Excellent photocatalytic degradation and antibiosis of WO$_3$/Fe$_2$O$_3$ heterojunction

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Abstract

The extensive light absorption, enhanced separation of photoinduced carriers and convenience of recycling are crucial for the practical application of WO$_3$ photocatalyst in the dye degradation and the antibiosis activity. Hence, in this work, we synthesize WO$_3$/Fe$_2$O$_3$ composite film on FTO conductive substrate through hydrothermal method. The higher degradation rate for methylene blue (MB) is achieved by WO$_3$/Fe$_2$O$_3$ composite film, and the value of $C/C_0$ is 0.28 which is lower than that of 0.58 for bare WO$_3$ with the irradiation for 4 h. Moreover, the sterilization rate of 28.99% is achieved for WO$_3$-based film with the deposition of Fe$_2$O$_3$ for 3 h. The deeper measurements indicate that the enhanced photocatalytic performances are attributed to the expand light absorption, improved transfer kinetics and separation efficiency of photoinduced carriers with the formation of heterojunction. This work establishes the effective template for WO$_3$-based film with the enhanced photocatalytic prosperities for dye degradation and antibiosis.

1. Introduction

The increasingly serious environmental problems and energy crisis have aroused the concern of scientists all over the world due to over application of fossil fuels and uncontrolled discharge of industrial wastewater [1–3]. The development of catalysts to degrade organic dyes and clean energy including hydrogen is crucial for resolving these problems [4, 5]. Since TiO$_2$ was applied to generate hydrogen by Fujishima and Honda for the first time in 1972 [6], photocatalytic reaction of semiconductors have become an extremely important method to improve the quality of the environment. Up to now, many semiconductors photocatalysts have been developed and applied, such as ZnO [7, 8], Fe$_3$O$_4$ [9, 10], BiVO$_4$ [11, 12], CuO [13, 14] and g-C$_3$N$_4$ [15, 16]. Compared with these semiconductors, more and more research interests have captured by n-type WO$_3$ due to suitable bandgap, stronger oxidation ability of photoinduced holes, excellent transfer rate of carriers and lower cost [17–19]. However, the photocatalytic application of WO$_3$ in the fields of environment and energy is not still realized due to the influences from the shortages of poor light absorption, low separation efficiency and sluggish surface reaction kinetics [20–22].

The various measurements including elements doping, surface medication and the loading of plasma metals have been applied to enhance the photocatalytic prosperities of WO$_3$ [23–25]. The coupling of different semiconductors with smaller bandgap has been seen as an effective method and attracted wide attention among above medication measurements. Widiyandari and his co-workers [26] prepared WO$_3$/CuO composite photocatalyst through the combining method of spray pyrolysis and flame, and the composite photocatalyst showed enhanced photocatalytic properties. Li and his co-workers [27] synthesized successfully WO$_3$/MoS$_2$-rGO nanocomposite photocatalyst, and the significantly improved photocatalytic performances are displayed by the photocatalyst, which include the photocatalytic degradation rate of 98.3% with photocatalytic reaction for 20 min. It is calculated for the construction of composite photocatalysts with high photocatalytic properties that the choice of semiconductors for coupling WO$_3$ is extremely important.
As an one of the typical n-type semiconductors, hematite (α-Fe₂O₃) have been extensively researched in filed photoelectromechanical and photocatalytic fields due to response activity for visible light with the bandgap of ∼2.2 eV, excellent chemical stability and low cost. It is nothing worth for the application of Fe₂O₃ that the theoretical feasibility is supported for the construction of type-II heterojunction due to suitable position with WO₃ for energy bands. Hence, Fe₂O₃ is selected to modify WO₃ as an ideal coupling semiconductor. Although there is a certain degree of support for the construction of WO₃/Fe₂O₃ composite photocatalyst in theory, the possibility of practical application may be not ideal due to the difficulty in recycle and recovery. Therefore, the film of WO₃/Fe₂O₃ grown in FTO conductive substrate is synthesized instead of traditional powder forms for photocatalysts. Furthermore, the photocatalys film without toxic can be utilized maximally in practical life and more field, such as the security of human health through sterilization effect in hospitals, kitchens, bathrooms, tableware and other places and appliances [28, 29].

