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Synthesis of α -Fe₂O₃/Bi₂WO₆ layered heterojunctions by *in situ* growth strategy with enhanced visible-light photocatalytic activity

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Layered heterojunction structure with larger interface region for electron migration has attracted much attention in recent years. In this work, layered α -Fe₂O₃/Bi₂WO₆ heterojunctions with strong interlayer interaction were successfully synthesized through a facile *in situ* growth method. The strong interaction between α -Fe₂O₃ and Bi₂WO₆ had resulted in excellent photoelectrochemical performance. It was found that such structure promoted the interfacial photogenerated charges separation according to EIS and Tafel analysis, except for the expansion of visible-light absorption range. PL and TRPL characterizations further demonstrated that the recombination ratio of photoexcited electron-hole pairs was greatly reduced. The toluene photocatalytic degradation tests had showed that α -Fe₂O₃/Bi₂WO₆ composites exhibited much well activity under visible-light irradiation. Especially, 4%-Fe₂O₃/Bi₂WO₆ sample displayed the highest photocatalytic activity, which was around 3 and 4 times higher than that of pure Bi₂WO₆ and α -Fe₂O₃. Based on ESR results and free radical trapping experiments, hydroxyl radicals (\cdot OH) and holes (h^+) were regarded as the main active species. The establishment of Fe₂O₃/Bi₂WO₆ with layered heterojunctions could provide new insights into the construction of novel photocatalysts.

In recent years, indoor air pollution caused by volatile organic pollutants (VOCs) has attracted lots of public attentions. Photocatalytic oxidation was considered as an environmental-friendly technology for indoor VOCs purification^{1–6}. Therefore, many kinds of photocatalysts have been extensively investigated, such as TiO₂^{7–9}, ZnO^{10,11}, SnO₂¹², SrTiO₃¹³ and so on. However, these semiconductors still have some common shortcomings, such as narrow light absorption range and high recombination ratio of photogenerated charges¹⁴. Thus, developing visible-light driven and highly active photocatalysts is one of the most urgent topics.

N-type Bi₂WO₆ has widely regarded as a promising photocatalyst for its outstanding photooxidation ability, nontoxicity, well thermal and chemical stability^{15,16}. Nevertheless, pure Bi₂WO₆ can't efficaciously utilize visible light due to the fact that it can only be driven by light shorter than 450 nm^{17,18}. Moreover, low separation ratio of photogenerated electrons and holes also impedes its application. Semiconductor heterojunction has been demonstrated to be an effective way to solve this issue above, such as the coupling of MoS₂/Bi₂WO₆¹⁹, g-C₃N₄/Bi₂WO₆²⁰, CeO₂/Bi₂WO₆²¹, BiOBr/Bi₂WO₆²² and so on.

Layered heterojunction photocatalyst possesses larger interfacial area compared to line contact and point contact heterojunction photocatalysts, which benefits the transfer of photogenerated electron-hole pairs²³. By taking this advantage into consideration, many photocatalysts with layered heterostructure have been fabricated, such as SnS₂/g-C₃N₄²³, g-C₃N₄/Bi₂WO₆²⁴, g-C₃N₄/Bi₂₀TiO₃₂²⁵, α -Fe₂O₃/graphene²⁶ and so on. Motivated by the above work, Bi₂WO₆ coupled with α -Fe₂O₃ (a low-price and narrow band gap semiconductor) nanosheets as layered heterojunction photocatalyst may exhibit significantly enhanced photoinduced interfacial charge transfer rate, which could effectively promote the photocatalytic activity.

In this work, layered α -Fe₂O₃/Bi₂WO₆ heterojunctions were fabricated via a facile *in situ* growth hydrothermal method. And toluene was chosen as a typical kind of indoor VOCs in the experiment. Then, the

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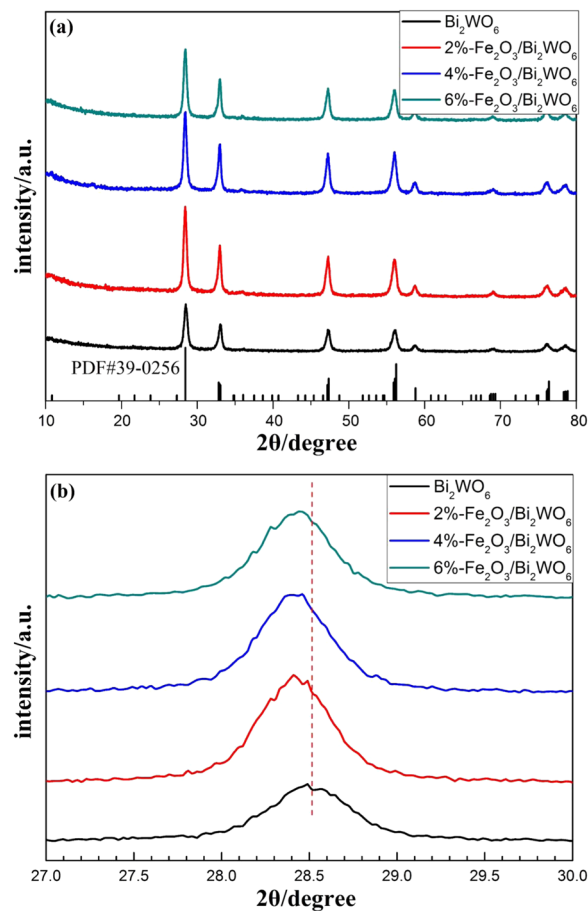


Figure 1. (a) XRD patterns of pure Bi_2WO_6 and $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composites. (b) Enlargement of XRD peaks in lattice (131) plane.

photodegradation efficiency of gaseous toluene under visible light irradiation was tested. After that, the inherent structure-performance relationship was then disclosed based on the physiochemical and photo-electrochemical characterizations. The main purpose of our work was to shed new light on the synthesis of layered heterojunctions and reveal the role of such structure in photocatalytic process.

