Synthesis of Ag_3VO_4 nanoparticles loaded on Bi_2MoO_6 nanoplates as heterostructure visible light driven photocatalyst by sonochemical method

Phonthep NUALKAEW, Anukorn PHURUANGRAT,^{*,†} Phattranit DUMRONGROJTHANATH,^{**}
Somchai THONGTEM^{***} and Titipun THONGTEM^{**}

Division of Chemistry, School of Science, Walailak University, Nakhon Si Thammarat 80161, Thailand

^{*}Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University,
Hat Yai, Songkhla 90112, Thailand

^{**}Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

^{***}Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

$\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanocomposites were successfully synthesized by sonochemical method. The as-synthesized products were characterized by X-ray powder diffraction (XRD), field emission scanning electron microscopy (FE-SEM), selected area electron diffraction (SAED), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). The results revealed the formation of heterostructure $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanocomposites. Photocatalytic activity of the nanocomposites was evaluated through the degradation of rhodamine B (RhB) dye under visible white light irradiation. Among them, heterostructure 10.0 wt% $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanocomposites exhibited the highest photocatalytic activity up to 56.26% for the degradation of RhB dye under visible white light within 240 min.

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1. Introduction

Bi_2MoO_6 belongs to bismuth oxide family with the structure consisting of perovskite layers between bismuth oxide layers of general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ ($\text{A} = \text{Ba}, \text{Bi}, \text{Pb}$, etc., $\text{B} = \text{Ti}, \text{Nb}, \text{W}, \text{Mo}$, etc.).¹⁾ It consists of alternating fluorite-like $(\text{Bi}_2\text{O}_2)^{2+}$ layers and perovskite-like $(\text{MoO}_4)^{2-}$ layers.^{2),3)} Bi_2MoO_6 is a highly promising photocatalyst for H_2 and O_2 evolution from water splitting under full-arc irradiation of a Xe lamp ($\lambda > 300 \text{ nm}$)^{4),5)} and degradation of organic compounds under visible light irradiation.⁶⁾ Moreover, the photocatalytic activity of Bi_2MoO_6 is a limited region of visible-light photo-response due to high recombination of photogenerated electron-hole pairs. To improve photocatalytic activity, a heterojunction by coupling Bi_2MoO_6 with the broadened range of visible-light and narrow band gap semiconductor is designed to promote the separation of photogenerated electron-hole pairs of Bi_2MoO_6 .^{2),7)} Among semiconductors, Ag_3VO_4 as an n-type semiconductor is very attractive because it has narrow band gap ($\sim 2.2 \text{ eV}$) and high photocatalytic activity.⁸⁾ It has been shown to have a visible-light catalytic activity for water splitting into H_2 and O_2 .⁹⁾ It can absorb most of the visible light and is a potential sensitizer to sense wide band gap semiconductors.

In this research, heterostructure 0.0–10.0 wt% $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanocomposites were fabricated by deposition-precipitation process which was proved to be a simple method to provide products with high crystallinity. The photocatalytic degradation of rhodamine B (RhB) under visible light and photodegradation

mechanism of $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanocomposites were also studied and discussed.

2. Experiment

All chemicals of the present research were analytical grade and were used without further treatment during the whole synthetic process. Typically, each of 5 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and Na_2MoO_6 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, tightly closed and heated at 180°C in an electric oven for 20 h. The obtained precipitates were washed with distilled water and ethanol, dried at 80°C for 24 h and collected for further studied.

To synthesize different contents of Ag_3VO_4 nanoparticles deposited on the Bi_2MoO_6 nanoplates, 0.0–10.0 wt% of AgNO_3 and Na_3VO_4 for each 1.0 g of Bi_2MoO_6 sample were dissolved in 100 ml RO water under ultrasonic radiation for 1 h. Subsequently, the samples were separated by filtering, washed with absolute ethanol and dried at 80°C in an electric oven for 24 h. The samples were characterized by an X-ray diffractometer (XRD), a field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray (EDX) spectrometer and a transmission electron microscope (TEM).

