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Construction of *in situ* self-assembled FeWO₄/g-C₃N₄ nanosheet heterostructured Z-scheme photocatalysts for enhanced photocatalytic degradation of rhodamine B and tetracycline†

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Although photocatalytic degradation is an ideal strategy for cleaning environmental pollution, it remains challenging to construct a highly efficient photocatalytic system by steering the charge flow in a precise manner. In this work, a novel, highly efficient, stable, and visible light active hybrid photocatalytic system consisting of FeWO₄ and g-C₃N₄ nanosheets (CNNs) has been successfully prepared by an *in situ* self-assembly solvothermal approach. Several characterization techniques were employed to study the phase structures, morphologies, optical properties, surface composition and chemical state of the as-prepared samples. SEM and TEM results demonstrated that the FeWO₄ nanoparticles are uniformly dispersed on the surface of CNNs with a diameter of about 10–20 nm, which could provide maximum interfacial contact and a synergistic coupling effect between FeWO₄ and CNNs. XPS and FTIR results confirmed that there was strong electrostatic interaction between FeWO₄ and CNNs, suggesting the formation of heterojunctions between them. In addition, UV-DRS and PL spectroscopy revealed that the FeWO₄/CNN composites exhibited increased visible light absorption and improved charge generation/separation efficiency. As a result, the photocatalytic activity of the FeWO₄/CNNs was enhanced in comparison with pure FeWO₄ and CNNs for rhodamine B (RhB) and tetracycline (TC) degradation under natural sunlight irradiation. The photocatalytic efficiency of the optimal FeWO₄/CNN composite (10 wt% FeWO₄/CNNs) for the degradation of RhB (TC) was about 13.26 (4.95) and 86.2 (31.1) times higher than that of pure FeWO₄ and CNNs, respectively. Meanwhile, the 10 wt% FeWO₄/CNN sample exhibits good photocatalytic stability in recycling experiments. The enhanced photocatalytic activity may be attributed to the formation of the Z-scheme system between FeWO₄ and CNNs, effectively prolonging the lifetime of the photoexcited electrons generated by CNNs and the photoexcited holes generated by FeWO₄, which was subsequently confirmed by the active species trapping experiments and the calculation of relative band alignments. This work opens up a new feasible avenue to synthesize visible light active Z-scheme photocatalysts for application in energy production and environmental remediation.

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1. Introduction

Over the past few decades, environmental pollution has become one of the greatest problems to society. The effluents produced by many industries, such as textile, pharmaceutical, cosmetic, leather, and food industries, are identified as the primary

source of water contamination, which is harmful to the environment, and hazardous to human health as well as ecosystems.^{1–3} Due to their stable chemical structures and recalcitrance to biological degradation, conventional wastewater treatment processes are not always efficient in the removal of these pollutants.^{4–6} As a result, they have been frequently detected in a variety of environmental matrices, including surface, ground and potable water, soils and even the food on our table. There is therefore a need for the development of efficient treatment technologies for the removal of these compounds from wastewater. A “green” photocatalytic strategy that utilizes solar energy has been considered as a sustainable solution to solve the above-mentioned problems.^{7–12} Nevertheless, the photocatalytic performance of most semiconductor photocatalysts available is located at a low level, and their

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practical application is hampered by some internal effects, such as poor visible light utilization, lower photogenerated electron-hole pair separation, and the lack of active species generation.^{13–15} Thus, to maximize the utilization of solar light, the development of visible light active photocatalysts with sufficient charge separation ability and high photocatalytic stability is still an arduous task in photocatalysis research. Hence, the fabrication of heterojunctions is an effective and attractive strategy to restrain the recombination rate of photogenerated charge carriers.^{16–18} Nevertheless, it is difficult to simultaneously achieve high charge separation efficiency and strong redox ability. Recently, the construction of artificial Z-scheme photocatalytic systems has emerged as an alternative method, because it can not only separate the photogenerated electron-hole pairs but also maintain the excellent redox capacity of the constituent semiconductors.^{19–21} However, the majority of the synthesized artificial Z-scheme photocatalytic systems usually had mediators (e.g. redox pairs ($\text{Fe}^{3+}/\text{Fe}^{2+}$ and IO_3^-/I^-))^{22,23} and noble metals (Ag and Au),^{24,25} which will bring about great difficulties in their practical application.¹⁹ Thus, developing a mediator-free direct Z-scheme photocatalytic system as an ideal and effective method has become a hotspot for application in environmental purification and hydrogen generation from water.^{26–31}

Recently, two-dimensional (2D) materials have been widely studied in photocatalysis due to their unique structural and optical properties, of which the $\text{g-C}_3\text{N}_4$ material gained special attention because it is abundant, sustainable, environmentally friendly and has a suitable band gap and high chemical stability, making it potentially suitable for solar energy conversion and environmental purification.^{32–36} Unfortunately, pure $\text{g-C}_3\text{N}_4$ seriously suffers from poor photocatalytic efficiency because of a high recombination rate of photogenerated charge carriers.^{37–40} Besides, it is reported that $\text{g-C}_3\text{N}_4$ nanosheets show considerably superior photocatalytic activity compared to the bulk $\text{g-C}_3\text{N}_4$ resulting from the reduction of internal defects and improvement of the specific surface area.^{41,42} It can be predicted that the photocatalytic activity of $\text{g-C}_3\text{N}_4$ -based photocatalysts may be further enhanced by increasing the specific surface area of bulk $\text{g-C}_3\text{N}_4$. Thus, it is accepted that the construction of $\text{g-C}_3\text{N}_4$ -based Z-scheme photocatalysts with a narrow band gap semiconductor may provide bright prospects for dealing with the increasingly serious environmental pollution.

Recent studies have investigated some metal tungstates as potential co-catalyst candidates for photocatalytic applications, which could effectively reduce the recombination of charge carriers for improving the degradation of pollutants.^{43–45} Among these tungstates, the investigation of iron tungstate (FeWO_4) has been widely reported in the literature due to its narrow band gap, and good magnetic and photocatalytic properties.^{46,47} Recently, FeWO_4 has been explored for photocatalytic reactions with no co-catalysts.^{48,49} Furthermore, suitable matching of the band levels of FeWO_4 with $\text{g-C}_3\text{N}_4$ nanosheets to form a direct Z-scheme photocatalytic system offers appropriate driving forces to separate and transfer photogenerated electron-hole pairs. As FeWO_4 and $\text{g-C}_3\text{N}_4$ are both visible light driven photocatalysts, after combining the FeWO_4 photocatalyst with

$\text{g-C}_3\text{N}_4$ nanosheets, the obtained $\text{FeWO}_4/\text{g-C}_3\text{N}_4$ nanosheet composite may be a promising candidate for efficient photocatalytic activity under visible light irradiation. However, to the best of our knowledge, no group has reported *in situ* growth of FeWO_4 nanoparticles on the surface of $\text{g-C}_3\text{N}_4$ nanosheets by a facile solvothermal method for the degradation of RhB and TC under sunlight irradiation.

Based on the above considerations, herein we grew FeWO_4 nanoparticles on the surface of $\text{g-C}_3\text{N}_4$ nanosheets by a facile solvothermal method to form composite catalysts for efficient degradation of organic pollutants and these composites were found to exhibit superior photocatalytic activity compared with the pure FeWO_4 , $\text{g-C}_3\text{N}_4$ nanosheets and mechanically mixed catalyst. It was found that the composite photocatalysts exhibited not only an improved photocatalytic activity but also excellent stability and reusability during the photocatalytic process, which can be mainly attributed to the synergistic effect between FeWO_4 and $\text{g-C}_3\text{N}_4$ nanosheets. Furthermore, a possible direct Z-scheme mechanism for the enhanced photocatalytic activity of the $\text{FeWO}_4/\text{g-C}_3\text{N}_4$ nanosheet composite was also discussed based on the relative band gap positions of these two semiconductors and the free radical trapping experimental results. Detailed characterization of the structure, composition, and optical properties of the as-prepared photocatalysts was also carried out.