Based on above analysis, we prepared WO₃/Fe₂O₃ composite film on FTO conductive glass through secondary hydrothermal method. A series of photocatalytic measurements shows the enhanced photocatalytic performances including degradation for MB and the higher sterilization rate for sulfur oxidizing bacteria are displayed by WO₃/Fe₂O₃ composite film. Deeper measurements indicates that the improved photocatalytic prosperities of WO₃/Fe₂O₃ composite film are attributed the more light absorption, the suppressed recombination and accelerated kinetics of photoinduced carriers. This work can play a good supporting role for the maximum application of WO₃-based films in photocatalytic dye degradation and antibiosis.

2. Experimental section

2.1. Synthesis of bare WO₃ Nanoplates arrays
The 0.462 g of sodium tungstate is dissolved in 60 ml of deionized water, and then the solution is slowly stirred for 5 min. The diluted hydrochloric acid (3 M, 20 ml) is gradually added into sodium tungstate solution with constant stirring and the epinephelos solution. The 60 ml of deionized water and 0.40 g of ammonium oxalate are added into the turbid solution and the cleaner precursor solution is obtained after stirring for 30 min. Subsequently, the hydrothermal reaction on FTO conductive substrate is carried out for 120 °C and 12 h. Finally, the offwhite WO₃ films are successfully obtained through the annealing for 450 °C and 1 h.

2.2. Synthesis of WO₃/Fe₂O₃ composite structure
The preparation of Fe₂O₃ on WO₃ is same as previous researches [30, 31]. Firstly, the 1.6 g of FeCl₃·6H₂O is dissolved in 40 ml of deionized water and then the solution is stirred for 10 min. Whereafter, the 3.4 g of NaNO₃ is added into FeCl₃ solution and dissolved completely with the stirring for 10 min. The pH of mixed solution is

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Figure 1. The SEM images of (a) bare WO₃, (b) WO₃/Fe₂O₃-2 h, (c) WO₃/Fe₂O₃-3 h and (d) WO₃/Fe₂O₃-4 h.
adjusted to 1.5 through the slow addition of HCl. Subsequently, the precursor solution of Fe₂O₃ and as-prepared are put together into stainless steel autoclave to construct the precursor of WO₃/Fe₂O₃ composite films. Finally, the WO₃/Fe₂O₃ composite films are prepared after the annealing for 450 °C and 1 h in air.

2.3. Characterization
The microtopography features of all as-synthesized photocatalysts are described through scanning electron microscope (SEM, JEOL JSM-7800F). The information for distribution of elements and atomic percent is obtained through energy-dispersive X-ray spectroscopy (EDS, AZtec from Oxford) attached to SEM. The crystal type and structure of all as-prepared samples is analysed with X-ray diffractometer (XRD, Rigaku-D/max-2500, Cu Kα radiation). The optical properties of all as-synthesized photocatalytic films are study via ultraviolet-visible spectroscopy (UV–vis, DU-8B). The light absorption of MB solution is measured through visible spectroscopy with fixed wavelength (Vis, 7230 G, 465 nm). The light source is supported by simulated sunlight (CHF-XM500, AM 1.5 G, 100 mW cm⁻²). Super depth of field 3D display system (Keyence, VHX-600e) is used to calculate the amount of sulfur oxidizing bacteria on counting boards. The electrochemical impedance spectroscopy and Mott-Schottky measurements are carried out with the frequency of 1000 Hz.

