Synergetic Effect of Bi$_2$WO$_6$ Photocatalyst with C$_{60}$ and Enhanced Photoactivity under Visible Irradiation

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Fullerene (C$_{60}$)-modified Bi$_2$WO$_6$ photocatalyst is prepared by a simple absorbing process. The as-prepared samples show the high efficiency for the degradation of nonbiodegradable azo dyes methylene blue (MB) and rhodamine B (RhB) under visible light ($\lambda > 420$ nm) and simulated solar light ($\lambda > 290$ nm). After being modified by C$_{60}$, the photocatalytic activities of Bi$_2$WO$_6$ samples increase about 5.0 and 1.5 times for the degradation of MB and RhB under visible light irradiation, whereas 4.6 and 2.1 times under xenon lamp irradiation, respectively. The enhanced photocatalytic activity for C$_{60}$-modified Bi$_2$WO$_6$ comes from the high migration efficiency of photoinduced electrons on the interface of C$_{60}$ and Bi$_2$WO$_6$ which is produced by the interaction of Bi$_2$WO$_6$ and C$_{60}$ with the conjugative $\pi$-system. The optimum synergetic effect is found at a weight ratio of 1.25 wt % (C$_{60}$/Bi$_2$WO$_6$). The photocatalytic reaction process of C$_{60}$-modified Bi$_2$WO$_6$ is mainly governed by direct holes and O$_2^-$ oxidation.

Introduction

Dye pollutants have been a major source of environmental pollution because of their resistance to biodegradation (1). Many conventional methods such as flocculation, reverse osmosis, and activated carbon adsorption have been used to deal with wastewaters containing dyes (2). However, many drawbacks still exist in these methods because of the increasing number of refractory materials in wastewater effluents and difficulties in the complete removal of color and expensiveness. Recent research shows that heterogeneous photocatalytic oxidation technologies are promising methods (3–5). Up to date, the majority of research on photocatalytic oxidation technologies is focused on dye/TiO$_2$ system (6–8). However, photoefficiency of the system and mineralization degree of dye is limited because of the slower interfacial electron transfer. Therefore, it is urgent to develop highly efficient visible-light induced photocatalysts for dye photodegradation.

Recent results reveal that Bi$_2$WO$_6$ photocatalyst can decompose water under visible light irradiation (9, 10). Furthermore, nanosized Bi$_2$WO$_6$ performs as an excellent visible-light-driven photocatalyst for the destruction of dye pollutants with a high degree of mineralization (11, 12). Fullerences with the delocalized conjugated structures have gained extensive attentions for the interesting properties. One of the most remarkable properties in electron-transfer processes is that it can efficiently arouse a rapid photoinduced charge separation and a relatively slow charge recombination (13). Many works have focused on the photochemical solar cells by the combination of C$_{60}$ and nanoparticles, which can greatly increase the photoconversion of solar energy (14, 15). In general, the photocatalytic activity of the photocatalyst can be promoted by increasing the separation efficiency of photoinduced electron–hole pairs. Thus, the combination of photocatalysts and C$_{60}$ may be an ideal system to achieve an enhanced charge separation by photoinduced electron transfer. Concerning the high photocatalytic activity of nanosized Bi$_2$WO$_6$, it is expected that the visible photoactivity of Bi$_2$WO$_6$ for degradation of dye can be enhanced via synergetic effect of C$_{60}$ and Bi$_2$WO$_6$. In this work, C$_{60}$-modified Bi$_2$WO$_6$ photocatalyst is obtained by chemically adsorbing C$_{60}$ on the surface of Bi$_2$WO$_6$. The photodegradation results of dyes over C$_{60}$-modified Bi$_2$WO$_6$ under visible-light irradiation and solar (simulated by xenon lamp) show that the photocatalytic activity can be significantly enhanced. It is postulated that the enhanced photoactivity of C$_{60}$-modified Bi$_2$WO$_6$ catalyst results from high migration efficiency of photoinduced electron–hole pairs.

