Huaiyin Normal University, Huai'an, Jiangsu 223300, PR China
$^b$Materials Science and Engineering, University of Washington, Seattle, WA 98195, USA
$^c$Key Laboratory of Soft Chemistry and Functional Materials, Nanjing University of Science and Technology, Nanjing 210097, China

Abstract

Series of composite-phase BiVO$_4$ (scheelite-tetragonal and scheelite-monoclinic) were synthesized by hydrothermal method. The mass content of monoclinic phase ($\eta_{\text{mono}} = \frac{I_{\text{mono}}}{I_{\text{mono}} + I_{\text{tetra}}} \times 100\%$) in composite-phase BiVO$_4$ was successfully controlled by adjusting the pH value of precursor solution, which was achieved by manipulating the dosage of 2 M NaOH during the synthetic reaction. Results indicated that the pH value of the precursor solution had great effect on the structure of BiVO$_4$. It took on pure tetragonal form with solid and spherical morphology when pH $\leq$ 3.8, but presented pure monoclinic structure with quadrilateral appearance when pH $\geq$ 8.5. Along with the increase of pH (3.8–8.5) and the $\eta_{\text{mono}}$, the tetragonal particles and monoclinic particulates began to link together, and the two phases interweave together to form a petal-like structure when $\eta_{\text{mono}}$ reached over 60% (pH = 4.7). The photocatalytic activities of obtained products were investigated by photodegradation of methylene blue under visible light. It was found that composite-phase BiVO$_4$ with $\eta_{\text{mono}} > 60\%$ presented better photocatalytic activity than that of pure phase BiVO$_4$, either monoclinic or tetragonal. About 95% of the 10 mg L$^{-1}$ methylene blue was degraded within 120 min catalyzed by the best catalyst BiVO$_4$ with $\eta_{\text{mono}} = 92.73\%$. Possible mechanism was put forward.

1. Introduction

Energy crisis and environmental security have come to the forefront of both global and national priorities. The sustainable development of human society will depend on how to solve the urgent resources and environment issues [1,2]. Semiconductor photocatalysis is an advanced technology which can convert the
harmless and inexhaustible solar energy into chemical energy and pollutants can be removed in the presence of converting chemical energy [3–6]. If successfully developed with an economic viability, this would be the ultimate technology that could solve both energy and environmental problems altogether in the future. Early studies on photocatalysts mainly focused on the TiO₂ because of its low cost, high efficiency, and photostability [7,8]. However, TiO₂ with the band gap of 3.2 eV responds only to ultraviolet (UV) light, which takes up only ca. 4% of the sunlight energy while visible-light accounts for ca. 43% [9,10]. Hereby, the development of visible-light-driven photocatalysts has now become one of the most challenging topics.

Recently, Bismuth vanadate (BiVO₄) has attracted increasing attention as one of the widely applied materials, a non-toxic yellow pigment, an excellent electric, magnetic materials and an effective photocatalyst for pollutant photodegradation under visible light (>420 nm) irradiation [11–15]. It was reported that there are three polymorphic forms of BiVO₄ [16]: zircon-tetragonal, scheelite-tetragonal, and scheelite-monoclinic. In general, the scheelite-monoclinic form of BiVO₄ has higher photocatalytic activity than the other two phases [17,18]. But there are quite few references about composites-phase BiVO₄ and its photocatalytic activity. It is well-known that TiO₂ also has various phases [19], including anatase, rutile, brookite, etc. But the acknowledged TiO₂ with optimal photocatalytic activity is Degussa P25, which consists of 80% anatase and 20% rutile [20,21]. Its best photocatalytic activity is due to a rutile sink, allowing an anatase-originating hole to move to the rutile surface and preventing anatase recombination [22]. Similarly, we speculated that the mixed-phase of BiVO₄ may have more efficient photocatalytic activity than that of pure phase BiVO₄. Zhang et al. [23] had synthesized a series of BiVO₄ samples using pure form and hybrid-phase by hydrothermal method and they found that one of the mixed-phase BiVO₄ presented better photocatalytic activity. But they didn’t discuss why the composite-phase BiVO₄ has better catalytic activity and did not study the effect of the content of monoclinic phase BiVO₄ on the photocatalytic activity of mixed-phase BiVO₄.