The photocatalytic activities of the products were evaluated via the photodegradation of RhB under visible white light irradiation. For each experiment, 20 mg photocatalyst was added to 200 ml of $1 \times 10^{-5} \text{ M}$ RhB aqueous solution and stirred in the dark for 30 min. Then the visible light was turned on, and each 5 ml of the suspension solution was sampled for RhB concentration determination by a UV-visible spectrophotometer. The decolorization

[†] Corresponding author: A. Phuruangrat; E-mail: phuruangrat@gmail.com

efficiency (%) was calculated by the equation

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

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 XRD patterns of the as-prepared Bi₂MoO₆ and Ag₃VO₄/Bi₂MoO₆ samples at different weight of Ag₃VO₄ loading. The diffraction peaks of the pure sample can be readily indexed to orthorhombic Bi₂MoO₆ (JCPDS no. 21-0102).¹⁰ In addition, all of the Ag₃VO₄/Bi₂MoO₆ patterns show additional diffraction peaks at $2\theta = 31.28^\circ$ which is attributed to the (121) crystal plane of orthorhombic Ag₃VO₄ structure (JCPDS no. 43-0543).¹⁰ The XRD pattern of Ag₃VO₄/Bi₂MoO₆ samples was detected both orthorhombic Bi₂MoO₆ structure as major phase and orthorhombic Ag₃VO₄ structure as minor phase, indicating the presence of Ag₃VO₄/Bi₂MoO₆ composites. Ag₃VO₄ was presented as a separated phase instead of being intercalated in the Bi₂MoO₆ lattice by forming heterostructure Ag₃VO₄/Bi₂MoO₆ composites.

In order to study the morphology of the as-synthesized Bi₂MoO₆ and Ag₃VO₄/Bi₂MoO₆ composites, they were probed by SEM. **Figure 2** shows SEM images of Ag₃VO₄/Bi₂MoO₆ samples containing different contents of Ag₃VO₄ loading. Obviously, Bi₂MoO₆ phase exhibits a smooth plate-like morphology. Upon modification of the Bi₂MoO₆ product, the Ag₃VO₄ nanoparticles with the size of <10 nm were highly dispersed on the surface of Bi₂MoO₆ nanoplates. The covering Ag₃VO₄ nanoparticles were gradually enhanced with the increasing Ag₃VO₄ content from 5.0 to 10.0 wt%. At high magnification of 10.0 wt% Ag₃VO₄/Bi₂MoO₆, the smaller Ag₃VO₄ nanoparticles appeared to be homogeneously dispersed on the surface of the as-synthesized nanoplates. The EDX results are in accordance with the elements of 10.0 wt% Ag₃VO₄/Bi₂MoO₆ nanocomposites containing the Ag, V, Bi, Mo and O.

The interaction of Ag₃VO₄ and Bi₂MoO₆ was investigated by TEM, SAED and HRTEM. **Figure 3(a)** shows that the as-synthesized Bi₂MoO₆ was composed of nanoplates. The SAED pattern of a single Bi₂MoO₆ nanoplate [Fig. 3(b)] shows single-crystal electron diffraction spots corresponding to the (060),

(062) and (002) planes. **Figures 3(c) and 3(d)** shows TEM and HRTEM images of 10.0 wt% Ag₃VO₄/Bi₂MoO₆ composites. Obviously, Bi₂MoO₆ nanoplates were covered with Ag₃VO₄ nanoparticles. The HRTEM image shows the clear lattice fringe of Ag₃VO₄ with planar space of 0.29 nm indexed to its (121) plane. Thus, an integration interface of Ag₃VO₄ and Bi₂MoO₆ was created which favored the diffusion of photoexcited carriers and enhanced the photocatalytic activity. This special structure promoted the efficiency of photogenerated electron-hole pairs and accelerated the interfacial charge diffusion, leading to improve the photocatalytic efficiency.

The photocatalytic activity of the samples was evaluated by tracing the temporal concentration change of RhB in an aqueous solution under visible white light irradiation. **Figure 4(a)** shows the UV-visible absorption spectral change during the photo-degradation of RhB solution by 10.0 wt% Ag₃VO₄/Bi₂MoO₆ sample under different lengths of time of visible light irradiation. They were found that the concentration of RhB solution was gradually reduced and the main absorption peak intensity of RhB decreased sharply with the time passed by, which indicated the decomposition of chromophoric structure of the RhB dye.¹¹

Fig. 2. SEM images of (a) pure Bi₂MoO₆, (b) 5.0 wt% Ag₃VO₄/Bi₂MoO₆ and (c, d) 10.0 wt% Ag₃VO₄/Bi₂MoO₆ samples.

Fig. 1. XRD patterns of Ag₃VO₄/Bi₂MoO₆ samples at different weight of Ag₃VO₄ loading.

Fig. 3. TEM images, SAED pattern and HRTEM image of (a, b) pure Bi₂MoO₆ and (c, d) 10.0 wt% Ag₃VO₄/Bi₂MoO₆ samples.

