Fe₃O₄-Loaded g-C₃N₄/C-Layered Composite as a Ternary Photocatalyst for Tetracycline Degradation

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ABSTRACT: A ternary photocatalyst, Fe₃O₄-loaded g-C₃N₄/C-layered composite (g-C₃N₄/C/Fe₃O₄) was fabricated by a facile sonication and in situ precipitation technique. Carbon nanosheets were prepared using the remaining non-metallic components of waste printed circuit boards as carbon sources. In this hybrid structure, g-C₃N₄ was immobilized on the surfaces of carbon nanosheets to form a layered composite, and 10−15 nm Fe₃O₄ nanoparticles are uniformly deposited on the surface of the composite material. The photocatalytic performance of the catalyst was studied by degrading tetracycline (TC) under simulated sunlight. The results showed that the photoactivity of the g-C₃N₄/C/Fe₃O₄ composite to TC was significantly enhanced, and the degradation rate was 10.07 times higher than that of pure g-C₃N₄, which was attributed to Fe₃O₄ nanoparticles and carbon nanosheets. Carbon sheets with good conductivity are an excellent electron transporter, which promotes the separation of photogenerated carriers and the Fe₃O₄ nanoparticles can utilize electrons effectively as a center of oxidation−reduction. Moreover, a possible photocatalytic mechanism for the excellent photocatalytic performance was proposed.

1. INTRODUCTION

In recent years, the existence of pharmaceutical residues in wastewater and its harm to the living ecosystem have attracted wide attention all over the world.¹ Tetracycline (TC), as a broad-spectrum antibiotic, has been widely used to prevent human and animal infections because of its antibacterial, bactericidal effect and low price.²,³ However, 70−90% of the administered dose of TC is excreted via urine and feces, which has been detected in several water sources.⁴ In order to effectively remove and degrade TC, various technologies have been developed, such as physical absorption, electrolysis, photocatalysis, microbial decomposition, electrochemical oxidation, and membrane separation.⁵⁻⁸ Moreover, semiconductor photocatalysis technology, as a green and efficient technology, has become the research hotspot of TC residue treatment in recent years. Graphitized carbon nitride (g-C₃N₄), as a typical metal-free polymer semiconductor material, has a unique two-dimensional structure, a suitable band gap to absorb visible light radiation and excellent chemical stability.⁹,¹⁰ Although g-C₃N₄ has already shown great potential in the photocatalysis field for water splitting,¹¹ degradation, and CO₂ reduction,¹² inevitable shortcomings such as low utilization efficiency of visible light, fast photo-induced carrier recombination, low BET surface area, and difficulty in restoring suspension dispersion limit its photocatalytic activity.¹³ Therefore, several strategies have been developed to enhance the photocatalytic performance of g-C₃N₄, such as porous structure design, metal or nonmetal element doping, surface modification, coupling with semiconductors, and so forth.¹⁴⁻¹⁶

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Of special notice, carbon materials are an excellent conductor of electrons and can transfer photoexcited electrons quickly to avoid carrier recombination.\(^{27}\) For instance, carbon dots, graphene, nanotubes, and others have been proven as effective components in g-C\(_3\)N\(_4\)-based hybrid systems due to their superior electrical, mechanical, thermal, and optical properties. Up to now, numerous significant research studies have been conducted via directly coupling carbon materials with g-C\(_3\)N\(_4\)-based materials, which include GO/g-C\(_3\)N\(_4\)/CDs,\(^{18}\) MWNTs/g-C\(_3\)N\(_4\),\(^{19}\) g-C\(_3\)N\(_4\)/graphene/Fe\(_3\)O\(_4\),\(^{20}\) and carbon/g-C\(_3\)N\(_4\) core−shell nanostructures.\(^{21}\) etc. Noticeably, since g-C\(_3\)N\(_4\) is also a π-conjugated semiconducting material, the electronic integration of g-C\(_3\)N\(_4\) with several carbonaceous materials including CNTs, carbon black, graphene, and carbon nanodots can significantly improve the delocalization, thus promoting the rapid migration of photoinduced electrons, hindering the recombination of carriers and improving the quantum efficiency of photocatalytic reactions.\(^{22}\) However, the present g-C\(_3\)N\(_4\)-based photocatalysts are difficult to recover and separate after photocatalytic reactions, which cannot meet the requirements of practical application. An effective strategy to solve this defect is to deposit magnetic materials on g-C\(_3\)N\(_4\) sheets. As a typical magnetic material, Fe\(_3\)O\(_4\) has been widely used in the synthesis of magnetic photocatalysts due to its good stability, low cost, good magnetism, and environmental friendliness. In addition, it can also be used as a good redox medium to store electrons and further improve photocatalytic performance.\(^{23−27}\)