2. Experimental section

2.1. Preparation of bulk $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4$ nanosheets

Bulk $\text{g-C}_3\text{N}_4$ (CN) was prepared by thermal polymerization of melamine at high temperature in a muffle furnace.⁵⁰ In detail, 5 g of melamine was placed in a crucible with a cover, and then, it was heated at 600 °C for 2 h with a ramp rate of about 3 °C min^{-1} . After cooling to room temperature, the obtained yellow agglomerates were collected and ground into fine powder. After that, $\text{g-C}_3\text{N}_4$ nanosheets (CNNs) were prepared by using the liquid exfoliation method.⁵⁰ In detail, 100 mg of the as-prepared CN was dispersed in 100 mL of double distilled water, then the mixture was sonicated for 16 h and then the resulting suspension was centrifuged at 5000 rpm to remove the residual un-exfoliated $\text{g-C}_3\text{N}_4$. Then, the final suspension was dried at 80 °C overnight.

2.2. Preparation of $\text{FeWO}_4/\text{g-C}_3\text{N}_4$ nanosheet composites

FeWO_4/CNN composites were synthesized through a solvothermal method.^{47,51} First, an appropriate amount of the as-prepared CNNs was dispersed in 36 mL of ethylene glycol by sonication for 30 min, to facilitate the uniform growth of FeWO_4 nanoparticles on their surface. Then, 5 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in 2 mL double distilled water was added to the CNN suspension and stirred magnetically for 30 min. Subsequently, 5 mmol of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ dissolved in 2 mL of double distilled water was added dropwise to the above mixture. 10 mmol of sodium acetate was then added to the above mixture with continuous stirring. After 30 min of stirring, the above suspension was transferred into a Teflon-lined stainless steel



autoclave (50 mL) and reacted at 200 °C for 12 h. After cooling down to room temperature naturally, the products obtained were collected by centrifugation, washed several times with double distilled water and ethanol, and dried in an oven at 80 °C for 12 h. The as-prepared FeWO₄/CNN composites with various FeWO₄ amounts of 5, 10, 15 and 20 wt% were denoted as 5-FWO/CNNs, 10-FWO/CNNs, 15-FWO/CNNs and 20-FWO/CNNs, respectively. Pure FeWO₄ nanoparticles were also synthesized under the same conditions without adding any CNN powder.

In addition, a control sample was also prepared by mechanical grinding of CNNs and FeWO₄. A mixture of FeWO₄ and CNNs was finely ground and then calcined at 200 °C for 12 h. After cooling to room temperature, the resultant product was collected and crushed to powder for further use. The mass ratio of FeWO₄ and CNNs in the sample was the same as that in the optimal composite catalyst of FeWO₄/CNNs [10-FWO/CNNs]. The control sample was denoted as FeWO₄ + CNNs. More details about the materials and characterization methods are provided in the ESI.†

2.3. Measurement of photocatalytic activity

The photocatalytic activities of the as-prepared photocatalysts were evaluated by the degradation of rhodamine B (RhB) and tetracycline (TC) under natural sunlight irradiation. All of the photocatalytic experiments were carried out during the same time on sunny days and the sunlight intensity was found to be around 100 000 lx to 110 000 lx. In a typical experiment, 50 mg of photocatalyst was suspended in an aqueous solution of RhB (50 mL, 10 mg L⁻¹) and TC (50 mL, 20 mg L⁻¹), and then the suspensions were stirred in the dark for 1 h to reach the adsorption-desorption equilibrium between the photocatalyst and model pollutants, after which the reaction suspension was irradiated for 90 min. At certain time intervals, 4 mL aliquots were sampled and centrifuged to remove the photocatalyst, and the concentrations of the remnant RhB and TC were analyzed by recording the absorbance using an UV-Vis spectrophotometer (UV-2600, Shimadzu). A blank test was also carried out without any photocatalyst under sunlight irradiation to evaluate the efficiency of the photocatalyst. Furthermore, the reusability of 10-FWO/CNNs was tested by four consecutive cycles for the

degradation of RhB. After each cycle, the catalyst was separated from the reaction mixture by centrifugation and washed with double distilled water and dried overnight in an oven at 80 °C for use in the next cycle.

2.4. Analysis of reactive species

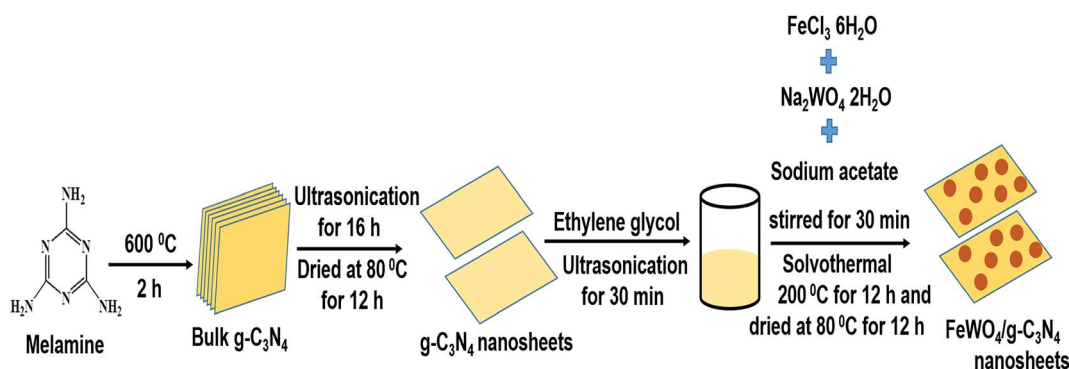
To investigate the active species generated during the photo-degradation process, ammonium oxalate (AO, 1 mM), isopropanol (IPA, 1 mM), and 1,4-benzoquinone (BQ, 1 mM) were used as the hole (h⁺), hydroxyl radical (·OH), and superoxide radical (·O₂⁻) scavengers,⁵⁰ respectively. The method was similar to the above photocatalytic activity test. The ·OH content was also measured by the PL technique, using terephthalic acid (TA) as a probe molecule.⁵²

3. Results and discussion

A facile *in situ* solvothermal method was designed for the preparation of FeWO₄/g-C₃N₄ nanosheet photocatalysts, and the preparation process is illustrated in Scheme 1. Firstly, the g-C₃N₄ nanosheets obtained from the bulk g-C₃N₄ through a liquid exfoliation method were dispersed in ethylene glycol by sonication. Then, upon addition of FeCl₃ solution to the above reaction mixture, the Fe³⁺ ions were reduced to Fe²⁺ ions because of the reducing ability of ethylene glycol. Then, with the addition of NaWO₄ solution and sodium acetate (here sodium acetate provided an alkaline environment), the Fe²⁺ ions reacted with WO₄²⁻ ions to generate FeWO₄ nuclei on the g-C₃N₄ nanosheet surface under constant stirring. As the solvothermal treatment time increased, the FeWO₄ nuclei grew into nanoparticles through a self-assembly growth mechanism.⁴⁷ In this case, g-C₃N₄ nanosheets not only act as the support to form heterostructures but are also employed as dispersants to hinder the aggregation of FeWO₄ nanoparticles. Finally, FeWO₄/CNN heterostructured photocatalysts were obtained.

3.1. Characterization of photocatalysts

The crystalline phases of the as-prepared samples were examined by XRD analysis. Fig. 1a shows the XRD patterns of the CN, CNNs, FeWO₄ and FeWO₄/CNN composites. The pure CN has two significant peaks at 27.4° and 13.1°, indexed to the (002)



Scheme 1 Schematic representation of the preparation of bulk g-C₃N₄, g-C₃N₄ nanosheets and FeWO₄/g-C₃N₄ nanosheet composites.



