Research Article

Synthesis and Characterization of Graphene Oxide-Modified Bi$_2$WO$_6$ and Its Use as Photocatalyst

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A Bi$_2$WO$_6$ photocatalyst modified with graphene was synthesized in a two-step template-free hydrothermal process. The prepared samples were characterized to explore their properties. The photocatalytic activities of the prepared samples were investigated by degrading dye model, Rhodamine B (RhB), under visible light irradiation. This showed that the modified Bi$_2$WO$_6$ photocatalyst with 1.2 wt% of graphene greatly improved photocatalytic activity during the degradation of dye pollutants, compared to pure Bi$_2$WO$_6$. The enhancement can be interpreted as the integrated effects of ultrahigh charge carriers’ mobility and high adsorption of RhB on graphene. Additionally, effects including catalysts dosage amount, pH of RhB solution, and temperature of reactor on the photocatalytically degrading RhB were also studied and discussed.

1. Introduction

The rapid developments in the field of nanotechnology in the 21st century have novel avenues for the study of semiconductor photocatalytic technology, especially relating to environmental and energy issues. Heterogeneous photocatalytic reaction process happens under room temperature [1–3]. Nanosemiconductor oxide acts as the carrier. This will be an ideal, broad prospect for environmental pollution control based on visible light induced irradiation for the unique properties of nanometer photocatalytic technology.

Titanium dioxide (TiO$_2$) nanoparticles are widely used in environmental pollution control, construction of solar cells, self-cleaning of glass or ceramic tiles, elimination of malignant bacteria, and other fields [4, 5]. However, TiO$_2$ has a wide band gap, at 3.2 eV; it can only absorb ultraviolet light with wavelengths of 387.5 nm or less. Currently, this is the major obstacle preventing the application of TiO$_2$ in the catalytic degradation of pollutants.

Recently, bismuth tungstate (Bi$_2$WO$_6$) has been studied for its photocatalytic properties. Its efficiency at degrading organic pollutants, chemical stability, low toxicity, reusability, and low cost make it an important discovery in the search for the optimal photocatalyst [6–9]. However, the compound has some limitations including photoresponse region and the efficiency for separating electron-hole pairs. For improving photocatalytic activity, some approaches have been investigated. Firstly, surface area of Bi$_2$WO$_6$ is increased by a different synthesis method [10]. Secondly, photoresponse region of Bi$_2$WO$_6$ is increased using doping ions, transition metals, or other semiconductors [11–13]. Thirdly, photoinduced electrons are migrated to restrict the recombination of photogenerated electrons and holes [14]. Together, these three approaches will enhance Bi$_2$WO$_6$’s response to visible light, resulting in greatly improving visible light photocatalytic activity.

Graphene is one of the most hotly researched nanomaterials to date; it bears a great potential to improve the electrical property, mechanical property, thermal property, and gas barrier property of polymer nanocomposites. Graphene is a single sheet structure composed of carbon atoms. It consists of a hexagonal honeycomb lattice formed by sp$^2$ hybrid orbitals carbon atoms [15]. Recently, graphene has been widely applied in the area of photocatalysis, owing to its ultrahigh charge carriers mobility and high adsorption property to organic molecules with benzene ring structure. Composites including TiO$_2$, [16], ZnO [17], and BiVO$_4$ [18] modified by graphene were reported with enhanced photocatalytic activities in degrading organic pollutants.
In this work, we reported the graphene modified Bi₂WO₆ which was prepared by the hydrothermal method. The photocatalytic activity was tested by degrading a dye organic model, Rhodamine B (RhB), under visible light irradiation. Properties of the prepared samples were characterized, and effects of parameters of photocatalytic reacting systems on removal efficiencies of RhB were also studied and discussed.

