Fabrication of hollow flower-like magnetic \( \text{Fe}_3\text{O}_4/C/\text{MnO}_2/\text{C}_3\text{N}_4 \) composite with enhanced photocatalytic activity

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The serious problems of environmental pollution and energy shortage have pushed the green economy photocatalysis technology to the forefront of research. Therefore, the development of an efficient and environmentally friendly photocatalyst has become a hotpot. In this work, magnetic \( \text{Fe}_3\text{O}_4/C/\text{MnO}_2/\text{C}_3\text{N}_4 \) composite as photocatalyst was synthesized by combining in situ coating with low-temperature reassembling of C/N precursors. Morphology and structure characterization showed that the composite photocatalyst has a hollow core–shell flower-like structure. In the composite, the magnetic \( \text{Fe}_3\text{O}_4 \) core was convenient for magnetic separation and recovery. The introduction of conductive C layer could avoid recombining photo-generated electrons and holes effectively. Ultra-thin g-C\(_3\)N\(_4\) layer could fully contact with coupled semiconductor. A Z-type heterojunction between g-C\(_3\)N\(_4\) and flower-like MnO\(_2\) was constructed to improve photocatalytic performance. Under the simulated visible light, 15 wt% photocatalyst exhibited 94.11% degradation efficiency in 140 min for degrading methyl orange and good recyclability in the cycle experiment.

In recent years, with the increase of wastewater discharge, a large amount of toxic and harmful organic pollutants are put into the water, which are difficult to completely degrade\(^1-8\). Advanced photocatalytic oxidation technology with strong oxidation capacity and high efficiency was considered as a very promising wastewater treatment means for the degradation of organic pollutants\(^7-14\). Among them, semiconductor-based photocatalysts with mild reaction conditions were most widely used\(^15-22\). In addition, various styles of self-assembled photocatalyst nanostructures were synthesized, such as one-dimensional nanotubes\(^23\), two-dimensional layered structure\(^24,25\), three-dimensional network structure\(^26\), three-dimensional flower-like structure\(^27\) and etc.

MnO\(_2\) has some advantages including low cost, high stability and environmental friendliness. Besides, its narrow band gap can increase the utilization of visible light, which is very promising as a photocatalyst\(^28-32\). The layered structure of \( \delta\)–MnO\(_2\) is formed by the MnO\(_6\) octahedral layer with shared edges, and there are some cations and H\(_2\)O molecules between the layers to maintain the charge balance\(^33\). \( \delta\)–MnO\(_2\) has been widely used as a catalyst to purify the environment\(^34-36\). However, while the narrow band gap increases the usage of visible light, it is also accompanied by the rapid recombination of photo-generated electrons and holes. The low photocatalytic efficiency restricts pure MnO\(_2\) for practical applications\(^37-39\).

Coupling MnO\(_2\) with other semiconductors to build a heterojunction is an effective method to prevent the recombination of photo-generated carriers. Wang et al.\(^40\) first reported that g-C\(_3\)N\(_4\) could decompose water to generate hydrogen by visible light irradiation. Subsequently, owing to excellent visible light activity and chemical stability, g-C\(_3\)N\(_4\) as photocatalyst has attracted a lot of attention\(^41-43\). Recently, Zhu et al.\(^44\) coated g-C\(_3\)N\(_4\) on the semiconductor surface to form an ultra-thin g-C\(_3\)N\(_4\) layer, avoiding the low contact rate between the bulk g-C\(_3\)N\(_4\) and the coupling semiconductor interface. Therefore, the design of the composite with ultra-thin g-C\(_3\)N\(_4\) layer and MnO\(_2\) is expected to achieve significant charge transfer at their interface by facilitating the separation of photo-generated carriers, thereby enhancing photocatalytic activity.