In this study, we synthesized a series of composite-phase BiVO₄ with different contents of monoclinic BiVO₄ by a simple and facile route based on the hydrothermal method. Photodecomposition of methylene blue (MB) was used as the model system to investigate the photocatalytic activity of the as-prepared BiVO₄ and a series of high effective mixed-phase BiVO₄ were obtained. The possible photocatalytic mechanism of its high efficiency was studied.

2. Experimental

2.1. Materials and synthesis of bismuth vanadate

Analytical grade of Ammonium metavanadate (NH₄VO₃ 99.0%) and Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O 99.0%) supplied by Sinopharm Chemical Reagent Co., Ltd, used without any purification. Other chemicals used were all analytical grade. Solutions were prepared using deionized water. A proper cation. Other chemicals used were all analytical grade.

The crystalline phase structure of the as-prepared samples was determined by ARL/XTRA X-ray diffractometer using Cu Kα radiation (λ = 0.15418 nm) in the range of 10°–80° at room temperature. The BET surface area was evaluated by N₂ adsorption in a constant volume adsorption apparatus (Coulter SA 3100). The morphology was determined by scanning electron microscopy (SEM) using LEO-1530VP SEM microscopy at 25 keV. The UV–vis diffuse reflectance spectra were obtained in the range of 200–800 nm at room temperature using a UV–visible spectrophotometer (UV–1100 spectrometer).

2.2. Characterization

Photocatalytic activities of the obtained BiVO₄ samples were determined by the decolorization of methylene blue (MB) using XPA photochemical reactor under visible-light irradiation of a 500-W Xe lamp with a 420 nm cutoff filter. Experiments were performed at ambient temperature as follows: First, 0.25 g of the as-prepared sample was added to 250 mL of 10 mg L⁻¹ methylene blue solution with constant magnetic stirring. Before illumination, the solution was stirred for 30 min in darkness in order to reach the adsorption–desorption equilibrium. At given time intervals, 5 mL of the suspension were sampled and centrifuged to remove the photocatalytic particles from the aqueous solution so as to obtain the supernatant for the analysis of residual MB. The concentrations of MB were monitored with a UV–visible spectrophotometer (UV–1100 spectrometer).

2.3. Photodegradation experiments

Table 1

<table>
<thead>
<tr>
<th>Item</th>
<th>Sample</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>(f)</th>
<th>(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of NaOH (mL)</td>
<td>17.0</td>
<td>17.2</td>
<td>17.4</td>
<td>17.6</td>
<td>17.8</td>
<td>18.0</td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td>pH values of precursor (x–a–g)</td>
<td>3.8</td>
<td>4.0</td>
<td>4.3</td>
<td>4.7</td>
<td>5.2</td>
<td>5.5</td>
<td>8.5</td>
<td></td>
</tr>
</tbody>
</table>

| Volume of NaOH (mL) | 17.0 | 17.2 | 17.4 | 17.6 | 17.8 | 18.0 | 18.5 |
| pH values of precursor (x–a–g) | 3.8 | 4.0 | 4.3 | 4.7 | 5.2 | 5.5 | 8.5 |

was sealed in a 100 mL Teflon-lined stainless autoclave and heated at 140 °C for 6 h under autogenous pressure [24,25]. Afterward, the precipitate was filtered, washed with distilled water and absolute alcohol, and then dried in vacuum at 80 °C for 12 h.

