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RESEARCH ARTICLE

Heterogeneous photocatalytic treatment of wastewater in ultraviolet light irradiation—photocatalyst Bi_2WO_6 microsphere with high repeatability

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Abstract The treatment of wastewater that includes toxic organic pollutants such as dyes, phenoaniline, phenols and their derivatives is still a challenge due to their biorecalcitrant and acute toxicity to the widespread acceptance of water recycling. Three-dimensional (3D) Bi_2WO_6 microsphere was synthesized by the hydrothermal method using $Bi(NO_3)_3$ and Na_2WO_4 as raw materials. This structure exhibits high photocatalytic activity for the dyes, toxic organic compounds. The degradation of methlyene blue is 100% in 30 min, 4-nitrylphenol is 95% in 60 min and p-nitrylphenol is 95% in 75 min in ultraviolet (UV) light irradiation. 3D Bi_2WO_6 microsphere is also a good photocatalyst to treat the printing and dyeing sewage, and exhibits high repeatability. After being used the 20th time, Bi_2WO_6 still has high activity to degrade the printing and dyeing sewage, which is very important for a photocatalyst to be used in industry. This study will pave a new way to treat industry wastewater.

Keywords photocatalyst, semiconductors, wastewater treatment

1 Introduction

The treatment of wastewater effluent that includes toxic organic pollutants such as dyes, phenoaniline, phenols and their derivatives is still a challenge due to their biorecalcitrant and acute toxicity to the widespread acceptance of water recycling [1,2]. Despite their low concentration, these contaminants are a major health concern because of their extremely high endocrine disrupting potency and genotoxicity [3]. In response, considerable efforts have been devoted to effectively remove the persistent organic pollutants from wastewater effluent to minimize the risk of pollution problems from such toxic chemicals and to enable its reuse. Conventional waste water purification systems, such as activated carbon adsorption, membrane filtration, chemical coagulation, ion exchange on synthetic adsorbent resins, etc., also generate wastes during the treatment of contaminated water, which requires additional steps and costs.

Photocatalysis has received enormous attention in recent years because of its application in organic synthesis [4,5], and in the abatement of pollutants in water or in air [6,7], since the reaction can be driven by sunlight at near ambient temperatures and pressure using molecular oxygen as an oxidant [8,9]. TiO_2 has been extensively investigated for its application in several fields and in particular for its activity in the oxidative photodegradation of a range of organic substrates [10,11]. There have been many reports on the mineralization of organic pollutants by heterogeneous photocatalytic oxidation with TiO_2 [12,13] or multimetal oxide materials such as Bi_2WO_6 [14].

Bi_2WO_6 and Bi_2MoO_6 are the member of cation-deficient Aurivillius phases, which have the potential for water splitting photocatalytic oxidative decomposition of organic pollutants under visible light irradiation [14–20]. The crystal of Bi_2WO_6 is composed of accumulated layers of corner-sharing WO_6 octahedral sheets and bismuth oxide sheets. The solution phase condition is proved to be fit for anisotropic crystal growth of Bi_2WO_6 and formation of rectangle-shaped nanoplates [15,20]. The Bi_2WO_6 microstructures with a flake-ball shape or rectangular-plate shape have exhibited high photocatalytic activity to induce photocatalytic decolorization of organic dies, such as rhodamine B, under visible-light irradiation. However, there have been few reports of other photocatlytic reactions, such as oxidative decomposition of toxic organic compounds, and photocatalytic degradation of the wastewater under ultraviolet light irradiation over hydrothermally prepared Bi_2WO_6 [21].

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In this article, we report the synthesis of the three-dimensional (3D) Bi_2WO_6 microspheres and their high photocatalytic activity for the dyes, toxic organic compounds and the printing and dyeing sewage. The Bi_2WO_6 has the best photocatalytic activity for the methylene blue (MB) dye, which is completely degraded only for 30 min. 3D Bi_2WO_6 microsphere is a very good photocatalyst to treat the printing and dyeing sewage in the ultraviolet (UV) light irradiation, and exhibits high stability and repeatability. After being used the 20th time, Bi_2WO_6 still has high activity to degrade the printing and dyeing sewage, and make its chemical oxygen demand (COD) value decrease to 78.4531 mg/L.

