Enhanced visible-light photocatalytic activity of plasmonic Ag and graphene co-modified Bi$_2$WO$_6$ nanosheets

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Photocatalytic degradation of pollutants in water has received much attention due to increasing environmental problems. In this study, a visible-light-driven plasmonic silver–graphene–bismuth tungsten (Ag–G–Bi$_2$WO$_6$) composite photocatalyst was prepared. Firstly, the graphite oxide (GO)–Bi$_2$WO$_6$ composite was prepared using a hydrothermal process, followed by a chemical reduction process using ethyl glycol (EG) as the reducing agent to form the G–Bi$_2$WO$_6$ composite. Then, Ag nanoparticles (NPs) were loaded onto the G–Bi$_2$WO$_6$ composite using a simple photochemical reduction process under xenon lamp irradiation to form the Ag–G–Bi$_2$WO$_6$ composite. The prepared samples were characterized using X-ray diffraction, transmission electron microscopy, nitrogen adsorption–desorption isotherm, UV-visible diffuse reflectance spectroscopy and electrochemical impedance spectroscopy. The photocatalytic activities of the prepared samples were evaluated by the photocatalytic degradation of rhodamine B (RhB) aqueous solution at ambient temperature under visible-light irradiation. The results showed that the photocatalytic activity of Bi$_2$WO$_6$ was significantly enhanced by the loading of Ag and graphene. The high photocatalytic activity is attributed predominantly to the hybridization of the surface plasmonic resonance (SPR) effect of Ag NPs and the specific electronics effect of graphene on the Bi$_2$WO$_6$ surface, thus enhancing the generation and separation of photogenerated charge carriers of Bi$_2$WO$_6$. Meanwhile, the excellent adsorption capacity of graphene also contributes to the enhancement of photocatalytic activity. This work highlights the design and preparation of new photocatalysts using plasmonic Ag and graphene as cocatalyst.

Introduction

Recently, photocatalytic degradation of harmful pollutants has become an increasingly important technology for water and air purification. It shows an extraordinary ability to decompose the pollutant into harmless substances directly from the contaminant source under sunlight irradiation.$^{1,2}$ Various efforts have been made in this field aiming for large-scale application of photocatalysts in daily human life. However, most photocatalysts, such as TiO$_2$ and ZnO, have broad bandgaps and absorb only small fractions of sunlight energy.$^{3,4}$ Besides that, photocatalytic activity is also limited due to the rapid recombination of photogenerated electron–hole pairs on the photocatalyst surface. In order to achieve practical use of photocatalysts, it is crucial to develop highly efficient photocatalysts for pollutant degradation under sunlight irradiation.

Bi$_2$WO$_6$ is believed to be one of the best photocatalysts due to its suitable characteristics, such as non-toxicity, low-cost, and relatively narrower bandgap ($E_g = 2.69$ eV).$^{5-7}$ Since the pioneering work on the Bi$_2$WO$_6$ photocatalyst was reported by Tang et al., extensive researches have been carried out to further enhance the photocatalytic activity of Bi$_2$WO$_6$. Generally, the photocatalytic activity of Bi$_2$WO$_6$ is intimately related to its morphology and the loaded cocatalyst.$^{8-12}$ In order to investigate the effect of morphology on the photocatalytic activity of Bi$_2$WO$_6$, several types of Bi$_2$WO$_6$ morphologies including nanoparticles,$^{13,14}$ nanosheets,$^{15,16}$ nanowires$^{17}$ and other complex morphologies$^{18,19}$ have been synthesized. Among them, Bi$_2$WO$_6$ nanosheets show great photocatalytic activity due to their high surface to volume ratio. On the other hand, the photocatalytic activity of Bi$_2$WO$_6$ is strongly dependent on the type and amount of cocatalyst. It is well-known that loading of cocatalysts, such as noble metals and carbon-based materials, can efficiently improve the charge-separation rate on the Bi$_2$WO$_6$ surface, and consequently facilitate photocatalytic activity.

Plasmonic metals such as gold (Au) and silver (Ag) are interesting cocatalyst materials for photocatalysts due to their unique SPR effect,$^{20-23}$ which can drastically enhance the light-absorption capability and charge-carrier generation rate of photocatalysts.$^{24,25}$ For example, Wang et al. reported
that Ag loading improved the visible light absorption of Ag$_2$O, and consequently led to higher photocatalytic activity. Meanwhile, Chen et al. showed that the extra electron magnetic field arising from plasmonic Au greatly accelerated the generation of electron–hole pair on the surface of the Au–TiO$_2$ composite.