Herein, as illustrated in Figure S1, we report a ternary heterojunction consisting of g-C\(_3\)N\(_4\) sheets and Fe\(_3\)O\(_4\) nanoparticles, with carbon layers attaching on the surfaces of the two components as an electron transfer mediator. The carbon material was prepared using the remaining nonmetallic fractions of waste printed circuit board (WPCB) as a carbon source according to our previous study.\(^{28}\) The magnetically separable g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\) nanocomposite was synthesized via a simple sonication technique followed by an in situ precipitation method. Under simulated sunlight, the photocatalytic degradation activity of the prepared g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\) ternary composite for antibiotic TC was significantly improved compared to pure g-C\(_3\)N\(_4\) and the g-C\(_3\)N\(_4\)/C composite. Moreover, the stability of the ternary g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\) photocatalyst and the mechanism of improving photocatalytic efficiency under solar light were studied.

2. RESULTS AND DISCUSSION

The XRD patterns of all as-prepared samples are shown in Figure 1. The carbon sample shows two peaks at around 26.1 and 41.8°, which can be indexed to the (002) and (100) diffraction planes of the amorphous carbon, respectively. The peaks located at 12.9 and 27.2° correspond to the (100) and (002) planes of g-C\(_3\)N\(_4\), which are attributed to the in-plane structural packing motif and interlayer stacking of the aromatic system, respectively. No carbon diffraction peak is observed in the g-C\(_3\)N\(_4\)/C, complex, which should be attributed to the low carbon content and weak diffraction intensity in the g-C\(_3\)N\(_4\)/C complex. As for g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\), the characteristic peaks of Fe\(_3\)O\(_4\) are found in the XRD pattern apart from that of g-C\(_3\)N\(_4\), in which the peaks at 35.5, 57.1, and 62.6° can be indexed to the (311), (511), and (440) crystal planes of Fe\(_3\)O\(_4\).\(^{30}\) The XRD results indicate that the g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\) photocatalyst was successfully prepared.

The morphology and microstructure of bare g-C\(_3\)N\(_4\) pure carbon, g-C\(_3\)N\(_4\)/C, and g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\) were investigated by TEM, and the results are shown in Figure 2. The sample of g-C\(_3\)N\(_4\) (Figure 2a) displays an irregular sheet structure, and the carbon (Figure 2b) shows a typical two-dimensional nanosheet morphology with thin thickness. Figure 2c,d shows TEM images of the g-C\(_3\)N\(_4\)/C nanocomposite. It can be seen that the carbon nanosheets and the g-C3N4 nanosheets are successfully combined to form a 2D−2D interface. g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\) exhibits a similar layer structure to g-C\(_3\)N\(_4\)/C. In addition, many nanoparticles with a diameter of about 10 to 15 nm are evenly distributed on the surface of carbon and g-C\(_3\)N\(_4\). In addition, the peaks of Fe, C, N, and O are clearly observed in the EDS result (Figure 2f) of g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\). The SAED pattern in Figure 2g consists of three diffraction rings, indicating the presence of Fe\(_3\)O\(_4\). The three ring patterns observed in SAED are indexed to (311), (511), and (440) planes of Fe\(_3\)O\(_4\) which are in good agreement with the XRD spectra.\(^{30}\) In the HRTEM images of Figure 2h,i, the lattice fringe of 0.25 nm corresponds to the (311) plane of Fe\(_3\)O\(_4\). All of the above observations suggested that the ternary hybrid photocatalyst g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\) was indeed formed.

