Synthesis and photocatalytic properties of MgBi$_2$O$_6$ with Ag additions

Liansheng Zhong$^1$, Chaohao Hu$^{1,2,3}$, Binqing Zhu$^1$, Yan Zhong$^{1,2}$ and Huaiying Zhou

$^1$School of Materials Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, P.R. China; $^2$Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin 541004, P.R. China.

Abstract. Ag-doped MgBi$_2$O$_6$ photocatalysts were synthesized by the low temperature hydrothermal method in combination with heat treatment reaction using NaBiO$_3$·2H$_2$O, MgCl$_2$·6H$_2$O, and AgNO$_3$ as raw materials. The products were characterized by using power X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Energy dispersive X-ray detector (EDS), and UV-Vis diffusion reflectance spectra. The photocatalytic activity of MgBi$_2$O$_6$ with Ag additions was evaluated by degrading MB (10 mg/L) under visible light irradiation ($\lambda$ > 420 nm). The results showed that in comparison with pure MgBi$_2$O$_6$, the photocatalytic activity of MgBi$_2$O$_6$ with about 5% Ag concentration is increased by about 24% after 120 min reaction. The enhancement of catalytic activity of Ag-doped MgBi$_2$O$_6$ photocatalysts should be related to the band structure, morphology and larger specific surface area.

1. Introduction

Nowadays, environmental pollution mostly induced by human activities has become a serious social problem. Among a great number of the advanced oxidation processes, semiconductor photocatalysis has become one of the green technologies to environmental management and has broad application prospect due to its advantages such as energy saving, high efficiency, and safety. TiO$_2$, as one of the most popular photocatalysts, has been widely studied owing to its nontoxicity, outstanding oxidative power, high stability, low cost, and photostability [1-4] since its photocatalytic activity was first reported by Fujishima and Honda in 1972 [5]. However, the wide band gap of TiO$_2$ (about 3.2 eV) leads to be excitable only under UV light irradiation wavelengths below 387 nm, which severely limits the efficient usage of solar energy. Furthermore, TiO$_2$ exhibits low quantum efficiency due to the high recombination rate of photogenerated electron-hole pairs [6-9]. In order to make full use of sunlight, exploring more efficient photocatalysts has become an important task. Metal bismuthates are potential candidates for photocatalytic materials for decomposing organic species [10,11]. For instance, some trivalent bismuthates like BiVO$_4$ [12], CaBi$_2$O$_4$ [13], and Bi$_2$WO$_6$ [14] have narrower band gaps in comparison with TiO$_2$. The electrons and empty holes which can oxidize some organic species can be excited under visible light [15-18]. On the other hand, pentavalent bismuthates have different electronic structure compared with trivalent bismuthates [19]. It has been reported that MgBi$_2$O$_6$ with the trirutile-type structure has efficient photocatalytic activities for degradading methylene blue under
visible light [20]. Currently, many studies have found that metal ion doping can reduce the recombination of electron-hole pairs [21,22], since metal additives can regulate the width of band gap of semiconductor photocatalysts efficiently to optimize the band structure. However, to the best of our knowledge, the photocatalytic performance of MgBi$_2$O$_6$ doped with metal ions has not been reported so far.

In this study, Ag-doped MgBi$_2$O$_6$ semiconductor photocatalysts were synthesized by using the low temperature hydrothermal method in combination with heat treatment reaction. A model dye of methylene blue (MB) solution was used to evaluate its photocatalytic efficiency under visible light irradiation. The potential mechanism for the improvement in the activity of Ag-doped MgBi$_2$O$_6$ composite catalysts was also discussed in detail.

2. Experimental procedures

2.1. Synthesis

All chemicals used in the present experiments were obtained from commercial sources as analytical reagents. In this work, pure MgBi$_2$O$_6$ catalyst was synthesized by the one-step low temperature hydrothermal method. Ag-doped MgBi$_2$O$_6$ composite catalysts were synthesized by the low temperature hydrothermal method in combination with heat treatment reaction. Single phase MgBi$_2$O$_6$ was obtained when using a starting Mg/Bi molar ration of 2. The whole process is as follows: 0.005 mol of NaBiO$_3$·2H$_2$O was dissolved in the 30 mL deionized water and also stirred for 10 min at room temperature to form solution A; 0.01 mol of MgCl$_2$·6H$_2$O was dissolved in the 30 mL deionized water and also stirred for 10 min at room temperature to form solution B. Then, two kinds of solution were mixed and stirred for 30 min at room temperature to form the orange-yellow and uniform suspension C. Then the suspension C was transferred into a 100 mL Teflon-lined autoclave up to 70% of the total volume. The autoclave was further heated in an oven at 130°C for 6 h. After the reaction, the as-prepared products were obtained by filtration and washed with deionized water and absolute ethanol several times and the products were dried at 60°C for 12 h in an oven. Subsequently, the precursor was obtained by rejoining AgNO$_3$ into MgBi$_2$O$_6$ (the mass ratio of MgBi$_2$O$_6$ to AgNO$_3$ is1:20) to create a homogeneous mixture, using a mortar and pestle, adding 20 ml of ethyl alcohol into the mixture and stirring for 30 min continuously. The sample was further transferred into an alumina crucible and heated in air at for 4 h at 100°C and then cooled to room temperature. Finally, Ag-doped MgBi$_2$O$_6$ with brown powders was obtained from this reaction.