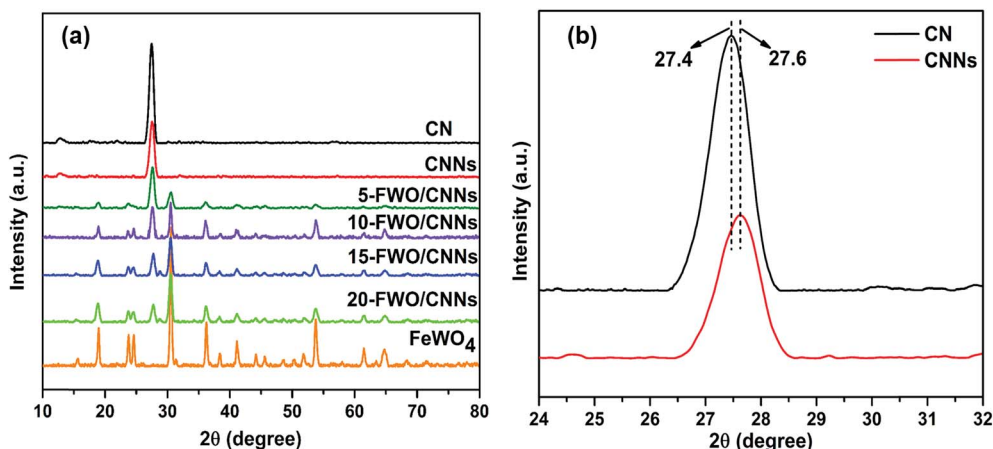


Fig. 1 (a) XRD patterns of CN, CNNs, FeWO₄ and the FeWO₄/CNNs composites and (b) magnified curves of CN and CNNs.

and (100) diffraction planes of g-C₃N₄, corresponding to the characteristic inter-layer stacking of aromatic systems and the in-plane structural packing motif of tri-*s*-triazine units,^{53–55} respectively. Interestingly, in the case of CNNs, the intensity of diffraction peaks significantly decreased, indicating that the CNN structure has been successfully obtained after exfoliation.⁵⁶ Besides, the dominant (002) peak in CNNs shifted slightly to a higher angle (Fig. 1b), which may be due to the decreased distance between the layers and which is in good agreement with previous reports.⁵⁷ For pure FeWO₄, the positions of all peaks can be well indexed to the monoclinic phase of FeWO₄ (JCPDS card no. 46-1446).⁵⁴ It can also be found that the diffraction peaks of FeWO₄/CNN composites consisted of the characteristic peaks of FeWO₄ and CNNs, which implied the coexistence of FeWO₄ and CNN phases in the as-prepared

FeWO₄/CNN composites. As the FeWO₄ concentration increases from 5 to 20 wt%, the diffraction peaks of FeWO₄ gradually intensify, whereas the peaks of CNNs are weakened and no phase structural changes have been detected, suggesting that the introduction of FeWO₄ did not change the phase structure of g-C₃N₄ during the *in situ* growth process. The above results confirm that the FeWO₄/CNN composites are successfully constructed.

The morphology and microstructure of the as-prepared samples were investigated by SEM and TEM. Fig. 2a–d show the SEM images of CN, CNNs, FeWO₄ and the 10-FWO/CNNs composite, respectively. As shown in Fig. 2a, the pure CN has a layered structure composed of tightly stacked g-C₃N₄ nanosheets several micrometers in size. And as expected, after exfoliation, the CNNs (Fig. 2b) exhibited a clear two-dimensional

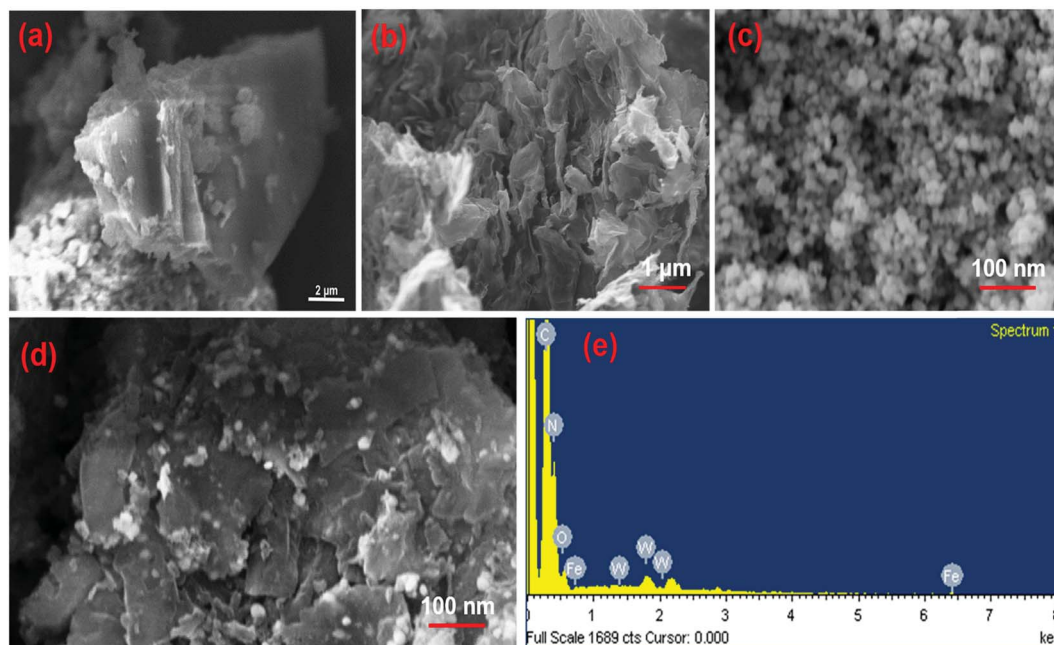


Fig. 2 SEM images of (a) CN, (b) CNNs, (c) FeWO₄ and (d) the 10-FWO/CNNs composite; and (e) the corresponding EDS image of the 10-FWO/CNN composite.



sheet-like structure with wrinkled edges, which further confirmed the successful exfoliation of CN.⁵⁰ Furthermore, the thickness of CNNs decreases dramatically, which may result in an increase in the specific surface area and reactive species.⁵⁷ From Fig. 2c, it can be seen that pure FeWO₄ exhibited spherical shapes with a diameter of 10–20 nm. In the case of the 10-FWO/CNN composite (Fig. 2d), we can clearly see that numerous FeWO₄ nanoparticles are well dispersed on the surface of CNNs. The EDS spectrum analysis of the 10-FWO/CNN composite (Fig. 2e) reveals that it contains of C, N, Fe, W, and O elements, which further confirmed the coexistence of CNN and FeWO₄ phases in the FeWO₄/CNN composites.

TEM was also performed to further confirm the morphology of CNNs and the FeWO₄/CNN composite formed. The TEM image shown in Fig. 3a further proved that the CNNs have a lamellar structure, with several stacking layers. The TEM image of 10-FWO/CNNs in Fig. 3b demonstrates that the FeWO₄ nanoparticles are uniformly dispersed on the surface of CNNs with a diameter of about 10–20 nm, which is in good agreement with the SEM results. Given the different morphologies of FeWO₄ and CNNs, the dark parts in the TEM image should be FeWO₄, while the light parts correspond to CNNs. These highly dispersed FeWO₄ nanoparticles could provide maximum interfacial contact with the CNN surface, which could further strengthen the synergistic coupling effect between FeWO₄ and CNNs. Moreover, the intimate contact between FeWO₄ and CNNs would further strengthen the photogenerated charge separation and transfer.⁵⁸ To observe in detail the interface between FeWO₄ and CNNs, HRTEM analysis was also performed. As shown in Fig. 3a and c, a lattice spacing of 0.326 nm that corresponds to the (002) crystallographic plane of g-C₃N₄

(ref. 38 and 59) and a clear lattice fringe of 0.37 nm ascribed to the (002) planes of FeWO₄ (ref. 51) were observed, which confirms the formation of heterojunctions *via* the *in situ* growth of FeWO₄ on the CNN surface. The formed interface is favorable for the transport of photogenerated charge carriers, and thereby promotes the separation of electron–hole pairs.