Graphene (G), a two-dimensional (2D) carbon based material, is widely used as catalyst support material in photocatalytic field due to its high surface area, excellent conductivity of charge carriers at room temperature (200 000 cm$^2$ V$^{-1}$ s$^{-1}$), high thermal conductivity ($\sim 5000$ W m$^{-1}$ K$^{-1}$) and nanoscale thickness characteristics. For example, Gao et al. demonstrated enhancement of the electron–hole separation efficiency of Bi$_2$WO$_6$ by the loading of graphene as cocatalyst. Furthermore, graphene nanosheets can act as an adsorption centre in a composite photocatalyst due to their large $\pi$-conjugation system and 2D planar structure, which make dye molecules adsorb easily onto their surface via strong $\pi$–$\pi$ interactions between G and RhB. For example, Liu et al. demonstrated that graphene as a capturer with excellent adsorption ability in the system would largely improve the photoactivity of photocatalysts.

To the best of our knowledge, limited work has been done on the combined effects of plasmonic Ag and graphene on the photocatalytic performance of photocatalyst materials. Herein, we report the effects of both plasmonic Ag and graphene on the photocatalytic activity of Bi$_2$WO$_6$ nanosheets for photocatalytic degradation of the RhB pollutant. Highly efficient degradation of the pollutant in water was achieved in the presence of the prepared Ag–G–Bi$_2$WO$_6$ nanocomposite photocatalysts. Finally, the performance of the Ag–G–Bi$_2$WO$_6$ was compared with Bi$_2$WO$_6$, Ag–Bi$_2$WO$_6$ and G–Bi$_2$WO$_6$, showing that the photocatalytic activity of the Ag–G–Bi$_2$WO$_6$ was higher than that of the other three materials.

**Experimental section**

**Materials**

All reactants were of analytical grade and were purchased from Shanghai Chemical Reagent Factory of China without further purification. Deionized (DI) water was used in all experiments. Graphite oxide (GO) was synthesized from natural graphite powder (> 99.8%) by a modified Hummers method. In detail, 3 g of graphite was added into a mixture of 15 mL of concentrated H$_2$SO$_4$, 2.5 g of K$_2$S$_2$O$_8$, and 2.5 g of P$_2$O$_5$. The solution was heated to 80 $^\circ$C and kept stirring for 8 h. After that, the mixture was diluted by 500 mL of DI water. The resulting product was filtered and dried. Then, the products were reoxidized by Hummers and Offeman method to obtain GO.

**Preparation of the G–Bi$_2$WO$_6$ composite**

The G–Bi$_2$WO$_6$ composite was prepared using a hydrothermal method. Typically, 0.035 g of the above prepared GO was dispersed in 20 mL of DI water and sonicated for 1 h. Simultaneously, 0.97 g of Bi(NO$_3$)$_3$ was added into 30 mL of nitric acid aqueous solution (4 mol L$^{-1}$) under vigorous stirring at ambient temperature for 15 min. Then, the above two solutions were mixed together under stirring for 1 h. Afterwards, 30 mL of Na$_2$WO$_4$ aqueous solution (1 mmol) was added into the mixture and was stirred continuously for 2 h. The obtained white brownish solution was transferred into a 100 mL Teflon-lined autoclave and held at 180 $^\circ$C for 20 h. After the hydrothermal reaction, the precipitate was collected by centrifuging, washed with DI water three times, and then dried in an oven at 80 $^\circ$C for 6 h. To further reduce GO in the composite and prepare the G–Bi$_2$WO$_6$ sample, 0.5 g of the as-prepared composite was mixed with 50 mL of EG by sonication for 30 min. The solution was then heated and was continuously stirred at 140 $^\circ$C for 2 h. After being cooled to room temperature, the obtained precipitate was washed with ethanol several times and dried at 80 $^\circ$C for 6 h.

**Preparation of the Ag–G–Bi$_2$WO$_6$ composite**

The Ag–G–Bi$_2$WO$_6$ composite was prepared using a photochemical reduction deposition method. Typically, the obtained G–Bi$_2$WO$_6$ composite samples were dispersed into 50 mL of DI water with constant stirring. A certain amount of AgNO$_3$ aqueous solution was added into the system to load 5 wt% Ag onto the surface of the G–Bi$_2$WO$_6$ composite. Then, the system was irradiated with a 350 W xenon lamp for 1 h to reduce Ag$^+$ ions to Ag$^0$ species on the G–Bi$_2$WO$_6$ surface. The mixture was filtered, washed and then dried at 80 $^\circ$C for 3 h, resulting in a nanocomposite of Ag–G–Bi$_2$WO$_6$.