Experimental

Chemicals. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Na_2SO_4 , $\text{NH}_3 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{C}_2\text{O}_4$, salicylic acid, benzoquinone, sodium acetate and ethanol were purchased from Sigma-Aldrich. All chemical reagents were of analytical grade and without any further purification.

Synthesis of $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composites. Bi_2WO_6 was synthesized via the same method as reported in our previous work¹⁵. Layered $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ heterojunctions were synthesized by *in situ* growth method. Typically, 2 g Bi_2WO_6 was ultrasonic dispersed in 120 mL ethanol for 30 minutes. Then, appropriate amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and sodium acetate were added into the above solution. After vigorous stirring for about 2 h, the mixture was transformed to a 200 mL Teflon-lined autoclave and then heated in an oven at 180 °C for 24 h. The obtained participates were collected by vacuum filtration and washed with deionized water and ethanol several times. Finally, these samples were dried in air at 70 °C before being used. Composites of 2, 4 and 6% $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ samples were prepared, respectively. Pure hexagonal nanoplates of $\alpha\text{-Fe}_2\text{O}_3$ were synthesized without the addition of Bi_2WO_6 via the method reported in the reference²⁶.

Characterization of samples. The crystal phase and composition of these as-prepared catalysts were obtained using an X-ray diffraction (XRD, model D/max RA, Rigaku Co., Japan with $\text{Cu K}\alpha$ radiation). Raman measurement was performed using a LABRAM-HR Ramascope fitted with a spectra physics argon ion laser. Laser radiation ($\lambda = 514 \text{ nm}$) was used as excitation source at 20 mW. The surface properties were performed using X-ray photoelectron spectroscopy (XPS) measurement (Thermo, ESCALAB 250). The standard binding energy of 284.8 eV from C1s value was chosen as a reference. The morphology and microstructure information of the catalysts were obtained by Scanning electron microscopy (SEM, FEI-quanta 200F, USA) and transmission electron microscopy (TEM, H-600, Hitachi, Ltd., Japan). The specific surface area of catalysts was ascertained by using a nitrogen adsorption apparatus (Beijing JWGB Sci. & Tech. Co., Ltd). The light adsorption ability of

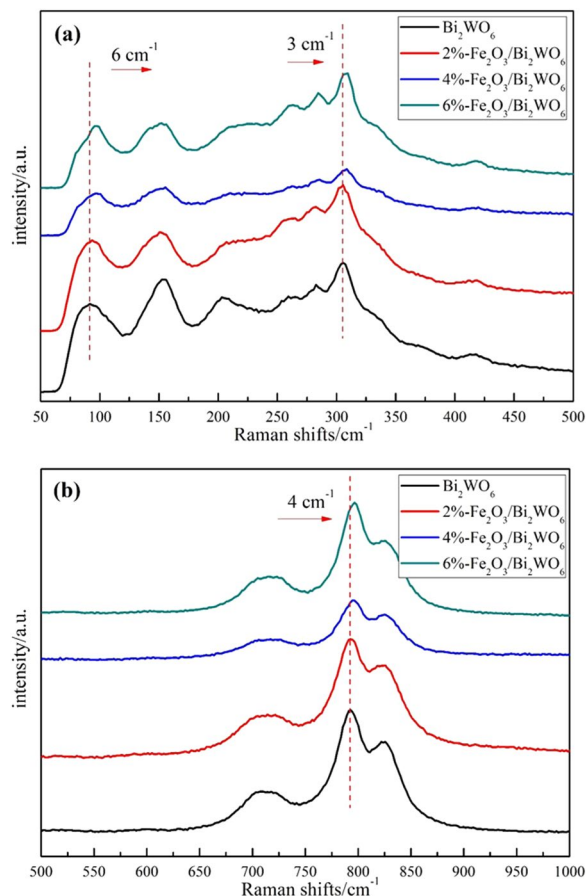


Figure 2. Raman spectra for pure Bi_2WO_6 and $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composites in the range of (a) $50\text{--}500\text{ cm}^{-1}$ and (b) $500\text{--}1000\text{ cm}^{-1}$.

these samples was obtained by using a Scan UV-visible spectrophotometer (UV-visible DRS: TU-1901, China) equipped with an integrating sphere assembly. The spectra were recorded at room temperature in air, ranging from 230 to 850 nm. Photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) spectra were recorded using a fluorospectrophotometer (PL: RAMANLOG 6, USA) with a 390 nm Ar^+ laser as excitation source. All these photoelectrochemical properties of the samples were measured on an electrochemical system (CHI 660B, Shanghai, China) using a three-electrode photo electrochemical cell. Platinum wire and saturated Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The working electrode was composed of indium tin oxide (ITO, $20 \times 30 \times 1.1\text{ mm}$, $15\ \Omega$) with an area of about 1 cm^2 , glass coated with the prepared samples. The details of preparing working electrode was reported in our previous work¹⁵. The electrolyte was 0.2 M Na_2SO_4 solution. Electron spin resonance (ESR) signals of radical species trapped by 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) were detected on a JES FA200 spectrometer.

Photocatalytic activity tests. Photocatalytic activity of as-prepared samples was evaluated via photodegradation of toluene. Experiment was performed in a 1.5 L batch reactor sealed with quartz plate. Circulating cooling water in the jacket around the reactor was used to control the reaction temperature. For each test, 0.1 g photocatalyst was uniformly dispersed onto a glass dish with a diameter about 10 cm. After that, the catalyst-coated dish was played on the bottom of the reactor. An appropriate amount of toluene was injected into the reactor with a micro-spring. Before each test, the system was maintained in the darkness to achieve adsorption-desorption equilibrium. The initial concentration of toluene was controlled at about 25 ppm. A 300 W Xe lamp (Celhx300UV, Ceaulight, China) equipped with two optical glass filters ($420\text{ nm} < \lambda < 780\text{ nm}$) was used as the light source. At given intervals (every 30 minutes), the concentration of toluene in the reactor was measured with a GC-FID (FULI 9790, China). The schematic of the photocatalytic reactor was provided in the supporting information (see Fig. S1).