2.2. Characterization

Crystal structures of MgBi$_2$O$_6$ and Ag-doped MgBi$_2$O$_6$ photocatalysts were characterized by using X-ray diffractometer (XRD) (Bruker D8-Advance, Germany) with Cu Kα radiation ($\lambda = 0.1541$ nm) from 10°-80°, with a scan speed of 5°/min. Field emission scanning electron microscopy (FESEM) (Quanta 450 FEG, American) was used to characterize the morphologies of samples. The composition of the samples was examined using energy dispersive X-ray detector (EDS) (Thermo Noran VANTAG-ESI, USA). The Brunauer-Emmett-Teller (BET) specific surface areas of the materials were detected by Micromeritics ASAP 2010 nitrogen adsorption apparatus. The UV-vis absorption spectra of photocatalysts were obtained by a UV-vis spectrometer (Puxi TU-1901, Beijing) in the range of 200-700 nm using BaSO$_4$ as the reference sample.

2.3. Photocatalytic activity test

The photocatalytic activity of pure MgBi$_2$O$_6$ and Ag-doped MgBi$_2$O$_6$ photocatalysts were evaluated by degrading MB (10 mg/L) under visible light irradiation at room temperature. The 0.20 g powder of photocatalyst was immersed in a quartz beaker containing 100 mL MB solution with a concentration of 10 mg/L. In order to ensure adsorption/desorption equilibrium between MB and the photocatalysts, the suspension was stirred in the dark for 30 min before the degradation with illumination. Then the photocatalytic degradation experiment was started by irradiating with a 300 W Xeon arc lamp with a
UV cut off to ensure all the incoming wavelengths longer than 420 nm to provide visible light irradiation (λ > 420 nm). Moreover, the 6 mL suspension was taken out using centrifuge tubes in an interval of 15 min and then was centrifuged to remove impurities and powder in order to collect the supernatant which was used in the later analysis. The absorbance of centrifugal solution was determined at 664 nm by UV-vis spectrophotometer.

3. Results and discussion

3.1. Structural and morphological characterization

The XRD patterns of as-prepared samples are shown in Figure 1. All characteristic peaks can be indexed to the trirutile-type structure of MgBi2O6 (JCPDS No. 86-2492). Moreover, no any secondary phase or impurities can be observed from the XRD patterns. Our results showed that Ag-doping does not change the phase structure of MgBi2O6 photocatalyst and Ag can be dissolved into MgBi2O6 as a solid solution. The characteristic peak intensity of the Ag-doped MgBi2O6 is stronger in comparison with that of pure MgBi2O6, which means that the degree of crystallinity of Ag-doped MgBi2O6 catalyst is better than that of the MgBi2O6 catalyst. As shown in Figure 1, the obvious characteristic diffraction peaks of Ag-doped MgBi2O6 slightly shift to a lower angle and the slight lattice expansion occurs in Ag-doped MgBi2O6, which is mainly ascribed to the larger ionic radii of Ag+ ions (1.00-1.28 Å) in comparison with that of replaced Bi3+ ion (0.096-1.117 Å).

![Figure 1. X-ray powder diffraction patterns of pure MgBi2O6 and Ag-doped MgBi2O6 photocatalysts.](image)

The morphology and microstructure of the obtained pure MgBi2O6 and Ag-doped MgBi2O6 catalysts were measured by FESEM images as presented in Figure 2(a)-(d). Apparently, it can be seen that the cuboid-like particles were observed for both photocatalysts with the size of about 100 to 250 nm. As can be seen in Figure 2(c) and (d), Ag-doped MgBi2O6 particles show better crystallinity and closer arrangement in comparison with pure MgBi2O6 and look more regular and compact. The higher crystallinity would promote to yield higher photocatalytic activity, since the recombination of photogenerated electron-hole pairs can be suppressed in the highly crystalline photocatalysts [23]. As presented in Figure 2(e), the EDS analysis was also carried out in order to determine the elemental composition of Ag-doped MgBi2O6. Mg, Bi, O and Ag elements can be found from the EDS energy spectrum, which indicates the doped Ag ions has entered into the lattice of MgBi2O6. This also agrees with the foregoing XRD results.
Figure 2. SEM images of pure MgBi$_2$O$_6$ (a, b), Ag-doped MgBi$_2$O$_6$ composite photocatalysts (c, d), and (e) EDS spectrum of Ag-doped MgBi$_2$O$_6$.