The elemental compositions and the surface chemical states of g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\) were obtained by XPS spectroscopy. As depicted in Figure 3a, the XPS survey spectra of g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\) illustrated that the prepared sample was composed of C, N, O, and Fe elements. Figure 3b shows the C 1s core spectra of the g-C\(_3\)N\(_4\)/C/Fe\(_3\)O\(_4\) sample. The peak at 284.6 eV is assigned to graphitic or hydrogenated C−C bonding. Also, the two other peaks located at 281.1 and 282.7 eV originate from the adventitious carbon.\(^{31}\) The adventitious carbon on the sample surface may originate from the atmosphere, sample handling, and the contamination in the XPS chamber. In Figure 3c, a main peak with the strongest intensity located at 395.3 eV is attributed to the C=N−C groups in the triazine rings, and the weaker peak located at 397.1 eV is assigned to the amino groups located at the edges of the polymeric g-C\(_3\)N\(_4\) sheets.\(^{32}\) The binding energies of the Fe 2p\(_{1/2}\) and Fe 2p\(_{3/2}\) were observed at 724.9 and 710.2 eV, which are associated with the spin−orbit peaks of Fe\(_3\)O\(_4\). (Figure 3d). The presence of Fe\(_3\)O\(_4\) can be further confirmed by the O 1s XPS peak at 530.1 eV (Figure 3e), which corresponds to the oxygen species in the Fe\(_3\)O\(_4\) phase; the small O 1s peak at 531.8 eV in Figure 4e indicates the presence of oxygen-containing groups.\(^{34}\) The specific surface area and porous nature of the as-prepared photocatalysts were analyzed by the N\(_2\) adsorption−
desorption technique. As depicted in Figure 4, the g-C3N4 sample exhibits a type IV with a H3 hysteresis loop, indicating the presence of a mesoporous structure within the sample.35

The N2 adsorption isotherm of carbon shows a sharp increase in adsorption at a low relative pressure (P/P0) range of 0.01−0.1, revealing their microporous characteristics,36 and the Brunauer−Emmett−Teller (BET) surface area was 2419.1 m2·g−1. The g-C3N4/C and g-C3N4/C/Fe3O4 nanocomposites exhibit a transitional isotherm from type I to type IV (Figure 3 inset), which indicates the coexistence of micropores and mesopores. Notably, an H3-type hysteresis loop was observed in the range of P/P0 = 0.5−1.0, indicating the presence of mesopores. The amount of nitrogen adsorbed can be found in the low-pressure zone, further proving that there are abundant micropores, which are derived from the voids of carbon nanosheets. Also, the pore size distributions (Figure S2) of the as-prepared carbon, g-C3N4/C, and g-C3N4/C/Fe3O4 samples showed a narrow pore size distribution and were mainly

Figure 2. TEM images of (a) g-C3N4, (b) carbon, (c, d) g-C3N4/C, and (e) g-C3N4/C/Fe3O4. (f) EDS of C3N4/C/Fe3O4, (g) SAED patterns, (h) HRTEM image of g-C3N4/C/Fe3O4, and (i) HRTEM image of Fe3O4.

Figure 3. (a) XPS survey spectra and high-resolution XPS spectra of (b) C 1s, (c) N 1s, (d) Fe 2p, and (e) O 1s core-level electrons of the g-C3N4/C/Fe3O4 sample.
microporous (<2 nm). This is consistent with the analysis of the N\textsubscript{2} adsorption−desorption isotherm. As shown in Table S1, the surface areas calculated using the BET method of g-C\textsubscript{3}N\textsubscript{4}/C and g-C\textsubscript{3}N\textsubscript{4}/C/Fe\textsubscript{3}O\textsubscript{4} were 146.6 and 125.1 m\textsuperscript{2}·g\textsuperscript{−1}, respectively, much higher than that of pure g-C\textsubscript{3}N\textsubscript{4} (17.4 m\textsuperscript{2}·g\textsuperscript{−1}). It is clear that the surface area of g-C\textsubscript{3}N\textsubscript{4}/C/Fe\textsubscript{3}O\textsubscript{4} decreased after loading of Fe\textsubscript{3}O\textsubscript{4} nanoparticles. This may be due to the covering and blocking of some parts of the g-C\textsubscript{3}N\textsubscript{4}/C surface by Fe\textsubscript{3}O\textsubscript{4} nanoparticles. The increased specific surface area was conducive to the adsorption and transfer of pollutant molecules and provided a large number of reaction sites for enhanced photocatalytic activity.