Results and Discussion

Structure and morphology.

The crystal structure and phase composition of these samples were detected by XRD analysis (Fig. 1a). For pure Bi_2WO_6 , distinct diffraction peaks at 28.5° , 32.8° , 47.1° , 55.7° , 58.5° and 75.8° were perfectly corresponding to (131), (200), (202), (133), (262) and (391) crystallographic planes (PDF#39-0256)²⁷, respectively. In addition, all the diffraction peaks of pure $\alpha\text{-Fe}_2\text{O}_3$ (see Fig. S2) were in good agreement with those for hematite (PDF#33-0664)²⁸. The intensity of the diffraction peaks of $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composites was stronger than that of pure Bi_2WO_6 (see Fig. 1a), which could be ascribed to the growth of crystals during the

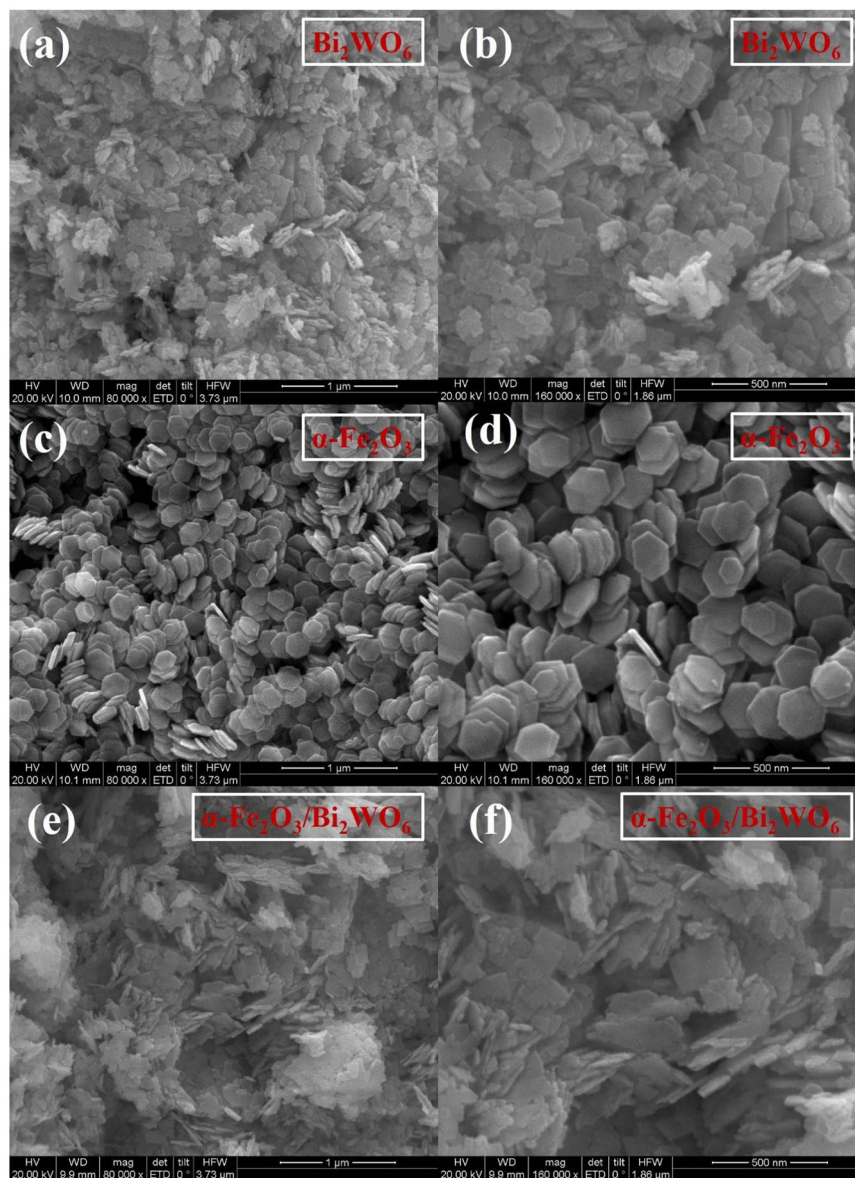


Figure 3. SEM images of (a,b) pure Bi_2WO_6 , (c,d) pure $\alpha\text{-Fe}_2\text{O}_3$ and (e,f) 4% $\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite.

hydrothermal process. It was noteworthy that no peaks of $\alpha\text{-Fe}_2\text{O}_3$ were observed for $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite photocatalysts, which may be ascribed to the high dispersion and low content of $\alpha\text{-Fe}_2\text{O}_3$ ²⁹. Moreover, a shift to lower 2θ value of the band related to (131) lattice plane for $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ could be observed (Fig. 1b). Based on Bragg's law, this fact verified the slight expansion of the interplanar spacing related to Bi_2WO_6 ³⁰. According to the reference³¹, the increase in d spacing of Bi_2WO_6 could be attributed to the partial substitution of Bi sites by Fe ions. From this viewpoint, it was confirmed that there existed strong interaction between $\alpha\text{-Fe}_2\text{O}_3$ and Bi_2WO_6 . Similar results were also reported by the reference²⁵.