2. Experimental

2.1. Preparation of Bi₂WO₆. All reagents were purchased from Fisher Scientific Company in analytical purity. Bi₂WO₆ in this work was prepared by the hydrothermal method. Typically, 0.33 g (Na₃WO₄·2H₂O) was dissolved in 20 mL distilled deionized water to make an aqueous sodium tungstate solution. This mixture was designated “solution a.” And 0.98 g of Bi(NO₃)₃·5H₂O was mixed with 40 mL acetic acid and magnetically stirred for 10 min until it is completely dissolved. This mixture is designated “solution b.” “Solution a” was added dropwise to “solution b” and stirred magnetically for 30 min. Concentrated hydrochloric acid solution was used to adjust the resultant suspension to pH 1. The suspension was then transferred into a 100 mL Teflon-lined stainless-steel autoclave (Parr Instrument Company). The autoclave was filled to 60% capacity (by volume). The autoclave was heated in an electric oven at 180°C for 20 hours and then gradually cooled down to room temperature. The resulting sample was firstly filtered by filter paper, washed twice with distilled deionized water, and dried at 60°C overnight. The dry residue was ground for 5 min to produce a white powder (precursor Bi₂WO₆).

2.2. Preparation of Graphene Modified Bi₂WO₆. The prepared Bi₂WO₆ with amount of 1 g was dispersed into 70 mL distilled deionized water and sonicated for 30 min. Then, 1 mL graphene oxide solution (Aldrich Chemistry, 4 mg/mL, dispersion in H₂O) was added to the Bi₂WO₆ suspension and magnetically stirred for two hours. To reduce the GO in the composite, the mixture was transferred to a Teflon-lined stainless-steel autoclave at 70% (the autoclave was filled to 70% capacity by volume) and heated in an electric oven at 140°C for 6 hours and then gradually cooled down to room temperature. The resulting sample was centrifuged for 15 min, the supernatant was discarded, and the solid precipitate was collected and dried overnight. The dry residue was ground for 5 min with a mortar and pestle to produce a grey powder which is 0.4% graphene-Bi₂WO₆ (0.4% G-BWO) by weight. A similar procedure was repeated to obtain G-BWO samples with different mass percentages of graphene. For 0.8% (g/g), use 2 mL GO dispersion solution. For 1.2% (g/g), use 3 mL GO dispersion solution. For 1.6% (g/g), use 4 mL GO dispersion solution.

2.3. Characterization. The crystal structures and the purity of the samples were characterized by X-ray diffraction (XRD) with a Cu-Kα radiation diffractometer recording with a 2θ scope ranging from 10 to 80°. Scanning electron microscopy (SEM) was used to take images of the prepared Bi₂WO₆ samples employing an accelerating voltage of 5 kV or 20 kV. Scanning transmission electron microscopy (STEM) was used to take images of the prepared GO-Bi₂WO₆ samples as graphene is too thin to be observed via SEM. The UV-Vis diffusion reflectance spectrum of the samples was analyzed using a UV-Vis spectrophotometer (Thermo Evolution 300) equipped with an accessory for analyzing powder samples.

2.4. Photocatalytic Activity Tests. The photocatalytic activity of each sample was evaluated by their ability to degrade the model pollutant, Rhodamine B (RhB). A 300-watt tungsten halide lamp (Ushio, wavelength mainly in the range of 310~800 nm) was used to simulate sunlight, and a filter (Kenko Zeta, transmittance > 90%) was used to cut off any radiation below 410 nm to ensure that the photocatalysis was proceeding under visible light irradiation. The temperature of the reaction vessel was controlled using a recirculating water jacket set to 20°C to avoid the effects of thermal catalytic reaction. Given amounts of GO-Bi₂WO₆ photocatalysts were added to a 500 mL beaker containing 200 mL Rhodamine B aqueous solution with concentration of 10 ppm. The pH value of the mixture was adjusted using sodium hydroxide or hydrochloric acid solution. Before illumination, the slurry was magnetically stirred in total darkness for 30 min to achieve adsorption/desorption equilibrium [19]. Aliquots were drawn every 10 min for 2 h (at each time point, the temperature of the bath was also recorded) and centrifuged at 12,000 rpm for 3 min. The absorbance of the liquid in the upper phase was determined using a Genyss UV-Vis spectrophotometer. Dark control was done to exclude the effect of adsorption and light control was done to control for the effect of dye photolysis. A calibration curve was created in a separate experiment to determine the relationship between absorbance intensity at \( \lambda_{\text{max}} = 552 \text{ nm} \) and concentration of RhB. Reusability of the prepared sample was also assessed by separating the photocatalysts from the suspension following a single run, after which they were mixed with fresh dye water to start another run. This was repeated for three runs.