3. Results and discussion

3.1. Characterization of the BiVO₄ powders

Fig. 1 shows the XRD patterns of the as-prepared samples at different pH values. For BiVO₄–a synthesized at pH = 3.8, all diffraction peaks can be assigned to the tetragonal BiVO₄ (JCPDS 14-0133). As the pH value increasing from 3.8 to 5.5, the peaks for the monoclinic BiVO₄ (JCPDS 14-0688) began to appear and the characteristic peak (121) corresponding to monoclinic BiVO₄ became stronger and stronger, whereas the typical peak (200) relating to tetragonal phase decreased gradually (Fig. 1b–f), indicating mixed phase of monoclinic and tetragonal BiVO₄ formed. As the pH increases to 8.5 (Fig. 1g), all diffractions peaks of the BiVO₄ can be assigned to the pure monoclinic BiVO₄. The results suggested that the pH value of the precursor solution is an important factor in preparing different phases of BiVO₄. The main reason of this phenomenon can be interpreted by the relevant chemical reactions following the synthesis route [26].
BiONO₃ and BiVO₄-c and BiVO₄-d is mainly orbicular (1 e the key role in the producing BiVO₄ nucleus. When pH concentration of BiONO₃ is low, and leads to a slow nucleation of its growth rate and BiVO₄ nucleus tends to heterogeneous nucleation. BiVO₄ presents a solid and smooth spherical particles have significant changes. As shown in Fig. 2a, the pure tetragonal phase BiVO₄ presents a solid and smooth spherical morphology (1–3 μm), which is similar to the results reported before [17,18,23]. The morphology of mixed-phase of BiVO₄-b, BiVO₄-c and BiVO₄-d is mainly orbicular (1–2 μm), containing some flake form (1–3 μm). The spherical particles (1–2 μm) were gradually reduced while the flake particles (0.3–1 μm) increased gradually with the enhancement of ηmono (seen in Fig. 2b–d). At the same time, spherical particles and flake granules begin to link together and the two phases interweave together to form a petal-like structure with reticulate framework when ηmono reaches over 60% (Fig. 2d, e). Also, the surface defect appeared in surface regions of it. The possible formation mechanism is illustrated in Scheme 1. With the increase of monoclinic phase, the surface environment of BiVO₄ changed, and the two phase linked together to achieve the stable status. In Fig. 3f, tetragonal particles and monoclinic particles clustered into a layered structure which is consistent with the data reported previously [28,29]. But it indicates that this synthetic route was advantageous to reduce the particles agglomeration.

The obtained BiVO₄ had different specific surface areas, which are summarized in Table 2. In general, the specific BET surface area of as-synthesized BiVO₄ with different ηmono changed in the sequence of pure monoclinic BiVO₄ (7.95 m² g⁻¹) > hybrid-phase BiVO₄ > pure tetragonal BiVO₄ (1.09 m² g⁻¹), which result from its different spatial structure since the monoclinic phase is flake-like and has layered structure, while the tetragonal phase presents solid orbicular form. The former may have more active absorption of site for N₂ than the latter. Besides, the BET surface area increased a little along with the increase of ηmono in the hybrid-phase BiVO₄ because of its unique reticulate framework. Obviously, the framework, specific area and surface defect are beneficial for the comprehensive performance in improving the photocatalytic activity of BiVO₄ [27,30,31].

![Diagram](image_url)

**Table 2**

<table>
<thead>
<tr>
<th>Item</th>
<th>Sample (a)</th>
<th>Sample (b)</th>
<th>Sample (c)</th>
<th>Sample (d)</th>
<th>Sample (e)</th>
<th>Sample (f)</th>
<th>Sample (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ηmono (%)</td>
<td>0</td>
<td>10.21</td>
<td>34.67</td>
<td>66.51</td>
<td>72.75</td>
<td>92.73</td>
<td>100</td>
</tr>
<tr>
<td>Aₜₜ (m² g⁻¹)</td>
<td>1.09</td>
<td>1.22</td>
<td>2.05</td>
<td>3.37</td>
<td>3.37</td>
<td>4.38</td>
<td>7.95</td>
</tr>
<tr>
<td>Eₜ (eV)</td>
<td>2.67</td>
<td>2.64</td>
<td>2.50</td>
<td>2.38</td>
<td>2.37</td>
<td>2.34</td>
<td>2.36</td>
</tr>
<tr>
<td>Absorption rate (%)</td>
<td>22.0</td>
<td>17.8</td>
<td>26.0</td>
<td>32.5</td>
<td>25.4</td>
<td>26.2</td>
<td>34.1</td>
</tr>
<tr>
<td>D (%) = (C₀ - C)/C₀ × 100%</td>
<td>48.1</td>
<td>50.3</td>
<td>57.3</td>
<td>93.1</td>
<td>92.1</td>
<td>94.7</td>
<td>90.9</td>
</tr>
</tbody>
</table>
3.2. Adsorption/photocatalytic properties of as-synthesized BiVO₄

