Photodegradation of rhodamine B by Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites under visible light illumination

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1. Introduction

Bismuth molybdenenum oxide (Bi$_2$MoO$_6$), a typically layered Aurivillius phase, has 2.6 eV energy gap [9] and can absorb visible light. It consists of perovskite slabs of (A$^+$_2B$^6$O$_{2n+1}$)$_2^+$ sandwiched between bismuth oxide (Bi$_2$O$_3$)$_2^+$ layers.[1,2] It is an ideal promising material for visible-light-driven photocatalytic process. Its photocatalytic properties are limited because it has high recombination rate of photo-excited electron–hole pairs.[3,4] Therefore, a number of efforts have been paid to improve photocatalytic performance such as metal ions doping, non-metal ions doping and coupling with composite semiconductors.[3–5] The Bi$_2$MoO$_6$ with coupling narrow-band gap semiconductor to improve diffusion efficiency of photogenerated electrons and holes across heterostructure photocatalytic junctions between the Bi$_2$MoO$_6$ and semiconductor.[5,7]

Ag$_3$PO$_4$ is an excellent photocatalyst, and is able to photodegrade organic pollutants under visible light radiation and to potentially separate photo-excited electrons and holes.[6,7] Thus the Ag$_3$PO$_4$-based composites are believed to be ideal photocatalysts because they can improve the optical absorption and simultaneously promote the separation of photo-induced electron–hole pairs.[3,4]

In this research, Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites were synthesized by direct precipitation of Ag$_3$PO$_4$ nanoparticles on surfaces of Bi$_2$MoO$_6$ nanoparticles. The heterostructure 10.0 wt% Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites exhibited excellent photocatalytic activity in degradation of rhodamine B (RhB) as compared to pure Bi$_2$MoO$_6$ phase.

2. Experiment

In a typical procedure, each of 5 mmol Bi(NO$_3$)$_3$·5H$_2$O and Na$_2$MoO$_4$ was dissolved in each 100 ml RO water and mixed together. The obtained solution was stirred and adjusted the pH to 6 by 3 M NaOH solution. The mixture was transferred to a 200 ml Teflon-lined stainless steel autoclave, which was tightly closed and maintained at 180°C in an electric oven for 20 h. The obtained precipitates were washed with distilled water and ethanol, dried, and collected for further characterization.

To synthesize different contents of Ag$_3$PO$_4$ nanoparticles deposited on the Bi$_2$MoO$_6$ samples, 0.0–15.0 wt% of AgNO$_3$ and Na$_2$PO$_4$ for each 1.0 g of Bi$_2$MoO$_6$ samples were dissolved in 100 ml RO water under magnetic stirring for 24 h. Subsequently, the products were separated by filtering, washed with absolute ethanol and dried in an electric oven for 24 h.

The 20 mg photocatalyst (Bi$_2$MoO$_6$, Ag$_3$PO$_4$ and 1.0–10.0 wt% Ag$_3$PO$_4$/Bi$_2$MoO$_6$) was added to 200 ml of 1 × 10$^{-5}$ M RhB solution. Before illumination, the suspensions were stirred in the dark for 30 min. Then the visible light was turned on, and each 5 ml of the suspension solution was taken for every interval times. The RhB concentration was determined by a UV–visible spectrophotometer and decolorization efficiency (%) was calculated by the equation

Decolorization efficiency (%) = \( \frac{C_0 - C_t}{C_0} \times 100 \), \( (1) \)

where $C_0$ is the initial concentration of RhB and $C_t$ is the concentration of RhB after visible white light irradiation within the elapsed time ($t$).
3. Results and discussion

Figure 1 shows X-ray diffraction (XRD) patterns of Bi$_2$MoO$_6$ and Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites. XRD pattern of the as-synthesized Bi$_2$MoO$_6$ sample can be indexed to orthorhombic Bi$_2$MoO$_6$ according to the JCPDS no. 21-0102.7 The Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites exhibited similar XRD patterns to that of pure Bi$_2$MoO$_6$, including the additional peaks of cubic Ag$_3$PO$_4$ (JCPDS no. 06-0505) were detected. They should be noted that the (210) peak at 2\(\theta\) = 33.29° of cubic Ag$_3$PO$_4$ overlapped the (002) peak at 2\(\theta\) = 33.29° of orthorhombic Bi$_2$MoO$_6$ phase. There was no detection of other peaks in the Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites, except for the 15.0 wt % Ag$_3$PO$_4$/Bi$_2$MoO$_6$. When the loading content of Ag$_3$PO$_4$ was 15.0 wt %, additional peaks of hexagonal Ag at 2\(\theta\) = 35.89° (JCPDS no. 41-1402) and unknown at 2\(\theta\) = 31.25° were detected.

