Synthesis of $\alpha$-Fe$_2$O$_3$/Bi$_2$WO$_6$ 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 $\alpha$-Fe$_2$O$_3$/Bi$_2$WO$_6$ heterojunctions with strong interlayer interaction were successfully synthesized through a facile in situ growth method. The strong interaction between $\alpha$-Fe$_2$O$_3$ and Bi$_2$WO$_6$ has 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 $\alpha$-Fe$_2$O$_3$/Bi$_2$WO$_6$ composites exhibited much well activity under visible-light irradiation. Especially, 4%-Fe$_2$O$_3$/Bi$_2$WO$_6$ sample displayed the highest photocatalytic activity, which was around 3 and 4 times higher than that of pure Bi$_2$WO$_6$ and $\alpha$-Fe$_2$O$_3$. Based on ESR results and free radical trapping experiments, hydroxyl radicals (·OH) and holes ($h^+$) were regarded as the main active species. The establishment of Fe$_2$O$_3$/Bi$_2$WO$_6$ 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 TiO$_2$$^{7-9}$, ZnO$^{10,11}$, SnO$_2$$^{12}$, SrTiO$_3$ and so on. However, these semiconductors still have some common shortcomings, such as narrow light absorption range and high recombination ratio of photogenerated charges$^{14}$. Thus, developing visible-light driven and highly active photocatalysts is one of the most urgent topics.

N-type Bi$_2$WO$_6$ has widely regarded as a promising photocatalyst for its outstanding photooxidation ability, nontoxicity, well thermal and chemical stability$^{15,16}$. Nevertheless, pure Bi$_2$WO$_6$ 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 MoS$_2$/Bi$_2$WO$_6$$^{19}$, g-C$_3$N$_4$/Bi$_2$WO$_6$$^{20}$, CeO$_2$/Bi$_2$WO$_6$,$^{21}$ BiOBr/Bi$_2$WO$_6$,$^{22}$ 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 pairs$^{23}$. By taking this advantage into consideration, many photocatalysts with layered heterostructure have been fabricated, such as SnS$_2$/g-C$_3$N$_4$,$^{24}$ g-C$_3$N$_4$/Bi$_2$WO$_6$,$^{25}$ g-C$_3$N$_4$/Bi$_2$O$_3$TiO$_2$,$^{26}$ $\alpha$-Fe$_2$O$_3$/graphene$^{27}$ and so on. Motivated by the above work, Bi$_2$WO$_6$ coupled with $\alpha$-Fe$_2$O$_3$ (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 $\alpha$-Fe$_2$O$_3$/Bi$_2$WO$_6$ 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
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.** Bi(NO$_3$)$_3$·5H$_2$O, Na$_2$WO$_4$·2H$_2$O, FeCl$_3$·6H$_2$O, Na$_2$SO$_4$, NH$_3$·H$_2$O, Na$_2$C$_2$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 $\alpha$-Fe$_2$O$_3$/Bi$_2$WO$_6$ composites.** Bi$_2$WO$_6$ was synthesized via the same method as reported in our previous work. Layered $\alpha$-Fe$_2$O$_3$/Bi$_2$WO$_6$ heterojunctions were synthesized by in situ growth method. Typically, 2 g Bi$_2$WO$_6$ was ultrasonic dispersed in 120 mL ethanol for 30 minutes. Then, appropriate amount of FeCl$_3$·6H$_2$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% $\alpha$-Fe$_2$O$_3$/Bi$_2$WO$_6$ samples were prepared, respectively. Pure hexagonal nanoplates of $\alpha$-Fe$_2$O$_3$ were synthesized without the addition of Bi$_2$WO$_6$ via the method reported in the reference.

**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 Cu Kα radiation). Raman measurement was performed using a LABRAM-HR Ramancope fitted with a spectra physics argon ion laser. Laser radiation ($\lambda = 514$ 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
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 × 30 × 1.1 mm, 15 Ω) with an area of about 1 cm², glass coated with the prepared samples. The details of preparing working electrode was reported in our previous work15. The electrolyte was 0.2 M Na₂SO₄ 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-springe. 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 nm < λ < 780 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

Figure 2. Raman spectra for pure Bi₂WO₆ and Fe₂O₃/Bi₂WO₆ composites in the range of (a) 50–500 cm⁻¹ and (b) 500–1000 cm⁻¹.