3. Results and discussion

The microtopographies of all as-prepared photocatalysts are investigated through the results of SEM images displayed in figure 1. As shown in figure 1(a), bare 2D WO₃ photocatalysts shows regular nanoplates array which is favourable to photocatalytic reaction of WO₃-based photocatalysts [32]. To be more specific, all 2D WO₃ nanoplates grow almost vertically on the FTO substrate which provides direct transmission channel for photogenerated electrons, that is, photoinduced electrons are quickly transmitted to FTO and the transmission distance is shorted, thus reducing the recombination probability of photogenerated electron-hole pairs. Meanwhile, the larger surface area is exposed due to larger gap between the nanoplates, which can enhance the progress of photocatalytic reaction. The high-resolution SEM images of bare 2D WO₃ is inserted in top right of figure 1(a), which shows that the thickness of WO₃ nanoplate is ~137 nm and smooth surface of bare WO₃ photocatalyst. With the deposition of Fe₂O₃ for 2 h, the numerous granular and small branchlike compound are generated, as shown in figure 1(b). Moreover, the high-resolution SEM image of WO₃/Fe₂O₃-2 h composite photocatalyst displays the rough surface and the larger surface area than bare 2D WO₃, which may imply the enhanced performances of photocatalytic reaction. In other words, the dispersed Fe₂O₃ particles are well coupled with WO₃ which is conductive to the separation and transportation of photoinduced carriers at the interface with the existence of the pathway from WO₃. Moreover, the deposition of Fe₂O₃ increase the total contact area of WO₃-based photocatalyst and electrolyte as well as light irradiation, which is beneficial to the occurrence of photocatalytic redox reaction and capture more photons. The granular compound almost disappeared and the branchlike compound almost covers the top of 2D WO₃ nanoplates when the hydrothermal
time of Fe₂O₃ is prolonged to 3 h, as shown in figure 1(c). Especially, the microtopography of WO₃/Fe₂O₃-3 h composite photocatalyst may imply the branchlike compound is formed though the growth of granular compound, which indicates that the granular and branchlike compound is Fe₂O₃. Furthermore, the phenomenon can be observed that the gap between every WO₃/Fe₂O₃-3 h composite photocatalyst unit is significantly decreased. The high-resolution SEM images of WO₃/Fe₂O₃-3 h composite photocatalyst shows the maximum diameter of branchlike Fe₂O₃ is ∼136 nm. As for WO₃/Fe₂O₃-4 h composite photocatalyst, the maximum diameter of branchlike Fe₂O₃ is ∼113 nm, and the change is almost negligible. It is worth noting that gap between every WO₃/Fe₂O₃-4 h composite photocatalyst unit is further decreased, which may hinder the application of improved photocatalytic performances for WO₃/Fe₂O₃ composite photocatalyst. The EDS spectrum and elements mapping of W, Fe and O elements attached to SEM image of WO₃/Fe₂O₃-3 h are shown in figure 2 in order to further analyze the construction of WO₃/Fe₂O₃ composite photocatalyst. Based on figure 2(b), the signals of Fe, W and O elements is detected. However, the atom percent of W, Fe and O elements does not match with theoretical value (1:2:6), that is, the proportion of O is less, which may be attributed to the common combination for O atoms by Fe and W at the interface of WO₃ and Fe₂O₃. Moreover, the elements mapping of W, Fe and O elements shows corresponding position, indicating that the WO₃/Fe₂O₃ heterojunction photocatalyst is well formed and corresponding with the results of SEM.

The results of XRD measurements are displayed in figure 3 in order to analyze the crystal structure of WO₃ and WO₃/Fe₂O₃-3 h photocatalyst. As for bare 2D WO₃ photocatalyst, the diffraction peaks attributed to FTO conductive glass is screened out and marked with *'. As for the four diffraction peaks including 2θ = 23.6°, 24.3°, 28.9° and 61.7° can be respectively indexed to crystal planes of (0 2 0), (2 0 0), (−1 1 2) and (4 2 2), which demonstrate the monoclinic phase of bare 2D WO₃ (JCPDS 83-0950). With the deposition of Fe₂O₃ for 3 h, the
diffraction peaks of monoclinic WO₃ at 2θ = 23.0° is observed, indicating that the crystal plane of (002) is more exposed and imply that the photocatalytic performances of WO₃/Fe₂O₃ composite photocatalyst is influenced by the (002) crystal plane of WO₃. Moreover, the feeble diffraction peaks at 2θ = 35.7°, 72.2° and 72.7° are observed, and these peaks can be respectively attributed to the crystal planes of (110), (119) and (220), which indicate that Fe₂O₃ belonged to hematite phase is well deposited on WO₃ substrate. It is worth noting that the diffraction peaks of (119) and (220) almost disappear due to the smaller thickness of Fe₂O₃. On the whole, the results of XRD prove the formation of WO₃/Fe₂O₃ composite photocatalyst and correspond with the results of SEM and EDS.