Experimental Section

Preparation of Photocatalysts. Bi$_2$WO$_6$ was synthesized by the hydrothermal method according to ref 11: the starting materials of Na$_2$WO$_4$ and Bi(NO$_3$)$_3$ were mixed together with the molar ratio of 1:2, deionized water (100 mL) was added, then white precipitates appeared immediately, and the mixed solution was ultrasonicated for 10 min to promote the precipitate reaction. The collected precipitate after washing several times was added into a 50 mL Teflon-lined autoclave and filled with deionized water up to 80% of the total volume. The autoclave was maintained at 180 °C for 20 h.

C$_{60}$-modified Bi$_2$WO$_6$ sample was prepared as follows: an appropriate amount of C$_{60}$ was added into toluene and sonicated for 30 min to make C$_{60}$ totally disperse. The as-prepared Bi$_2$WO$_6$ powder (1 g) was added into the above solution and stirred for 24 h. The solvent was evaporated at 80 °C for 10 h and opaque powder was obtained after drying. C$_{60}$-modified Bi$_2$WO$_6$ samples with other different mass ratio from 0.65 to 3.00% were prepared by following a similar procedure.

To investigate the transition of photogenerated electrons before and after C$_{60}$ modification, Bi$_2$WO$_6$ film was prepared as follows: 0.02 mol Diethylaminedipentaneacetic acid (H$_2$DTPA) and 7.5 mL concentrated ammonia water (ca.13.0 mol L$^{-1}$) were added in hot distilled water (200 mL). 0.005 mol Bi$_2$O$_3$ and 0.005 mol 5(NH$_4$)$_2$O–12H$_2$O powders were added afterward. The mixture was stirred and heated to promote the dissolution and reaction. After being slowly vaporized at 80 °C, transparent glass-like material was obtained. The as-prepared glass-like material was ground and redissolved in water to get the colorless transparent precursor solution with a concentration of 15 wt %, ITO (Indium Tin Oxide) glass substrates (3 cm × 2 cm) with a sheet resistance of 15 Ω were dipped into the complex precursor for 2 min and then were pulled out with a velocity...
of 3 cm·min⁻¹. After being dried, the sample was heated to 450 °C and calcined for 4 h in air flow. Bi₂WO₆ film was dipped in a certain amount of C₆₀ toluene solution for 20 h. The ITO glass covered with thin Bi₂WO₆ film and C₆₀ were used as photoanode and named ITO/Bi₂WO₆ and ITO/Bi₂WO₆/C₆₀, respectively.

Characterization. HRTEM (high-resolution transmission electron microscopy) images were obtained by JEM 2010F field emission transmission electron microscope with an accelerating voltage of 200 kV. UV–visible absorption spectra of the samples were recorded on a UV–vis spectrophotometer (Hitachi UV-3100) with an integrated sphere attachment in the range of 200–800 nm. BaSO₄ was used as the reflectance standard. The Brunauer–Emmett–Teller (BET) surface area measurements were performed by a Micromeritics ASAP 2010V5.02H surface area analyzer. The nitrogen adsorption and desorption isotherms were measured at 77 K after degassing the samples on a Sorptomatic 1900 Carlo Erba Instrument.

Photocatalytic and Photoelectrochemical Performance. The photocatalytic activities were evaluated for the degradation of RhB and MB solution under visible light and simulated solar irradiation. A 500 W xenon lamp (λ > 290 nm Institute of Electric Light Source, Beijing) with a 420 nm cutoff filter was used as light resource, and the average light intensity was 30 mW·cm⁻². 100 mg of the C₆₀-modified Bi₂WO₆ photocatalyst was dispersed in 1 × 10⁻³ mol·L⁻¹ RhB or MB solution (100 mL). Prior to the irradiation, the suspension was magnetically stirred in the dark for 30 min to reach an absorption–desorption equilibrium. At a given time interval, 3 mL aliquots were sampled and centrifuged to remove the particles. The degradation of RhB and MB were monitored by a Hitachi U-3010 UV–vis spectrophotometer. The concentration of RhB and reaction intermediates were measured by HPLC (high performance liquid chromatography) using an Intersil ODS-3C-18 inverted-phase column. All samples were detected by a UV–vis detector at 505 nm. The solution gradient was regulated by water and methanol (from 60 to 90% methanol over 25 min) with a flow rate of 1 mL·min⁻¹.

