Hydrothermal synthesis of Bi$_2$WO$_6$ and photocatalytic reduction of aqueous Cr(VI) under visible light irradiation

Jing Li*, Qingzhu Shi, Yan Chen, Ming Song
School of Chemistry and Chemical Engineering, Xuzhou University of Technology, Xuzhou, 221111
*corresponding author’s e-mail address: lijinxz111@163.com

Abstract. Bi$_2$WO$_6$ was synthesized via a facile hydrothermal method using different inorganic acid or alkali varied pH of the solution at 180°C for 12 h, and characterized by X-ray diffraction, FESEM and photocurrent. Furthermore, the photocatalytic activity of Bi$_2$WO$_6$ was investigated in the reduction of aqueous Cr(VI) under visible light (λ > 420 nm) irradiation. As a result, as-synthesized Bi$_2$WO$_6$ was an orthorhombic phase, and well-crystallized with 3D hierarchical structure constructed by arranged 2D layers of nanoplates. All the as-synthesized Bi$_2$WO$_6$ exhibited the visible light photocatalytic activities on aqueous Cr(VI), and Bi$_2$WO$_6$-(2) exhibited the highest photocatalytic reduction efficiency based on much higher separation and transfer efficiency of photogenerated electrons and holes.

1. Introduction
Chromium(VI) is a common heavy metal pollutant in the aquatic environments from electroplating, electrochemical, leather tanning and steel manufacturing industries [1, 2]. Cr(VI) is high mobility and high toxicity which can be absorbed by living organisms. Therefore, it is important for industrial production and human life to develop an efficient and clean technology in Cr(VI) wastewater treatment.

The popular treatment technologies explored for the remediation of Cr(VI) are chemical precipitation, ion exchange, bio-oxidation and adsorption [3, 4]. However, these techniques often utilize potentially polluting materials and led to the secondary water pollution [3]. Semiconductor-base photocatalytic reduction method is widely considered to be a promising way in treating aqueous Cr(VI) [5, 6]. However, industrial applications of photocatalytic reduction technology are hampered to a large extent by the lack of high-performance visible-light-activated photocatalysts. Therefore, it is of great importance to develop highly active photocatalysts that possess both high visible-light-activity and good stability in the reduction of aqueous Cr(VI) [7, 8].

Among the visible-light driven photocatalysts, possessing a layered structure of bismuth tungstate (Bi$_2$WO$_6$) has attracted extensive attentions due to its excellent intrinsic physical and chemical properties [9]. More importantly, it has been found that Bi$_2$WO$_6$ exhibits the highest photocatalytic activity among the above Bi$^{3+}$-based oxides under visible light irradiation [9] dependent on their structure, crystallization, composition, morphology.

In the present study, we report Bi$_2$WO$_6$ hierarchical architecture with various morphologies were synthesized via hydrothermal method using Bi(NO$_3$)$_3$·5H$_2$O and Na$_2$WO$_4$·2H$_2$O as the reactants and by adjusting pH of reaction solution with citric acid (HCA), HNO$_3$, NaOH or NaHCO$_3$. Besides, the photocatalytic activities of the as-synthesized Bi$_2$WO$_6$ are tested in the reduction of aqueous Cr(VI) under visible light (λ > 420 nm) irradiation, and the proposed mechanism of the photocatalytic activity of Bi$_2$WO$_6$ was also discussed in detail.
2. Experiment procedures

2.1. Preparation of \( \text{Bi}_2\text{WO}_6 \) hierarchical structure

All the reagents used were analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd. \( \text{Bi}_2\text{WO}_6 \) was fabricated by hydrothermal synthesis method. Solution A was obtained as follows: 2 mmol \( \text{Bi(NO}_3\text{)}_3\cdot5\text{H}_2\text{O} \) and 2 ~ 8 mmol HCA were dissolved in 20 mL distilled water under rigorous stirring. Solution B was prepared by adding 1 mmol \( \text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O} \) and 4 mmol \( \text{NaHCO}_3 \) or \( \text{NaOH} \) into 20 mL distilled water under stirring. The as-obtained solution B was drop-by-drop added into solution A by continuous magnetic stirring in a Teflon-lined stainless steel autoclave of 50 mL capacity, and then obtained a homogeneous solution. Subsequently the mixed solution was kept in the autoclave at 180 ℃ for 12 h, then cooled naturally to room temperature. The as-formed yellow precipitates were filtered, washed with distilled water, and dried in vacuum at 100 ºC for 4 h.