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In our previous research, Fe₃O₄ was introduced as a magnetic core to construct a magnetically recyclable core–shell structure photocatalyst. The existence of magnetic core was beneficial to the recycle of the catalyst⁴⁵,⁴⁶. In this paper, hollow Fe₃O₄ microspheres were also synthesized by using a hydrothermal method as magnetic cores. Subsequently, the carbon layer was obtained by calcining the polymer layer formed on the periphery of Fe₃O₄ microspheres, which can protect the core and act as an electronic conductor simultaneously. Then, flower-like MnO₂ was grown on the periphery of Fe₃O₄/C microspheres through the hydrothermal method. Finally, the transparent CN precursor produced with the aid of the neutral hydrothermal process was polymerized in situ on the surface of above microspheres at a low temperature. A flower-like Fe₃O₄/C/MnO₂/C₃N₄ composite photocatalyst with core–shell structure was obtained. The photocatalyst displayed remarkable photocatalytic activity for degrading the organic dye methyl orange (MO). The specific synthetic steps are shown in Fig. 1.

**Experimental section**

**Preparation of Fe₃O₄/C core–shell composite.** First, hollow Fe₃O₄ microspheres were obtained by the hydrothermal method⁴⁷. Then the polymer layer was prepared through a distillation precipitation process. 0.10 g Fe₃O₄ microspheres were ultrasonically dispersed in 80 mL acetonitrile. 1.0 mL divinylbenzene (DVB), 1.0 mL methyl methacrylate (MMA), and 0.040 g 2,2-azobisisobutyronitrile (AIBN) were also added into the above solution. The system was heated in 90 °C water bath for 2 h. Afterwards, Fe₃O₄/P(MMA-DVB) microspheres were obtained by using an external magnet, and washed three times. Then, the Fe₃O₄/P(MMA-DVB) sample was calcined at 600 °C for 2.0 h to obtain Fe₃O₄/C microspheres.

**Preparation of Fe₃O₄/C/MnO₂ flower-like composite.** 0.30 g Fe₃O₄/C microspheres were fully dispersed to 80 mL 0.055 M KMnO₄ solution. Next, 1.0 mL HCl was added to the mixture dropwise. Thereafter, the mixture was transferred to an autoclave and heated to 100 °C for 6.0 h. At last, flower-like Fe₃O₄/C/MnO₂ microspheres with core–shell structure were obtained by using an external magnet, and washed three times and lyophilized.

**Preparation of Fe₃O₄/C/MnO₂/C₃N₄ composite.** 6.0 g dicyandiamide was calcined at 550 °C for 4.0 h to produce g-C₃N₄. Thereafter, 2.0 g g-C₃N₄ powder was dispersed in 80 mL deionized water, and then heated at 210 °C for 6 h to form a CN transparent precursor. Fe₃O₄/C/MnO₂ microspheres were added to the precursor (5.0, 10, 15, 20, 30 wt%). The solvent was slowly removed through a lyophilized process. Finally, Fe₃O₄/C/MnO₂/C₃N₄ flower-like photocatalyst was obtained via annealing at 200 °C for 4.0 h in a tube furnace under N₂ protection.

**Characterization.** Scanning electron microscope (SEM, JSM-6700F, JEOL Ltd., Japan) was employed to obtain a surface topography image of the samples. Transmission images were gotten by using a high-resolution transmission electron microscope (TEM, JEM-3010, Hitachi Co., Japan). X-ray diffraction patterns of samples were obtained by the use of an X-ray diffractometer (XRD, Shimadzu XRD-7000, Shimadzu Co., Japan). X-ray photoelectron spectrometer (XPS, JPS-9010 MC, JEOL Ltd., Japan) was utilized to obtain the samples’ surface elemental composition of the samples. Brunauer–Emmett–Teller (BET, ASAP 2020, Quantachrome, US) means was used to test the pore size and specific surface area of the catalyst. The saturation magnetization of the samples was obtained by employing a vibrating sample magnetometer (VSM, Lake Shore 7307, Lake Shore Ltd., USA). A photochemical reactor (BL-GHX-V, Shanghai Bilang Instruments Co., Ltd., China) was used to simulate the illumination. The ultraviolet–visible absorption spectra were measured on an ultraviolet–visible spectrophotometer (UV–vis, UV-5200PC, YuanXi, China).