Photoelectrochemical measurements were carried out in a conventional three-electrode, single-compartment glass cell, fitted with a synthesized quartz window, using a potentiostat. The quartz electrolytic cell was filled with 0.5 M Na₂SO₄ and 10⁻² M MB solution (100 mL). The ITO/Bi₂WO₆/C₆₀ or ITO/Bi₂WO₆ electrodes served as the working electrode. The counter and the reference electrodes were platinum black wire and saturated calomel electrode (SCE), respectively. A 30 W germicidal lamp was used as the excitation light source. The incident light was irradiated onto electrodes from the front face through the quartz window and the electrolyte unless noted otherwise. The irradiated light intensity was 1 mW·cm⁻². The photoelectrochemical experiment was measured on electrochemical system (CHI-660B, China).

Results and Discussion

Structure and Optical Properties of C₆₀-modified Bi₂WO₆ Photocatalyst. Figure 1 shows the morphologies and lattice structure of Bi₂WO₆ and C₆₀-modified Bi₂WO₆. It was found that the lattice structure of Bi₂WO₆ was clear from the center to the boundary (Figure 1A), and there was no change of lattice structure of Bi₂WO₆ after C₆₀ adsorbed on the surface. However, the outer boundary of Bi₂WO₆ modified by C₆₀ was distinctly different. A coverture layer with noncrystal structure surrounded the surface of Bi₂WO₆ nanosheet. The thickness of the coverture layer was estimated to be about 1 nm, which was close to the diameter of C₆₀ molecular. Therefore, it can be estimated that the outer layer was C₆₀, which dispersed on the surface of Bi₂WO₆ with a monolayer structure. XRD (X-ray diffraction) patterns of Bi₂WO₆ sample showed no change when Bi₂WO₆ was modified by C₆₀, indicating the absorption of C₆₀ did not influence the lattice structure of Bi₂WO₆. No XRD diffraction peaks assigned to C₆₀ was observed because the C₆₀ layer was too thin.

The diffuse-reflection spectra (DRS) of Bi₂WO₆ and C₆₀-modified Bi₂WO₆ with different C₆₀/Bi₂WO₆ mass ratios are depicted in Figure 2. Bi₂WO₆ sample showed an absorption edge around 470 nm, which could be responsible for the visible-light induced photocatalytic activity. With the loading of C₆₀, the C₆₀/Bi₂WO₆ displayed the same absorption edge as Bi₂WO₆. However, the samples exhibited a greater light attenuation throughout the visible wavelengths consistent with the grayed color of the catalyst. It also could be found
FIGURE 4. Photocatalytic degradation of (A) MB and (B) RhB by C$_{60}$-modified Bi$_2$WO$_6$ and Bi$_2$WO$_6$ under visible light irradiation (Bi$_2$WO$_6$ sample before and after modified by C$_{60}$ are shown in Figure 3). The sample with 1.25% C$_{60}$ showed the highest activity, 80% MB can be photodegraded by Bi$_2$WO$_6$ under visible light in 2 h. All the modified Bi$_2$WO$_6$ samples exhibited higher photocatalytic activities than pure Bi$_2$WO$_6$. The sample with 1.25% C$_{60}$ showed the highest activity, 80% of MB can be photodegraded under the same condition. Results showed that the loading amount of C$_{60}$ had a great influence on the photocatalytic activity of the as-prepared photocatalyst. The influence of C$_{60}$ loading amounts upon the photodegradation rate of MB is shown in Figure 4A, the apparent reaction rate constant $k$ was 0.0037, 0.0099, 0.0069, 0.0033, and 0.0020 min$^{-1}$, respectively, for C$_{60}$/Bi$_2$WO$_6$ ratio of 0.65%, 1.25%, 2.0%, 3.0%, and Bi$_2$WO$_6$ samples. When the loading amount was below 1.25%, the photocatalytic activities increased with the increase of loading amount of C$_{60}$. The
decreased as the amount of C60 increased. The optimal loading amount of C60 on Bi2WO6 for increasing the photocatalytic activity was 1.25%. As mentioned in the result of DRS, C60 tended to aggregate on the surface of Bi2WO6 when the mass ratio of C60 above 1.25%, which resulted in the slower transmission of the photoinduced electrons. 1.25% C60 and Bi2WO6 mechanical mixture as a reference was prepared by merely stirring. Its photocatalytic activity was similar to that of Bi2WO6 and much lower compared with 1.25% C60-modified Bi2WO6 catalyst. The photocatalytic activity of Bi2WO6 modified by C60 was enhanced by about 4 times compared with that of Bi2WO6 sample. This result implied that the interaction between C60 and Bi2WO6 photocatalyst took an important role in the enhancement of photoactivity. The photocatalytic decomposition of RhB by 1.25% C60-modified Bi2WO6 and Bi2WO6 samples under visible light irradiation was also carried out (Figure 4B). C60-modified Bi2WO6 sample showed much higher photocatalytic activity for the decomposition of RhB than Bi2WO6. The apparent reaction rate constant k was 0.0454 and 0.0296 min\(^{-1}\) for C60-modified Bi2WO6 and Bi2WO6 samples, respectively. Therefore, it was a novel way to enhance the photocatalytic activity of Bi2WO6 by modifying with C60.