Transmission electron microscopic (TEM) images and selected area electron diffraction (SAED) pattern of the Bi$_2$MoO$_6$ and Ag$_3$PO$_4$/Bi$_2$MoO$_6$ samples are shown in Fig. 2. The morphology of Bi$_2$MoO$_6$ shows good-quality nanoplates with edge length of 100–150 nm. The SAED pattern of individual Bi$_2$MoO$_6$ nanoplate shows regular square diffraction spot array, revealing the presence of single crystalline nanoplate. The calculated SAED spots correspond to the (060), (062) and (002) planes projected along the [100] direction. Generally the top and bottom facets of the Bi$_2$MoO$_6$ nanoplate are the (001) planes, and the side facets are the ±(100), ±(010) and ±(110) planes. The TEM images of 5.0 and 10.0 wt % Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites reveal the dark spots of nanoparticles <20 nm dispersed on the surface of Bi$_2$MoO$_6$ nanocomposites. At high magnification, Ag$_3$PO$_4$ nanoparticles with 5–10 nm in size were distributive across the Bi$_2$MoO$_6$ surface of the 10.0 wt % Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites. High resolution transmission electron microscopic (HRTEM) image of Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites shows two lattice fringes of Bi$_2$MoO$_6$ nanoplate with Ag$_3$PO$_4$ nanoparticle on top. The measured lattice spaces of 0.237 and 0.318 nm correspond with the (211) crystallographic plane of cubic Ag$_3$PO$_4$ and the (131) crystallographic plane of orthorhombic Bi$_2$MoO$_6$ phase, respectively. The HRTEM result clearly shows that Ag$_3$PO$_4$ nanoparticles closely connect with the Bi$_2$MoO$_6$ nanoparticles, which favor the formation of nanoparticle-nanoplate junctions. Thus the photodegradation can be improved by charge diffusion through these junctions. The content of Ag$_3$PO$_4$ in Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites was analyzed by energy dispersive X-ray spectroscopy (EDS). The weight percent of Ag$_3$PO$_4$ is 0.89, 4.78 and 9.75 in 1 wt %, 5 wt % Ag$_3$PO$_4$/Bi$_2$MoO$_6$, 5 wt % Ag$_3$PO$_4$/Bi$_2$MoO$_6$ and 10 wt % Ag$_3$PO$_4$/Bi$_2$MoO$_6$, respectively.

X-ray photoelectrons spectroscopy (XPS) (Fig. 3) was used to determine elemental components of Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites, which were demonstrated to compose of Ag, P, Bi, Mo and O. All of these results confirm the coexistence of Ag$_3$PO$_4$ and Bi$_2$MoO$_6$ in the heterostructure Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites.

RhB dye was used to evaluate the photocatalytic activity of the Ag$_3$PO$_4$/Bi$_2$MoO$_6$ composites. The temporal UV-vis spectral absorption of 10.0 wt % Ag$_3$PO$_4$/Bi$_2$MoO$_6$ in RhB solution as a function of exposure time by visible white light is shown in Fig. 4(a). It should be noted that RhB solution has a maximum peak at 553 nm which was used to specify the degradation of RhB dye. Under exposure to visible white light, the intensity absorption at 553 nm of RhB solution was gradually decreased when the reaction time was prolonged. The absorbance of RhB

![Fig. 1](image1.png)

Fig. 1. XRD patterns of 0.0, 1.0, 2.5, 5.0, 10.0 and 15.0 wt % Ag$_3$PO$_4$/Bi$_2$MoO$_6$.

![Fig. 2](image2.png)

Fig. 2. TEM images, SAED pattern and HRTEM images of (a, b) pure Bi$_2$MoO$_6$, (c) 5.0 wt % Ag$_3$PO$_4$/Bi$_2$MoO$_6$ and (d–f) 10.0 wt % Ag$_3$PO$_4$/Bi$_2$MoO$_6$.

![Fig. 3](image3.png)

Fig. 3. XPS spectra of (a–e) Ag 3d, P 2p, Bi 4f, Mo 3d and O 1s of 10.0 wt % Ag$_3$PO$_4$/Bi$_2$MoO$_6$ nanocomposites, respectively.
peaks shifted from 553 to 496 nm due to N-deethylation of RhB molecules in accordance with the gradual color change of the solution from pink to colorless.\(^\text{14}\) The stepwise blue-shift of the main peaks from 553 nm of RhB is attributed to the blue-shift step-by-step deethylation of RhB molecules to N,N,N-triethyl rhodamine (539 nm), N,N'-diethyl rhodamine (522 nm), N-ethyl rhodamine (510 nm) and rhodamine (496 nm).\(^\text{14}\)