**Characterization**

X-ray diffraction (XRD) patterns were recorded using X-ray diffractometer (type HZG41BPC) using a monochromatic Cu K$\alpha$ radiation source ($\lambda = 0.15418$ nm) at a scan rate of 0.05° 20 s$^{-1}$ to determine the crystallite phase of the prepared samples. The accelerating voltage and the applied current were 40 kV and 80 mA, respectively. Transmission electron microscopy (TEM) images were obtained on a JEM-2100F electron microscope (JEOL, Japan), using a 200 kV accelerating voltage. UV-vis diffuse reflectance spectra of the samples were measured using a UV-vis spectrophotometer (UV2550, Shimadzu, Japan). BaSO$_4$ was used as a reflectance standard. Raman analysis was carried out on a micro-Raman spectrometer (Renishaw InVia) in the backscattering geometry of a 514.5 nm Ar$^+$ laser as an excitation source. X-ray photoelectron spectroscopy (XPS) studies were conducted with an ultrahigh vacuum VG EXCALAB 210 electron spectrometer using Mg K$\alpha$ (1253.6 eV) as the radiation source. The Brunauer–Emmett–Teller (BET) surface area ($S_{BET}$) of the samples was measured using an ASAP 2020 nitrogen adsorption apparatus (Micromeritics Instruments, USA). Prior to the nitrogen adsorption measurements, all the samples were subjected to a degassing treatment at 120 $^\circ$C for 12 h. Adsorption data in the relative pressure ($P/P_0$) range of 0.05–0.3 were used to determine $S_{BET}$ using the multi-point BET method. The Barret–Joyner–Halender (BJH) method was used to determine the pore size distribution of the samples by assuming a cylindrical pore modal. The nitrogen adsorption volume at the relative pressure ($P/P_0$) of 0.994 was used to determine the pore volume and average pore size.
Electrochemical measurement and photocatalytic activity

In order to investigate the electron transportation properties of the samples, the electrochemical impedance spectroscopy (EIS) test was carried out at the open circuit potential. An electrochemical analyzer (CHI660C instruments, CHI, China) in a standard three-electrode system was used to perform the electrochemical measurements. The photocatalyst sample was coated onto a 2 cm × 1.5 cm fluorine-tin oxide (FTO) glass electrode. The weight and thickness of the sample on the FTO were fixed at ca. 10 mg and 15 μm, respectively. Then, the FTO was sintered at 400 °C for 1 h. The sample coated FTO, Pt wire and Ag/AgCl were used as the working electrode, counter electrode, and reference electrode in the electrochemical analyzer system, respectively. Na2SO4 aqueous solution (1 M) was used as the electrolyte in this system.

Photocatalytic activity of the samples was evaluated by photocatalytic degradation of RhB aqueous solution under visible-light irradiation. In order to exclude the effects of adsorption on the reduction of RhB concentration, 50 mg of the prepared sample was first saturated with 20 mL of RhB solution (5 × 10^{-5} M) and kept under dark conditions for 4 h. After adsorption equilibrium, the saturated sample was separated from the solution. Then, the saturated sample was dispersed again in 20 mL of RhB solution (1 × 10^{-5} M) in a culture dish with a diameter of 95 mm. The mixed solution was kept under dark conditions for 2 h to further reach the adsorption–desorption equilibrium between photocatalysts and RhB molecules. Finally, a 350 W xenon lamp (Shanghai Lansheng Electronic Co., China) with a 420 nm cutoff filter was used as the visible-light source, which was located vertically at ca. 25 cm from the culture dish. At every 15 min interval, 3 mL of the RhB solution was sampled and its concentration was detected using a UV-vis spectrometer in the range of 300–700 nm. The photocatalytic activity test was then repeated with the phenol aqueous solution (5 × 10^{-5} M).