3. Results and Discussions

3.1. XRD Analysis. XRD patterns of pure Bi₂WO₆ and G-BWO composites were shown in Figure 1. In the patterns of pure Bi₂WO₆, all peaks were indexed to characteristic peaks of Bi₂WO₆ (PDF Card number 01-075-5628) [20]. This indicates that the obtained Bi₂WO₆ had a good degree of crystallinity and was expected to have good catalytic activity. Modification of this material by graphene oxide with different contents (0.4 wt%~1.6 wt%) did not produce any changes in the peak positions or shapes, compared to the patterns of the pure Bi₂WO₆. The main reason why graphene oxide has such a small impact on Bi₂WO₆ is that the crystallinity degree of graphene oxide is not as good as most crystals [21]. XRD peaks belonging to amorphous-type crystals have low intensities, and such a small amount (0.4 wt%~1.6 wt%) of modification is not sufficient to change the XRD diffraction peaks positions or peak shapes of Bi₂WO₆. From the XRD data, it was concluded that graphene modification on pure
3.2. Morphologies. Morphologies of the prepared samples were observed by SEM and STEM. For pure Bi$_2$WO$_6$ (Figure 2(a)), it is composed of regular 2-dimensional nanosheets with size of 100–300 nm stacked together. After modification by graphene, the morphology of G-BWO composite was shown in Figure 2(b). It can be found that there was negligible influence of G on Bi$_2$WO$_6$, resulting from the fact that G was too thin to be observed [22]. Furthermore, the STEM images of G-BWO are shown in Figures 2(c) and 2(d). Bi$_2$WO$_6$ can be found in the form of nanoplates; comparatively, graphene shows typical crumpled and stacking layered structure. Bi$_2$WO$_6$ was covered well by the graphene.

3.3. Diffuse Reflectance Spectra (DRS). The optical properties of GO, pure Bi$_2$WO$_6$, and 1.2% G-BWO composite were evaluated by UV-Vis diffuse reflectance spectroscopy, shown in Figure 3. Pure Bi$_2$WO$_6$ exhibited excellent photoabsorption properties in the UV-visible light spectrum with a wavelength lower than 450 nm. A steep decrease in the spectrum of pure Bi$_2$WO$_6$ was observed, indicating that the absorption in the visible light region resulted from a band gap transition as opposed to a transition from the impurity level [23]. Specifically, electrons on the valence band (hybrid orbital of O 2p and Bi 6s) were activated by photon energy and jumped to the conduction band (W 5d orbital with a small contribution from Bi 6p orbital). The band gap value can be calculated as about 2.75 eV. By introducing graphene on the surface of Bi$_2$WO$_6$, there was a similar absorption edge with an intense transition from the UV to visible region, indicating that the graphene was not incorporated into the lattice of Bi$_2$WO$_6$ and just got adsorbed on its surface. Meanwhile, the absorbance intensity in the range of 450–700 nm was enhanced, which is helpful for the composite to absorb more incident light.