The results of UV–vis measurements is applied to investigate the optical performances of all as-synthesized photocatalysts, as shown in figure 4(a). As for bare 2D WO₃, the smaller absorption edge for stimulated sunlight is shown, which is only ∼462 nm. The significant red-shift are observed for the absorption edge of WO₃/Fe₂O₃-2 h, and the absorption edge is about 546 nm. With the increased time for depositing Fe₂O₃ on WO₃, the absorption edge of WO₃-based photocatalyst is further extended to 563 nm. Compared with bare WO₃, the photoresponse range of WO₃-based expanded by 21.86%. However, the absorption edge of WO₃/Fe₂O₃-4 h is smaller than WO₃/Fe₂O₃-2 h, and the value is same as that of WO₃/Fe₂O₃-3 h, which is attributed to the more amount of Fe₂O₃ deposited on WO₃ [33]. Moreover, the deeper optical mechanism of Fe₂O₃ on WO₃ through bandgap spectrum shown in figure 4(b) according the results of UV–vis measurements and equation (1) as following [34]:

\[
\alpha hν^n = A(hν - E_g)
\]  

In which, \(E_g\) means the optical bandgap of all as-prepared photocatalysts, \(h\) and \(ν\) is respectively Planck constant and frequency of photons. Moreover, the constants of absorbance and proportion is noted by \(A\) and \(α\). Especially, for the indirect semiconductors such as WO₃, the value of \(n\) is 1/2. Corresponding with the absorption edge, the bandgap value of bare 2D WO₃ is 2.68 eV. With the deposition of Fe₂O₃, the bandgap of WO₃-based composite photocatalysts decrease to 2.27 eV, 2.2 eV and 2.27 eV, which indicate that Fe₂O₃ with smaller bandgap help WO₃ capture more light as light absorber.

The photocatalytic activities of all as-prepared photocatalysts are first evaluated through the degradation of MB. As shown in figure 5(a), the concentration changes of methylene blue (MB) solution are not so distinct in the first 15 min with the occurrence of photocatalytic reaction, which is mainly attributed to the occurrence of
absorption-desorption reaction. The concentration of MB decrease rapidly as time goes on, and the final proportion of concentration at corresponding time \( (C) \) and original concentration \( (C_0) \) reaches 0.58 for bare 2D WO\(_3\) photocatalyst. As for WO\(_3\)/Fe\(_2\)O\(_3\)-2 h, the degradation efficiency is significantly improved, and the value of \( C/C_0 \) reaches 0.48 with photocatalytic activity for 4 h. The value of \( C/C_0 \) is further decreased to 0.28 for WO\(_3\)/Fe\(_2\)O\(_3\)-3 h, which indicates enhanced photocatalytic performances and is attributed to the generation of more photoinduced carriers with the deposition of adequate Fe\(_2\)O\(_3\) on WO\(_3\). However, the final value of \( C/C_0 \) is improved to 0.36 for WO\(_3\)/Fe\(_2\)O\(_3\)-4 h, which may be attributed to decreased light absorption and increased recombination of photoinduced carriers due to longer migration length with the deposition of more Fe\(_2\)O\(_3\). Moreover, the decreased degradation efficiencies are observed at 150 min for WO\(_3\)/Fe\(_2\)O\(_3\)-3 h and WO\(_3\)/Fe\(_2\)O\(_3\)-4 h composite photocatalysts as well as the significant obvious turning point is at 120 min for bare 2D WO\(_3\) photocatalysts, and the difference of 30 min demonstrates the enhanced photocatalytic stability of WO\(_3\)-based photocatalysts when Fe\(_2\)O\(_3\) is deposited on WO\(_3\). The results of UV–vis measurements for MB solution with the photocatalytic application of WO\(_3\)/Fe\(_2\)O\(_3\)-3 h is applied to support the analysis of figure 5(a). It can be observed for MB solution with the photocatalytic degradation under different time that the characteristic peaks generated at 554 nm. With the occurrence of photocatalytic reaction, the intensity of characteristic peaks decrease gradually due to the decomposition of MB. In order to obtain the constants for degradation of MB, the first order kinetic model of photocatalytic degradation of all as-prepared photocatalysts is constructed through equation (2) \[35, 36]\:

\[
\ln \left( \frac{C_0}{C} \right) = kt
\]

in which, \( k \) and \( t \) are the degradation rate constant of MB and the time of photocatalytic reaction, respectively. As shown in figure 5(d), the degradation constant of bare 2D WO\(_3\) film is only 0.00191 min\(^{-1}\), which demonstrates the slow microscopic photocatalytic degradation. After the deposition of Fe\(_2\)O\(_3\) for 2 h, the degradation constant of WO\(_3\)-based photocatalyst is 1.75 folds higher than that of bare WO\(_3\) film, which reaches 0.00336 min\(^{-1}\). The maximum degradation constant of 0.00513 min\(^{-1}\) is achieved by WO\(_3\)/Fe\(_2\)O\(_3\)-3 h film, which is 1.12 folds higher than that of 0.00457 min\(^{-1}\) for WO\(_3\)/Fe\(_2\)O\(_3\)-4 h film. In a word, the highest photocatalytic performances are achieved by WO\(_3\)/Fe\(_2\)O\(_3\)-3 h (named WO\(_3\)/Fe\(_2\)O\(_3\) in next analysis) among all as-prepared films for photocatalytic reaction.

The antibacterial activities of as-prepared photocatalytic films including bare WO\(_3\) and WO\(_3\)/Fe\(_2\)O\(_3\) composite structure are evaluated through the destruction of sulfur oxidizing bacteria with the irradiation of stimulated sunlight, and the amount of sulfur oxidizing bacteria is counted through equation (3) \[35, 36\]:
in which, \( N_s \) means the total amount of sulfur oxidizing bacteria per milliliter of bacterial solution and \( A \) notes the total amount of sulfur oxidizing bacteria for five counting squares. Furthermore, \( B \) represents multiple of dilution for bacterial solution, and the multiple is 30 times. As shown in figure 6, it is can be observed for pure FTO conductive glass that the proportion of destroyed bacteria is only 5.07\%, which indicate that the influence of FTO conductive glass on the performances of antibacterial activities for as-prepared photocatalytic films may be negligible. The effect of photocatalytic antibiosis for bare WO\(_3\) is more significant, and the surplus amounts of sulfur oxidizing bacteria per milliliter of bacterial solution are \( 5.15 \times 10^8, 4.82 \times 10^8, 4.52 \times 10^8 \) and \( 4.39 \times 10^8 \) after photocatalytic antibiosis for 1 h, 2 h, 3 h and 4 h, respectively. The antibacterial performances are further enhanced with the deposition of Fe\(_2\)O\(_3\) on WO\(_3\), and the surplus amounts of sulfur oxidizing bacteria per milliliter of bacterial solution are \( 4.61 \times 10^8, 4.43 \times 10^8, 4.11 \times 10^8 \) and \( 3.92 \times 10^8 \) after photocatalytic antibiosis for 1 h, 2 h, 3 h and 4 h, respectively. More precisely, after the photocatalytic antibiosis for 4 h, the sterilizing rate of 28.99\% for WO\(_3\)/Fe\(_2\)O\(_3\) composite film is 1.42 folds higher than that of 20.47\% for bare WO\(_3\) film. The enhanced antibacterial performances is attributed to two reasons as following [37]: (I) the introduction and dissolution of Fe\(^{3+}\) with the deposition of Fe\(_2\)O\(_3\), (II) the enhanced destruction for the mechanism of electrons transfer and the interrupt of respiration process for sulfur oxidizing bacteria due to the utilization of more photoinduced carriers with the formation of WO\(_3\)/Fe\(_2\)O\(_3\) heterojunction.