XPS analysis was performed to investigate the surface chemical states and bonding configuration of the pure CNNs and 10-FWO/CNN composite and the results (survey and high resolution spectra) are shown in Fig. 4. The survey XPS spectrum (Fig. 4a) of the 10-FWO/CNN composite exhibited strong C 1s and N 1s peaks related to the g-C₃N₄ phase, together with Fe 2p, W 4f and O 1s peaks related to the FeWO₄ phase without any contamination, and the survey XPS spectrum of CNNs contains C 1s, N 1s and O 1s peaks. In addition, the small peak of O 1s in CNNs is assigned to adsorbed oxygen species. Fig. 4b shows the high-resolution spectra of C 1s. Pure CNNs show two peaks at 284.6 eV and 288.1 eV, which can be assigned to the sp² C–C bond and sp² bonded carbon of N–C=N coordination present in the triazine rings of g-C₃N₄, respectively.⁴³ The 10-FWO/CNN composite also displayed the two C 1s peaks. However, compared with pure CNNs, the binding energy of 10-FWO/CNNs at 288.1 eV was shifted to 288.4 eV, while the position of the peak at 284.6 eV remained unchanged. The N 1s spectrum of CNNs (Fig. 4c) was deconvoluted into three peaks at 398.8, 399.8 and 401.1 eV, which could be assigned to sp² hybridized aromatic nitrogen atoms bonded to carbon atoms (C–N=C), tertiary nitrogen groups (N–(C)₃), and uncondensed amino groups (C–N–H), respectively.⁴³ The N 1s binding energies of CNNs shifted to 339.1, 400.4 and 401.5 eV for 10-FWO/CNNs, respectively. These results indicate that the carbon and nitrogen

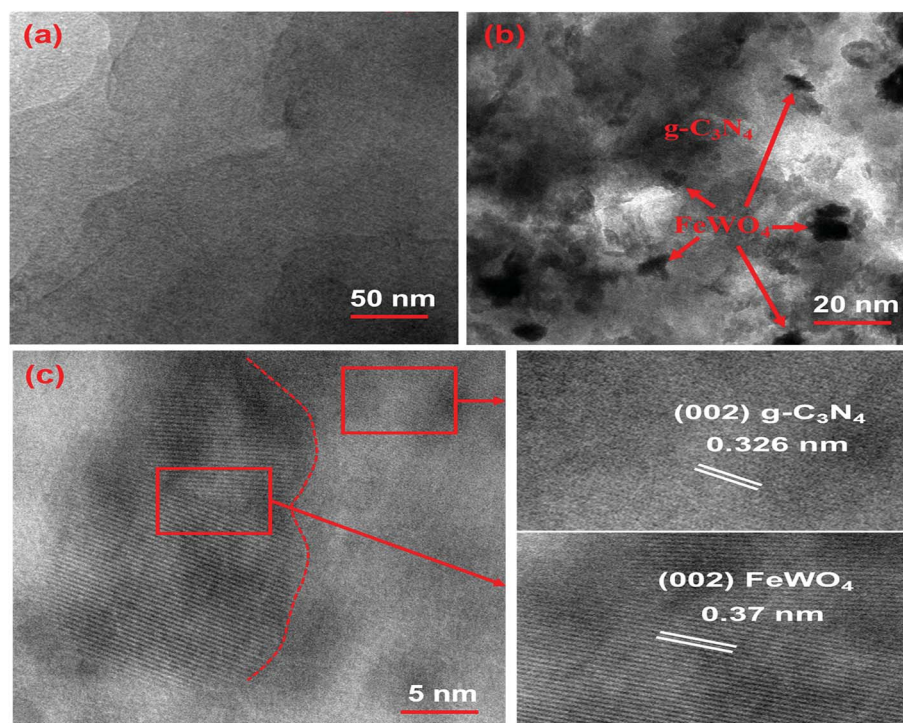


Fig. 3 TEM images of the (a) CNNs and (b) 10-FWO/CNN composite; and (c) HRTEM image of the 10-FWO/CNN composite.



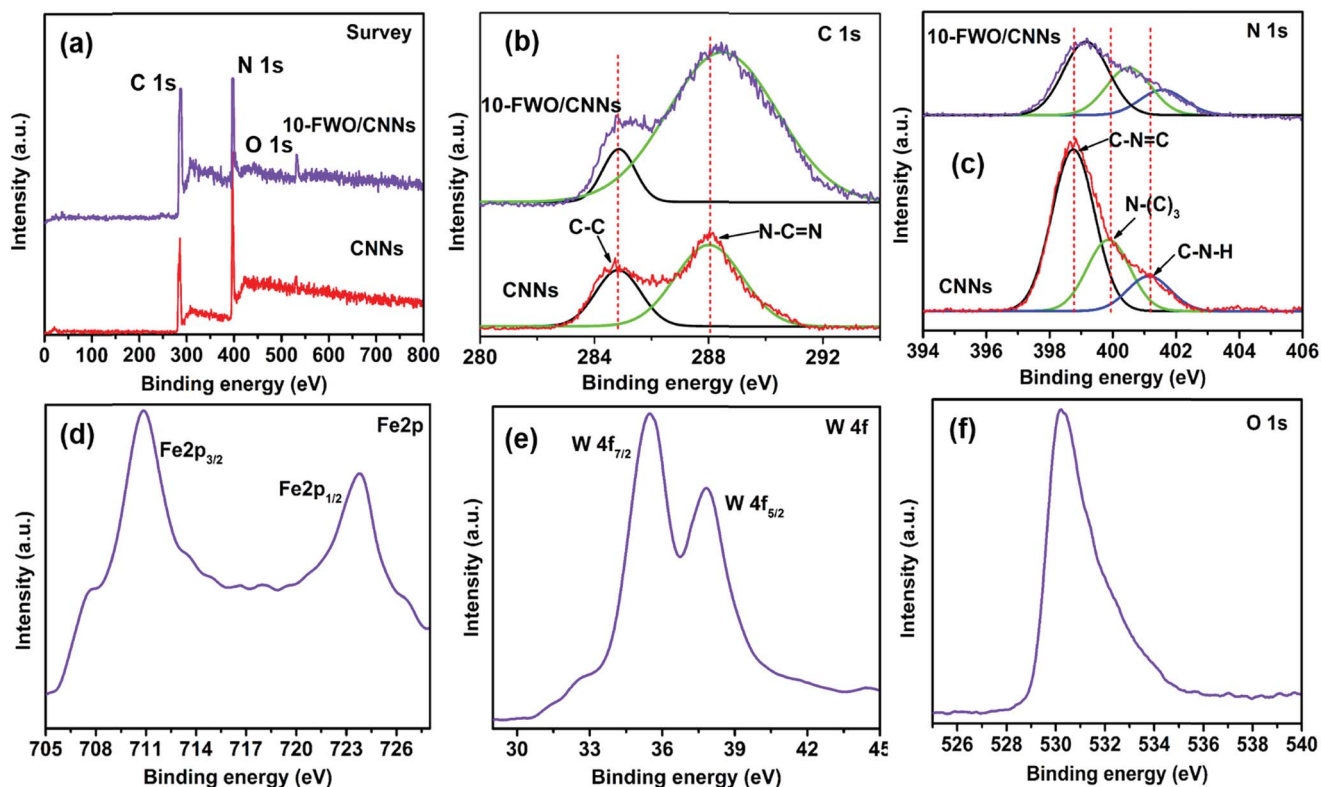


Fig. 4 (a) XPS survey spectra of the CNNs and 10-FWO/CNN composite; high-resolution XPS spectra of (b) C 1s and (c) N 1s for CNNs and the 10-FWO/CNN composite; and high-resolution XPS spectra of (d) Fe 2p, (e) W 4f and (f) O 1s for the 10-FWO/CNN composite.

atoms present in CNNs formed the binding interaction with metal species of FeWO_4 . In Fig. 4d, the peaks at 710.4 and 723.9 eV are assigned to the binding energies of Fe $2p_{3/2}$ and $2p_{1/2}$ respectively, and are characteristic of Fe^{2+} in the FeWO_4 material.⁵¹ The W 4f peaks at 35.5 and 37.8 eV in Fig. 4e correspond to the W $4f_{7/2}$ and W $4f_{5/2}$ binding energies of W^{6+} in FeWO_4 ,⁶⁰ respectively. The O 1s peak at 530.1 eV (Fig. 4f) corresponds to the FeWO_4 oxygen atom.⁶⁰ The shifting of C 1s and N 1s peaks and presence of Fe 2p, W 4f and O 1s peaks in the 10-FWO/CNN composite can be ascribed to the fact that FeWO_4 hybridized with CNNs during the *in situ* growth process, also indicating that certain chemical interactions are possibly formed between them, as observed in TEM images.