The temporal evolution of the spectral changes taking place during the photodegradation of RhB over Bi2WO6 were displayed (Figure 4B, inset). During the degradation, the absorption maximum of the degraded solution with irradiation time exhibited hypsochromic shifted to some extent with the cleavage of the conjugated structure (>12), while, the MB decomposition under visible irradiation mainly occurred via the destruction of the conjugated structure (Figure 4A, inset) (>19). The photodecomposition process of RhB under visible-light irradiation was demonstrated by HPLC. The typical HPLC chromatograms in the presence of Bi2WO6 and C60-modified Bi2WO6 were recorded by UV–visible detector. After 70 min, the concentration of RhB in C60-modified Bi2WO6 system (see Supporting Information Figure S2B) was much lower than that in Bi2WO6 system (see Supporting Information Figure S2A). The evidence further proved that the reaction rate of Bi2WO6 modified by C60 was faster. At the same time, no new intermediates or products formed, indicating the photocatalytic decomposition process for pollutants was similar with Bi2WO6 even after being modified by C60.

The photocatalytic performance of Bi2WO6 modified by C60 under simulated solar irradiation was also studied. In this work, xenon lamp was used to simulate the solar irradiation. The photocatalytic performances of C60-modified Bi2WO6 sample are shown in Figure 5. The apparent reaction rate constants k were 0.0175, 0.0038 min\(^{-1}\) of C60-modified Bi2WO6 and Bi2WO6 for the decomposition of MB, and 0.0504, 0.0244 min\(^{-1}\) for the decomposition of RhB. C60-modified Bi2WO6 sample can effectively decompose dyes under simulated solar condition, which was similar to the result under visible light irradiation. It was well-known that the photocatalytic activity was governed by various factors such as surface area, phase structure, interfacial charge transfer, and separation efficiency of photoinduced electrons and holes (>20). Results showed that the surface area and phase structure of Bi2WO6 almost remained the same before and after being modified by C60. It could be concluded that the difference of photocatalytic activity was not determined by the factor of surface area and phase structure. Therefore, the enhancement of photocatalytic activity may be attributed to the high separation efficiency of electron and hole pairs.