Raman spectra were also collected to further analyze the phase structure of photocatalysts. In Fig. 2, the peaks in the $60\text{--}160\text{ cm}^{-1}$, $200\text{--}400\text{ cm}^{-1}$ and $600\text{--}1000\text{ cm}^{-1}$ regions could be assigned to translational motions of Bi^{3+} and W^{6+} , WO_6 bending modes and Bi-O stretching and bending modes, and W-O bands stretching modes³², respectively. In detail, the bands at about 95 cm^{-1} and 305 cm^{-1} were associated with translational modes involving simultaneous motions of Bi^{3+} and WO_6 ⁶⁻³³. The peak at about 710 cm^{-1} could be ascribed to an antisymmetric bridging mode of the tungstate chain^{33,34}. Two bands at about 790 cm^{-1} and 820 cm^{-1} matched well with anti-symmetric and symmetric A_g modes of terminal O-W-O groups^{33,35}. No Raman vibrational peaks of $\alpha\text{-Fe}_2\text{O}_3$ were detected, which may be due to a lower $\alpha\text{-Fe}_2\text{O}_3$ loading²⁹. As illustrated in Fig. 2a,b, three bands at 95 cm^{-1} , 305 cm^{-1} and 790 cm^{-1} of the $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composites migrated to higher wave numbers, indicating the *in situ* growth of $\alpha\text{-Fe}_2\text{O}_3$ on Bi_2WO_6 crystal had an influence on the phase structure of Bi_2WO_6 . This finding fitted well with the results obtained from XRD characterization above.

The microstructure and morphology of the obtained samples were visualized by SEM, TEM and HR-TEM measurements. Figure 3 showed the SEM images of pure Bi_2WO_6 , pure $\alpha\text{-Fe}_2\text{O}_3$ and 4% $\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$

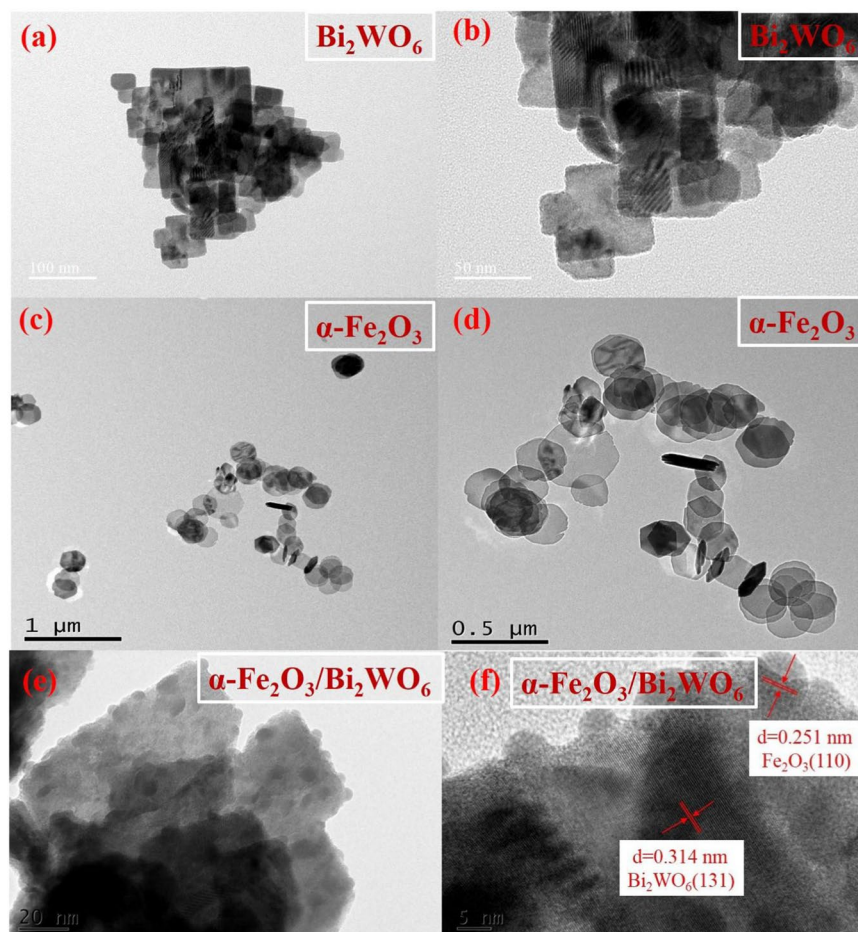


Figure 4. TEM images of pure (a,b) Bi_2WO_6 , (c,d) pure $\alpha\text{-Fe}_2\text{O}_3$, (e) TEM and (f) HR-TEM images of 4% $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite.

composite, respectively. It could be clearly seen that the geometric shape of pure Bi_2WO_6 was a laminated structure (Fig. 3a,b). Pure $\alpha\text{-Fe}_2\text{O}_3$ had a uniform and hexagonal nanoplate structure (Fig. 3c,d). No significant change could be observed in the SEM images of 4% $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite (Fig. 3e,f) compared with that of pure Bi_2WO_6 , indicating the prepared process hardly damaged the origin layered structure of pure Bi_2WO_6 . Additionally, no hexagonal nanoplate structure of $\alpha\text{-Fe}_2\text{O}_3$ could be found as well, which may be ascribed to the low content of $\alpha\text{-Fe}_2\text{O}_3$ ²⁹. The TEM images of pure Bi_2WO_6 (Fig. 4a,b) and pure $\alpha\text{-Fe}_2\text{O}_3$ (Fig. 4c,d) showed layered structure as well. Figure 4e displayed that $\alpha\text{-Fe}_2\text{O}_3$ nanosheets randomly grew on the laminated structure of Bi_2WO_6 . A typical HR-TEM image of $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite was given in Fig. 4f. The lattice with interplanar distances of 0.314 nm and 0.251 nm attached to (131) lattice plane of Bi_2WO_6 ³⁰ and (110) lattice plane of Fe_2O_3 ²⁶, respectively. In view of long-time ultrasonication pretreatment in the TEM process, it could be concluded that there existed strong interlayer interaction between $\alpha\text{-Fe}_2\text{O}_3$ and Bi_2WO_6 nanoplates³⁶.