2 Experimental

2.1 Synthesis of Bi_2WO_6 microstructures

In a typical procedure, $Bi(NO_3)_3 \cdot 5H_2O$ (1.212 g, 2.5 mmol) was added to 40 mL of deionized water. Then, $Na_2WO_4 \cdot 2H_2O$ (0.412 g, 1.25 mmol) was added to the solution, and the mixture was vigorously stirred for 30 min to ensure that all reagents were dispersed homogeneously. The mixture was translated into a 50 mL Teflonlined autoclave, maintained at 180°C for 24 h, and cooled to room temperature naturally. The precipitate was collected and rinsed several times with distilled water and absolute ethanol, respectively. Then, the sample was dried in a vacuum at 60°C for 6 h.

2.2 Characterization

The obtained product was characterized by X-ray powder diffraction (XRD) using a Rigaku (Japan) D/max-γA X-ray diffractometer with Cu–K radiation (λ = 0.154178 nm). Field-emission scanning electron microscopy (FESEM) was captured on a Hitachi model S-4800 instrument operating at 15 kV. Room temperature UV-Vis absorption was recorded on a UV-2550 spectrophotometer in the wavelength range of 200–800 nm.

2.3 Photocatalytic activity measurements

Photocatalytic activity of as-prepared Bi_2WO_6 samples were tested by decomposing different dyes, toxic organisms and the printing and dyeing sewage under UV light irradiation of a 300 W UV lamp (main wavelength 365 nm). In a typical experiment, as-prepared Bi_2WO_6 (40 mg) was added into 100 mL of the printing and dyeing sewage, or 100 mL 10 mg/L of dye (or toxic organism) to obtain suspension for degradation reaction at room temperature under air. Prior to UV light irradiation, the suspensions were stirred in the dark for 30 min to ensure an adsorption/desorption equilibrium of dye on surfaces of Bi_2WO_6 particles. After a given irradiation time, the suspensions were withdrawn, and centrifuged to remove the particles. The degradation process as a function of irradiation time was monitored by measuring the absorption of dyes in the solution with UV–Vis absorption spectra. The COD value of the treated printing and dyeing sewage is measured with $K_2Cr_2O_7$ method.

3 Results and discussion

3.1 Structure and morphology of Bi_2WO_6 sample

The morphology of the as-synthesized Bi_2WO_6 was investigated by FESEM. Figure 1(a) shows the morphology of the product in large scale. It reveals that the product is composed of a large quantity of nearly monodispersed flower-like spheres with an average diameter of about 3.0 μm. No other morphologies can be detected, indicating a high yield of these 3D microspheres. The as-prepared Bi_2WO_6 sample possesses a superstructure of a flower-like appearance (Fig. 1(b)). The hierarchical flower-like Bi_2WO_6 structures are built by a large quantity of two-dimensional nanoplates with a thickness of about 15.0 nm. The aggregation and/or assembly of the nanoplates may produce abundant hierarchical pores on nanoscale.

Figure 1(c) shows the typical XRD pattern of the as-prepared hierarchical flower-like Bi_2WO_6. All peaks for this sample could be indexed to the orthorhombic phase of Bi_2WO_6 (JCPDS card no. 73-1126), No characteristic peaks of the other impurities were observed.

3.2 Photocatalytic degradation of dyes and organic compounds

Methyl red (MR), Rhodamine-B (RhB) and methylene blue (MB), a widely used dyes, the widespread occurrence of toxic organisms phenols, phenoaniline in wastewater were selected as the model pollutants to evaluate the photocatalytic activity of the Bi_2WO_6. Figure 2 displayed the photodegradation curve of these pollutions by the Bi_2WO_6 sample under UV light illumination. The MR solution gradually was decolored in the 75 min upon UV light irradiation in the presence of photocatalyst. However, the dyes MB and RhB were diminished quickly and 100% photodegration efficiencies in 30 and 45 min. The results showed that photocatalyst Bi_2WO_6 has an elective ability to degraded the dyes MB and RhB. The degradation rate of the toxic organic compounds is relatively slow, o-nitrylaniline needed 90 min to degrade completely, and p-nitrylphenol needed 75 min. A comparison experiment showed that these pollutions did not degrade in the dark with the presence of Bi_2WO_6 photocatalysts. On the other hand, the blank test revealed that the degradation of these pollutions were very slow when illuminated by UV light in