Interestingly, it is found that the enhancement degree of photocatalytic activity for the photodegradation of MB and RhB by 1.25% C60-modified Bi2WO6 under simulated solar irradiation is different. The photocatalytic activity increased much more for the degradation of MB than for the degradation of RhB. The difference in enhancement of photocatalytic activity may result from the difference in photocatalytic reaction mechanism. For the photodegradation of RhB, the photosensitization process mainly governed photocatalytic reaction process. RhB molecules absorbed the incident photon flux, and the photogenerated electrons transferred to the excited-state of the dye (>21). Then the photoelectrons of the excited-state were immediately injected into the conduction band (W 5d level) of Bi2WO6 (>12). Finally, the RhB absorbed on the surface of Bi2WO6 react with the active species generated on the surface. However, the electron cannot migrate from RhB to Bi2WO6 after being modified by monomolecular layer C60 for the incompatibility of energy level. The photosensitization process for RhB was inhibited; therefore, the photocatalytic activity was decreased. However, the existence of C60 can greatly promote the transfer of the photoinduced electron which resulted in the enhancement of the separation efficiency for electron and hole pairs. The above two competitive effects finally caused the photodecolorization activity for RhB to only be improved by 1.5 times. For the photocatalytic degradation of MB, direct photocatalytic reaction was the main process and no inhibition effect of photosensitization process could occur in the system (>22). Therefore, the promotion of electron transfer by modified C60 caused the drastic enhancement of photocatalytic activity (4.3 times). The photocatalytic reaction process was also studied by adding a scavenger of radicals and capture of holes. As shown in Figure 4, the addition of a scavenger of hydroxyl radicals (tert-butanol) only caused small change in the degradation rate of RhB, indicating that the free hydroxyl radicals was not the main active oxygen species in the photochemical process. On the contrary, the photocatalytic
The activity of Bi$_2$WO$_6$ after being modified by C$_{60}$ could be greatly inhibited by the addition of capture for holes (EDTA-Na). ESR (electron spin resonance) spin-trap technique (with DMPO) was employed to monitor the reactive oxygen species generated during the irradiation of the present system (see Supporting Information Figure S3). No DMPO-OH signals appeared when the RhB/Bi$_2$WO$_6$ and the RhB/C$_{60}$-modified Bi$_2$WO$_6$ suspension were irradiated by a Quanta-Ray Nd:YAG pulsed laser system ($\lambda = 532$ nm, 10 Hz) (Figure S3A). But the “OOH/O$_2^-$” adducts were observed for the RhB/C$_{60}$-modified Bi$_2$WO$_6$ system under this pulsed laser irradiation (Figure S3B). The radical scavenger technologies and kinetic studies by using ESR suggested that “OH radical oxidation reaction was not the dominant photioxidant pathway. Direct hole transfers and O$_2^-$ oxidation reaction mainly govern the photocatalytic process. The enhancement of photocatalytic activity could be attributed to the higher separation efficiency of electron–hole pairs caused by the rapid photoinduced charge separation and the inhibition of recombination for electron–hole pairs of C$_{60}$, resulting in the increasing of number of holes participated in the photooxidation process and enhancing of photocatalytic activity.

**Photocatalytic Mechanism.** As discussed above, the C$_{60}$-modified Bi$_2$WO$_6$ photocatalyst showed a high photocatalytic activity under both visible and simulated solar irradiation. The reason should be closely attributed to the interaction between Bi$_2$WO$_6$ and C$_{60}$ which increased the photogenerated electron mobility in Bi$_2$WO$_6$. In this work, C$_{60}$ molecule was mainly covered on the surface of Bi$_2$WO$_6$. C$_{60}$ acted as an electron shuttle that could effectively transfer the photoinduced electron (15). Accordingly, the photogenerated electrons in the modified Bi$_2$WO$_6$ photocatalyst could easily migrate from the inner region to the surface to take part in the surface reaction. Based on the above discussion, the schematic of photocatalytic mechanism was shown in Scheme 1.