Surface composition analysis. X-ray photoelectron spectroscopy (XPS) measurement was used to identify the oxidation state and surface composition of $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composites. For pure Bi_2WO_6 , two peaks with binding energy of 164.60 eV and 159.25 eV were the split signals of Bi 4f (Fig. 5a), which could be assigned to the Bi^{3+} species in the sample³⁷. Two characteristic peaks in the W 4f spectrum (Fig. 5b) at 37.70 eV and 35.50 eV were ascribed to W 4f_{5/2} and W 4f_{7/2}³⁷, respectively. As displayed in Fig. S3, the peaks at 724.58 eV and 710.68 eV belonged to Fe 2p_{1/2} and Fe 2p_{3/2}³⁸, suggesting the presence of Fe^{3+} . The peaks of Bi^{3+} 4f and W^{6+} 4f both showed a slightly positive shift (see Fig. 5), which indicated the surface electron density for Bi and W had changed^{39,40}. This result indicated that the heterostructure interface between Fe_2O_3 and Bi_2WO_6 could have been formed^{15,36}. It agreed well with the abovementioned XRD, Raman and HR-TEM results.

Optical properties. Expanding the visible light absorption range played a crucial role for the modification of photocatalysts towards improving the visible-light photocatalytic activity. Optical diffuse reaction spectra (DRS) was used to estimate the visible light adsorption property of as-obtained photocatalysts. As shown in Fig. 6, pure $\alpha\text{-Fe}_2\text{O}_3$ displayed an excellent light absorption ability among almost the whole visible light range due to its narrow band gap⁴¹. The spectrum of $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composites showed obvious red-shift compared with pure

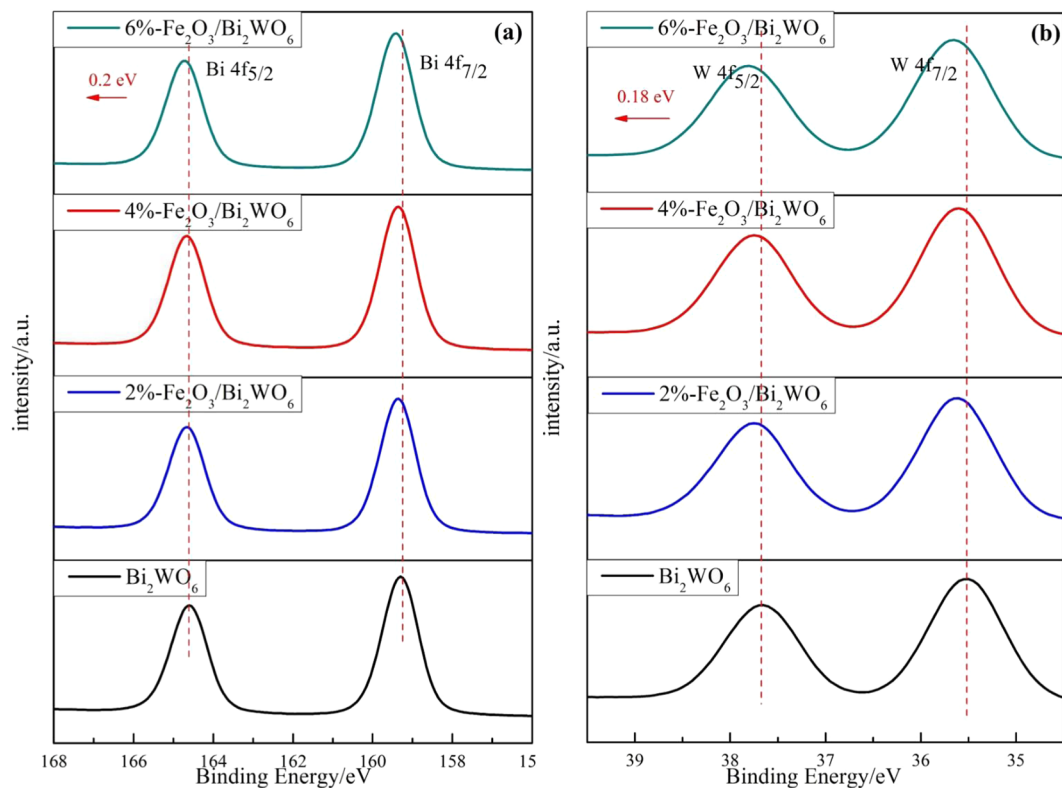


Figure 5. High-resolution XPS spectra of (a) Bi 4f (b) W 4f for different photocatalysts.

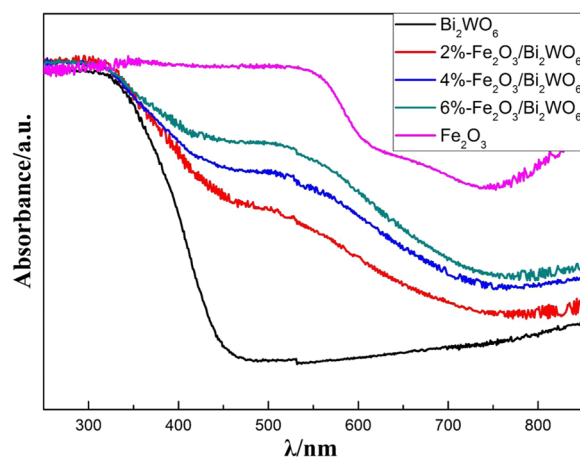


Figure 6. UV-vis absorption spectra of pure Bi_2WO_6 , pure $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composites.

Bi_2WO_6 , implying the improvement of the utilization of visible light⁴². Furthermore, the band gap of pure Bi_2WO_6 and pure Fe_2O_3 was calculated based on Kubelka-Munk theory to be about 2.65 eV and 1.95 eV, respectively (see Fig. S4). These results agreed well with the references^{43,44}.