Structure and morphology. The crystal structure and phase composition of these samples were detected by XRD analysis (Fig. 1a). For pure Bi₂WO₆, 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 α-Fe₂O₃ (see Fig. S2) were in good agreement with those for hematite (PDF#33-0664)28. The intensity of the diffraction peaks of α-Fe₂O₃/Bi₂WO₆ composites was stronger than that of pure Bi₂WO₆ (see Fig. 1a), which could be ascribed to the growth of crystals during the
hydrothermal process. It was noteworthy that no peaks of $\alpha$-Fe$_2$O$_3$ were observed for $\alpha$-Fe$_2$O$_3$/Bi$_2$WO$_6$ composite photocatalysts, which may be ascribed to the high dispersion and low content of $\alpha$-Fe$_2$O$_3$\(^{29}\). Moreover, a shift to lower $2\theta$ value of the band related to (131) lattice plane for $\alpha$-Fe$_2$O$_3$/Bi$_2$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$_2$WO$_6$\(^{30}\). According to the reference\(^{31}\), the increase in d spacing of Bi$_2$WO$_6$ 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 $\alpha$-Fe$_2$O$_3$ and Bi$_2$WO$_6$.

Similar results were also reported by the reference\(^{25}\). Raman spectra were also collected to further analyze the phase structure of photocatalysts. In Fig. 2, the peaks in the 60–160 cm\(^{-1}\), 200–400 cm\(^{-1}\) and 600–1000 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 modes\(^{32}\), 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$_6$\(^{6–}\). 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 antisymmetric and symmetric $A_g$ modes of terminal O–W–O groups\(^{33,35}\). No Raman vibrational peaks of $\alpha$-Fe$_2$O$_3$ were detected, which may be due to a lower $\alpha$-Fe$_2$O$_3$ loading\(^{29}\). As illustrated in Fig. 2a,b, three bands at 95 cm\(^{-1}\), 305 cm\(^{-1}\) and 790 cm\(^{-1}\) of the $\alpha$-Fe$_2$O$_3$/Bi$_2$WO$_6$ composites migrated to higher wave numbers, indicating the in situ growth of $\alpha$-Fe$_2$O$_3$ on Bi$_2$WO$_6$ crystal had an influence on the phase structure of Bi$_2$WO$_6$. 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$_2$WO$_6$, $\alpha$-Fe$_2$O$_3$ and 4%-Fe$_2$O$_3$/Bi$_2$WO$_6$ composite.
composite, respectively. It could be clearly seen that the geometric shape of pure Bi$_2$WO$_6$ was a laminated structure (Fig. 3a,b). Pure α-Fe$_2$O$_3$ had a uniform and hexagonal nanoplate structure (Fig. 3c,d). No significant change could be observed in the SEM images of 4%-Fe$_2$O$_3$/Bi$_2$WO$_6$ composite (Fig. 3e,f) compared with that of pure Bi$_2$WO$_6$, indicating the prepared process hardly damaged the origin layered structure of pure Bi$_2$WO$_6$. Additionally, no hexagonal nanoplate structure of α-Fe$_2$O$_3$ could be found as well, which may be ascribed to the low content of α-Fe$_2$O$_3$.

The TEM images of pure Bi$_2$WO$_6$ (Fig. 4a,b) and pure α-Fe$_2$O$_3$ (Fig. 4c,d) showed layered structure as well. Figure 4e displayed that α-Fe$_2$O$_3$ nanosheets randomly grew on the laminated structure of Bi$_2$WO$_6$. A typical HR-TEM image of α-Fe$_2$O$_3$/Bi$_2$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$_2$WO$_6$ and (110) lattice plane of Fe$_2$O$_3$, respectively. In view of long-time ultrasonication pretreatment in the TEM process, it could be concluded that there existed strong interlayer interaction between α-Fe$_2$O$_3$ and Bi$_2$WO$_6$ nanoplates.