For the convenience of description, the products obtained at different synthetic conditions were named \( \text{Bi}_2\text{WO}_6-(1) ~ (5) \) shown in Table 1.

| Samples  | HCA mmol | 16 mol/L HNO\(_3\) mL | NaHCO\(_3\) mmol | NaOH mmol | Distilled water mL | reduction rates of Cr(VI) % |
|----------|----------|------------------------|------------------|-----------|-------------------|----------------------------|
| \( \text{Bi}_2\text{WO}_6-(1) \) | 2        | \( \backslash \)        | 4                | \( \backslash \) | 40                | 25.7                       |
| \( \text{Bi}_2\text{WO}_6-(2) \) | 4        | \( \backslash \)        | 4                | \( \backslash \) | 40                | 41.9                       |
| \( \text{Bi}_2\text{WO}_6-(3) \) | 8        | \( \backslash \)        | 4                | \( \backslash \) | 40                | 15.6                       |
| \( \text{Bi}_2\text{WO}_6-(4) \) | \( \backslash \) | 1                      | 4                | \( \backslash \) | 39                | 30.5                       |
| \( \text{Bi}_2\text{WO}_6-(5) \) | \( \backslash \) | 1                      | \( \backslash \) | 4          | 39                | 35.9                       |

2.2. Characterization of \( \text{Bi}_2\text{WO}_6 \)

The samples were characterized by Powder X-ray diffraction (XRD, German Bruker AXS D8 ADVANCE X-ray diffractometer), FESEM (Japan Hitachi S-4800 Field Emission SEM). Photocurrent response (Shanghai Chenhua instrument Co., Ltd. CHI660E electrochemical workstation). Photocatalytic activities of the samples were evaluated by photocatalytic reduction of Cr(VI) under a 200 W Xe lamp with \( \lambda \geq 420 \) nm irradiation using an optical filter. The experiments were performed at 25 ºC as follows: 300 mg photocatalyst was added into 300 mL of 50 mg/L \( \text{K}_2\text{Cr}_2\text{O}_7 \) aqueous solution. An hour magnetically stirred in the dark to ensure the adsorption-desorption equilibrium between Cr(VI) and photocatalyst powders.

3. Results and discussion

Fig. 1 a ~ d show the XRD patterns of \( \text{Bi}_2\text{WO}_6-(1) ~ (5) \) synthesized via hydrothermal reaction with different reaction solution at 150 ℃ for 18 h, respectively. All the five samples displayed only the XRD peaks characteristic of orthorhombic phased \( \text{Bi}_2\text{WO}_6 \), which is in good agreement with the literature value (JCPDS No. 73- 1126) [9]. NO other diffraction peaks arising from possible impurities were detected. Compared with the sample of \( \text{Bi}_2\text{WO}_6-(1) ~ (3) \), the intensity of the diffraction peaks of \( \text{Bi}_2\text{WO}_6-(4) \) and \( \text{Bi}_2\text{WO}_6-(5) \) were much stronger. It was indicated that \( \text{Bi}_2\text{WO}_6-(4) \) and \( \text{Bi}_2\text{WO}_6-(5) \) were of higher crystallinity [10]. Using the Scherrer formula based on the half-width of their \((131)\) peak, the crystal sizes (or nanosheets) of \( \text{Bi}_2\text{WO}_6-(1) ~ (5) \) were calculated to be about 11 nm, 10 nm, 7nm, 16 nm, 15 nm, respectively.
It is known that the morphologies of the final products are depending upon the intrinsic structure of the product, but also relate to the growth kinetics of the reaction process. From the FESEM images, different morphology of Bi$_2$WO$_6$ can be obtained by adjusting the reaction solution with acid and alkali, or controlling the concentration of acid and alkali. Fig. 2 shows the morphology of the as-synthesized Bi$_2$WO$_6$ by FESEM, respectively. The images showed that Bi$_2$WO$_6$ held hierarchical structure with many nanoplates with a lateral size of a few hundred nanometers. Fig. 2 a and b illustrate that the Bi$_2$WO$_6$
were spindle morphology with diameters of about 2 μm. Fig.2 c and e show that spindle morphology
was destroyed in the higher citrate acid solution, and the microspheres were obtained with shorter flakes.
It was observed that the flower-like nanostructure is composed on numerous thin petals with thickness
of about 30 nm in Fig.2 d. Clearly, morphology was obtained by adjusting the pH of the reaction solution
using different acid and alkali.