Results and discussion

Phase structure and morphology

XRD patterns were used to identify the crystallite phases of the Bi2WO6, Ag–Bi2WO6, G–Bi2WO6 and Ag–G–Bi2WO6 samples. Fig. 1 shows the comparison of the XRD patterns of the Bi2WO6, Ag–Bi2WO6, G–Bi2WO6 and Ag–G–Bi2WO6 samples. All diffraction peaks of these samples can be well indexed to orthorhombic Bi2WO6 (JCPDS Card No. 39-0256). When the Bi2WO6 sample was loaded with Ag NPs and graphene, there are no significant changes observed in the XRD pattern. The absence of an Ag diffraction peak is due to the low content of Ag NPs on the Bi2WO6 surface. On the other hand, there is no graphene peak observed. This is also due to graphene having low content (5 wt%) and weak diffraction peaks. Therefore, it is not surprising that the characteristic diffraction peaks of graphene and Ag were shielded by the strong diffraction peaks of Bi2WO6. Similarly, no significant changes are observed from the XRD pattern of Ag–G–Bi2WO6.

The morphology of the Ag–G–Bi2WO6 sample was investigated using TEM. As shown in Fig. 2a, the Ag–G–Bi2WO6 sample consists of many nanosheets, which seem to aggregate together due to their highly active surface. Bi2WO6 nanosheets with a size of several tens to several hundred nanometers are deposited on the surface of graphene. The graphene shows a typical crumpled
and stacking layered structure. Ag NPs with diameters in the range of 10 to 50 nm can also be observed in Fig. 2a. In addition, Bi$_2$WO$_6$ nanosheets were found to have close contact with the Ag NPs. The intimate contact between Ag and Bi$_2$WO$_6$ may significantly enhance the SPR effect on the Bi$_2$WO$_6$. The energy-dispersive X-ray (EDX) spectrum (Fig. 2b) further confirms that the sample contains bismuth, tungsten, oxygen and silver elements.

XPS analysis

The chemical composition and element chemical status of Ag–G–Bi$_2$WO$_6$ sample was characterized using XPS. Fig. 3 shows the C1s XPS spectra for GO and the Ag–G–Bi$_2$WO$_6$ composite. Four main peaks of C1s from GO at 284.5, 287.0, 287.9 and 288.9 eV are attributed to the C–C, C–O, C=O and O–C=O, respectively, indicating a high percentage of oxygen-containing functional groups in GO. In contrast, in the XPS spectrum of C1s from the Ag–G–Bi$_2$WO$_6$ composite, the peak for C–O, C=O and O–C=O almost vanishes and the peak for C–C remains almost the same. This indicates that most of the oxygen-containing functional groups are successfully removed. The XPS results clearly show that GO is successfully reduced to graphene in the Ag–G–Bi$_2$WO$_6$ composite. The reduction of GO to graphene will dramatically improve the electrical conductivity of the composite, and hence significantly enhance the photocatalytic activity.

Raman analysis

The presence of graphene and Ag in the Ag–G–Bi$_2$WO$_6$ sample was further confirmed using Raman analysis. Raman spectra of GO, Bi$_2$WO$_6$, Ag–Bi$_2$WO$_6$, G–Bi$_2$WO$_6$ and Ag–G–Bi$_2$WO$_6$ samples are shown in Fig. 4. For the Bi$_2$WO$_6$, the peaks in the range from 600 to 1000 cm$^{-1}$ in the Raman spectrum are assigned to the stretching of the W–O band. In detail, the peaks at 763 and 817 cm$^{-1}$ are attributed to antisymmetric and symmetric Ag modes of the O–W–O group terminus, respectively. The peak at 303 cm$^{-1}$ is assigned to the translation modes involving simultaneous motions of Bi$^{3+}$ and WO$_6^{6–}$. All of these Raman peaks show that the Bi$_2$WO$_6$ crystals in the composite are of orthorhombic phase structure, which is well consistent with the XRD results. For the Raman spectra of Ag–Bi$_2$WO$_6$, there is no significant shift of the Raman peak position in comparison with that of Bi$_2$WO$_6$. However, the intensity of Raman peaks of Ag–Bi$_2$WO$_6$ is greatly enhanced compared with that of the Bi$_2$WO$_6$. This phenomenon is attributed to the surface enhanced Raman scattering effect (SERS) of the Ag NPs. When the Ag NPs are irradiated by an Ar$^+$ laser, the electrons on the Ag NP surface could be excited to a high energy state. Then, a strong near field is produced by these high energy state electrons which leads to Raman intensity enhancement of Bi$_2$WO$_6$. In the Raman spectra of G–Bi$_2$WO$_6$, all the Raman peaks of Bi$_2$WO$_6$ can still be observed. The two additional Raman peaks at about 1352 cm$^{-1}$ (D band) and 1610 cm$^{-1}$ (G band) for graphitized structures are also observed in the Raman spectra of G–Bi$_2$WO$_6$ and shown in the inset of Fig. 4. The two peaks for G and D band of the composite are slightly blue-shifted compared with the D band (1348 cm$^{-1}$) and the G band (1599 cm$^{-1}$) of GO (inset), which is similar to the previous reports. Such a blue shift is possibly attributed to the charge transfer between Bi$_2$WO$_6$ and graphene nanosheets and provides evidence for the intimate contact between them. Furthermore, the D/G integral intensity ratio ($I_D/I_G$) for graphene in the G–Bi$_2$WO$_6$ sample (0.93) is higher than that for GO (0.86). This is because the amount of oxygen functional groups in G for G–Bi$_2$WO$_6$ sample decreased during the chemical reduction process, and the conjugated graphene networks were re-established. The deoxygenated graphene is beneficial for...
the enhancement of the electron–hole separation in the system. For the Raman spectrum of Ag–G–Bi₂WO₆, the SERS enhancement of Ag NPs can be also found. Moreover, graphene can also be observed in the Raman spectrum of Ag–G–Bi₂WO₆. The Raman spectra show that Ag NPs and graphene sheets are successfully loaded onto the Bi₂WO₆, which is consistent with the TEM results. The results prove that the Ag NPs and graphene are tightly connected with Bi₂WO₆ nanosheets.