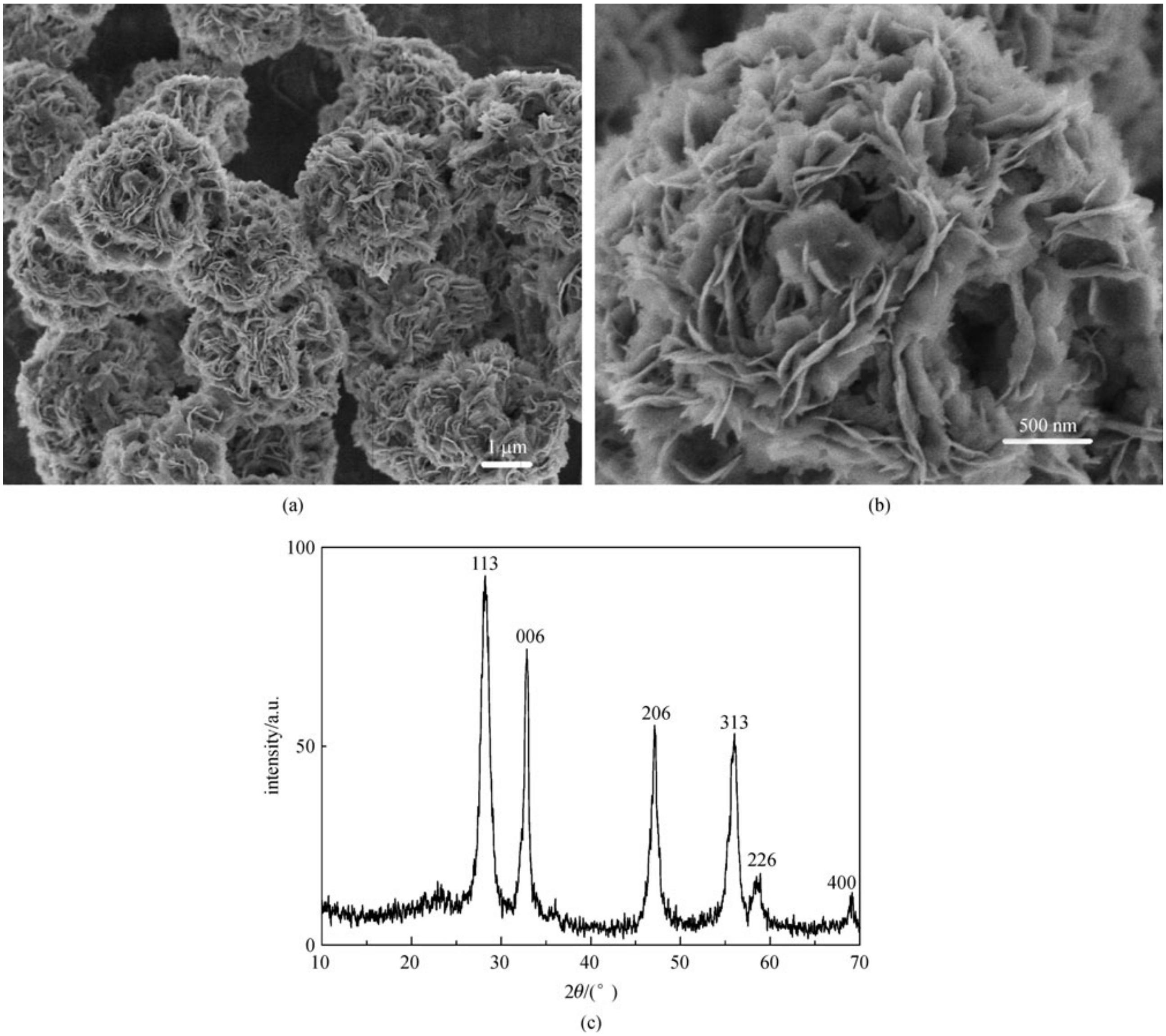

Fig. 1 SEM images (a)–(b) and XRD patterns (c) of Bi_2WO_6 samples

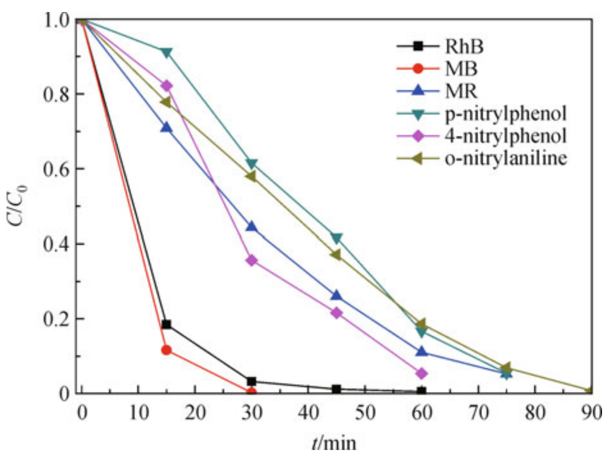

Fig. 2 Photodegration efficiencies of dyes and toxic organic compounds as function of irradiation time by Bi_2WO_6 photocatalyst

the absence of photocatalysts. These results confirmed that the catalyst and UV light are indispensable to the photodegradation of these pollutions.

For a photocatalyst to be useful, it should be stable and has high repeatability under the photocatalytic application. To test the repeatability of MB dye degrading on the Bi_2WO_6, we repeated ten times under the same conditions. As shown in Fig. 3, the MB dye was still quickly degraded in the tenth experiment. It is noticeable that, the photodegradation rates of MB dyes almost remain unchanged in the degradation processes of all 20 experiments, indicating that the Bi_2WO_6 photocatalyst was stable under repeated application.

3.3 Photocatalytic treatment of printing and dyeing sewage

Printing and dyeing sewage is the wastewater discharged from printing and dyeing plants in processing of cotton,