Figure 4(b) shows the photocatalytic activity of RhB degradation by blank, pure Bi\(_2\)MoO\(_6\), pure Ag\(_3\)PO\(_4\) and 2.5, 5.0 and 10.0 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) nanocomposites under visible white light irradiation. The blank test without photocatalytic adding shows no photodegraded RhB solution under visible white light, implying that RhB molecules are stable under visible white light. Clearly, these photocatalysts show photodegraded RhB activity under visible white light irradiation. The decolorization efficiency of Bi\(_2\)MoO\(_6\) is about 40.7% within 100 min. When Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) nanocomposites were used instead of Bi\(_2\)MoO\(_6\), the photocatalytic rate became faster. For 10.0 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) loading, the rate was the highest. They were found that the specific surface area of products are 18.35, 16.57, 15.75 and 13.25 m\(^2\) g\(^{-1}\) for Bi\(_2\)MoO\(_6\), 1 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\), 5 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) and 10 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\), respectively. The presence of Ag\(_3\)PO\(_4\) loading greatly affects the photodegradation of RhB due to photogenerated charged carriers diffusion between the Bi\(_2\)MoO\(_6\) and Ag\(_3\)PO\(_4\). The heterostructure 10.0 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) nanocomposites have the highest photocatalytic activity of 98.0%, or 2.4 times of the photocatalytic activity of pure Bi\(_2\)MoO\(_6\) under visible white light within 100 min.

The RhB degradation rate under visible-light illumination by Bi\(_2\)MoO\(_6\), Ag\(_3\)PO\(_4\), Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) samples follows pseudo-first-order reaction

\[
\ln(C_0/C) = kt, \tag{2}
\]

where \(k\) is the apparent rate constant [7, 8, 12, 15], calculated from slope of the degradation regression line of pure Bi\(_2\)MoO\(_6\), pure Ag\(_3\)PO\(_4\) and Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) nanocomposites [Fig. 4(c)].\(^\text{14}\) For linear relationship (R→1), the photocatalytic degradation line fitted well with the first-order reaction.\(^\text{14}\) The calculated rates were 0.0455, 0.0431, 0.0138, 0.0112 and 0.0069 min\(^{-1}\) for 10.0 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\), pure Ag\(_3\)PO\(_4\), 2.5 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\), 5.0 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) and pure Bi\(_2\)MoO\(_6\) samples, respectively. The photocatalytic rate constant of 10.0 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) nanocomposites is 6.6 times that of pure Bi\(_2\)MoO\(_6\) and is a little higher than that of the pure Ag\(_3\)PO\(_4\). These results indicate the preferable photocatalytic performance of the 10.0 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) nanocomposites. The improved photocatalytic efficiency of Bi\(_2\)MoO\(_6\) by Ag\(_3\)PO\(_4\) loading was attributed to the unique property of Ag\(_3\)PO\(_4\) on Bi\(_2\)MoO\(_6\) which can provide more active sites, lead to the promotion of the separation of photo-excited electron–hole pairs, reduce the recombination rate of photogenerated charged carriers and accelerate charge diffusion through the Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) interfaces.\(^\text{4,15}\)

The photocatalytic stability of Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) nanocomposites was studied for practical application. The cyclic photocatalysis for photodegradation of RhB solution by 10.0 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) photocatalytic nanocomposites was performed under visible white light irradiation for five cycles, as the results shown in Fig. 4(d). After the first cycle, the filtered photocatalyst was washed with deionized water, dried in an electric oven and reused for the next test for photocatalysis. The recyclability of photocatalytic activity exhibited a little significant loss in RhB photodegradation after five-cycle run. The efficiency of photocatalytic degradation of RhB at the end of fifth cycle is 85.0%, 13.0% lower than that of the first. In general, the degradation efficiency can be controlled by the photocatalytic and dye concentrations, surface area to volume ratio of the photocatalytic material, frequency of the visible light, pH of the solution and testing temperature. Due to the high activity, stability and recyclability, the 10.0 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) nanocomposites are promising practical photocatalyst in reducing organic contaminants in water resources.

4. Conclusions

Heterostructure Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) nanocomposites were successfully synthesized by a deposition–precipitation method at high temperature and pressure. The effect of Ag\(_3\)PO\(_4\) content as supporting load on photocatalytic properties of Bi\(_2\)MoO\(_6\) was investigated by evaluating the degradation of RhB under visible white light. In this research, the 10.0 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) nanocomposites exhibited higher photocatalytic activity than any other samples. The recyclability of 10.0 wt % Ag\(_3\)PO\(_4)/Bi\(_2\)MoO\(_6\) nanocomposites exhibited a little significant loss in RhB photodegradation after five-cycle run. They were attributed to be a promising practical application in removing of organic contaminants in water resources with very high efficiency.

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