**Photocatalytic experiment.** Firstly, 20 mg Fe₃O₄/C/MnO₂/C₃N₄ photocatalyst were added to 65 mL, 10 mg/L MO solution. Under dark environment, the mixture was agitated to reach adsorbed-desorbed equilibrium. Secondly, photocatalytic reaction was carried out with simulate light stemming from a 400 W metal halide lamp. The absorbance of the solution at intervals was monitored with the help of UV–visible spectrophotometer. Ultimately, the degradation curves of the MO solution were recorded, followed by the calculation of photocatalytic degradation rate.
Results and discussion

SEM and TEM images of samples are shown in Fig. 2. In Fig. 2a, Fe3O4 microspheres prepared by the hydrothermal method have good dispersibility and uniform size of about 200 nm. Figure 2b shows Fe3O4/P(MMA-DVB) microspheres prepared by distillation precipitation process. Compared with the former, the surface of the latter becomes much smoother, which proves the successful formation of polymer coating. And these polymer core–shell microspheres have a diameter of 225 nm. To obtain the conductive carbon layer, the polymer microspheres were calcined and carbonized. The SEM image of Fe3O4/C microspheres is displayed in Fig. 2c. One can see that the original core–shell structure of the material is not destroyed after the calcination treatment. And the agglomeration that originally occurred in Fe3O4/P(MMA-DVB) polymer microspheres has been slightly weakened due to the carbonization treatment. From Fig. 2d,e, it can be found out that the flower-like morphology of the composite microspheres produced by the hydrothermal method is composed of MnO2 intersecting sheets. And the overall particle size is about 480 nm. As shown in Fig. 2f, the overall flower-like morphology has not changed, but the thickness of the MnO2 flower sheets has increased significantly. This case indicates that the ultra-thin C3N4 layer is successfully formed on the surface of MnO2 to form a flower-like Fe3O4/C/MnO2/C3N4 composite photocatalyst. It can be seen from Fig. 2g that the synthesized magnetic microspheres have a clear hollow structure with a particle size of about 200 nm. Figure 2h shows the TEM image of the Fe3O4/C microspheres, which have a core–shell structure with 13 nm thickness of C shell. Figure 2i is the TEM image of the flower-like Fe3O4/C/MnO2/C3N4 microspheres. It can be found out that the composite photocatalyst with a complete magnetic core and flower-like shell exhibits the diameter of around 480 nm. According to these results, the composite photocatalyst with a magnetic core and flower-like shell was successfully prepared.

The crystal phase composition of the composite was demonstrated by XRD characterization, as shown in Fig. 3I. Figure 3I-a is the diffraction curve of the bulk g-C3N4 obtained by pyrolysis of dicyandiamide. The strong peak near 27.4° belongs to the (002) plane, corresponding to the crystal plane stack of the CN aromatic system48. The broad peak at 13.0° belongs to the triazine repeat unit45. Figure 3I-b is the diffraction curve of Fe3O4 microspheres showing the diffraction peaks at 30.12°, 35.41°, 43.10°, 53.43°, 57.11°, and 62.52°, which are attributed to (220), (311), (400), (422), (511) and (440) crystal planes of Fe3O4 (JCPDS 19-0629).
further formation of g-C3N4, the value is 30.02 emu/g (Fig. 5d). This value still meets the needs of magnetic separation. As shown in the illustration, when the magnet is placed next to the Fe3O4/C/MnO2/C3N4 photocatalyst spheres is 70.58 emu/g. After the carbon layer is recombined, the value of Fe3O4/C microspheres decreases to microspheres.

CN precursor successfully becomes g-C3N4 after low temperature polymerization and high temperature calcination spectrum (Fig. 4e), promoting the transfer and separation of photo-generated carriers. In the case of the N1s the peaks at 399.4 eV, 400.5 eV, 401.8 eV, and 405.3 eV are separately designated as carbon-bonded sp2, aromatic C=N–C, a tertiary nitrogen bonded to a carbon atom in the form N–(C)3, NH and the charge effect or positive charge localization in the heterocyclic ring. The XPS spectra powerfully verify the surface chemical composition of the Fe3O4/C/MnO2/C3N4 photocatalyst. (II): Raman spectrum of Fe3O4/C microspheres.