The optical properties of g-C\textsubscript{3}N\textsubscript{4}, carbon, g-C\textsubscript{3}N\textsubscript{4}/C, and g-C\textsubscript{3}N\textsubscript{4}/C/Fe\textsubscript{3}O\textsubscript{4} were investigated by UV−vis DRS, and the results are shown in Figure 5a. For pristine g-C\textsubscript{3}N\textsubscript{4}, the response cutoff wavelength is 460 nm, and the high selectivity to the visible spectral range corresponds to its band gap; thus, the photoconversion efficiency in the visible range is rather low. It is known that the narrow gap of sp\textsuperscript{2}carbon clusters embedded in the carbon layer has excellent optical absorption capacity in almost the whole wavelength, so the introduction of carbon materials can improve the optical absorption efficiency of the g-C\textsubscript{3}N\textsubscript{4}/C sample.\textsuperscript{37} As expected, compared with pristine g-C\textsubscript{3}N\textsubscript{4}, the g-C\textsubscript{3}N\textsubscript{4}/C and g-C\textsubscript{3}N\textsubscript{4}/C/Fe\textsubscript{3}O\textsubscript{4} samples show wider light absorption capacity and improved adsorption strength in the whole UV−visible region.

The photoluminescence spectroscopy (PL) was used to study the separation and recombination of photoelectrons and holes in semiconductor catalysts.\textsuperscript{38} As shown in Figure 5b, compared with g-C\textsubscript{3}N\textsubscript{4}, the PL peak intensity of g-C\textsubscript{3}N\textsubscript{4}/C is significantly reduced, which is related to the inhibition of light-induced carrier recombination. The PL intensity of g-C\textsubscript{3}N\textsubscript{4}/C/Fe\textsubscript{3}O\textsubscript{4} is much weaker than that of g-C\textsubscript{3}N\textsubscript{4} and g-C\textsubscript{3}N\textsubscript{4}/C, indicating that the carbon layer can effectively transfer photoelectrons and extend the life of photoelectron−hole pairs. The results demonstrated that the introduction of a carbon layer and Fe\textsubscript{3}O\textsubscript{4} can effectively inhibit the recombination rate of photocarriers, thus producing more active groups and improving the photocatalytic performance.

In order to determine the separation efficiency of the carrier, photochemical measurements were performed.\textsuperscript{39} Figure 6a displays the transient photocurrent responses of g-C\textsubscript{3}N\textsubscript{4}, g-C\textsubscript{3}N\textsubscript{4}/C, and g-C\textsubscript{3}N\textsubscript{4}/C/Fe\textsubscript{3}O\textsubscript{4} samples in several light on−off cycles. Compared with g-C\textsubscript{3}N\textsubscript{4} and g-C\textsubscript{3}N\textsubscript{4}/C, g-C\textsubscript{3}N\textsubscript{4}/C/Fe\textsubscript{3}O\textsubscript{4} significantly improves the photocurrent performance. The results show that it has the lowest electron and hole recombination rate, indicating that Fe\textsubscript{3}O\textsubscript{4} and carbon nanosheets play an important role in the ternary photocatalyst. In Figure 6b, the charge migration rate was evaluated according to the arc radius in the EIS. Obviously, g-C\textsubscript{3}N\textsubscript{4}/C/Fe\textsubscript{3}O\textsubscript{4} shows the minimum radius of curvature, indicating its highest electron−hole pair separation and electron transfer efficiency, which agreed well with the results of PL and photocurrent response.