Fig. 4. (a) UV-visible absorption of RhB solution containing 10.0 wt% $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ photocatalyst under visible white light within 240 min. (b) Decolorization efficiency and (c) first-order plot for the photocatalytic activity of Bi_2MoO_6 , 2.5 wt% $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$, 5.0 wt% $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ and 10.0 wt% $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ under visible white light within 240 min. The photodegradation of RhB solution without any photocatalysts is also shown in (b). (d) A schematic diagram for the photocatalytic mechanism of $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanocomposites.

Figure 4(b) displays the change of RhB concentration versus the reaction time by the Bi_2MoO_6 and $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanophotocatalysts. The photodegradation of RhB solution in the absence of any photocatalysts under visible light radiation shows a little degraded RhB within 240 min of visible light irradiation, in accordance with the previous reports^{(12), (13)} because of the oxygen radical form reduction of molecular oxygen in photoexcited RhB molecules under visible light radiation.⁽¹⁴⁾ The pure Bi_2MoO_6 phase exhibits poor activity due to its insensitivity to the light. $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanocomposites present higher degradation potential for RhB than pure Bi_2MoO_6 . As the Ag_3VO_4 content increases from 2.5 to 10.0 wt%, the photocatalytic activity of $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanocomposites increases. The 10.0 wt% $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ sample exhibits the highest photocatalytic efficiency of 56.26% or 2.69 times that of Bi_2MoO_6 . In addition, photodegradation through the catalysts was fitted for Langmuir-Hinshelwood pseudo-first-order kinetics.^{(1), (15)} Figure 4(c) shows the $\ln(C_0/C_t)$ versus reaction time of the photodegradation of RhB in the presence of Bi_2MoO_6 and $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ photocatalysts. The rate constant was calculated from the slope of the straight line. The calculated reaction rate constant (k) was 8.75×10^{-4} , 1.04×10^{-3} , 1.62×10^{-3} and $3.37 \times 10^{-3} \text{ min}^{-1}$ for the Bi_2MoO_6 , 2.5 wt% $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$, 5.0 wt% $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ and 10.0 wt% $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ samples, respectively. Thus, the 10.0 wt% $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ sample has the best activity which leads to the highest RhB degradation rate.

The photocatalytic property of the nanocomposites is closely related to their corresponding band structures. The conduction band potential (V_{CB}) and valence band potential (V_{VB}) of Bi_2MoO_6 reported in literature is -0.32 V and $+2.71 \text{ V}$ w.r.t. NHE,^{(16), (17)} and V_{CB} and V_{VB} of Ag_3VO_4 is $+0.04 \text{ V}$ and $+2.24 \text{ V}$,⁽⁸⁾ respectively. The overall band structure of $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ system is shown in Fig. 4(d). During visible irradiation, the photogenerated electron-hole pairs formed in both Bi_2MoO_6 and Ag_3VO_4 components. Since the V_{CB} of Bi_2MoO_6 is more negative than that of Ag_3VO_4 , the photoelectrons in the CB of Bi_2MoO_6 nanoplates were transferred to Ag_3VO_4 nanoparticles.

The V_{VB} of Bi_2MoO_6 is more positive than that of Ag_3VO_4 . Thus, the recombination of electron-hole in Bi_2MoO_6 was inhibited because electron and hole of Bi_2MoO_6 were transferred to Ag_3VO_4 due to the difference their V_{CB} and V_{VB} . The electrons in the CB of Ag_3VO_4 were scavenged by oxygen to generate H_2O_2 ($\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$, $E^\circ = +0.682 \text{ V}$).⁽⁸⁾ Subsequently, the as-produced H_2O_2 combined with the trapped electron to form $\cdot\text{OH}$ ($\text{H}_2\text{O}_2 + \text{e}^- \rightarrow \text{OH}^- + \cdot\text{OH}$). The V_{VB} of Ag_3VO_4 is lower than the standard redox potential of $\cdot\text{OH}/\text{H}_2\text{O}$ ($+2.38 \text{ V}$ w.r.t. NHE).^{(2), (18)} Thus, it is unlikely to transform H_2O into hydroxyl radicals. These hydroxyl radicals have been recognized as the major reactive species for the photocatalytic degradation of organic pollutants such as RhB dye.

4. Conclusions

In summary, heterostructure $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanocomposites were successfully synthesized by a sonochemical method. The experimental results showed the presence orthorhombic Ag_3VO_4 nanoparticles with $< 10 \text{ nm}$ supported on the orthorhombic Bi_2MoO_6 nanoplates. The heterostructure $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanocomposites exhibit remarkable photocatalytic activities for the degradation of RhB dye under visible white light. Hence, $\text{Ag}_3\text{VO}_4/\text{Bi}_2\text{MoO}_6$ nanocomposites are the promising photocatalysts for wastewater treatment.

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