85-1436)59. The sharp peaks indicate that the synthesized Fe3O4 are well crystallized. In Fig. 3I-c, in addition to the diffraction peaks of Fe3O4 component, the diffraction peaks at 12.20°, 36.70°, and 65.70° correspond to (002), (006), and (119) crystal planes, in consistence with the crystal planes of MnO2 (JCDPS 18-0802)59. This case indicates that the MnO2 is successfully synthesized. The diffraction curve of the Fe3O4/C/MnO2/C3N4 photocatalyst in Fig. 3I-d reveals that except for the diffraction peaks of Fe3O4 and MnO2, the diffraction peaks appear at 13.00° and 27.40° are separately assigned to the (100) and (002) crystal planes of g-C3N4. This situation indicates that CN precursor successfully becomes g-C3N4 after low temperature polymerization and high temperature calcination. XRD results show that the Fe3O4/C/MnO2/C3N4 composite photocatalyst were successfully synthesized.

The XRD patterns cannot verify the existence of the C layer. For further confirming the formation of the C layer, the Raman test was used to characterize the Fe3O4/C sample. The spectrum in Fig. 3II indicates two different peaks at 1344 cm−1 and 1596 cm−1, corresponding to D-band and G-band of carbon material, respectively. These results confirm the carbonization of Fe3O4/P(MMA-DVB) material, and Fe3O4/C microspheres are successfully obtained. These two bands are related to the A1g phonon of sp2 carbon atoms in disordered graphite and the in-plane vibration of sp2 carbon atoms in the crystalline graphite, respectively50. The peak intensity ratio (I_D/I_G) can evaluate the carbon material’s crystallinity. The smaller the value is, the higher the degree of atomic order is52. Herein, the value is 0.79, meaning that the carbon material is graphitized partially. Therefore, the presence of the carbon matrix can improve the electronic conductivity and help avoid the recombination of photo-generated electron holes.

The surface chemical composition and the chemical state of the products were demonstrated by XPS characterization. Figure 4a is the full-scan spectrum of the photocatalyst, presenting the peaks of Mn, O, N, and C elements. From Fig. 4b, as for the Mn 2p spectrum, two peaks at 653.9 eV and 642.3 e V correspond to Mn 2P1/2 and Mn 2P3/2. With respect to the O1s, as illustrated in Fig. 4c, three peaks at 529.7 eV, 531.3 eV, 533.2 eV are fitted, which are separately attributed to the Mn–O–Mn lattice oxygen, surface hydroxyl and surface adsorbed oxygen. The C1s spectrum in Fig. 4d shows the sub-bands centered at 284.8 eV and 288.5 eV, which are ascribed to the C–C coordination of the surface-unstable carbon and N=C–N of g-C3N4. In addition, there is another peak centering at 286.3 eV, which is assigned to the C–O bond formed between the C of C3N4 and the O of MnO2. This result indicates that MnO2 and g-C3N4 are closely connected and form a solid MnO2/g-C3N4 interface, promoting the transfer and separation of photo-generated carriers. In the case of the N1s spectrum (Fig. 4e), the peaks at 399.4 eV, 400.5 eV, 401.8 eV, and 405.3 eV are separately designated as carbon-bonded sp2 hybrid aromatic C=N–C, a tertiary nitrogen bonded to a carbon atom in the form N–(C)n, NH and the charge effect or positive charge localization in the heterocyclic ring. The XPS spectra powerfully verify the surface chemical composition of the Fe3O4/C/MnO2/C3N4 photocatalyst.

The specific surface area and the pore structure of Fe3O4, Fe3O4/C, Fe3O4/C/MnO2 and Fe3O4/C/MnO2/C3N4 products are listed in Table 1. The former of the Fe3O4/C/MnO2 and Fe3O4/C/MnO2/C3N4 products are 119.56 m2/g and 120.25 m2/g, and the latter of them are 0.35 cm3/g and 0.31 cm3/g. Since C3N4 does not significantly affect the morphology of the composite structure, these parameters of the two samples are almost similar. The higher values are owing to the flower-like structure of the composite photocatalyst. The increase in specific surface area is conducive to exposing more active sites and increasing more surface adsorption, followed by improving catalytic performance.