The performance of degradation of TC by all synthesized samples under simulated sunlight is displayed in Figure 7a. As depicted in Figure S3, in the dark adsorption step, adsorption−desorption equilibrium was reached within 60 min and 30.2 and 28.6% of CIP can be adsorbed by g-C\textsubscript{3}N\textsubscript{4}/C and g-C\textsubscript{3}N\textsubscript{4}/C/Fe\textsubscript{3}O\textsubscript{4}, respectively. It is noted that the g-C\textsubscript{3}N\textsubscript{4}/C and g-C\textsubscript{3}N\textsubscript{4}/C/Fe\textsubscript{3}O\textsubscript{4} photocatalysts exhibited a higher adsorption ability than pure g-C\textsubscript{3}N\textsubscript{4}, which can be ascribed to the increased specific surface area and the interactions between the graphitic carbon layer (sp\textsuperscript{2} bonding) and the aromatic rings of the TC molecules. In the control experiment, TC basically did not degrade without the photocatalyst, indicating that the self-decomposition of TC can be ignored. Under the same conditions, the carbon and pure g-C\textsubscript{3}N\textsubscript{4} samples only degraded 3.6 and 28.8% of the TC in 120 min. Compared to pure g-C\textsubscript{3}N\textsubscript{4}, the coupling of carbon and g-C\textsubscript{3}N\textsubscript{4} obviously improved

![Figure 4. N\textsubscript{2} adsorption−desorption isotherms of as-prepared g-C\textsubscript{3}N\textsubscript{4}, carbon, g-C\textsubscript{3}N\textsubscript{4}/C and g-C\textsubscript{3}N\textsubscript{4}/C/Fe\textsubscript{3}O\textsubscript{4}.](image)

![Figure 5. (a) UV−vis absorption spectra and (b) PL emission spectra of the as-prepared samples.](image)
the photodegradation efficiency. As expected, g-C₃N₄/C/Fe₃O₄ had the best degradation efficiency, with the photodegradation rate of TC, approaching 96.4% under the same irradiation time. According to the first-order kinetics model, the apparent rate constants (k_{app}/min⁻¹) of g-C₃N₄, carbon, g-C₃N₄/C, and g-C₃N₄/C/Fe₃O₄ are calculated to be 0.0029, 0.0003, 0.0063, and 0.0292 min⁻¹, respectively (Figure 7b). It is worth noting that the rate constant of the g-C₃N₄/C/Fe₃O₄ sample is the highest, which is 10.07 times that of the original g-C₃N₄. The enhanced activity of g-C₃N₄/C/Fe₃O₄ can be attributed to the formation of heterojunctions that can effectively separate photocarriers, and the introduction of carbon in the composite material also helps to expand the optical response range and realize more effective electron transfer.
Photocatalytic stability and recyclability are the main parameters of its practical application. Figure 8a shows the photocatalytic TC degradation performance of the g-C3N4/C/Fe3O4 sample under simulated sunlight for five successive runs. It can be seen that after five cycles, the removal rate of TC remains at 88.1%, indicating that the g-C3N4/C/Fe3O4 photocatalyst possesses high stability and can be used for repeated treatment of TC. Additionally, XRD patterns presented in Figure S4 shows that the position of the diffraction peaks for g-C3N4/C/Fe3O4 before and after the fifth use remained unchanged, with a slight decrease in the peak intensities. In this study, EDTA, p-benzoquinone, and t-BuOH were used to scavenge h+, O2−, and ·OH, respectively, in order to investigate in depth the photocatalytic mechanism. In Figure 8b, it can be seen that the degradation rate of TC is significantly reduced after adding p-benzoquinone (1 mM) and EDTA (1 mM), indicating that O2− and h+ play significant roles in the degradation process. However, little efficiency reduction with the addition of t-BuOH (1 mM) demonstrated that ·OH might not the predominant active species. Based on the analysis of tapping experiments, it can be concluded that O2− and h+ primarily contributed to the photocatalytic removal of TC over the g-C3N4/C/Fe3O4 photocatalyst.