Fig. 3 The photocatalytic activities of Bi2WO6 in the reduction of aqueous Cr(VI) under visible light
irradiation

The photocatalytic activities of Bi2WO6-(1) ~ (5) hierarchical structures is evaluated using Cr(VI)
as target molecule under visible light irradiation. The comparison of photocatalytic reduction efficiency
of Bi2WO6 under different reaction condition is displayed in Fig. 3. All the as-synthesized Bi2WO6
exhibited the photocatalytic activities on aqueous Cr(VI) under visible light irradiation, and Cr(VI) was
removed with increasing irradiation time. The photocatalytic activities of the as-synthesized Bi2WO6
followed the order of Bi2WO6-(2) > Bi2WO6-(5) > Bi2WO6-(4) > Bi2WO6-(1) > Bi2WO6-(3). For
instance, the reduction rates of Cr(VI) over them were in turn 41.9%, 35.9%, 30.5%, 25.7% and 15.6%
after 100 min irradiation.

Fig. 4 First-order plots for the photocatalytic reduction of aqueous Cr(VI) by Bi2WO6

To quantitatively investigate the reaction kinetics of the photocatalytic reduction of aqueous Cr(VI)
in the experiment, the experimental data were fitted by applying a first order model as expressed by
equation (1) [11], which is well established for the photocatalytic experiments when the pollutant is in
the milligram concentration range.

\[-\ln\left(\frac{c}{c_0}\right) = k t\] (1)
Where $k$ is the first-order rate constant and $t$ is the visible light illumination, $c_0$ and $c$ are the concentration of Cr(VI) in the reaction solution at times 0 and $t$, respectively.

Fig. 4 shows the plots of illumination time ($t$) versus the $\ln(c_0/c)$ displayed a nearly straight line. Apparent rate constants of Bi$_2$WO$_6$-(1) ~ (5) are estimated to be $1.91 \times 10^{-3}$, $3.94 \times 10^{-3}$, $1.05 \times 10^{-3}$, $8.31 \times 10^{-4}$, $2.26 \times 10^{-3}$. It can be seen directly from the first-order plots that the Bi$_2$WO$_6$-(2) exhibited the highest photocatalytic reduction efficiency.

The difference in the photocatalytic activities of the Bi$_2$WO$_6$ samples was a result of combined action of many factors, such as size, adsorption capacity for Cr(VI), specific surface area, morphology, crystallinity, etc. In essence, the separation and transfer efficiency and quantity of the photocatalyst are the key factors, much higher photogenerated electrons and holes contributed to the greatly improved photocatalytic activity.