Photoelectrochemical performances. Electrochemical impedance spectroscopy (EIS) was applied to shed light on the interface charge separation and transfer efficiency of different photocatalysts under visible light irradiation. The arc radius of $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composites was smaller than that of pure Bi_2WO_6 and Fe_2O_3 (see Fig. 7a), revealing that the photoexcited electrons could easily transfer across the interface and efficiently migrate to the surface due to the $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ layered heterojunction^{39,45}. Especially, the 4% $\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite had the smallest arc radius, indicating it possessed the least electrons transfer resistance. Tafel analysis was performed to get a vivid view of the current density values of the photocatalysts investigated under visible light irradiation⁴⁶. Generally, larger values of corrosion current density and anodic Tafel slope meant more photogenerated pairs and faster electron transfer rate¹², which benefitting the photocatalytic process. As displayed in Fig. 7b, 4% $\text{-Fe}_2\text{O}_3/$

Sample	τ_1 /ns	A_1 /%	τ_2 /ns	A_2 /%	χ^2	τ_{av} /ns
Bi_2WO_6	0.7402	63.41	3.5458	36.59	1.407	2.8005
4%- $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$	1.2237	60.52	5.8734	39.48	1.186	4.7478

Table 1. Kinetic parameters of the emission Decay of different samples.

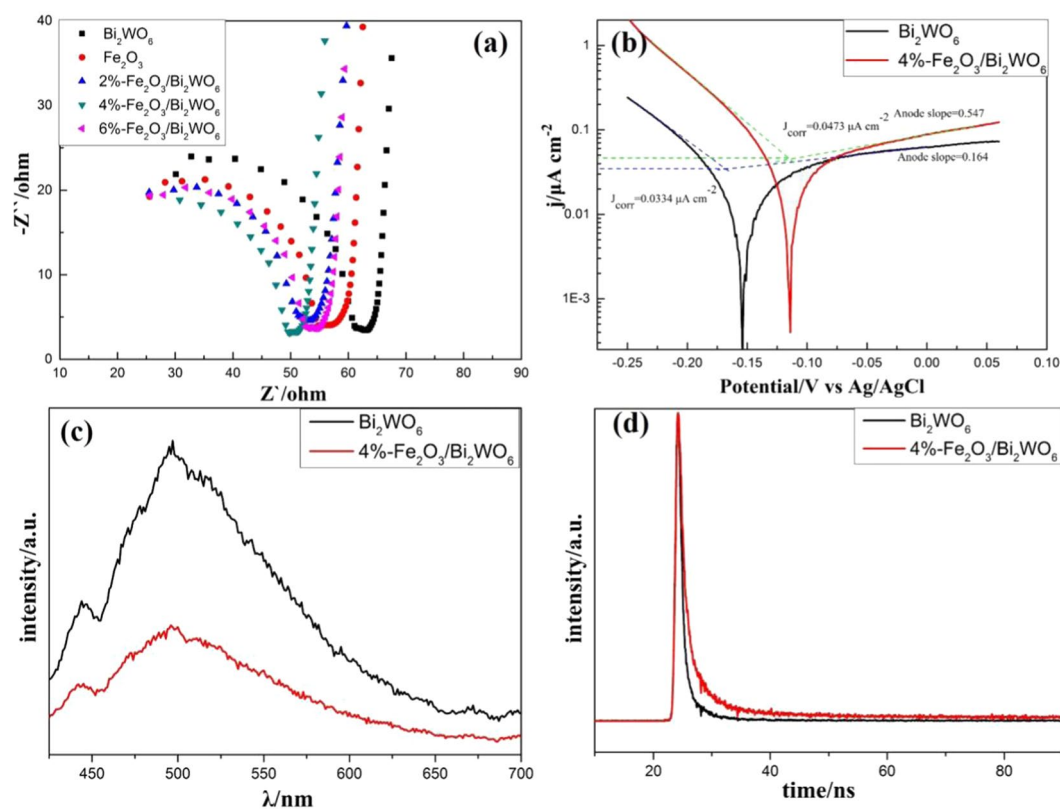


Figure 7. (a) Electrochemical impedance spectroscopy spectra of different catalysts, (b) Tafel polarization curves of the various electrodes under visible light irradiation, (c) Photoluminescence (PL) spectra and (d) time-resolved photoluminescence (TRPL) spectra of different samples.

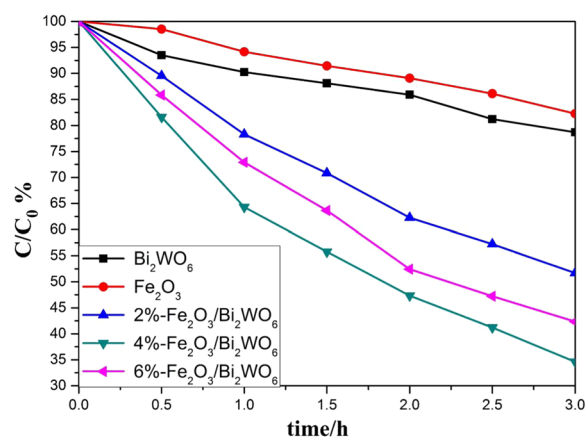


Figure 8. Photocatalytic degradation of gaseous toluene in the presence of different samples under visible light irradiation.