In order to clarify the photodegradation pathway of TC under the action of the g-C3N4/C/Fe3O4 photocatalyst, the main intermediate products converted by TC in the photodegradation process were accurately identified by HPLC-MS, and the result is shown in Figure S5 and Table S2. Obviously, TC is completely transformed into seven main photoproducts, which are designated as P2−P7 in the order of retention time. Combining with these detection results and references, degradation and removal processes can be divided into three main pathways (Figure 9). Briefly, the m/z of 445.1 (P1) is the molecular ion of TC and also appeared in the mass spectrum at the early stage of degradation. The first pathway is that the TC was transformed into P2 with m/z 427.1, which is due to dehydration. Meanwhile, deprotonated product P3 with m/z 397 was generated via loss of the N-dimethyl group due to the relative low bond energy of C−N and loss of the hydroxyl group. When further increasing the reaction time, the formation of P4 with m/z 318.3 was proposed to form via dihydroxylation. Subsequently, the loss of methyl group occurred from intermediate P4 and then intermediate P5 was produced. The third possible degradation route is that the tetracycline molecule was attacked by OH to form its hydroxylated product P6 with m/z 453.3. The product P7 with m/z 362.3 was formed through the further oxidation of product P6 and ring opening. These ring-opening products were finally oxidized into CO2 and H2O.

Figure 10 shows the schematic representation of the proposed mechanism for target pollutant degradation over the g-C3N4/C/Fe3O4 ternary photocatalyst. First, the introduction of carbon nanosheets resulted in a larger specific surface area of the g-C3N4/C/Fe3O4 sample, thus providing more active reaction sites. According to previous studies, the CB and VB edge potentials of g-C3N4 were at −1.12 and 1.57 eV, respectively. The g-C3N4 yields photoinduced electrons and holes after exciting by simulated solar light. Because the carbon nanosheets in the ternary complex have good electron transport capability, the electrons generated in the VB of g-C3N4 are quickly transferred to the Fe3O4 nanoparticles resulting in the decrease of the electron−hole recombination rate and the prolongation of positive hole half-life, along these lines, high photocatalytic activity was expected in the test of g-C3N4/C/Fe3O4. In addition, g-C3N4 and carbon nanosheets...
are layered systems with a tri-triazine structure and have electron delocalization, leading to high charge separation. On the other hand, these captured electrons by Fe₃O₄ nanoparticles could react with oxygen to form active species O₂⁻, and OH radicals also can be produced via multistep reduction of O₂. Moreover, the Fe³⁺ existing in Fe₃O₄ captures the electrons to generate Fe²⁺ and combines with O₂ to generate more O₂⁻. Meanwhile, the photogenerated holes left in the VB of g-C₃N₄ reacted with the target pollutants directly instead of oxidized H₂O to produce active species OH/H₂O₂ (+2.68 eV). These active substances produced in the photocatalytic process would further react with organic pollutants to achieve degradation.

3. CONCLUSIONS

In summary, the g-C₃N₄/C/Fe₃O₄ ternary nanocomposite was synthesized by a facile sonication and in situ precipitation technology. The as-prepared g-C₃N₄/C/Fe₃O₄ has significantly enhanced photocatalytic activity for the degradation of antibiotic TC, and the degradation rate is nearly ten times higher than that of g-C₃N₄ under simulated solar light. The significantly improved photocatalytic activity should be attributed to the enhancement of optical absorption, enlarged specific surface area, and effective separation efficiency of photogenerated carriers. According to the determination of free radical capture experiments, the main active substances responsible for photocatalytic degradation are photoinduced holes and O₂⁻ free radicals. Finally, the ternary photocatalyst showed reasonable stability during five successive runs.