The chemical structure and functional groups of the as-prepared samples were studied using FTIR spectra and the results are shown in Fig. 5a. For the FTIR spectrum of pure FeWO_4 , the absorption bands appearing at 834 and 877 cm^{-1} were due to the symmetrical vibrations of bridging oxygen atoms of Fe–O–W. The absorption band at 650–680 cm^{-1} can be due to the stretching mode of W–O in WO_6 octahedra and the absorption band at 556 cm^{-1} is the characteristic stretching vibration of the Fe–O bond in hematite particles.⁴³ In the FTIR spectrum of CN, the series of bands observed in the region of 1200–1650 cm^{-1} are ascribed to the stretching vibration of C–N heterocycles, while the broad band at 3000–3500 cm^{-1} is ascribed to the stretching vibration of N–H groups and surface adsorbed hydroxyl groups. In addition, the band at 810 cm^{-1} originates from a breathing mode of *s*-triazine units.^{28,54,61} It can be seen that the characteristic

FTIR spectrum of CNNs is similar to that of CN, indicating that the $g\text{-C}_3\text{N}_4$ chemical structure has not been destroyed after the exfoliation process. Moreover, the FTIR spectra of the $\text{FeWO}_4/\text{CNNs}$ composites are similar to that of pure CNNs, and all the characteristic absorption bands of CNNs appear in the composites, suggesting that no structural change of CNNs occurs during the composite formation. After introducing FeWO_4 into CNNs, the characteristic bands from the C–N heterocycles of CNNs appear as blue shifts (Fig. 5b), indicating that there might be some interactions between the C–N heterocycles of $g\text{-C}_3\text{N}_4$ and FeWO_4 . From the TEM, XPS and FTIR results, we concluded that there was strong electrostatic interaction between FeWO_4 and CNNs, which could promote photogenerated electron–hole pair separation and transfer, and further enhance the photocatalytic performance of the FeWO_4/CNN composites.

The light absorption properties of the as-prepared samples were examined by UV-vis DRS analysis (Fig. 6). As shown in Fig. 6a, CNNs show a slight blue shift of the absorption edge with respect to that of CN, which is ascribed to the quantum confinement effect of $g\text{-C}_3\text{N}_4$ nanosheets and is consistent with previous reports.⁶² The pure FeWO_4 exhibited profound absorption over a wide spectral region from UV to visible light. After the introduction of FeWO_4 into CNNs, the composite samples exhibited stronger optical absorption in the visible region compared with CNNs, and the absorption intensities of these composites are strengthened with an increase in the FeWO_4 content. This demonstrates well that the *in situ* grown FeWO_4 nanoparticles can act as a sensitizer for enhancing the



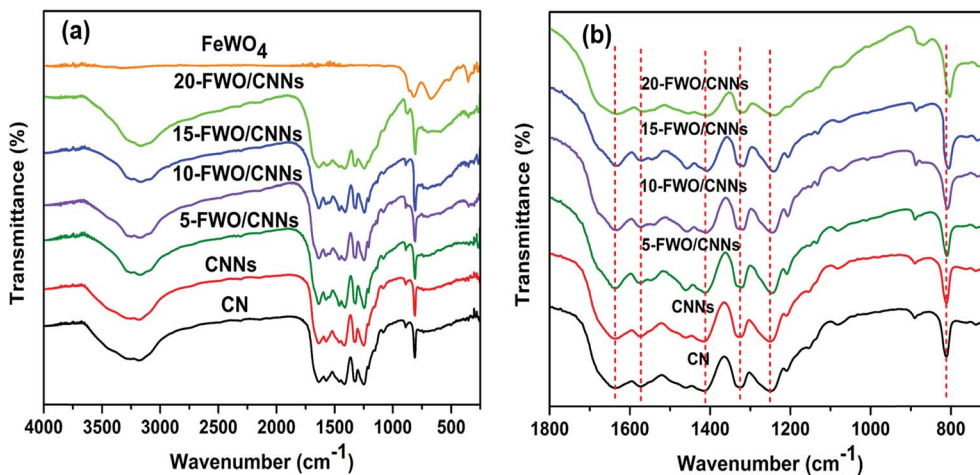


Fig. 5 (a) FTIR spectra of CN, CNNs, FeWO₄ and the FeWO₄/CNN composites; and (b) magnified curves in the range of 700 to 1800 cm⁻¹.

visible light absorption of CNNs, suggesting that the FeWO₄/CNN composites can harvest more light energy and produce more photogenerated charge carriers.

The energy level and band gap of the semiconductors play a crucial role in determining their physical properties. The band gap energies of the as-prepared photocatalysts can be calculated using the following formula⁴⁵

$$\alpha h\nu = A(h\nu - E_g)^{n/2}$$

where α , h , ν , A and E_g represent the absorption coefficient, Planck's constant, light frequency, proportionality constant

related to the material, and energy band gap, respectively. The band gap energy for FeWO₄ was determined from a plot of $(\alpha h\nu)^2$ versus $h\nu$ ($n = 1$ for direct transition)⁶³ and that for the CNNs was obtained from a plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ ($n = 4$ for indirect transition).⁶⁴ As shown in Fig. 6b and c, the band gap energies of CN, CNNs and FeWO₄ are estimated to be around 2.7, 2.73 and 2.1 eV, respectively.

Generally, the PL spectra of photocatalysts can be used to illustrate the recombination rate of the photogenerated electron-hole pairs; it is known that higher PL intensity usually means more recombination of electron-hole pairs and lower photocatalytic activity. Fig. 7 shows the PL spectra of the as-