To study the adsorption and photocatalytic activities of these BiVO₄ products, methylene blue (MB), with a major absorption band at 664 nm, was chosen as a model pollutant. It is well known that the adsorption ability of the reactant on the catalyst surface is an important factor influencing photocatalytic performance. The adsorption rates of the MB over all samples are shown in Table 2. After stirring for 30 min in darkness to reach the adsorption–desorption equilibrium, the absorption rate was 22.0% and 34.1% for the pure tetragonal BiVO₄ and the monoclinic BiVO₄ respectively, which may be accounted for the different amount active absorption site of BiVO₄. When associated with the BET results, we calculated the absorption capacity for per unit area in pure

![Image of SEM images of BiVO₄ with different h mono](image)

Fig. 2. SEM images of BiVO₄ with different h mono (a) h mono = 0, (b) h mono = 10.21%, (c) h mono = 34.37%, (d) h mono = 66.51%, (e) h mono = 72.75%, (f) h mono = 92.73%, (g) h mono = 1.
tetragonal BiVO$_4$-1 (2.02 mg m$^{-2}$), and found that it was higher than that of pure monoclinic BiVO$_4$-g (0.43 mg m$^{-2}$), indicating the adsorptive affinity of tetragonal BiVO$_4$ for MB is higher than that of monoclinic BiVO$_4$. Therefore, the adsorptive ability of MB dye was not only related to the surface areas of catalyst, but also related to the crystal structure of catalyst. Accordingly, although the surface area of BiVO$_4$-e sample was estimated to be 3.37 m$^2$ g$^{-1}$, the absorption rate was up to 32.5%, which was close to BiVO$_4$-g. This is very helpful for a photocatalyst in the latter photodegradation reaction.

Fig. 4 shows the variation of the MB absorbance as a function of irradiation time in the presence of as-fabricated BiVO$_4$-x ($x = d, e, f, g$). The MB absorbance decreased clearly with irradiation time and no new absorbance band was observed in the UV--Vis absorption spectrum, indicating the absolute degradation of MB molecules and no formation of intermediate product [30,31].

The corresponding plot for the photodegradation rate of different samples is shown in Fig. 5. The plot of the maximum

\[ \text{Scheme 1. The sketch map of crosslink structure with tetragonal BiVO}_4 (\text{ }) \text{ and monoclinic BiVO}_4 (\text{ }).} \]

Fig. 3. (A) UV--vis diffuse reflectance spectra and (B) plots of the ($ahv)^2$ versus $hv$ of the (a) BiVO$_4$-a, (b) BiVO$_4$-b, (c) BiVO$_4$-c, (d) BiVO$_4$-d, (e) BiVO$_4$-e, (f) BiVO$_4$-f, (g) BiVO$_4$-g.

Fig. 4. UV--visible spectral changes of MB (10 mg L$^{-1}$) as a function of irradiation time for different photocatalysts under visible-light illumination.
under visible-light irradiation. It is generally believed that the absorption band is
shortly into the visible region; (2) the better adsorptive ability of the
factors: (1) the smaller band gap of catalysts extends the useful
range into the visible region; (2) the better adsorptive ability of the
organic compounds helps to improve the external reaction content;
(3) the stabilization of charge separation by electron transfer from
tetragonal particles to monoclinic particles helps to slow down the
recombination of light-induced electrons and holes.

4. Conclusions

Series of composite-phase BiVO₄ with different morphology were controlling synthesized by a facile hydrothermal method, in
which the pH value of the reaction solution is playing an important role. Photocatalytic evaluation of MB revealed that hybrid-phase
BiVO₄ presented higher photocatalytic performance than that of pure phase BiVO₄. From the data we have gathered, these mixed-
phase BiVO₄ exhibiting greater photo-efficiency was due to three factors: (1) the smaller band gap of catalysts extends the useful
range into the visible region; (2) the better adsorption ability of the
organic compounds helps to improve the external reaction content;
(3) the stabilization of charge separation by electron transfer from
tetragonal particles to monoclinic particles helps to slow down the
recombination of light-induced electrons and holes.

Acknowledgments

The authors thank the Program for Jiangsu Higher Institutions
Key Basic Research Projects of Natural Science (10KJA430005),
Natural Science Foundation of Jiangsu Province (BK2010289),
technological Research Foundation of Huai′an City (HAG2011008)
and Jiangsu Government Scholarship for Overseas Studies for
financial support.

References

1847.
133 (2011) 931.
(2012) 600.
Creative Patent, Open number: 201110323655.X.
115 (2011) 3794.