**BET surface area and pore size distributions**

The BET surface area and the porous structure of the prepared samples were investigated using nitrogen adsorption–desorption measurement. It is found that the Ag–G–Bi₂WO₆ sample shows slightly higher \( S_{\text{BET}} \) (14.5 m² g⁻¹) than that of the Bi₂WO₆ sample (12.3 m² g⁻¹). This implies the presence of a larger surface area in the Ag–G–Bi₂WO₆ sample by the loading of graphene. However, the improvement of the specific surface area is not significant because the density of the Ag–G–Bi₂WO₆ sample increases due to the addition of Ag. Fig. 5 shows the comparison of nitrogen adsorption–desorption isotherms and the corresponding pore size distribution curves (inset) of the Bi₂WO₆ and Ag–G–Bi₂WO₆ samples. The Bi₂WO₆ sample has an adsorption–desorption isotherm of type IV according to the Brunauer–Deming–Deming–Teller (BDDT) classification. The high adsorption at relative pressure \( (P/P_0) \) approaching 1.0 indicates the coexistence of mesopores (2–50 nm) and macropores (>50 nm) in the sample. In addition, the shape of the hysteresis loop is of type H3, indicating the presence of slit-like pores that are associated with aggregates of platelike particles, consistent with their nanosheet-like morphology (see Fig. 2a). Similarly, the Ag–G–Bi₂WO₆ sample also shows higher adsorption at relative pressures \( (P/P_0) \) approaching 1.0. The pore size distribution curves indicate that the Bi₂WO₆ and Ag–G–Bi₂WO₆ samples have wide pore size distribution ranging from ca. 2 to 100 nm. Such special porous structures might be useful for photocatalytic activity because it supplies an efficient transport pathway for the photogenerated charge carriers to the interior void space.

**UV-vis spectroscopy measurements**

Optical properties of the prepared samples were tested using UV-vis diffuse reflectance spectroscopy. A comparison of the UV-vis diffuse reflectance spectra of the Bi₂WO₆, Ag–Bi₂WO₆, G–Bi₂WO₆ and Ag–G–Bi₂WO₆ samples is displayed in Fig. 6. The colors of the corresponding samples are shown in the inset of Fig. 6. Particularly, Ag nanoparticles make the color of the Bi₂WO₆ powders change from light yellow (a) to grey (b), and graphene makes the color of Bi₂WO₆ change into dark yellow (c), while Ag and graphene together make Bi₂WO₆ a color of dark grey (d). All the samples display similar absorption edge with an intense transition from the visible to UV region, implying that Ag and graphene do not incorporate into the lattice of Bi₂WO₆ or influence its bandgap width. For the Ag–Bi₂WO₆ and G–Bi₂WO₆ samples, the background absorption from 420–700 nm is enhanced due to the black body effect of Ag. This is helpful for the composite to absorb more incident light. Also, an additional peak is observed at around 500 nm in the UV-visible spectrum of the Ag–Bi₂WO₆ sample. This peak is attributed to the SPR effect of plasmonic Ag. Noticeably, the Ag–G–Bi₂WO₆ sample shows the highest absorption intensity in the visible-light range, and the SPR peak of Ag also still remains at ca. 500 nm. The increased peak intensity for the Ag–G–Bi₂WO₆ sample is due to the synergic effect of graphene and plasmonic Ag.