3.2. UV-visible absorption spectra
The diffuse reflectance spectra of MgBi$_2$O$_6$ and Ag-doped MgBi$_2$O$_6$ samples were depicted in Figure 3. According to the DRS spectra, pure MgBi$_2$O$_6$ shows different photoabsorption properties from UV light region to visible light and the absorption edge of pure MgBi$_2$O$_6$ is at about 725 nm. The optical band gap is estimated to be about 1.71 eV by the extrapolation method. However, compared with pure MgBi$_2$O$_6$, the absorption of Ag-doped MgBi$_2$O$_6$ has blue shifts and its absorption edge is at about 708 nm. The estimated optical band gap is about 1.75 eV. MgBi$_2$O$_6$ has the greater probability of the recombination of electron-hole pairs because of relatively small optical band gap, while Ag doping in MgBi$_2$O$_6$ can reduce the combination of electron-hole pairs.
3.3. Photocatalytic activity

The photocatalytic activity of pure MgBi$_2$O$_6$ and Ag-doped MgBi$_2$O$_6$ photocatalysts were evaluated by degrading MB (10 mg/L) under visible light irradiation ($\lambda > 420$ nm). The concentration rate $C/C_0$ of MB solution as a function of reaction time under visible light irradiation is shown in Figure 4. As a comparison, the degradation of MB without any photocatalyst and over pure MgBi$_2$O$_6$ were also performed under the same conditions and are shown in Figure 4. Our results show that MB solution is relatively stable under visible light irradiation and cannot be degraded in the case without catalyst since no change in the concentration can be observed. For pure MgBi$_2$O$_6$ catalyst, the total degradation rate of MB is about 89.1% after 135 min of reaction, while the total degradation rates of MB for Ag-doped MgBi$_2$O$_6$ catalyst is about 98.6% within the 120 min. In comparison with pure MgBi$_2$O$_6$, the significant enhancement in the photocatalytic activity of Ag-doped MgBi$_2$O$_6$ should be related with the following reasons. First of all, it is well known that the crystallite size, shape, assembly morphology, and specific surface area can obviously affect the photocatalytic activity of solid. Ag-doped MgBi$_2$O$_6$ has higher crystallinity and larger surface area (5.85 m$^2$/g) than the pure MgBi$_2$O$_6$ (4.6 m$^2$/g) which can provide the more active sites and plays a key role in improving the photocatalytic activity. Another important reason for enhancing the photocatalytic activity of MgBi$_2$O$_6$ is that the recombination of electron-hole pairs can be reduced by the doped Ag ions, since the Ag ions can act as trap sites for capturing the photogenerated electrons when the photogenerated electrons are excited under visible light irradiation.
Figure 4. Degradation rate of MB solution as a function of irradiation time under visible light ($\lambda > 420$ nm): (a) without any photocatalysts, (b) pure MgBi$_2$O$_6$, and (c) Ag-doped MgBi$_2$O$_6$.

4. Conclusions

In conclusion, Ag-doped MgBi$_2$O$_6$ photocatalysts have been successfully synthesized by the low temperature hydrothermal in combination with heat treatment reaction using NaBiO$_3$·2H$_2$O and MgCl$_2$·6H$_2$O as raw materials and AgNO$_3$ as silver source. Our results show that Ag-doped MgBi$_2$O$_6$ has better crystallinity and larger surface area and exhibits higher photocatalytic activity for the decomposition of MB solution in comparison with pure MgBi$_2$O$_6$. Degradation experiments on MB solution have suggested that compared with pure MgBi$_2$O$_6$ the photodegradation rate of MB under visible light irradiation was increased about 24% in Ag-doped MgBi$_2$O$_6$ with about 5% of mass ration concentration of AgNO$_3$ after 120 min. Meanwhile, the doped Ag ions can reduce the recombination of electron-hole pairs during photodegradation, which can also enhance the catalytic activity of Ag-doped MgBi$_2$O$_6$ composite photocatalyst.

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