![Fig. 5 Photocurrent response of as-synthesized Bi$_2$WO$_6$](image)

Fig. 5 shows the photocurrent response of Bi$_2$WO$_6$-(1) ~ (5) electrodes subjected to the intermittent irradiation with a 35 W Opple LED bulb. The photocurrent response was quick and reproducible in each switch-on and switch-off cycle for all Bi$_2$WO$_6$-(1) ~ (5) electrodes. The photocurrent of Bi$_2$WO$_6$-(2) electrode was about five times that other Bi$_2$WO$_6$ electrode, so suggesting the much more efficient separation and transfer of photo-generated electrons and holes in Bi$_2$WO$_6$-(2). Thus, Bi$_2$WO$_6$-(2) exhibited much higher separation and transfer efficiency of photogenerated electrons and holes, which contributed to the greatly improved photocatalytic activity.

4. Conclusions
Morphology-tunable synthesis of Bi$_2$WO$_6$ hierarchical structure was achieved by hydrothermal method at 180 ºC, simply using different inorganic acid or alkali varied pH of the solution. The as-synthesized Bi$_2$WO$_6$-(2) exhibited the highest photocatalytic reduction efficiency that attributed to much higher separation and transfer efficiency of photogenerated electrons and holes.

Acknowledgments
This work was financially supported by the Natural Science Foundation of Jiangsu Province (grant number BK20171168, BK20170169), Science and Technology Project of Xuzhou (KC16SG246), Key cultivation project of Xuzhou University of Technology (XKY2014103).

References
[1] R J Kieber, J D Willey, S D Zvalaren. Chromium speciation in rainwater: temporal variability and atmospheric deposition. Environmental Science and Technology, 2002, 36(24): 5321-5327.
[2] J J Testa, M A Grela, M I Litter. Heterogeneous photocatalytic reduction of chromium(VI) over TiO₂ particles in the presence of oxalate: Involvement of Cr(V) species. Environmental Science and Technology, 2004, 38(5): 1589-1594.

[3] M Qamar, Z H Yamani. Bismuth oxychloride-mediated and laser-induced efficient reduction of Cr(VI) in aqueous suspensions. Applied Catalysis A: General, 2012, 439-440(16): 187-191.

[4] V N H Nguyen, R Amal, D Beydoun. Effect of formate and methanol on photoreduction/removal of toxic cadmium ions using TiO₂ semiconductor as photocatalyst. Chemical Engineering science, 2003, 58 (19): 4429-4439.

[5] J Yang, XH Wang, XL Zhao, et al. Synthesis of uniform Bi₂WO₆-reduced graphene oxide nanocomposites with significantly enhanced photocatalytic reduction activity. The Journal of physical chemistry, 2015, 119(6): 3068-3078.

[6] H Tong, S Ouyang, Y Bi, et al. Nano-photocatalytic materials: possibilities and challenges. Advanced Materials 2012, 24: 229-251.

[7] X Liu, L Pan, Q Zhao, et al. UV-assisted photocatalytic synthesis of ZnO-reduced graphene oxide composites with enhanced photocatalytic activity in reduction of Cr(VI). Chemical Engineering Journal, 2012, 183 (4): 238-243.

[8] H T Hsu, S S Chen, Y S Chen. Removal of chromium(VI) and naphthalenesulfonate from textile wastewater by photocatalysis combining ionic exchange membrane processes. Separation & Purification Technology, 2011, 80 (3): 663-669.

[9] L Zhang, H Wang, Z Chen, et al. Bi₂WO₆ micro/nano-structures: Synthesis, modifications and visible-light-driven photocatalytic applications. Applied Catalysis B: Environmental, 2011, 106 (1): 1-13.

[10] H Wang, J M Song, H Zhang, et al. Controlled synthesis of three-dimensional hierarchical Bi₂WO₆ microspheres with optimum photocatalytic activity. Materials Research Bulletin, 2012, 47 (2): 315-320.

[11] L Ge, J Liu. Efficient visible light-induced photocatalytic degradation of methyl orange by QDs sensitized CdS-Bi₂WO₆. Applied Catalysis B: Environmental, 2011, 105 (3): 289-297.