**Electrochemical characterization**

The photocatalytic activity of the semiconductor is intimately related to its electrical conductivity. In order to investigate the electrical conductivity of the prepared samples, the EIS test was carried out. The typical Nyquist plot of the EIS measurements is shown in Fig. 7. The Randles electrical equivalent-circuit model

![Fig. 5](image-url)  
**Fig. 5** Nitrogen adsorption–desorption isotherms and corresponding pore diameter distribution curves (inset) of the Bi₂WO₆ (a) and Ag–G–Bi₂WO₆ (b) samples.

![Fig. 6](image-url)  
**Fig. 6** UV-vis diffuses reflectance spectra of the Bi₂WO₆ (a), Ag–Bi₂WO₆ (b), G–Bi₂WO₆ (c), and Ag–G–Bi₂WO₆ (d) samples. Inset shows the colors of the corresponding samples.
is used to simulate the EIS test and is shown in the inset of Fig. 7, where CPE1 is ascribed to the interfacial resistance at the interface between the electrolyte and counter electrode, $R_p$ and $R_s$ are the electron-transfer resistance and the Ohmic resistance of the electrolyte solution, respectively. Generally, the electron-transfer properties of the samples are reflected by the arc of the EIS spectra, and the smaller arc indicates a faster rate of electron–hole separation and transfer. It can be clearly seen from Fig. 7 that the arc of spectrum becomes smaller when Ag or graphene is introduced into the Bi$_2$WO$_6$ sample, suggesting that loading of Ag or graphene onto Bi$_2$WO$_6$ reduces the electron transfer resistance of the Bi$_2$WO$_6$ sample and makes the charges transfer faster. The faster charge transfer rate is expected to improve photocatalytic degradation efficiency. Noticeably, the G–Bi$_2$WO$_6$ sample shows a smaller arc compared to the Ag–Bi$_2$WO$_6$ sample. This suggests that graphene has a better charge transfer rate than that of Ag NPs. Furthermore, the smallest arc is observed in the spectrum of the Ag–G–Bi$_2$WO$_6$ sample. This is not surprising because the hybridization of Ag and graphene on the Bi$_2$WO$_6$ synergizes both the plasmonic effect of Ag and excellent charge carrier conductivity of graphene, thus leading to ultrafast charge transfer and separation rate on the Ag–G–Bi$_2$WO$_6$ sample. Overall, the hybridization of Ag and graphene can function as an effective electron collector and ultrafast charge transporter in the Ag–G–Bi$_2$WO$_6$ nanocomposite and inhibit the charge recombination, which is beneficial for the enhancement of photocatalytic activity.

**Adsorption measurement**

In order to test the adsorption ability of the samples, the concentration changes of RhB solution in the presence of the Bi$_2$WO$_6$, Ag–Bi$_2$WO$_6$, G–Bi$_2$WO$_6$ and Ag–G–Bi$_2$WO$_6$ samples under dark conditions were recorded and shown in Fig. 8. It can be clearly seen that ca. 20% of RhB was adsorbed by the Bi$_2$WO$_6$ sample. Adsorption of RhB was slightly reduced to ca. 17% by the loading of Ag onto the Bi$_2$WO$_6$. This is because the loading of Ag may prohibit the surface of the Bi$_2$WO$_6$ to contact RhB molecules. On the other hand, the adsorption of RhB was enhanced in the presence of the G–Bi$_2$WO$_6$ and Ag–G–Bi$_2$WO$_6$ samples, reaching ca. 65% and 58%, respectively. Similar to the above results, loading of Ag slightly reduce the adsorption of G–Bi$_2$WO$_6$. Apparently, loading of graphene significantly enhanced the adsorption of the sample to the RhB molecule. This is because the π-conjugation and 2D planar structures of G in the G–Bi$_2$WO$_6$ and Ag–G–Bi$_2$WO$_6$ samples can make dye molecules easily adsorb on its surface via strong π–π interactions between G and the dye.

