Hydrothermal synthesis and characterization of visible-light-driven Mo-doped Bi₂WO₆ photocatalyst

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In this research, Bi₂WO₆ nanoplates doped with 0, 1, 3 and 4% by weight of Mo were successfully synthesized by hydrothermal method. X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy and ultraviolet-visible spectroscopy certified that the as-synthesized products were uniform orthorhombic Bi₂WO₆ nanoplates with absorbance of the pure product in ultraviolet region and of the doped ones in both ultraviolet and visible regions. Photocatalysis of the products was also evaluated through the degradation of rhodamine B under visible light irradiation. The Bi₂WO₆ nanoplates doped with 3% by weight of Mo have the highest rate constant of 0.023 min⁻¹.

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1. Introduction

Bi₂WO₆ as n-type semiconductor has attracted much attention in recent years because of its unique chemical and physical properties.¹,² It was found to have prominent photocatalytic efficiency for photodegradation of organic contaminants in water and air under visible light irradiation.³⁻⁶ For example, Bi₂WO₆ lamellas have an excellent photodegradation performance for damaging to rhodamine B (RhB) under simulated sunlight irradiation.⁷ Hierarchical flower-like Bi₂WO₆ microspheres of assembled nanosheets were hydrothermally synthesized using EO₁₀₀−PO₆₅−EO₁₀₀ as a non-ionic surfactant.⁸ They have high photodegradation of RhB within 180 min due to their high surface area and efficient charge-carrier separation. Furthermore, photocatalytic performance of Bi₂WO₆ is limited by fast recombination of photogenerated electron-hole pairs.⁵,⁶ Thus, improvement of photocatalytic performance of Bi₂WO₆ is a top priority of the current research. There have been many techniques used for improving photocatalytic performance of photocatalysts such as controlling of morphology,¹,³ combining with noble metals and other semiconductors,⁵⁻⁷ and loading with metal ions.⁸⁻¹⁰

In this research, Bi₂WO₆ nanoplates doped with 0, 1, 3 and 4% by weight of Mo was synthesized by hydrothermal process. Effect of Mo content on phase, morphology and photocatalytic activity was investigated and explained according to the experimental results.

2. Experiment

All chemical reagents were analytical grade and were used without further purification. In a typical synthesis, Bi(NO₃)₃·5H₂O, Na₂WO₄·2H₂O and Na₂MoO₄·2H₂O (0, 1, 3 and 4 wt% Mo) were dissolved in 100 ml deionized water at room temperature. The pH of solutions was adjusted to 10 by NH₄OH solution under continuous stirring. Subsequently, each solution was transferred into a 200 ml Teflon-lined stainless steel autoclave which was sealed and heated in an electric oven at 180°C for 24 h. The as-synthesized precipitates were filtered, thoroughly washed, dried and characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray photoelectron spectroscopy (XPS) and ultraviolet (UV)-visible spectroscopy.

In order to test for photocatalysis, 0.2 g of each photocatalyst was suspended in 200 ml of 1×10⁻³ M rhodamine B (RhB) solution. The suspensions were stirred in the dark condition for 30 min to establish an adsorption–desorption equilibrium. Then, the suspensions were ex-
posed by visible light irradiation (λ > 420 nm) of Xe lamp as light source at 30 cm apart. Every 20 min interval of visible-light irradiation, 5 ml suspended solutions were sampled and centrifuged at 4000 rpm for 8 min to remove the residual photocatalyst before spectroscopic measurement. The concentration of RhB was determined by UV-visible spectroscopy at λ_{max} of 554 nm.

3. Results and discussion

XRD patterns of the products (Fig. 1) exhibit the sharp and strong eight diffraction peaks at 2θ = 28.28, 32.75, 47.04, 55.77, 58.56, 68.59, 76.17 and 78.23° for Bi_{2}WO_{6}; 28.28, 32.70, 47.05, 55.79, 58.53, 68.67, 76.23 and 78.21° for 1 wt% Mo-doped Bi_{2}WO_{6} and 28.29, 32.69, 47.09, 55.89, 58.51, 68.97, 76.23 and 78.22° for 3 wt% Mo-doped Bi_{2}WO_{6}. They can be indexed to the (113), (200), (220), (313), (226), (400), (319) and (406) planes of orthorhombic Bi_{2}WO_{6} phase of the JCPDS database no. 73-1126.10)