Bi_2WO_6 composite exhibited larger J_{corr} value and anodic slope as compared with pure Bi_2WO_6 . Consequently, the results further demonstrated that the heterojunction between Fe_2O_3 and Bi_2WO_6 could improve charge transfer rate and efficiently separate photoexcited electrons and holes. Moreover, as shown in Fig. S5, the photocurrent of

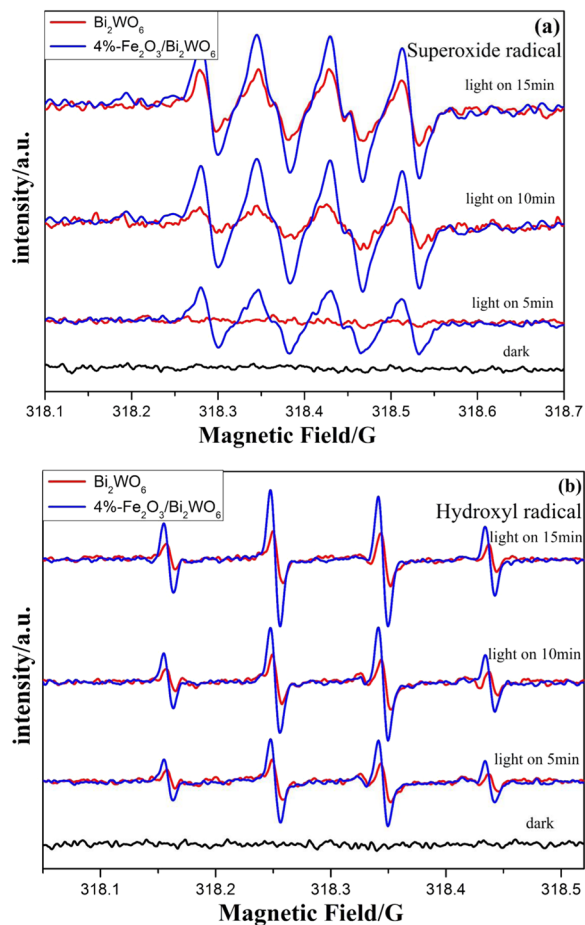


Figure 9. DMPO spin-trapping ESR spectra in Bi_2WO_6 and 4%- $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite in dark or under visible light irradiation: (a) in aqueous dispersion for DMPO- O_2^- and (b) in methanol dispersion for DMPO- OH .

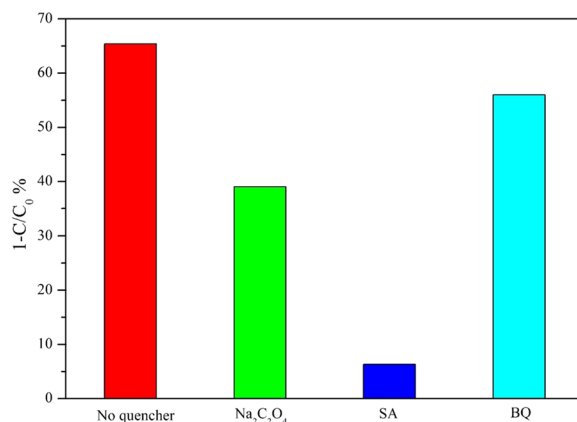


Figure 10. Photocatalytic activities of 4%- $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite for the photooxidation of toluene in the presence of different quenchers.

$\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite was much higher than that of pure Bi_2WO_6 , suggesting the separation ratio of photoexcited charges enhanced. Photoluminescence (PL) spectra was further used to demonstrate the recombination ratio of photoinduced pairs. As displayed in Fig. 7c, the intensity of 4%- $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ was much lower than that of pure Bi_2WO_6 , indicating that the recombination of photogenerated charge carriers was effectively inhibited^{15,47}. Time-resolved photoluminescence (TRPL) spectra (Fig. 7d) was also used to assess recombination kinetics of photoinduced electron-hole pairs. The TRPL decay spectrum waves were fitted by exponential decay kinetics displayed as Eq. (1)⁴⁸:

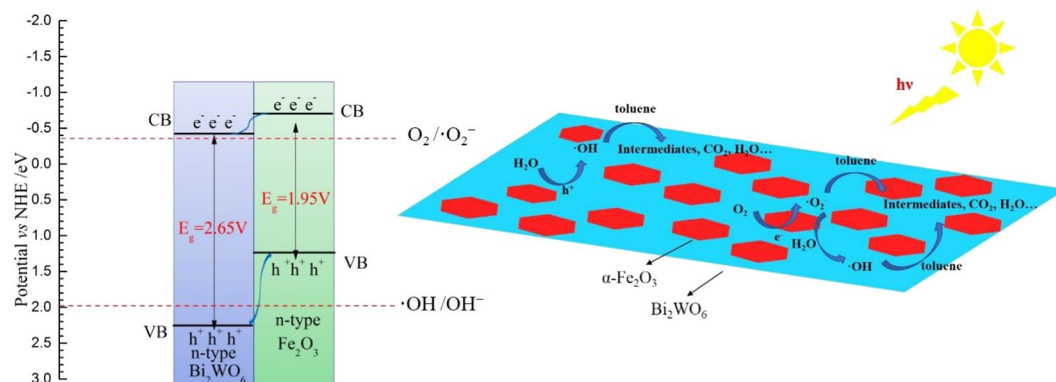


Figure 11. Diagram of the energy band levels of $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite and proposed possible photodegradation of toluene process.

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

The average emission time was calculated based on Eq. (2)⁴⁸:

$$\tau_{\text{av}} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \quad (2)$$

where τ_1 and τ_2 were lifetimes, A_1 and A_2 were the corresponding weighting factors. Based on the fitted results listed in Table 1, the average lifetime of 4%- $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite was longer than that of pure Bi_2WO_6 , enhancing the likelihood of photoinduced pairs to participate in the reaction of gas-phase toluene photodegradation³⁹, thereby implying higher photocatalytic activity for $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composites.

Photocatalytic performances. To evaluate the photocatalytic efficiency of as-prepared photocatalysts, gaseous toluene was chosen as a probe indoor air contaminant. The toluene degradation efficiency for the samples investigated was displayed in Fig. 8 and the relative apparent rate constant (k) based on pseudo-first-order kinetic model was obtained (see Fig. S6). Pure Bi_2WO_6 and $\alpha\text{-Fe}_2\text{O}_3$ showed rather poor photocatalytic activity under three-hour visible light irradiation. In stark contrast, the gaseous toluene removal efficiency was remarkably enhanced over $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composites owing to their well photoelectrochemical property as discussed above. Among all the samples, 4%- $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ catalyst showed the highest photocatalytic activity, whose k value (0.3469 h^{-1}) was much higher than those of pure Bi_2WO_6 (0.0749 h^{-1}) and pure $\alpha\text{-Fe}_2\text{O}_3$ (0.0649 h^{-1}). Besides, the surface area didn't play an important role in enhancing the photocatalytic activity, as the surface area of 4%- $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ sample was modest (see Table S1). Based on the above analysis, it could be concluded that the layered heterojunctions between Fe_2O_3 and Bi_2WO_6 played a key role in promoting the photocatalytic process.