4. EXPERIMENTAL SECTION

4.1. Preparation of Samples. Preparation of g-C₃N₄: 5 g of melamine was heated at 550 °C (2 °C·min⁻¹) for 4 h. Then, the obtained yellow product was collected and ground into powder. Synthesis of carbon nanosheets: the remaining WPCB nonmetallic fraction was carbonized in a microwave oven for 20 min at 600 W. The cooled product was mixed and ground with KOH at a mass ratio of 1:2 and then activated at 850 °C for 90 min under nitrogen protection at a heating rate of 1 °C·min⁻¹. Finally, the samples were washed with DI water until the pH value was neutral and dried at 120 °C for 12 h. Synthesis of g-C₃N₄/C/Fe₃O₄ photocatalyst: first, g-C₃N₄ (2.5 g) and carbon powder (0.25 g) were dispersed in 200 mL of ethanol/water (ν/ν, 1/3) and ultrasonicated for 2 h at ambient temperature. After that, FeCl₃·6H₂O (0.1081 g) and FeCl₂·4H₂O (0.0398 g) were dissolved separately in 5 mL of deionized water and added to the above suspension. The resulting mixture was stirred at 80 °C for 120 min, and then 8 mL of ammonia solution was quickly injected into the above reaction mixture and then stirred for 60 min. The products were collected, washed several times with deionized water and alcohol, and dried overnight at 65 °C vacuum.

4.2. Characterization of Photocatalysts. X-ray diffraction (XRD) data were obtained on an X-ray diffractometer (SmartLab, Rigaku) with Cu Kα radiation in the range of 10–70° (2θ). The morphology and microstructure of the samples were studied by transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) and high-resolution TEM (HRTEM). The elements of the sample prepared were analyzed by energy-dispersive spectroscopy (EDS). UV–vis diffuse reflectance spectra (DRS) of the samples were measured using a UV–vis spectrophotometer (UV-3600, Shimadzu). Photoluminescence (PL) with an excitation wavelength of 325 nm was obtained using a fluorescence spectrophotometer (Shimadzu RF-5301). The specific Brunauer–Emmett–Teller (BET) surface areas were determined by nitrogen adsorption using Micromeritics ASAP 2020 nitrogen adsorption apparatus. The analysis of intermediates was performed using an HPLC-MS system (Agilent 1290/6460, Triple Quad MS) equipped with a Zorbax XDB-C18 column (150 × 2.1 mm, 3.5 μm). The electrochemical measurement was performed with an electrochemical workstation (CHI660B, Chen Hua Instruments, Shanghai, China).

4.3. Photocatalytic Experiments. The photodegradation of tetracycline (TC) was performed in a photochemical reactor at room temperature. Also, a 500 W xenon lamp was used as the simulated solar light source. Typically, 10 mg of the as-prepared photocatalyst was suspended in 40 mL of TC solution (10 mg·L⁻¹) and stirred magnetically for 60 min in the dark to ensure the establishment of the adsorption/desorption equilibrium between the catalyst and the simulated pollutant. In the course of the experiment, 1 mL of the sample was taken out every 5 min and a PTFE syringe filter (0.45 μm) was used to remove the particles. The concentration of TC was monitored by a high-performance liquid chromatograph (HPLC, Shimadzu LC-20A) equipped with an Inertsil ODS-SP column. The mobile phase consisted of acetonitrile and ultrapure water (with the addition of 0.2% formic acid) with a volume ratio of 25:75 at a flow rate of 0.8 mL min⁻¹.

ASSOCIATED CONTENT

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03905.

Supporting Information

Schematic illustration of the preparation processes of the g-C₃N₄/C/Fe₃O₄ photocatalyst (Figure S1), Barrett–Joyner–Halenda pore size distribution curves of the as-prepared materials (Figure S2), pore structure parameters of the as-prepared materials (Table S1), TC adsorption capacities of the as-prepared samples (Figure S3), XRD pattern of the g-C₃N₄/C/Fe₃O₄ sample before and after five cycle run photocatalytic experiments (Figure S4), mass spectra of the TC and intermediates eluted at different retention times (Figure S5), and identification of TC and its possible transformation products during photodegradation (Table S2) (PDF)

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Notes

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