Surface composition analysis. X-ray photoelectron spectroscopy (XPS) measurement was used to identify the oxidation state and surface composition of α-Fe$_2$O$_3$/Bi$_2$WO$_6$ composites. For pure Bi$_2$WO$_6$, 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 sample. 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$_{7/2}$, 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$_{3/2}$, 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. This result indicated that the heterostructure interface between Fe$_2$O$_3$ and Bi$_2$WO$_6$ could have been formed. 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 α-Fe$_2$O$_3$ displayed an excellent light absorption ability among almost the whole visible light range due to its narrow band gap. The spectrum of α-Fe$_2$O$_3$/Bi$_2$WO$_6$ composites showed obvious red-shift compared with pure
Bi$_2$WO$_6$, implying the improvement of the utilization of visible light. Furthermore, the band gap of pure Bi$_2$WO$_6$ and pure Fe$_2$O$_3$ 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.

*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 Fe$_2$O$_3$/Bi$_2$WO$_6$ composites was smaller than that of pure Bi$_2$WO$_6$ and Fe$_2$O$_3$ (see Fig. 7a), revealing that the photoexcited electrons could easily transfer across the interface and efficiently migrate to the surface due to the Fe$_2$O$_3$/Bi$_2$WO$_6$ layered heterojunction. Especially, the 4%-Fe$_2$O$_3$/Bi$_2$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 irradiation. Generally, larger values of corrosion current density and anodic Tafel slope meant more photogenerated pairs and faster electron transfer rate, which benefitting the photocatalytic process. As displayed in Fig. 7b, 4%-Fe$_2$O$_3$/
Bi$_2$WO$_6$ composite exhibited larger $J_{corr}$ value and anodic slope as compared with pure Bi$_2$WO$_6$. Consequently, the results further demonstrated that the heterojunction between Fe$_2$O$_3$ and Bi$_2$WO$_6$ could improve charge transfer rate and efficiently separate photoexcited electrons and holes. Moreover, as shown in Fig. S5, the photocurrent of

| Sample            | $\tau_1$/ns | $A_1$/% | $\tau_2$/ns | $A_2$/% | $\chi^2$ | $\tau_{av}$/ns |
|-------------------|-------------|---------|-------------|---------|----------|---------------|
| Bi$_2$WO$_6$      | 0.7402      | 63.41   | 3.5458      | 36.59   | 1.407    | 2.8005        |
| 4%-Fe$_2$O$_3$/Bi$_2$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$_2$WO$_6$ composite exhibited larger $J_{corr}$ value and anodic slope as compared with pure Bi$_2$WO$_6$. Consequently, the results further demonstrated that the heterojunction between Fe$_2$O$_3$ and Bi$_2$WO$_6$ could improve charge transfer rate and efficiently separate photoexcited electrons and holes. Moreover, as shown in Fig. S5, the photocurrent of
Fe$_2$O$_3$/Bi$_2$WO$_6$ composite was much higher than that of pure Bi$_2$WO$_6$, suggesting the separation ratio of photo-excited 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%-Fe$_2$O$_3$/Bi$_2$WO$_6$ was much lower than that of pure Bi$_2$WO$_6$, indicating that the recombination of photogenerated charge carriers was effectively inhibited. 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 function displayed as Eq. (1):

\[ I(t) = I_0 e^{-kt} \]

Figure 9. DMPO spin-trapping ESR spectra in Bi$_2$WO$_6$ and 4%-Fe$_2$O$_3$/Bi$_2$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%-Fe$_2$O$_3$/Bi$_2$WO$_6$ composite for the photooxidation of toluene in the presence of different quenchers.
The average emission time was calculated based on Eq. (2) \(^{48}\):

\[
\tau_{uv} = \sum A_i \tau_i / \sum A_i
\]