Figure 2 shows FTIR spectra of the Bi_{2}WO_{6} and 3 wt% Mo-doped Bi_{2}WO_{6} samples. The small band at 827 cm⁻¹ is ascribable to the bending vibration of W–O–W.11) The strong band at 734 cm⁻¹ is attributed to the W–O vibration in WO_{6} octahedrons.12),13) Two weak bands at 572 and 445 cm⁻¹ are identified to the Bi–O vibration of BiO_{6} octahedrons containing in Bi_{2}WO_{6}.13) The broadband located at 3400–3600 cm⁻¹ corresponds with the O–H stretching of adsorbed water on the surface of samples.12)

Figure 3 shows XPS spectra of Bi 4f, W 4f, O 1s and Mo 3d of 3 wt% Mo-doped Bi_{2}WO_{6}. The strong Bi 4f binding energies appeared as symmetrical peaks at 159.34 eV for Bi 4f_{7/2} and 164.66 eV for Bi 4f_{5/2}, suggesting the presence of trivalent oxidation state Bi containing in Bi_{2}WO_{6}.7),8),12),13) The XPS spectrum of W 4f consists of two peaks with binding energies at 35.53 eV for W 4f_{7/2} and 37.67 eV for W 4f_{5/2} with oxidation state of 6+.7),8),12),13) The XPS spectrum of oxygen presents an asymmetric O 1s peak corresponding to the crystal lattice oxygen and adsorbed oxygen. The asymmetric O 1s peak can be deconvoluted into three peaks at 530.13, 531.00 and 531.80 eV. Two main peaks of O 1s at 530.13 and 531.00 eV are assigned to oxygen lattice of Bi–O and W–O in Bi_{2}WO_{6}.7),8),13) The shoulder peak of O 1s at 531.80 eV is attributed to O–H from absorbed water on the surface of 3 wt% Mo-doped Bi_{2}WO_{6}.12) The binding energies at 232.67 eV for Mo 3d_{5/2} and 235.81 eV for Mo 3d_{3/2} of Mo^{6+} were detected in the XPS analysis.14),15) Furthermore, the quantitative determination of actually Mo dopant in 3 wt% Mo-doped Bi_{2}WO_{6} was found to be 2.72% by weight.

Morphology and phase of Bi_{2}WO_{6} and 3 wt% Mo-doped Bi_{2}WO_{6} were further investigated by TEM and SAED as the results shown in Fig. 4. The TEM analysis revealed that the products were uniform two-dimensional nanoplates with the size of 200–300 nm for Bi_{2}WO_{6} and 50–150 nm for 3 wt% Mo-doped Bi_{2}WO_{6}. They should be noted that the doped product was composed of Bi_{2}WO_{6} as the host (majority) and of Mo as the doping material (minority). Their SAED patterns show clear electron dif-
fraction spots, indicating a well-defined single crystalline orthorhombic Bi$_2$WO$_6$ phase. The diffraction spots were specified as the (200), (220) and (020) planes. The formation mechanism of Bi$_2$WO$_6$ nanoplates can be explained by the anisotropic growth process. The orthorhombic Bi$_2$WO$_6$ phase was built up the corner-sharing structure of WO$_6$ octahedrons with (Bi$_2$O$_2$)$_2^{2+}$ layers sandwiched between the WO$_6$ octahedral layers, stacking along the [100] and [010] axes. They have much lower potential energy as compared to those of other facets. Thus, growth rate along the [100] and [010] directions were the highest, resulting in two-dimensional growth and the eventual formation of two-dimensional nanoplates with the (001) plane as the planar facet.\textsuperscript{1,16,17)

The UV–visible spectra of Bi$_2$WO$_6$ and 3 wt % Mo-doped Bi$_2$WO$_6$ are shown in Fig. 5. The Bi$_2$WO$_6$ sample shows a strong absorption band centered at 258 nm due to the O$^2-$ to W$^{6+}$ charge transfer of the isolated WO$_6$ in Bi$_2$WO$_6$ lattice.\textsuperscript{19} Comparing to 3 wt % Mo-doped Bi$_2$WO$_6$, the doped product shows higher UV absorption than Bi$_2$WO$_6$, including the detection of a broadband in visible-light region attributed to the band-gap transition instead of impurity level.\textsuperscript{19} Clearly, the presence of Mo$^{6+}$ does not change the position of valence band edge of Bi$_2$WO$_6$. Instead, a new energy level of the molybdenum dopant in the band gap region of Bi$_2$WO$_6$ is created.\textsuperscript{20}