3.4. Photocatalytic Activity Tests

3.4.1. Effect of the Quantity of Graphene. Aiming at eliminating the effect of adsorption on the RhB removal efficiency, before each photocatalytic process, the adsorption-desorption equilibria between RhB and the photocatalysts were first obtained. In Figure 4(a), it is indicated that 30 min is enough to reach equilibrium. And RhB can be more easily adsorbed by GO (RhB removal efficiency ∼85%) than by Bi$_2$WO$_6$ (RhB removal efficiency ∼3%). The adsorption capacity was enhanced when GO was introduced on Bi$_2$WO$_6$. The performances of the prepared samples, including pure Bi$_2$WO$_6$ and Bi$_2$WO$_6$ modified by graphene with different quantity, were investigated with regard to the degradation of RhB under visible light irradiation, the results of which were illustrated in Figure 4(b). Additionally, one control experiment was conducted: no more than 2% of RhB was decomposed by photolysis without photocatalyst. This suggested that the negligible influence of photolysis can be ignored. In the presence of pure Bi$_2$WO$_6$, 58% of RhB was removed over 90 min under visible light irradiation. By introducing graphene on the surface of Bi$_2$WO$_6$, the performance of photocatalytically degrading RhB was greatly enhanced. Specifically, with improving the amount of graphene from 0.4% to 1.2% in the G-BWO composite, the removal efficiencies of RhB were significantly improved from 68% to 98% over 90 min. And further improving the amount of graphene reduced the photocatalytic activity, with only 70% of RhB being removed in 90 min. This suggests that graphene with an amount of 1.2% in the G-BWO composite performs the best in removing organic pollutants in wastewater under visible light irradiation.

3.4.2. Effect of Photocatalysts Dosage. The effect of photocatalysts (1.2% G-BWO) composite dosage on the photocatalytic degradation of RhB was studied and shown in Figure 5. The dosage amount was varied from 0.5 g/L to 6 g/L. All the tests were tested at pH 7 at 20°C. It can be concluded that, with the increase of catalyst dosage from 0.5 to 4 g/L, the removal efficiencies were greatly improved. And further increase of the catalysts dosage quantity from 4 to 6 g/L will slightly decrease the efficiency of the removal of RhB. These phenomena, maybe because of the increase in the amount of catalysts dosage, would increase the reactive sites that can correspondingly produce more reactive oxidative species. However, too much catalysts dispersed in the system will possibly increase light scattering and decrease light penetration [24], resulting in the reduction of removal efficiency of RhB in a system with excessive photocatalysts.

3.4.3. Effect of pH of Initial RhB Solution. Considering that the pH of wastewater is possibly different, its effect on the photocatalytically degrading RhB in the presence of G-BWO under visible light irradiation was explored, the results of which were shown in Figure 6. It has been reported that, with the increase of the pH of RhB solution, it may reduce the adsorption of RhB on the photocatalyst [25]. This resulted in the improvement of removal efficiencies when pH of the RhB solution increased from 4 to 10. However, when pH of

![Figure 1: XRD patterns of pure Bi$_2$WO$_6$ and G-BWO composites.](image-url)
Figure 2: SEM images of (a) pure Bi$_2$WO$_6$ and (b) 1.2% G-BWO composite and STEM images of 1.2% G-BWO composite in low (c) and high (d) magnification.

Figure 3: UV-Vis diffuse reflectance spectra of GO, pure Bi$_2$WO$_6$, and 1.2% G-BWO composite.

the RhB solution was equal to 3, the photocatalytic activity was worse than that when pH of the RhB solution was equal to 4. This may be attributed to Bi$_2$WO$_6$ being unstable and transforming into H$_2$WO$_4$ and Bi$_2$O$_3$ in the acidic solution [25, 26]. And the transformation of Bi$_2$WO$_6$ damages the G-BWO structure and eventually reduces the photocatalytic activity.