where \(\tau_i\) and \(\tau_j\) were lifetimes, \(A_i\) and \(A_j\) were the corresponding weighting factors. Based on the fitted results listed in Table 1, the average lifetime of 4%-Fe\(_2\)O\(_3\)/Bi\(_2\)WO\(_6\) composite was longer than that of pure Bi\(_2\)WO\(_6\), enhancing the likelihood of photoinduced pairs to participate in the reaction of gas-phase toluene photodegradation\(^{39}\), thereby implying higher photocatalytic activity for Fe\(_2\)O\(_3\)/Bi\(_2\)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\(_2\)WO\(_6\) and α-Fe\(_2\)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 Fe\(_2\)O\(_3\)/Bi\(_2\)WO\(_6\) composites owing to their well photoelectrochemical property as discussed above. Among all the samples, 4%-Fe\(_2\)O\(_3\)/Bi\(_2\)WO\(_6\) catalyst showed the highest photocatalytic activity, whose k value (0.3469 h\(^{-1}\)) was much higher than those of pure Bi\(_2\)WO\(_6\) (0.0749 h\(^{-1}\)) and pure α-Fe\(_2\)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%-Fe\(_2\)O\(_3\)/Bi\(_2\)WO\(_6\) sample was modest (see Table S1). Based on the above analysis, it could be concluded that the layered heterojunctions between Fe\(_2\)O\(_3\) and Bi\(_2\)WO\(_6\) 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 ·OH and ·O\(_2^-\) emerged once the obtained samples were irradiated by visible light. Both intensity for ·OH and ·O\(_2^-\) became stronger with increasing irradiation time. Notably, the 4%-Fe\(_2\)O\(_3\)/Bi\(_2\)WO\(_6\) exhibited stronger intensity for ·OH and ·O\(_2^-\) than that of pure Bi\(_2\)WO\(_6\) under the same condition, implying the oxidation ability of the composite photocatalyst had been effectively promoted\(^{49}\). As reported in the references\(^{50–52}\), the involvement of active radical species (such as ·O\(_2^-\), ·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, Na\(_2\)C\(_2\)O\(_4\)\(^{53}\), salicylic acid (SA)\(^{54}\) and benzoquinone (BQ)\(^{55}\) were applied as scavengers of h\(^+\), ·OH and ·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 Na\(_2\)C\(_2\)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 ·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\(_2\)WO\(_6\) and α-Fe\(_2\)O\(_3\),\(^{56}\) respectively. For n-type semiconductor, the conduction band (CB) edge was more negative (about 0–0.2 eV) than Fermi level\(^{57}\). 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\(_2\)WO\(_6\) and pure α-Fe\(_2\)O\(_3\) could be obtained. The \textit{in situ} growth strategy could guarantee the intimate contact between Bi\(_2\)WO\(_6\) and α-Fe\(_2\)O\(_3\) with stronger interfacial interaction. Once the heterojunction was irradiated by visible light, both Bi\(_2\)WO\(_6\) and α-Fe\(_2\)O\(_3\) could generate electron-hole pairs. Due to the type-II heterojunction and intimate contact between Bi\(_2\)WO\(_6\) and α-Fe\(_2\)O\(_3\), the photoexcited electrons on the CB of α-Fe\(_2\)O\(_3\) had the tendency to transfer to that of Bi\(_2\)WO\(_6\), whereas photoinduced holes spontaneously moved to the VB of α-Fe\(_2\)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\(_2\)WO\(_6\) was more negative than that of O\(_2^-\)/O\(_2^-\) (−0.33 eV), thus
the photoexcited electrons could reduce oxygen molecules absorbed on the surface to $-\text{O}_2^-$ species. What's more, part of $\text{O}_2$ could be reduced to $\text{H}_2\text{O}_2$ by photo-generated electrons based on the fact that the redox potential of $\text{O}_2/\text{H}_2\text{O}_2$ was $0.695 \text{ eV}^{59}$, then the formed $\text{H}_2\text{O}_2$ could produce $\alpha$-Fe$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$. The $\alpha$-Fe$_2$O$_3$/Bi$_2$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%-Fe$_2$O$_3$/Bi$_2$WO$_6$ sample with strong interlayer interaction exhibited the highest photocatalytic activity. Given the results of ESR and trapping experiments, $\alpha$-Fe$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$-Fe$_2$O$_3$ had strong oxidation ability to destroy toluene molecule.

Conclusions

In summary, $\alpha$-Fe$_2$O$_3$/Bi$_2$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$_2$WO$_6$ and $\alpha$-Fe$_2$O$_3$. The $\alpha$-Fe$_2$O$_3$/Bi$_2$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%-Fe$_2$O$_3$/Bi$_2$WO$_6$ sample with strong interlayer interaction exhibited the highest photocatalytic activity. Given the results of ESR and trapping experiments, $\alpha$-Fe$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$-Fe$_2$O$_3$ and $\alpha$-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
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