In this research, the photocatalytic reaction of 3 wt % Mo-doped Bi$_2$WO$_6$ is higher than that of pure Bi$_2$WO$_6$ due to the improvement and utilization of visible light and the electronic transition between Mo$^{6+}$ 3d and Bi$_2$WO$_6$ conduction band.\textsuperscript{19,20}

Figure 6(a) shows the absorbance of RhB solution after being degraded by 3 wt % Mo-doped Bi$_2$WO$_6$ for different lengths of time within 180 min. The absorption intensity was monotonically decreased with the prolonged period of time. The color of RhB solution was changed from pink to light yellow-green and transparency in sequence within 180 min under visible light irradiation. The absorption peak of RhB at $\lambda_{\text{max}} = 554$ nm was blue shift to lower wavelength at 539, 522, 510 and 498 nm because of the RhB degradation of ethyl groups.\textsuperscript{8,11} They correspond to N,N,N'-triethylated rhodamine, N,N'-diethylated rhodamine, N-ethylated rhodamine and rhodamine, respectively.\textsuperscript{11} In the end, they were broken into CO$_2$ and H$_2$O as
final products. Figure 6(b) revealed photodegradation of RhB solution by Bi2WO6 nanoplates loading with different contents of Mo dopant under visible light irradiation. Upon loading with 4 wt% Mo, the percent yield is very low. Thus, the content of Mo dopant was limited to 3% by weight. In this research, the 0, 1, and 3 wt% Mo-doped Bi2WO6 samples were studied for photocatalysis under visible light irradiation of Xe lamp ($\lambda > 420$ nm). Obviously, photodegradation of RhB solution by pure Bi2WO6 nanoplates was 93.74% and that at the same condition by 3 wt% Mo-doped Bi2WO6 was able to reach 97.93%. The photodegradation improvement was due to the existence of a broadband in visible-light region of the 3 wt% Mo-doped Bi2WO6 nanoplates, as the UV–visible absorbance shown above. When visible light was exposed on the photocatalyst, electrons and holes were produced in the conduction band and valence band. They diffused to the surface of Bi2WO6 and reacted with O2 and OH−/H2O to produce the ‘$O_2^-$’ and OH− as strong oxidizing radicals. Furthermore, ‘$O_2^-$’ and OH− radicals reacted with RhB molecules by transforming RhB into CO2 and H2O as final products.7,17) The photocatalytic performance was limited due to a high rate of electron–hole recombination. When the Mo-doped Bi2WO6 photocatalyst was irradiated by the visible light, Mo dopant as an electron–hole recombination center would produce more defects, leading to inhibit the recombination of photo-generated electrons and holes.21) Thus, Mo-doped Bi2WO6 has higher photocatalytic performance than pure Bi2WO6. The photodegradation of RhB by Bi2WO6 and Mo-doped Bi2WO6 under visible light irradiation was fitted through the pseudo-first-order kinetic model as the results shown in Fig. 6(c).7,12) Obviously, the photoreaction rates for photodegradation of RhB are in a particular sequence: 3 wt% Mo-doped Bi2WO6 > 1 wt% Mo-doped Bi2WO6 > Bi2WO6.

The apparent reaction rate constants of photocatalysts were calculated from slopes of the plots. The 3 wt% Mo-doped Bi2WO6 photocatalyst exhibited the rate constant of 0.023 min$^{-1}$ which is higher than those of 1 wt% Mo-doped Bi2WO6 (0.017 min$^{-1}$) and pure Bi2WO6 (0.014 min$^{-1}$).

4. Conclusions

In summary, Bi2WO6 and Mo-doped Bi2WO6 were successfully synthesized by hydrothermal method. XRD and TEM results certified that the products consisted of high crystalline orthorhombic Bi2WO6 nanoplates. The photocatalytic properties of Bi2WO6 and Mo-doped Bi2WO6 nanoplates were investigated through photodegradation of RhB solutions. The results demonstrated that 3 wt% Mo-doped Bi2WO6 is an excellent visible-light-driven photocatalyst for photodegradation of RhB molecules in water.

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