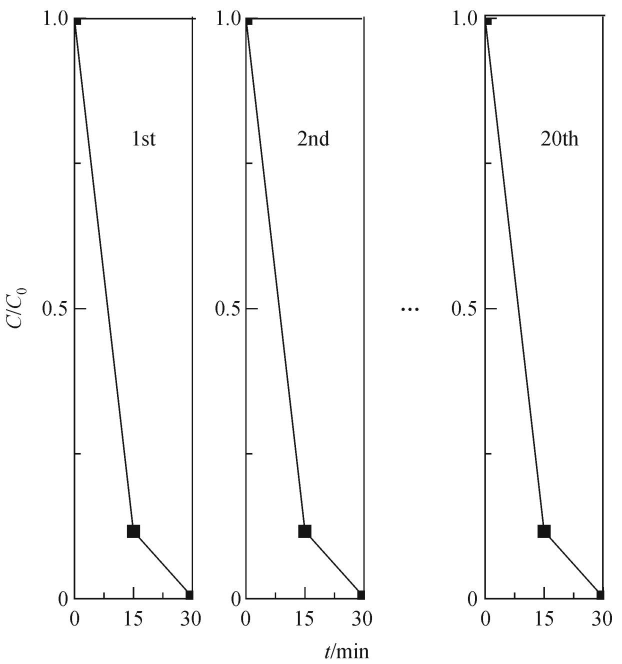

Fig. 3 Repeated photocatalytic experiments use Bi_2WO_6 to degraded MB dye under UV light

bast fiber, synthetic fiber and their blended product. This sewage contains dye, sizing material, auxiliaries, oiling agent, acid, alkali, fiber impurities, sand, inorganic salt, etc. It is very difficult to treat this kind of sewage due to the large quantity, high colority and poor biochemical purification ability of the sewage. Here, the Bi_2WO_6 sample was used to treat the printing and dyeing sewage (without being any treatment) through photocatalytical reaction. After 60 min of irradiation, the suspensions were centrifuged and the COD values were obtained via $K_2Cr_2O_7$ method. As shown in Table 1, before the treatment, the COD value of the sewage is 386.0000 mg/L, which reduces to 8.2368 mg/L after 60 min of UV light irradiation in the presence of Bi_2WO_6 sample. After reused 20 times, the photocatalyst Bi_2WO_6 still exhibits high activity for the sewage, with the COD value 78.4531 mg/L. The colority of water is very low, and no suspended matter from the treated sewage is found at the bottom of the bottle after one week.