To evaluate the saturation magnetization value of Fe3O4, Fe3O4/C, Fe3O4/C/MnO2 and Fe3O4/C/MnO2/C3N4, VSM measurement is conducted. It can be seen from Fig. 5a that the magnetization value of the Fe3O4 microspheres is 70.58 emu/g. After the carbon layer is recombined, the value of Fe3O4/C microspheres decreases to 56.97 emu/g (Fig. 5b). After the flower-like MnO2 was fabricated, the content of Fe3O4 component is decreasing, which leads to the value of Fe3O4/C/MnO2 microspheres decreases obviously to 37.62 emu/g (Fig. 5c). With the further formation of g-C3N4, the value is 30.02 emu/g (Fig. 5d). This value still meets the needs of magnetic separation. As shown in the illustration, when the magnet is placed next to the Fe3O4/C/MnO2/C3N4 photocatalyst
Figure 4. XPS spectra of FeO\(_4\)/C/MnO\(_2\)/C\(_3\)N\(_4\) photocatalyst (a), Mn 2p (b), O1s (c), C1s (d) and N1s (e).

Table 1. Specific surface area and pore parameters of samples.

| Entry | Sample               | Surface area (m\(^2\)/g) | Pore width (nm) | Pore volume (cm\(^3\)/g) |
|-------|----------------------|---------------------------|-----------------|---------------------------|
| 1     | FeO\(_4\)            | 38.47                     | 4.01            | 0.17                      |
| 2     | FeO\(_4\)/C          | 59.87                     | 2.23            | 0.21                      |
| 3     | FeO\(_4\)/C/MnO\(_2\)| 119.56                    | 6.94            | 0.35                      |
| 4     | FeO\(_4\)/C/MnO\(_2\)/C\(_3\)N\(_4\)| 120.25                | 6.35            | 0.31                      |
suspension, the photocatalyst can be quickly attracted to the side of the cuvette in a short time. The results show that the photocatalyst has a good magnetic response to the magnetic field, favoring the magnetic separation from the mixed solution.

Determining the adsorption capacity of the photocatalyst in dark reaction, then degrading MO under simulated light is used to investigate the photocatalytic activity of the prepared photocatalyst, and the results are shown in Fig. 6. Figure 6a reveals the mixture reached adsorption–desorption equilibrium within 60 min. And Fe₃O₄/C/MnO₂/C₃N₄ can adsorb about 22% of MO within 60 min, which is related to its higher specific surface area (120.25 m²/g). Figure 6b displays that UV–Vis is employed to monitor the change in the absorbance of the solution during the photocatalytic reaction. In Fig. 6b, one can clearly view that MO was almost completely degraded with adding Fe₃O₄/C/MnO₂/C₃N₄ composite photocatalyst after 140 min. The photocatalytic degradation MO over Fe₃O₄/C/MnO₂/C₃N₄ could be described by the following reactions:

\[
\text{photocatalyst} + \text{hv} \rightarrow \text{photocatalyst}\left(e^{-}\right) + \text{photocatalyst}\left(h^{+}\right) \\
H₂O + h^{+} \rightarrow \cdot OH + H^{+} \\
O₂ + e^{-} \rightarrow O₂⁻ \\
\text{MO} + \cdot OH/O₂⁻ \rightarrow \text{Mineralisation products}
\]

Figure 6c indicates the change of the MO concentration ratio Cₜ/C₀ with varying the light time, in which C₀ and Cₜ are the initial concentration of MO and the concentration of MO during the reaction, respectively. The degradation rate of MO solution with Fe₃O₄/C/MnO₂/C₃N₄ photocatalyst reaches 94.11%. From Fig. 6d, this reaction is attributed to a pseudo first-order reaction, which belongs to the Langmuir–Hinshelwood model with ln (Cₜ/C₀) = −k t. In the formula, k is the apparent first-order rate constant. The calculated rate constant k of Fe₃O₄/C/MnO₂/C₃N₄ photocatalyst is 0.022 min⁻¹. The excellent photocatalytic performance of Fe₃O₄/C/MnO₂/C₃N₄ composite material benefits from the synergistic effect between the various components.