Possible photocatalytic mechanism. DMPO spin-trapping ESR technique was employed to verify the active radicals produced in the photocatalytic system. As presented in Fig. 9, no peaks could be observed in the darkness. Clearly, characteristic peaks for $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ emerged once the as-obtained samples were irradiated by visible light. Both intensity for $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ became stronger with increasing irradiation time. Notably, the 4%- $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ exhibited stronger intensity for $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ than that of pure Bi_2WO_6 under the same condition, implying the oxidation ability of the composite photocatalyst had been effectively promoted⁴⁹. As reported in the references^{50–52}, the involvement of active radical species (such as $\cdot\text{O}_2^-$, $\cdot\text{OH}$ and h^+) was very important in the photocatalytic process. Thus, free radicals trapping experiment was performed to further figure out the role of the radical species during the photocatalytic reaction. In a typical experiment, $\text{Na}_2\text{C}_2\text{O}_4$ ⁵³, salicylic acid (SA)⁵⁴ and benzoquinone (BQ)⁵⁵ were applied as scavengers of h^+ , $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, respectively. As illustrated in Fig. 10, the addition of BQ had little effect on the photocatalytic activity. However, the toluene removal efficiency obviously decreased in the presence of $\text{Na}_2\text{C}_2\text{O}_4$ and SA. In particular, the degradation efficiency of toluene was whittled down into about 5% when adding appropriate amount of SA. Therefore, it could be inferred that h^+ and $\cdot\text{OH}$ played dominant roles in the toluene photodegradation process.

Based on the Mott-Schottky analysis (see Fig. S7), the value of Fermi energy level was -0.30 eV and -0.60 eV (vs NHE) for Bi_2WO_6 and $\alpha\text{-Fe}_2\text{O}_3$ ⁵⁶, respectively. For n-type semiconductor, the conduction band (CB) edge was more negative (about $0\text{--}0.2 \text{ eV}$) than Fermi level⁵⁷. Herein, the difference value was set to 0.1 eV . Therefore, as illustrated in Fig. 11, the conduction band (CB) bottom and valence band (VB) top values of pure Bi_2WO_6 and pure $\alpha\text{-Fe}_2\text{O}_3$ could be obtained. The *in situ* growth strategy could guarantee the intimate contact between Bi_2WO_6 and $\alpha\text{-Fe}_2\text{O}_3$ with stronger interfacial interaction. Once the heterojunction was irradiated by visible light, both Bi_2WO_6 and $\alpha\text{-Fe}_2\text{O}_3$ could generate electron-hole pairs. Due to the type-II heterojunction and intimate contact between Bi_2WO_6 and $\alpha\text{-Fe}_2\text{O}_3$, the photoexcited electrons on the CB of $\alpha\text{-Fe}_2\text{O}_3$ had the tendency to transfer to that of Bi_2WO_6 , whereas photoinduced holes spontaneously moved to the VB of $\alpha\text{-Fe}_2\text{O}_3$ (see Fig. 11). Therefore, the photogenerated electrons and holes could be separated efficiently, which greatly enhanced the photocatalytic activity. The CB bottom level of Bi_2WO_6 was more negative than that of O_2/O_2^- (-0.33 eV)⁵⁸, thus

the photoexcited electrons could reduce oxygen molecules absorbed on the surface to $\cdot\text{O}_2^-$ species. What's more, part of O_2 could be reduced to H_2O_2 by photo-generated electrons based on the fact that the redox potential of $\text{O}_2/\text{H}_2\text{O}_2$ was 0.695 eV⁵⁹, then the formed H_2O_2 could produce $\cdot\text{OH}$ by capture the photo-generated electrons^{60,61}. Although the VB top value of $\alpha\text{-Fe}_2\text{O}_3$ was less positive than the potential of $\cdot\text{OH}/\text{OH}^-$ (1.99 eV)⁵⁸, characteristic signals of $\cdot\text{OH}$ (1:2:2:1 quartet pattern) could still be obviously observed in the ESR spectrum (see Fig. 9). This may be ascribed to the fact that part of the photogenerated holes remaining in the VB top of Bi_2WO_6 could also oxidize absorbed H_2O into $\cdot\text{OH}$. Similar phenomenon was also founded by Li. *et al.*³⁹. Hence, these radical species had strong oxidation ability to destroy toluene molecule.

Conclusions

In summary, $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ layered heterojunctions were successfully synthesized via a simple *in situ* growth method in this work. XRD, Raman, HR-TEM and XPS results demonstrated there existed strong interaction between Bi_2WO_6 and $\alpha\text{-Fe}_2\text{O}_3$. The $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ layered heterojunctions could effectively broaden visible light absorption range and improve photoexcited charges separation efficiency according to the characterization results of UV-vis, EIS, Tafel curve, PL and TRPL. Especially, 4% $\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ sample with strong interlayer interaction exhibited the highest photocatalytic activity. Given the results of ESR and trapping experiments, h^+ and $\cdot\text{OH}$ species played a crucial role during the photocatalytic process of toluene removal. Such layered heterojunction photocatalyst had potential applications for indoor air purification.

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Author Contributions

Taiping Xie designed, performed most of the experiments and wrote the manuscript. Yue Liu, Haiqing Wang and Zhongbiao Wu supervised the research work. All authors were contributed to discussion and writing the manuscript.

Additional Information

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