**Photocatalytic activity**

The photocatalytic activity of the prepared samples was evaluated by photocatalytic degradation of RhB aqueous solution. Fig. 9 displays the concentration changes of RhB aqueous solution in the presence of the Ag–G–Bi$_2$WO$_6$ sample under visible-light. During the photocatalytic degradation, the intensity of the main absorption peak of RhB at about 550 nm decreased gradually.
upon increasing the time, indicating the degradation of the RhB molecule in the solution. After 45 min of visible-light irradiation, the absorption peak of RhB solution has almost vanished. Accordingly, the color of the RhB solution becomes almost completely colorless from intense pink, as can be seen in the inset of Fig. 9. The results indicate that RhB is mostly degraded within 45 min by the Ag–G–Bi2WO6 photocatalyst.

To further investigate the effects of the hybridization of graphene and Ag on the enhancement of photocatalytic activity, a series of the RhB photocatalytic degradation experiments with the Bi2WO6, Ag–Bi2WO6, G–Bi2WO6 and Ag–G–Bi2WO6 as the photocatalysts were carried out and the comparison of photocatalytic activity of the samples is shown in Fig. 10. It can be seen that the Ag–G–Bi2WO6 sample exhibits the highest visible-light photocatalytic activity, with ca. 92% of RhB decolorized within 45 min. In contrast, ca. 82%, 80%, and 72% of RhB is decolorized by the G–Bi2WO6, Ag–Bi2WO6, and Bi2WO6 samples, respectively. The order of the photocatalytic activity of the samples is well consistent with the order of charge carrier conductivity of the above EIS results, viz. Ag–G–Bi2WO6 > G–Bi2WO6 > Ag–Bi2WO6 > Bi2WO6 (Fig. 7). This is not surprising because higher charge carrier mobility leads to faster electron–hole separation rate and thus higher photocatalytic activity of the Bi2WO6 photocatalyst.

Fig. 11 shows the comparison of the RhB degradation rate constants for Bi2WO6, Ag–Bi2WO6, G–Bi2WO6 and Ag–G–Bi2WO6 before and after being normalized with surface areas. It can be seen that the specific surface areas have no great influence on photocatalytic activity because the prepared samples have similar specific surface areas. Pure Bi2WO6 presents the lowest normalized apparent rate constant which is only ca. 0.018 (g m−2 min−1). Meanwhile, the RhB degradation rate constant normalized was enhanced in the presence of Ag–Bi2WO6 and G–Bi2WO6, reaching ca. 0.035 and 0.038 (g m−2 min−1), respectively. The results are in good agreement with EIS measurements, which show that loading of Ag and graphene on the Bi2WO6 significantly inhibits the recombination of photogenerated electron–hole pairs due to faster electron transfer rate. Apparently, the Ag–G–Bi2WO6 exhibits the highest apparent rate constant among all four samples, which is about three-fold higher than that of pure Bi2WO6. This is because the combination of Ag and G leads to higher separation rate of electron–hole pairs in the Ag–G–Bi2WO6 system.

In order to further evaluate the advantages of Ag–G–Bi2WO6 for decomposing the pollutant, the visible light photocatalytic degradation of phenol were also tested. Phenol is transparent in its aqueous solution; thus, it is more difficult to be degraded than other dye pollutants. Fig. 12 shows the comparison of visible-light photocatalytic degradation rates of phenol in the presence of Bi2WO6, Ag–Bi2WO6, G–Bi2WO6 and Ag–G–Bi2WO6. In the absence of Ag or graphene, Bi2WO6 exhibits a low photocatalytic degradation activity under visible light irradiation, which is about 5% in 90 min. In contrast, Ag–Bi2WO6 and G–Bi2WO6 show higher photocatalytic activity than Bi2WO6, which are 11% and 10%, respectively. The reduction of phenol concentration was further improved to 19% in 90 min when both Ag NPs and graphene were loaded onto the Bi2WO6 surface. This is because introduction of plasmonic metal Ag NPs and graphene on the Bi2WO6 efficiently enhances the charge separation of photogenerated electron–hole pairs and prolongs the light absorption range of Bi2WO6, resulting in higher visible light photocatalytic degradation activity.
Photocatalytic mechanism