Table 1 COD values of sewage with different reused times of Bi_2WO_6 sample

used times of Bi_2WO_6	COD values of treated printing and dyeing sewage/($mg \cdot L^{-1}$)
0	386.0000
1st	8.2368
5th	21.7152
10th	38.5632
15th	60.2147
20th	78.4531

Table 2 gives out the COD value of prior to treatment and post-treatment and light irradiation time for the printing and dyeing sewages come from different wastewater treatment factory using Bi_2WO_6 as photocatalyst. It could be found that the Bi_2WO_6 was a good photocatalyst for the wastewater treatment.

3.4 Photocatalytic mechanism of Bi_2WO_6 sample

In the photocatalytic oxidation process, organic pollutants are destroyed in the presence of semiconductor photocatalyst Bi_2WO_6, an energetic light source, and an oxidizing agent such as oxygen or air. Figure 4 illustrates the mechanism of Bi_2WO_6 photocatalysis. The illumination of the photocatalytic surface with sufficient energy leads to the formation of a positive hole (h^+) in the valence band and an electron (e^-) in the conduction band (CB). The positive hole oxidizes either pollutant directly or water to produce $\cdot OH$ radicals, whereas the electron in the conduction band reduces the oxygen adsorbed on the catalyst Bi_2WO_6.

The activation of Bi_2WO_6 by UV light can be represented by the following steps:

$$Bi_2WO_6 + h\nu \rightarrow e^- + h^+$$

Table 2 COD value of prior to treatment and post-treatment and light irradiation time for printing and dyeing sewages come from different wastewater treatment factories using Bi_2WO_6 as photocatalyst

wasterwater pants	prior to treatment COD value/($mg \cdot L^{-1}$)	post-treatment COD value/($mg \cdot L^{-1}$)	light irradiation time/h
Sheng-Luo textile factory in Wuhu City	240	9.8762	0.5
Ke-Run printworks in Shaoxing City	400	50.6123	1
Wan-Hong printworks in Hangzhou City	2000*	70.6901	1
Sheng-Du-Da printworks in Hangzhou City	700*	62.5678	1.5
Chong-Xian wasterwater plant in Hangzhou City	300	43.2510	0.5

Note: * stand for some flocculant was used prior to photocatalytic treatment

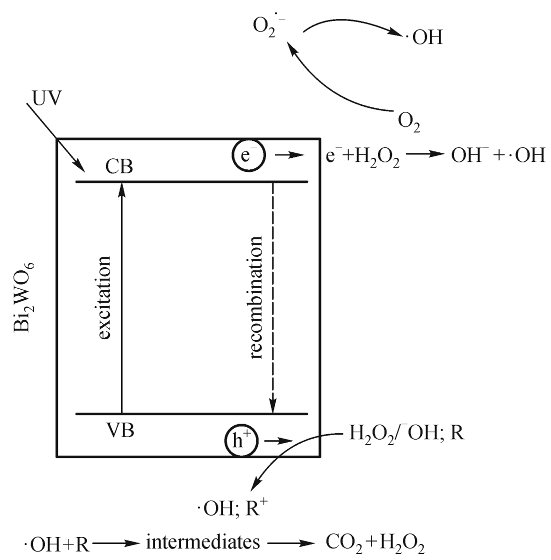

Fig. 4 Schematic diagram of principle of Bi_2WO_6 photocatalysis

$$e^- + O_2 \rightarrow O_2^-$$

In this reaction, h^+ and e^- are powerful oxidizing and reductive agents respectively. The oxidative and reductive reaction steps are expressed as

Oxidative reaction:

$$h^+ + \text{organic} \rightarrow CO_2$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+$$

Reductive reaction:

$$\cdot OH + \text{organic} \rightarrow CO_2$$

Hydroxyl radical generation by the photocatalytic oxidation process is shown in the above steps. In the degradation of organic pollutants, the hydroxyl radical, which is generated from the oxidation of adsorbed water where it is adsorbed as OH^-, is the primary oxidant; and the presence of oxygen prevents the recombination of an electron-hole pair.

4 Conclusions

3D Bi_2WO_6 microsphere, which was synthesized by the hydrothermal method, exhibits high photocatalytic activity for the dyes, toxic organic compounds, and the printing and dyeing sewage in UV light irradiation. Furthermore, in the degradation processes, the Bi_2WO_6 sample also showed high stability and repeatability, which is very important for a photocatalyst to be used in industry.