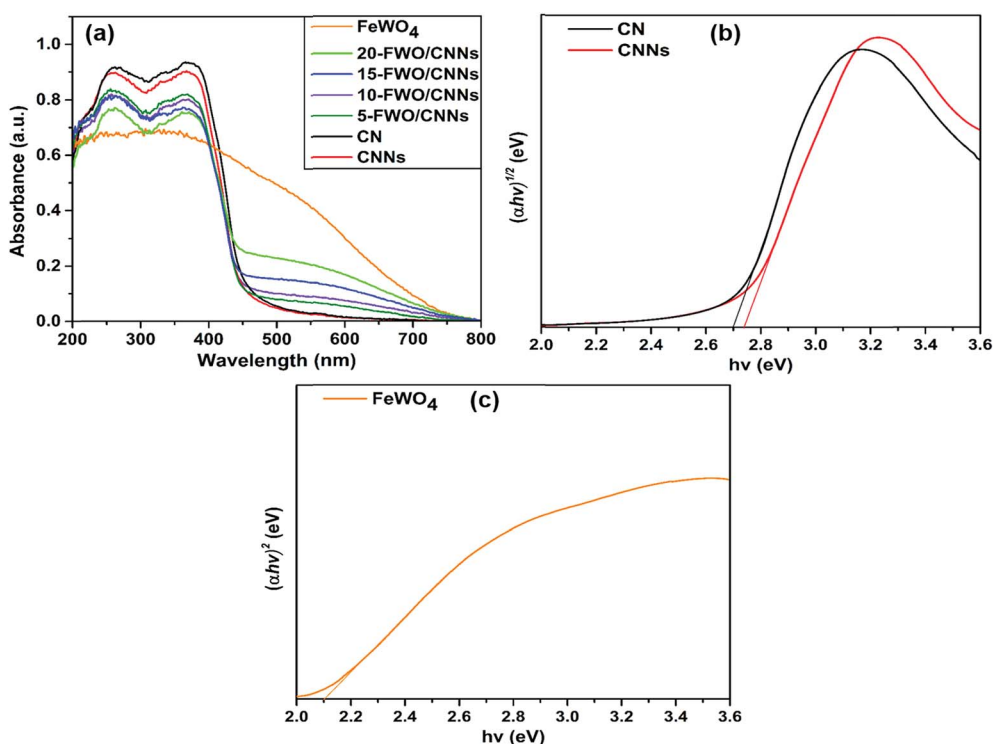


Fig. 6 (a) UV-vis diffuse reflectance spectra of CN, CNNs, FeWO₄ and the FeWO₄/CNN composites; (b) $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot of CNNs and CN; and (c) $(\alpha h\nu)^2$ versus $h\nu$ plot of FeWO₄.



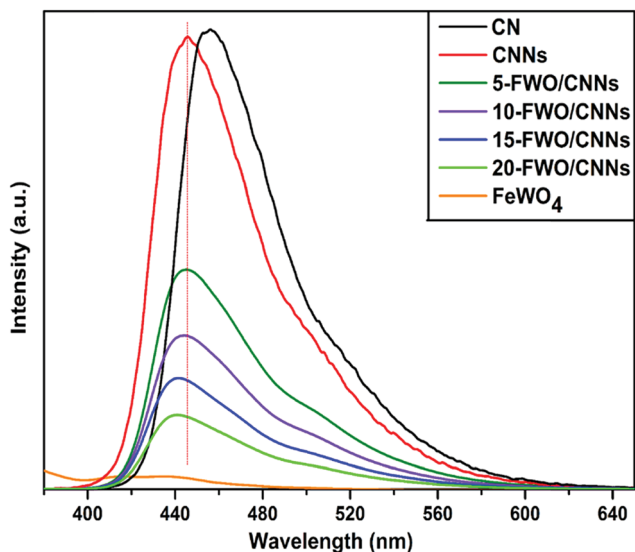


Fig. 7 PL spectra of CN, CNNs, FeWO₄ and the FeWO₄/CNN composites.

prepared samples. It can be observed that both the CN and CNNs have a strong PL peak at an excitation wavelength of 360 nm, which could be related to the recombination of the photogenerated electron-hole pairs in *g*-C₃N₄. A blue shifted peak for CNNs compared with that for CN is mainly due to

shifted conduction band and valence band edges, which is caused by the well-known quantum confinement effect.⁶² After coupling CNNs with FeWO₄, the emission peak intensities decreased significantly, indicating that the recombination of electron-hole pairs is greatly suppressed by the introduction of FeWO₄. One reason might be that coupling with FeWO₄ may change the transition path of photogenerated electrons to the ground state for CNNs, which may result from interactions between CNNs and FeWO₄. As a result, the charge separation could be promoted on the FeWO₄/CNN composites, leading to the higher photocatalytic activity of the composite photocatalysts. From Fig. 7, it can also be seen that the PL peak positions shifted to lower wavelengths with the increase in the amount of FeWO₄. This may be caused by the strong interaction between the FeWO₄ and CNNs in the composite samples, which also occurred in the *g*-C₃N₄-WO₃ system.⁵⁹

3.2. Photocatalytic performance

In order to investigate the photocatalytic activities of the as-prepared samples, RhB and TC were chosen as model pollutants for photocatalytic degradation (Fig. 8). Negligible self-degradation was observed for RhB and TC under sunlight irradiation for ~90 min (Fig. 8a and b). As expected, all FeWO₄/CNN composites exhibited higher photocatalytic activities than pure FeWO₄, CN and CNNs with a hierarchical order of 10-FWO/CNNs > 5-FWO/CNNs > 15-FWO/CNNs > 20-FWO/CNNs,

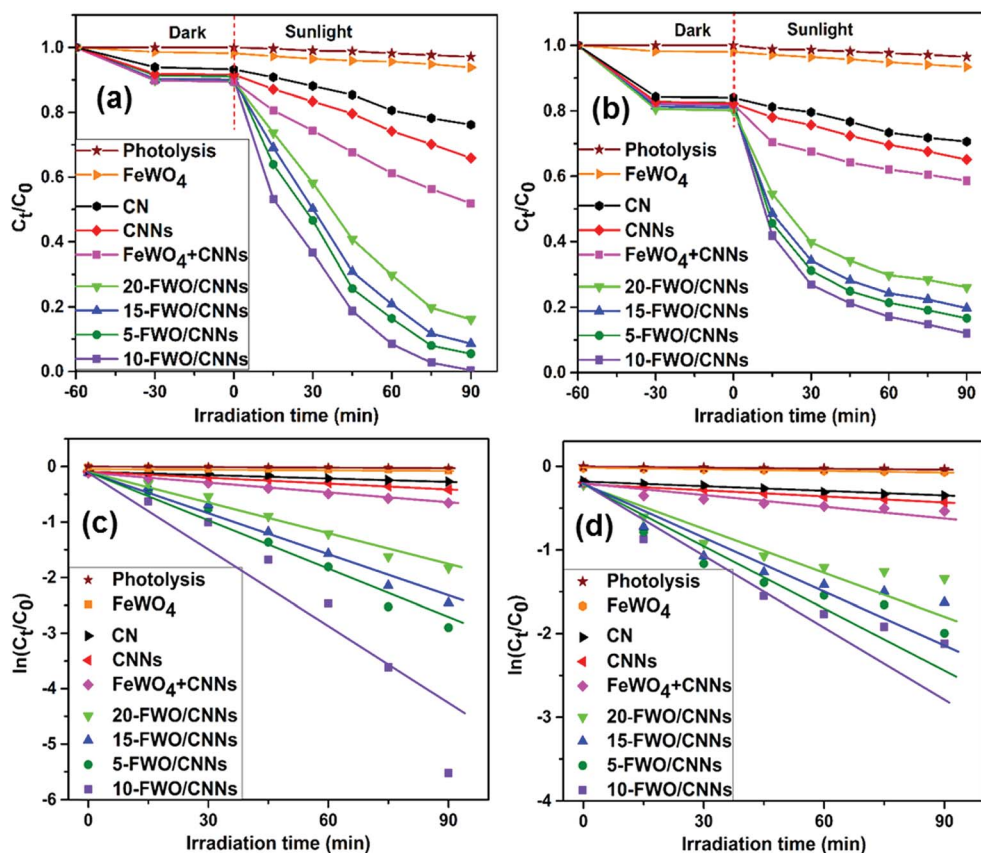


Fig. 8 Photocatalytic degradation rate of (a) RhB, and (b) TC over CN, CNNs, FeWO₄ and the FeWO₄/CNN composites; the pseudo-first-order kinetics fitted curves of (c) RhB, and (d) TC over CN, CNNs, FeWO₄ and the FeWO₄/CNN composites under sunlight irradiation.



indicating that the FeWO_4 content influenced the photocatalytic activity of the as-prepared composites notably. This could be explained by the effective separation of photo-generated electron-hole pairs due to the formation of heterojunctions between FeWO_4 and CNNs in the composites. Moreover, the activities of the composite samples were found to increase with the increase in the FeWO_4 content from 5 wt% (94.5% for RhB, 83.4% for TC) to 10 wt% (99.6% for RhB, 88% for TC), and then decrease with further increase in the FeWO_4 content from 10 wt% to 20 wt% (83.9% for RhB, 73.9% for TC), suggesting that the FeWO_4/CNN composites had the highest photocatalytic activity with the optimum FeWO_4 content of 10 wt%. The reason for this may be that when the amount of FeWO_4 is lower than its optimum amount, the trapping sites of carriers increase with the increase of the FeWO_4 amount, which prolongs the lifetime of carriers, thus improving the photocatalytic activity. However, when the amount of FeWO_4 is higher than its optimum amount, excessive FeWO_4 (15 wt% and 20 wt%) may be clustered and effective heterojunction photocatalysts are not formed. Furthermore, the excessive deposition of FeWO_4 may increase the light opacity, preventing CNNs from absorbing light effectively, which leads to a decrease in the photocatalytic activity. Therefore, CNNs coated with an appropriate amount of FeWO_4 form an effective heterojunction photocatalyst, so that the photocatalytic performance will be maximum.