In this investigation, a new strategy is proposed to improve the photocatalytic activity of Bi$_2$WO$_6$ by hybridizing with both plasmonic noble metal Ag and graphene. On the basis of the above-mentioned characterization and analysis, the enhancement of the photocatalytic activity of Ag–G–Bi$_2$WO$_6$ composite could be well explained. Fig. 13 shows the proposed mechanism for RhB adsorption on graphene. The RhB molecule has π-bonding from its benzene ring structure. On the other hand, G in the Ag–G–Bi$_2$WO$_6$ sample has a large π-conjugation and 2D planar structure, hence RhB molecules are easily adsorbed by graphene in the sample via π–π interactions between G and RhB, thus enhancing the photocatalytic activity of the sample. For example, it has been reported previously by Liu et al. that capturing dye molecules on the photocatalyst surface would increase the photocatalytic degradation rate of dyes. In addition, graphene with ultrahigh charge carrier mobility at room temperature, thus, can significantly enhance the transfer and separation of photogenerated electrons. This makes graphene an electron acceptor and electron transport “highway” in the composite photocatalytic system, which will suppress the recombination of photogenerated electron–hole pairs.

Furthermore, when Ag NPs are deposited on the Bi$_2$WO$_6$ nanosheets, Schottky barriers are formed due to the Fermi level equilibrium between Bi$_2$WO$_6$ and Ag. This unique metal–semiconductor interface allows only the movement of electrons from the semiconductor to metal particles, which will hinder electron transfer back across the Schottky barrier and prevent recombination of the photogenerated electron–hole pairs. Moreover, the plasmonic Ag NPs are very efficient at scattering and absorbing visible light. When the Ag NPs are excited by the visible light, the electrons on the metal surface undergo a collective oscillation, known as the SPR effect. The oscillation results in a peculiar enhancement of the electric near-field on the Ag NP surface and all around Ag NPs. As displayed in Fig. 14, the electrons are transferred from the valence band to the conduction band of the Bi$_2$WO$_6$ under the visible light irradiation. The electric near-field produced by the Ag NP SPR effect will enhance the separation of photogenerated electrons and holes on the Bi$_2$WO$_6$, thus, reducing their recombination.

Finally, the visible-light photocatalytic degradation mechanism of RhB in the presence of the Ag–G–Bi$_2$WO$_6$ sample can be explained. Firstly, graphene easily captures the RhB dye in the solution due to strong π–π interactions between G and RhB, thus RhB molecules can intimately contact the surface of...
the Ag–G–Bi$_2$WO$_6$ sample. Then, under the visible-light, the photogenerated electrons from the conduction band of Bi$_2$WO$_6$ tend to transfer to the graphene surface due to the excellent charge carrier conductivity of graphene, which facilitates the electron–hole separation on the Bi$_2$WO$_6$. Further, the electric near-field produced by the Ag NP SPR effect may significantly enhance energy intensity of electrons and consequently boost the separation of photoinduced electron–hole pairs and migration of the electron to the graphene or Ag NPs. Then, these transferred electrons are trapped by molecular oxygen on the graphene surface to produce superoxide anion radicals (*O$_2^−$), which is a strong oxidative species to degrade RhB molecules. On the other hand, hydroxyl radicals (*OH) is almost impossible to be produced by the photogenerated electron on the Bi$_2$WO$_6$. This is because the valence band position (+1.63 eV) of Bi$_2$WO$_6$ is higher than that of *OH/*OH’ (1.99 eV).

However, the RhB could be directly degraded by the strong oxidizing hole on the Bi$_2$WO$_6$. In short, the photocatalytic degradation of RhB by Bi$_2$WO$_6$ is primarily caused by superoxide radicals and photogenerated holes.

Conclusions

In summary, a visible-light-driven Ag–G–Bi$_2$WO$_6$ composite photocatalyst was prepared using a hydrothermal and photochemical reduction method. The photocatalytic activity of Bi$_2$WO$_6$ was significantly enhanced by loading of plasmonic Ag and 2D graphene for degradation of RhB. The enhanced photocatalytic activity is due to the combined effects including the surface plasmonic resonance and extra strong electron magnetic field of Ag NPs, and the excellent charge carrier conductivity and strong adsorption for RhB dye of graphene on the Bi$_2$WO$_6$ surface, thus improving the generation and separation of photogenerated charge carriers of the Bi$_2$WO$_6$. This work will provide new insight into the design and fabrication of new photocatalysts by using the surface plasmonic resonance effect of noble metal NPs and the excellent charge carrier conductivity of 2D graphene. The prepared Ag–G–Bi$_2$WO$_6$ composite should also find potential applications in catalysis, solar-cell, separation, and purification processes and so on.

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Notes and references