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References

1. Mahmoodi N M, Armani M. Limaee N.Y, Gharanjig K. Photocatalytic degradation of agricultural *N*-heterocyclic oimmobilized nanoparticles of titania. Journal of Hazardous Materials, 2007, 145: 65–71
2. Department of Environment Conservation. Managing Urban Stormwater: Harvesting and Reuses. NSW DEC, 2007, 137
3. Arques A, Amat A M, García-Ripoll A, Vicente R. Detoxification and/or increase of the biodegradability of aqueous solutions of dimethoate by means of solar photocatalysis. Journal of Hazardous Materials, 2007, 146(3): 447–452
4. Fox A, Chen C C, Park K, Younathan N J. Controlled organic redox reactivity on irradiated semiconductor surfaces. ACS Symposium Series, 1985, 278: 69–78
5. Fox M A. Organic heterogeneous photocatalysis: chemical conversions sensitized by irradiated semiconductors. Accounts of Chemical Research, 1983, 16(9): 314–321
6. Matthews R W. Photooxidation of organic impurities in water using thin films of titanium dioxide. Journal of Physical Chemistry, 1987, 91(12): 3328–3333
7. Yao W, Ye J. Photophysical and photocatalytic properties of $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$ solid solutions. Journal of Physical Chemistry B, 2006, 110(23): 11188–11195
8. Hu C, Lan Y Q, Qu J H, Hu X X, Wang A. Ag/AgBr/TiO_2 visible light photocatalyst for destruction of azodyes and bacteria. Journal of Physical Chemistry B, 2006, 110(9): 4066–4072
9. Arends I, Sheldon R A. Activities and stabilities of heterogeneous catalysts in selective liquid phase oxidations: recent developments. Applied Catalysis A: General, 2001, 212(1–2): 175–183
10. Chong M N, Jin B, Chow C W K, Saint C. Recent developments in photocatalytic water treatment technology: a review. Water Research, 2010, 44(10): 2997–3027
11. Konstantinou I K, Albanis T A. TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: A review. Applied Catalysis B: Environmental, 2004, 49(1): 1–14
12. Sajjad A K L, Shamaila S, Tian B, Chen F, Zhang J. Comparative studies of operational parameters of degradation of azo dyes in visible light by highly efficient WO_x/TiO_2 photocatalyst. Journal of Hazardous Materials, 2010, 177(1–3): 781–791
13. Hu C, Hu X, Wang L, Qu J, Wang A. Visible-light-Induced photocatalytic degradation of azodyes in aqueous AgI/TiO_2 dispersion. Environmental Science & Technology, 2006, 40(24): 7903–7907
14. Tang J, Zou Z G, Ye J H. Photocatalytic decomposition of organic contaminants by Bi_2WO_6 under visible light irradiation. Catalysis Letters, 2004, 92(1–2): 53–56
15. Zhang C, Zhu Y F. Synthesis of square Bi_2WO_6 nanoplates as high-activity visible-light-driven photocatalysts. Chemistry of Materials, 2005, 17(13): 3537–3545
16. Kudo A, Hijii S. H_2 or O_2 evolution from aqueous solutions on layered oxide photocatalysts consisting of Bi^{3+} with $6s^2$ configuration and d^0 transition metal ions. Chemistry Letters, 1999, 10(10): 1103–1104

17. Zhang L S, Wang W, Zhou L, Xu H. Bi_2WO_6 nano- and microstructures: shape control and associated visible-light-driven photocatalytic activities. Small, 2007, 3(9): 1618–1625
18. Li G S, Zhang D, Yu J C, Leung M K. An efficient bismuth tungstate visible-light-driven photocatalyst for breaking down nitric oxide. Environmental Science & Technology, 2010, 44(11): 4276–4281
19. Amano F. Nogami K, Abe R, Ohtani B. Preparation and characterization of bismuth tungstate polycrystalline flake-ball particles for photocatalytic reactions. Journal of Physical Chemistry C, 2008, 112: 9320–9326
20. Fu H B, Zhang L W, Yao W Q, Zhu Y F. Photocatalytic properties of nanosized Bi_2WO_6 catalysts synthesized via a hydrothermal process. Applied Catalysis B: Environmental, 2006, 66(1–2): 100–110
21. Amano F, Nogami K, Abe R, Ohtani B. Facile hydrothermal preparation and photocatalytic activity of bismuth tungstate polycrystalline flake-ball particles. Chemistry Letters, 2007, 36 (11): 1314–1315