The effect of C$_{60}$ modification on the recombination of e$^-$/h$^+$ produced by Bi$_2$WO$_6$ was also investigated. PL spectra were measured for Bi$_2$WO$_6$ nanoparticles and C$_{60}$-modified Bi$_2$WO$_6$ (see Supporting Information Figure S4). There were two peaks at about 486 and 461 nm at room temperature for the Bi$_2$WO$_6$ sample, which were attributed to the radiative recombination process of self-trapped excitons (23). The position of the emission peaks of Bi$_2$WO$_6$ after being modified with C$_{60}$ on the surface remained almost unchanged, suggesting that the interaction between C$_{60}$ and Bi$_2$WO$_6$ was chemical absorption. The PL peak intensity of C$_{60}$-modified Bi$_2$WO$_6$ sample was weaker than that of pure Bi$_2$WO$_6$. The great reduction of PL intensity indicated the decrease of radiative recombination process. Thus, the recombination of e$^-$/h$^+$ excited in Bi$_2$WO$_6$ under visible light could be inhibited by modifying with C$_{60}$. Furthermore, electrochemical impedance spectroscopy (EIS) was also used to investigate the photogenerated charge separations process on ITO/Bi$_2$WO$_6$ film and ITO/Bi$_2$WO$_6$/C$_{60}$ film. Figure 6 shows EIS response of ITO/Bi$_2$WO$_6$ film sample and ITO/Bi$_2$WO$_6$/C$_{60}$ film sample under visible light ($\lambda > 420$ nm) irradiation. The radius of the arc on the EIS Nyquist plot reflects the reaction rate occurring at the surface of electrode. The arc radius on EIS Nyquist plot of ITO/Bi$_2$WO$_6$/C$_{60}$ film was smaller than that of ITO/Bi$_2$WO$_6$ film sample, which meant that an effective separation of photogenerated electron–hole pairs and fast interfacial charge transfer to the electron donor/electron acceptor occurred as suggested (24, 25). Under simulated solar irradiation ($\lambda > 290$ nm), a similar result was obtained. The arc radius on EIS Nyquist plot of ITO/Bi$_2$WO$_6$/C$_{60}$ film sample became smaller after being modified by C$_{60}$ on the film of ITO/Bi$_2$WO$_6$. Hence, it could be concluded that there also existed an effective separation of the photogenerated electron–hole pair and a fast interfacial charge transfer to the electron donor/electron acceptor after Bi$_2$WO$_6$ film was modified by C$_{60}$ under visible and simulated solar irradiation. Figure S5 shows the applied potential dependence of the photocurrent for ITO/Bi$_2$WO$_6$/C$_{60}$ film and ITO/Bi$_2$WO$_6$ film (450 W Xe lamp; electrolyte, 0.1 M Na$_2$SO$_4$ solution). An obvious anodic photocurrent was obtained when anodic bias potential was present. No photocurrent can be found for ITO/Bi$_2$WO$_6$ film at V = 0.9 V in the dark. The photocurrent of ITO/Bi$_2$WO$_6$ increased to $1.41 \times 10^{-4}$ A when illuminated by Xe lamp. It is interesting that the photocurrent of ITO/Bi$_2$WO$_6$/C$_{60}$ film increased to $2.56 \times 10^{-4}$ A, which increased about two times after being modified by C$_{60}$, suggesting the improvement of separation efficiency and inhibition of recombination of photoinduced electron–hole pairs. These photoelectric characteristics further proved that the combination of Bi$_2$WO$_6$ and electron acceptor (C$_{60}$) was an effective way to improve photocatalytic efficiency.

The stability of the photocatalyst was also studied. The DR spectra of C$_{60}$-modified Bi$_2$WO$_6$ changed very little after
UV irradiation for 10 days (see Supporting Information Figure S6), further confirming that the interaction between C_{60} and Bi_{2}WO_{6} was strong and the modified Bi_{2}WO_{6} photocatalyst was very stable under irradiation. The photocatalytic activity after irradiation was nearly the same as before, indicating that the C_{60}-modified Bi_{2}WO_{6} photocatalyst is fairly stable under the studied conditions.

The storing and shutting photoinduced electrons role of C_{60} in a photocatalytic process is realized by coating Bi_{2}WO_{6} with monomolecular layer C_{60}. It is the electronic contact between semiconductor and C_{60} that lead to the efficient separation of electron–hole pairs to reduce electron–hole recombination, which exhibits high photocatalytic activity under visible light and simulated solar light irradiation. In conclusion, the modified photocatalyst is an interesting and promising photocatalytic material which has good potential for application to pollutants purification.

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Supporting Information Available
ESR experiment, Figures S1–S6. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited
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