The direct evidences of photocatalytic antibiosis are shown in figure 7 in order to qualitatively assess the antibacterial activities of as-prepared photocatalytic films. As for the bacterial solution through photocatalytic reaction for 1 h, the maximum transparency is displayed by the bacterial solution containing WO\(_3\)/Fe\(_2\)O\(_3\) film, demonstrating the best antibacterial performances. The transparency of bacterial solution is further improved.

\[
N_s = A / 5 \times 25 \times 10^4 \times B
\]
and the content of white sediment is obviously increased when the photocatalytic antibiosis for 4 h is carried out, demonstrating that the destruction of sulfur oxidizing bacteria, as shown in figure 7(b). Moreover, the amount of sulfur oxidizing bacteria is approximate combining and qualitatively described combining with results of ultra-diameter deep microscope. It is can be observed that the amounts of alive sulfur oxidizing bacteria is significantly decreased with the occurrence of photocatalytic antibiosis, and the least amount of alive sulfur

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**Figure 8.** (a) Linear Sweep Voltammetry measurements, (b) Chronoamperometry with light on and light off, (c) injection efficiencies of photoinduced carriers and (d) Surface Photovoltage Spectroscopy of pure WO$_3$ and WO$_3$/Fe$_2$O$_3$ composite film.

**Figure 9.** (a)–(c) The EIS spectrum and Mott-Schottky curves with and without the irradiation of stimulated sunlight for bare WO$_3$ and WO$_3$/Fe$_2$O$_3$ composite film, (d) the schematic diagram of enhanced photocatalytic performances for WO$_3$/Fe$_2$O$_3$ composite film.
oxidizing bacteria is obtained with photocatalytic reaction form WO₃/Fe₂O₃ film, which further support the analysis of figure 6.

In order to further investigate the catalytic performances under irradiation of WO₃ and WO₃/Fe₂O₃ film, some photoelectrochemical measurements are carried out with the application of three-electrode system as well as 0.2 M Na₂SO₄ electrolyte. As shown in figure 8(a), the results of Linear Sweep Voltammetry can indicate the change of PC and PEC in its entirety [34]. The photocurrent density of 0.67 mA cm⁻² (1.23 V versus RHE) is achieved by WO₃/Fe₂O₃ composite film which is 3.19 folds higher than the value of pure WO₃ (0.21 mA cm⁻²).

The significant enhancement can be attributed to the generation of more photogenerated carriers with the extend of absorption edge as well as the suppressed recombination of photoinduced electron-hole pairs. The results of Chronoamperometry with light on and off can be used to demonstrate the importance of irradiation. It is observed for pure WO₃ and WO₃/Fe₂O₃ composite film that the curve rise rapidly and stabilize with light on as well as decline rapidly, indicating the excellent optical excitation performance. Moreover, for all as-prepared photocatalysts, the current density in dark extremely smaller in contrast to the results under irradiation, demonstrating that generation of current derived from the transfer of photoinduced carriers.

Furthermore, the enhanced photocurrent density of WO₃/Fe₂O₃ composite film may imply the improved charges transfer dynamics than pure WO₃. As shown in figure 8(c), the injection efficiencies of photoinduced carriers is respectively 28.39% and 44.43% for pure WO₃ and WO₃/Fe₂O₃ composite film which indicate the enhanced surface reaction kinetics and correspond with the results of Chronoamperometry. As a direct means of characterization for photoinduced carriers separation efficiency, surface photovoltage spectroscopy of the photocatalysts is obtained with light irradiation on positive surface of photocatalyst. The SPV signals of 18.96 μV for WO₃/Fe₂O₃ is captured at 464 nm, which is much higher than 5.33 μV (395 nm), strongly proving the enhanced carriers separation efficiency in space with the formation of WO₃/Fe₂O₃ heterojunction.