A physical mixture of FeWO_4 and CNNs (defined as $\text{FeWO}_4 + \text{CNNs}$) was also tested for RhB and TC degradation, and it exhibited much weaker photocatalytic activity as compared to the *in situ* synthesized FeWO_4/CNN composites. This fact indicates that intimate contact between FeWO_4 and CNNs is crucial for the interfacial charge transfer between the two semiconductors, which improves the separation efficiency of photo-generated electron-hole pairs and ultimately enhances the photocatalytic activity.

To quantitatively study the reaction kinetics of RhB and TC degradation, the experimental data were analyzed using the pseudo-first-order kinetic model, $\ln(C_t/C_0) = -kt$,⁵² where k is the rate constant, C_0 is the initial concentration of RhB or TC, and C_t is the concentration of RhB or TC at time t . This equation is well built for photocatalytic experiments when the pollutant is in the millimolar concentration range. The k value can be determined by a linear fit of the plot of $\ln(C_t/C_0)$ versus reaction time, as shown in Fig. 8c and d. The calculated k values for RhB and TC degradation over all the photocatalysts are listed in Table 1; it can be seen that the k values of 10-FWO/CNNs for RhB and TC photodegradation were 86.2 times and 31.1 times higher than that of pure FeWO_4 , and 13.26 and 4.95 times as high as that of individual CNNs, respectively, revealing that the introduction of FeWO_4 greatly influences the performance of the composite photocatalysts. As a result, the 10-FWO/CNNs were the optimal performing sample among all composites.

The time-dependent UV-vis absorption spectral changes of the RhB and TC under sunlight irradiation in the presence of 10-FWO/CNNs are shown in Fig. S1a and b.† The characteristic peak intensities of RhB and TC gradually decreased by prolonging the irradiation time, revealing the degradation of the

Table 1 The calculated reaction rate constants (min^{-1}) for FeWO_4 , CN, CNNs, $\text{FeWO}_4 + \text{CNNs}$, 5-FWO/CNNs, 10-FWO/CNNs, 15-FWO/CNNs and 20-FWO/CNNs toward photodegradation of RhB and TC

Photocatalyst	Rate constant (min^{-1})	
	Rhodamine B	Tetracycline
FeWO_4	0.000711	0.000757
CN	0.00302	0.00368
CNNs	0.00463	0.00476
$\text{FeWO}_4 + \text{CNNs}$	0.00728	0.00593
5-FWO/CNNs	0.0322	0.0222
10-FWO/CNNs	0.0614	0.0236
15-FWO/CNNs	0.0272	0.0181
20-FWO/CNNs	0.0203	0.0150

pollutants. The shifts of the characteristic peaks indicate the presence of decomposition products of the pollutants.

In addition to the photocatalytic activity, the stability of photocatalysts is another important parameter for practical application. To evaluate the stability and reusability of the FeWO_4/CNN composites, recycling reactions were performed for the photodegradation of RhB over the optimized catalyst (10-FWO/CNNs) under sunlight irradiation (Fig. 9). As shown in Fig. 9, very interestingly, no significant reduction of photocatalytic efficiency was observed up to the fourth cycle (there was a slight decrease derived from the loss of the photocatalyst during the cycling process), which implies the high stability of the photocatalyst during photodegradation. The XRD and FTIR patterns of the 10-FWO/CNN composite were also investigated after four recycling runs. As shown in Fig. S2a and b,† the XRD and FTIR patterns of the 10-FWO/CNN composite before and after reaction reveal that the phase and structure remained unchanged. Therefore, it is evident that the FeWO_4/CNN composite does not undergo any photocorrosion or photo-bleaching during the degradation experiments.

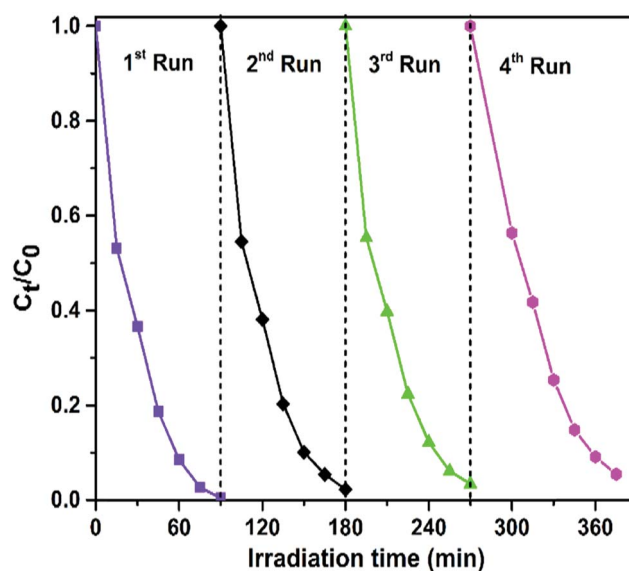


Fig. 9 Recycling photocatalytic tests of the 10-FWO/CNN composite for RhB degradation.



3.3. Photocatalytic mechanism

To investigate the photocatalytic degradation mechanism of the FeWO₄/CNN composites, a series of sacrificial agents were used to quench the relevant active species during the photocatalytic process, and the results are shown in Fig. 10a. As shown in Fig. 10a, when AO was added to the reaction system, the photocatalytic efficiency was not obviously changed. Therefore, it seems that holes are not the reactive species. However, when BQ and IPA were added to the reaction system, the photocatalytic efficiencies were reduced from 99.6% to 14.1 and 19.3% for RhB, respectively. Based on the results, it is suggested that [•]O₂⁻ and [•]OH are the major reactive species in the photocatalytic reaction system. To further confirm the presence of [•]OH in the FeWO₄/CNN system during sunlight irradiation, [•]OH trapping PL experiments using terephthalic acid (TA) as a probe molecule were also carried out (Fig. 10b). As shown in Fig. 10b, after 30 min of irradiation, a strong PL signal is observed at 425 nm and the intensity significantly increased with the irradiation time as compared to dark treatment, which indeed indicates the generation of [•]OH radicals.

For the sake of theoretical investigation of the mechanism of photodegradation, the valence band (VB) and conduction band (CB) edge potentials of the FeWO₄ and g-C₃N₄ were determined using the following empirical equations:⁴⁵

$$E_{\text{VB}} = \chi - E^{\text{c}} + 0.5E_{\text{g}}$$

$$E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}}$$

where E_{VB} and E_{CB} are the valence and conduction band edge potentials, respectively; χ is the absolute electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms; E^{c} is the energy of free electrons on the hydrogen scale (about 4.5 eV vs. NHE); and E_{g} is the bandgap energy of the semiconductor (the E_{g} values for FeWO₄ and CNNs are 2.10 eV and 2.73 eV, respectively). The χ values for FeWO₄ and g-C₃N₄ are calculated to be 6.3 eV (ref. 60) and 4.73 eV,⁴⁵ respectively. Accordingly, the VB values of semiconductors FeWO₄ and CNNs are calculated to be 2.85 and 1.595 eV, and the CB values of semiconductors FeWO₄ and CNNs are calculated to be 0.75 and -1.135 eV, respectively.