3.4.4. Effect of Temperature. Temperature of the photocatalytic reacting system was also varied from 0 to 80°C to explore its effect on the photocatalytic performances of the prepared samples under visible light irradiation, which were shown in Figure 7. When the temperature of the reacting system is in the range of 20–60°C, the photocatalytic performances in degrading RhB were similar, and only slight increases were found with the increase in temperature. However, when the temperature was fixed at 0°C, the photocatalytic activity was significantly reduced. This might be because the mass transfer of pollutants to the surface of photocatalysts was decreased and the generation rate of oxidative species was also reduced. When the temperature was as high as 80°C, the photocatalytic activity was greatly decreased. This might be resulting from the notion that high temperature favors the recombination of charge carriers and desorption of adsorbed organics on the photocatalysts. The results can be regarded as evidence of temperature controller needed for solar devices.

3.4.5. Reusability. The reusability of the prepared sample was assessed by recycling 1.2% G-BWO composite three times,
Figure 4: (a) Adsorption capacity of RhB on pure Bi$_2$WO$_6$, 1.2% G-BWO, and GO. (b) Degradation curves of RhB in the presence of different prepared samples under visible light irradiation (catalyst dosage amount: 1 g/L; $c_0 = 10$ ppm; $T = 20^\circ$C).

Figure 5: Removal efficiencies of RhB in the presence of 1.2% G-BWO with different catalysts dosage amount under visible light irradiation ($c_0 = 10$ ppm; pH 7; $T = 20^\circ$C).

Figure 6: Removal efficiencies of RhB with different pH of initial solution in the presence of 1.2% G-BWO under visible light irradiation (catalyst dosage: 1 g/L; $c_0 = 10$ ppm; $T = 20^\circ$C).

and the profiles of RhB concentrations were illustrated in Figure 8. The removal efficiency of RhB was 98% in the first run and 94.5% in the third run over 90 min under visible light irradiation. The slight decrease can be attributed to the loss of photocatalysts between two runs and some refractory intermediates adsorbed on their surface which are difficult to be destroyed [27]. Despite this slight reduction in removal efficiency, the stability of the reused G-BWO photocatalysts after degradation of RhB is still significant.
Figure 7: Removal efficiencies of RhB in the presence of 1.2% G-BWO at different temperature under visible light irradiation (catalyst dosage: 1 g/L; \(c_0 = 10\) ppm; pH 7).

Figure 8: Reusability test by recycling 1.2% G-BWO composite three times.

3.5. Photocatalytic Mechanism. In this investigation, the photocatalytic activity of Bi

\(2\)WO

\(6\) was significantly improved by introducing graphene on its surface. The possible reasons can be attributed to the presence of \(\pi\)-conjugation and 2D planar structures of graphene in the G-BWO composite which can adsorb organic molecules easily on its surface via strong \(\pi-\pi\) interactions (Figure 9) [28]. Additionally, graphene possesses high charge carrier mobility and can be regarded as an electrons acceptor. It can greatly decrease the recombination rate of photogenerated electrons and holes. So, the process can be described as follows: electrons on the valence band (VB) of Bi

\(2\)WO

\(6\) activated by incident photons jump to the conduction band (CB) with holes left on the VB; electrons can be either transferred to graphene or directly reacted with...
adsorbed $O_2$ to produce $O_2^-$; photogenerated holes accumulated on the VB can directly oxidize the adsorbed organic pollutants.

4. Conclusions

Graphene-$Bi_2WO_6$ composite photocatalysts with different graphene contents were successfully prepared using a template-free hydrothermal reaction. Photocatalytic activity was studied by degradation of Rhodamine B. The prepared samples showed excellent photocatalytic performance under visible light. The photocatalytic activity of G-BWO was greatly enhanced compared to that of pure $Bi_2WO_6$ because of the synergetic effects of high adsorption of RhB and electrons mobility on graphene. The activity of G-$Bi_2WO_6$ was also found to be a function of photocatalyst dosage, initial pH value of solution, and temperature.

Competing Interests

The authors declare that they have no competing interests.

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