In order to find the optimal ratio, the effect of amount of g-C₃N₄ on the photocatalytic efficiency was investigated. Meanwhile, determining the minimum optimal amount of photocatalyst in practical applications is important to reduce the costs. The composite photocatalyst containing different amounts of g-C₃N₄ (5%, 10%, 15%, 20%, 30%) were used to degrade MO dyes under the same conditions. From Fig. 7a,b, when the amount of g-C₃N₄ is 15%, the Fe₃O₄/C/MnO₂/C₃N₄ composite photocatalyst has the highest value. In Fig. 7c, the effect of the amount of photocatalyst on the degradation efficiency is examined. The results show that the photocatalytic efficiency gradually increases when the amount of photocatalyst increases in the range of 0–20 mg. When the amount of photocatalyst continues to increase, the photocatalytic efficiency does not change significantly, which may be caused by the particle agglomeration affecting the increase of active sites. Therefore, the optimal dosage of Fe₃O₄/C/MnO₂/C₃N₄ photocatalyst is 20 mg. Considering the industrial application of Fe₃O₄/C/MnO₂/C₃N₄ nanoparticles, it is essential to investigate the recyclability and stability of the photocatalyst. The Fe₃O₄/C/MnO₂/C₃N₄ was reused four times to examine their
performances. And Fig. 7d reveals the results that the degradation rates for the four cycles are 94.11%, 90.42%, 88.37% and 79.69%, respectively. There is no doubt that after the photocatalyst is recycled, the conversion rate will decrease, which might result from the loss of sample during the cycle. However, even after four cycles, the value still has 79.69% that might be related with the structure stability of the used photocatalysts, strongly demonstrating that the designed photocatalyst has excellent recyclability.

In this study, Fe₃O₄/C/MnO₂/C₃N₄ photocatalyst was synthesized by compounding g-C₃N₄ on the surface of MnO₂. In terms of enhanced photocatalytic activity, it is assumed that the charge transfer in the photocatalyst uses the Z-type mechanism, as shown in Fig. 8. For the individual g-C₃N₄ or MnO₂ component, due to thermodynamic effects, photo-generated holes in g-C₃N₄ cannot oxidize OH⁻ to form •OH radicals, while photo-generated electrons in MnO₂ cannot generate •O₂⁻ radicals effectively. Therefore, individual g-C₃N₄ or MnO₂ material cannot possess good photocatalytic performances. However, after a heterojunction was fabricated between these two components, the photo-generated electrons in the conduction band of MnO₂ can be transferred to the valence band of g-C₃N₄ and combined with the photo-generated holes there. This configuration of the Z-type scheme makes the utilization of holes from MnO₂ and electrons from g-C₃N₄ remarkably enhanced. In addition, the conductive C layer can also increase the photo-generated electron–hole pairs’ separation in MnO₂, which effectively prevents the recombination of photo-generated carriers. In the meantime, the higher specific surface area supplies much more active sites for photocatalytic activities. The prepared flower-like Fe₃O₄/C/MnO₂/C₃N₄ photocatalyst forms a Z-type photocatalytic system, which effectively enhances the separation of carrier, so that the composite material has excellent photocatalytic degradation efficiency.

Conclusions

In summary, a magnetic recyclable flower-like Fe₃O₄/C/MnO₂/C₃N₄ heterojunction photocatalyst was prepared for degrading organic dyes. The Fe₃O₄ core was used to facilitate magnetic separation and recovery. The C layer could conduct photo-generated electrons in MnO₂ and protect the core. The thin g-C₃N₄ layer was compounded on the surface of MnO₂, which greatly improved the specific surface area and the reactive sites of the material. The obtained Fe₃O₄/C/MnO₂/C₃N₄ composites exhibited enhanced photocatalytic performance for the degradation of MO solution (65 mL, 10 mg/L) under simulated light irradiation. The maximum photocatalytic degradation efficiency was 94.11% within 140 min. It was assumed that a Z-type heterojunction was fabricated between
MnO₂ and g-C₃N₄, which stimulated the electron transfer from the valence band of MnO₂ to the conduction band of g-C₃N₄. This structure promoted the photo-generated electron–hole pairs' separation, inhibited the free charges' recombination, and improved effective use of visible light. In here, an effective method to construct heterostructure nanomaterials was provided for efficient photocatalytic degradation.

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M.M., Y.Y. and Y.C. wrote the main manuscript text. Y.Y. drew the flow chart and mechanism diagram. Y.M. analyzed the data. J.J., Y.M., Z.W., W.H., S.W., M.L., D.M. and X.Y. collected data. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
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