In theory, the photogenerated electrons in the CB of FeWO₄ cannot reduce O₂ to give [•]O₂⁻, because the CB edge potential of FeWO₄ (0.75 eV vs. NHE) is more positive than the standard redox potentials of O₂/[•]O₂⁻ (-0.33 eV vs. NHE).^{27,45} However, the photogenerated holes in the VB of FeWO₄ can oxidize H₂O to give [•]OH, because the VB potential of FeWO₄ is more positive than the standard redox potentials of H₂O/[•]OH (2.68 eV vs. NHE).^{26,58} For the CNNs, because the CB edge potential of CNNs (-1.135 eV vs. NHE) is more negative than the standard redox potentials of O₂/[•]O₂⁻, the photogenerated electrons can reduce O₂ to give [•]O₂⁻. Meanwhile, since the VB potential of CNNs is lower than the standard redox potentials of H₂O/[•]OH, the photogenerated holes in the VB of CNNs cannot oxidize H₂O to give [•]OH.

If the charge carrier transfer in the FeWO₄/CNN composites occurs through a type-II heterojunction mechanism (Fig. 11a), the electrons in the CB of CNNs will migrate to the CB of FeWO₄, and the holes in the VB of FeWO₄ will migrate to the VB of CNNs. As a result, the electrons get accumulated in the CB of FeWO₄ and cannot reduce O₂ to [•]O₂⁻, and the holes get accumulated in the VB of CNNs and cannot oxidize H₂O to [•]OH. Hence, this kind of electron-hole transfer process is not favorable for the formation of active species, and leads to lower photocatalytic activity of the reaction system. Nevertheless, the radical trapping experiment and TAPL analysis implied that [•]O₂⁻ and [•]OH are the major reactive species in the FeWO₄/CNN photocatalytic system, and the photocatalyst exhibited higher photocatalytic activity. Therefore the separation process of the photogenerated electron-hole pairs in this system did not follow the type-II heterojunction mechanism, but might have occurred through the Z-scheme mechanism.

On the basis of the above experimental results and band structure analysis of FeWO₄ and CNNs, a Z-scheme mechanism was proposed to explain the enhanced photocatalytic performance of the FeWO₄/CNN composites and is schematically illustrated in Fig. 11b. Under illumination of sunlight, both FeWO₄ and CNNs can be excited to generate electron-hole pairs. The photogenerated electrons in the CB of FeWO₄ tend to transfer and recombine with the photogenerated holes in the VB of CNNs. In this way, the larger number of photogenerated

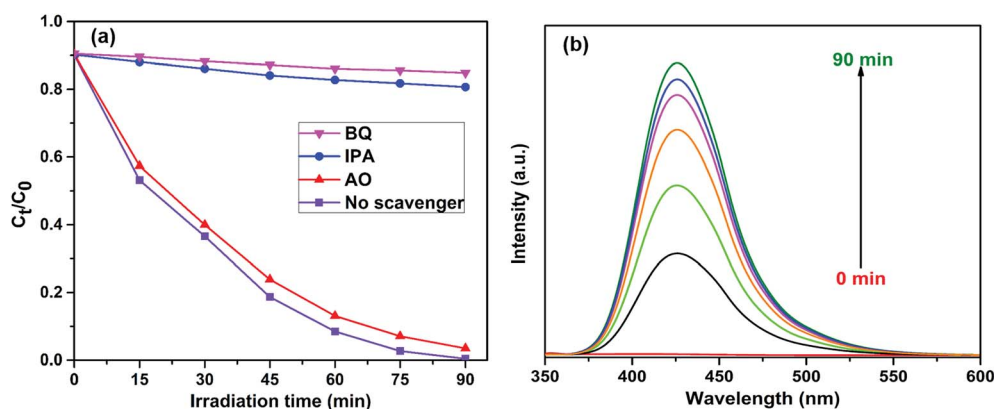


Fig. 10 (a) Effect of different scavengers on degradation of RhB in the presence of the 10-FWO/CNN composite; and (b) [•]OH trapping PL spectra of the 10-FWO/CNN composite with TA solution under sunlight irradiation.



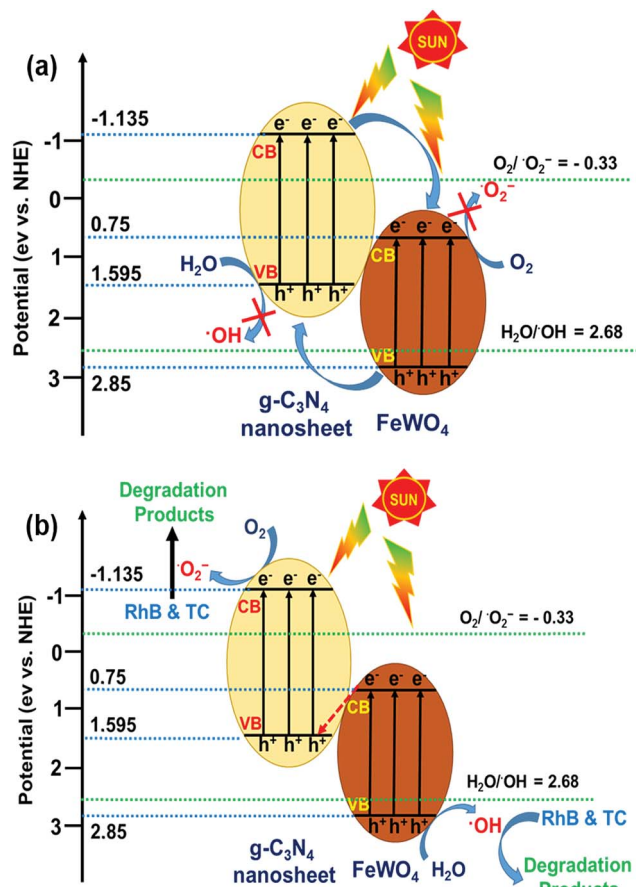


Fig. 11 (a) Schematic diagram for the impossible generation of reactive species in the FeWO_4/CNN composites; and (b) schematic diagram for the charge transfer in the direct Z-scheme FeWO_4/CNN composites.

electrons accumulated in the CB of CNNs can reduce the adsorbed O_2 to form more $\cdot\text{O}_2^-$. Meanwhile, the photo-generated holes left behind in the VB of FeWO_4 can oxidize the adsorbed H_2O to give $\cdot\text{OH}$. Therefore, the photocatalytic activity of the FeWO_4/CNN system is significantly increased, and RhB or TC is decomposed by $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ reactive species. Therefore, a conclusion can be drawn that the photocatalytic reaction of the as-prepared FeWO_4/CNN composites followed a direct Z-scheme mechanism, which could improve the photo-generated electron-hole pair separation and transfer and show a strong oxidation and reduction ability for the effective degradation of organic pollutants.

4. Conclusions

In summary, a series of FeWO_4/CNN composites with various contents of FeWO_4 have been successfully synthesized through *in situ* growth of self-assembled FeWO_4 nanoparticles on the surface of CNNs via a facile solvothermal method. The as-prepared FeWO_4/CNN composites exhibited excellent photocatalytic activity compared to the pure FeWO_4 , CN, CNNs and mechanically mixed catalyst in the degradation of RhB and TC

under sunlight irradiation. This enhancement could be attributed to the high separation and easy transfer of photogenerated electron-hole pairs in the hybrid system, which can be reasonably attributed to the suitable matching of conduction and valence band levels between FeWO_4 and CNNs. Besides, a novel Z-scheme photocatalytic mechanism in the FeWO_4/CNN system was confirmed by active species trapping experiments and band energy potentials. Moreover, the FeWO_4/CNN composites are very stable and reusable during the photocatalytic reactions. Therefore, the novel FeWO_4/CNN photocatalysts may have potential for application in pollutant removal as well as water splitting in the future. This work opens up a new feasible avenue to synthesize visible light active Z-scheme photocatalysts for application in energy production and environmental remediation.

Conflicts of interest

There are no conflicts of interest to declare.

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