The deeper mechanism of enhanced photocatalytic performances for WO₃/Fe₂O₃ composite film can be investigated through additional photoelectrochemical measurements, and the smaller radius of EIS arc means the more excellent electrochemical performances [38]. As shown in figure 9(a), the results of EIS measurements for bare WO₃ and WO₃/Fe₂O₃ composite film under dark shows enhanced electrical conductivity with the deposition of Fe₂O₃ on WO₃, which is instrumental in the transfer of photoinduced carriers. With the irradiation of stimulated sunlight, the radius of EIS arc is further decreased, indicating that photocatalytic performances for bare WO₃ and WO₃/Fe₂O₃ composite film. Especially, WO₃/Fe₂O₃ composite film shows the enhanced surface reaction kinetic than that of bare WO₃ film, which indicates the recombination of photoinduced carriers is further suppressed. Subsequently, the physicochemical information of interface between WO₃ and Fe₂O₃ through Mott-Schottky measurements. As displayed in figures 9(b) and (c), the flat potential of bare WO₃ is 0.48 V with light off, and the value is higher than that of WO₃/Fe₂O₃ composite film, which may be attributed to the effect of buffer layer for Fe₂O₃ [39]. With the irradiation of stimulated sunlight, the obvious negative shift is accomplished for bare WO₃ and WO₃/Fe₂O₃ composite film, and the flat potential is respectively 0.43 V and 1.07 V, which indicate the effective photoresponse for all as-prepared films. Moreover, the difference of the flat potential for bare WO₃ and WO₃/Fe₂O₃ composite illustrates the formation of built-in electric filed due to the construction of WO₃/Fe₂O₃ heterojunction. Based on above analysis, the schematic diagram can be obtained, as shown in figure 9(d). The more photons is captured due to the effect of light absorber for Fe₂O₃ when WO₃/Fe₂O₃ composite films is irradiated by stimulated light, and then photoinduced electron-hole pairs are generated. With the coupling of WO₃ and Fe₂O₃, the bend of energy bands is generated at the interface of WO₃/Fe₂O₃, which suppress the recombination of photoinduced electron-hole pairs. Afterwards, the photogenerated carriers are transferred to surface of composite photocatalyst to participate in the reaction of photocatalytic degradation or photocatalytic antibiosis.

4. Conclusion

We prepared successfully WO₃/Fe₂O₃ composite film on FTO conductive glass through convenient hydrothermal method. The WO₃-based composite film displays excellent optical prosperity and the photocatalytic performances for degradation and antibiosis. The absorption edge of 563 nm is achieved by WO₃/Fe₂O₃ composite photocatalyst, which is higher than that of 462 nm for bare WO₃. With the irradiation of stimulated sunlight for 4 h, the degradation efficiency of MB for WO₃/Fe₂O₃ composite film is significantly higher than that of bare WO₃, and the values of C/C₀ 0.28 and 0.58 for WO₃/Fe₂O₃ composite film and bare WO₃, respectively. Meanwhile, the more outstanding ability of photocatalytic antibiosis is displayed by WO₃/Fe₂O₃ composite film, and the sterilization rate of 28.99% is achieved as well as the corresponding rate for bare WO₃ in only 20.47%. The deeper optical measurements indicate that the generation of more photogenerated carriers is crucial to the enhanced photocatalytic prosperities of WO₃/Fe₂O₃ composite film due to the more photons absorbed. Moreover, the improved photocatalytic performances are influenced by the
decreased recombination of photogenerated carriers with the formation of WO$_3$/Fe$_2$O$_3$ heterojunction as well as the enhanced electrical conductivity and the transfer kinetics of photoinduced carriers. We believe that this work plays a favorable demonstration role for the modification and application of WO$_3$-based photocatalytic film in degradation and antibiosis with assistance of sunlight.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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