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# Enhancement of the heterogeneous photo-Fenton performance of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> heterostructures for erythromycin degradation through accelerating Fe(II) generation

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The slow rate of the Fe<sup>3+</sup>/Fe<sup>2+</sup> cycle has decreased the efficiency of photo-Fenton technology for wastewater treatment. Here, a novel GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> heterostructure was constructed by growing Fe<sub>3</sub>O<sub>4</sub> nanoparticles and MIL-100(Fe) onto GO, thus accelerating the Fe<sup>3+</sup>/Fe<sup>2+</sup> cycle and improving catalytic activity, and it was used as a heterogeneous photo-Fenton catalyst for ERY degradation. The catalyst was fully characterized by TEM, XRD, Raman spectroscopy, XPS, N<sub>2</sub> adsorption–desorption and UV-vis DRS. The influences of initial solution pH, H<sub>2</sub>O<sub>2</sub> concentration and catalyst dosage on ERY degradation were investigated. Under optimal conditions (initial pH of 4.03, 10.0 mM H<sub>2</sub>O<sub>2</sub>, 0.1 g L<sup>-1</sup> catalyst), the GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> + vis system removed 97.3% of ERY (0.1 mmol L<sup>-1</sup>) within 60 min, and the pseudo-first-order rate constant was 0.0575 min<sup>-1</sup>. Furthermore, the catalyst showed favorable stability, maintaining excellent catalytic activity even after 4 cycles. A possible degradation mechanism of ERY was proposed based on the results of characterization, ERY degradation, and reactive species analysis. Fe<sub>3</sub>O<sub>4</sub>, MIL-100(Fe) and GO in the catalyst showed synergistic effects; the photo-induced electrons from MIL-100(Fe) could be immediately transferred to Fe<sub>3</sub>O<sub>4</sub>, promoting Fe<sup>3+</sup> reduction to Fe<sup>2+</sup> in the photo-Fenton reaction. GO in the catalyst could promote electron transfer from MIL-100(Fe) and organics to Fe<sub>3</sub>O<sub>4</sub>, significantly promoting the Fe<sup>3+</sup>/Fe<sup>2+</sup> cycle.

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## 1. Introduction

Erythromycin (ERY) is usually used when people are allergic to penicillin, and it can exist in the natural environment for a long time with antibiotic activity, which may ultimately threaten human health.<sup>1</sup> ERY can be degraded *via* the biliary and renal tract by the human body, but undecomposed ERY enters the environment with excretion. However, more than 60% of ERY in the environment is maintained unchanged because of its chemical stability, and it has been detected in various environments.<sup>2</sup> The United States Environmental Protection Agency added ERY into its Contaminant Candidate List 3, while the European Union regards ERY as a high-risk priority pollutant.<sup>3</sup> In China, ERY has been identified as a precedence-controlled pollutant because of its frequent detection in water sources,

natural waters, underground waters and wastewater treatment plants.<sup>4</sup>

To date, various methods have been used to remove ERY from wastewater: advanced oxidation,<sup>5</sup> membrane separation,<sup>6</sup> adsorption,<sup>7</sup> biological treatment technology<sup>8</sup> and phytoremediation.<sup>9</sup> Advanced oxidation technologies, such as ozonation, catalytic wet oxidation, electrochemical oxidation and Fenton oxidation, can produce free radicals (such as <sup>•</sup>OH and <sup>•</sup>O<sub>2</sub><sup>-</sup>) and they have usually been used for antibiotic wastewater treatment.<sup>10</sup> Among them, Fenton oxidation has attracted wide attention for its strong oxidation ability and simple operation.<sup>11</sup> However, there are still inherent drawbacks with Fenton technology, such as the generation of iron-containing sludge, a narrow range of working pH (2–3.5), great difficulty in catalyst regeneration, and excessive consumption of H<sub>2</sub>O<sub>2</sub>.<sup>12</sup> In order to overcome these drawbacks, heterogeneous Fenton technology was developed, an iron-based solid was used to replace soluble iron ions, and the cycling of Fe<sup>2+</sup>/Fe<sup>3+</sup> could ensure the successive reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>.<sup>13</sup>

For iron-based heterogeneous Fenton technology, <sup>•</sup>OH was generated mainly *via* the Hubble–Weiss cycle (eqn (1) and (2)), where Fe<sup>3+</sup> reduction to Fe<sup>2+</sup> (eqn (2)) was regarded as the rate-

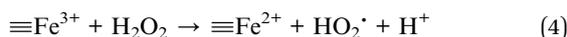
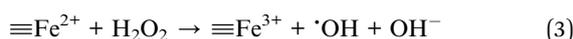
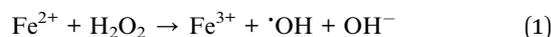
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controlling step, which significantly influenced the production of  $\cdot\text{OH}$ ,<sup>14</sup> and the active sites at the catalyst interface directly catalyzed the decomposition of  $\text{H}_2\text{O}_2$  (eqn (3) and (4)).<sup>15</sup> Therefore, accelerating the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  cycle is a crucial method to promote the production of  $\cdot\text{OH}$ . There are three main methods for improving heterogeneous Fenton reactions: (1) incorporating  $\text{Fe}^{2+}$ :<sup>16</sup>  $\text{Fe}^{2+}$  has been introduced into the catalysts *via* different methods; (2) facilitating the regeneration of  $\text{Fe}^{2+}$ :<sup>13</sup> additional energy, materials and reagents (such as light, metals and redox mediators) were introduced to heterogeneous Fenton reactions; (3) accelerating the Hubble–Weiss cycle:<sup>14</sup> some catalyst modification methods (such as regulation of surface/interface and fabrication of composite materials) have been applied to promote the Hubble–Weiss cycle in heterogeneous Fenton reactions.



$\text{Fe}_3\text{O}_4$  nanoparticles (NPs) have been proven to be an efficient heterogeneous Fenton catalyst for a higher content of  $\text{Fe}^{2+}$  in the structure,<sup>17</sup> and rapid electron transfer between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  can be achieved in a unique octahedral structure.<sup>18</sup>  $\text{Fe}^{2+}$  in an  $\text{Fe}_3\text{O}_4$  octahedron was oxidized to  $\text{Fe}^{3+}$  by  $\text{H}_2\text{O}_2$  to produce  $\cdot\text{OH}$  (eqn (1),  $k = 40\text{--}80 \text{ M}^{-1} \text{ s}^{-1}$ ), and the structure of  $\text{Fe}_3\text{O}_4$  remained unchanged.<sup>18</sup> Nevertheless, further reduction of the produced  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  by  $\text{H}_2\text{O}_2$  was hindered, because the reaction rate was as low as  $0.001\text{--}0.01 \text{ M}^{-1} \text{ s}^{-1}$  (eqn (2)).<sup>19</sup> Furthermore, the utilization efficiency for  $\text{H}_2\text{O}_2$  was always relatively low because of  $\text{Fe}_3\text{O}_4$  aggregation and a slow  $\text{Fe}^{3+}/\text{Fe}^{2+}$  cycle.<sup>20</sup> Therefore, excessive  $\text{H}_2\text{O}_2$  ( $10\text{--}50 \text{ mmol L}^{-1}$ ) should be added for the complete degradation of organic pollutants ( $0.01\text{--}0.3 \text{ mmol L}^{-1}$ ).<sup>20</sup> Since  $\text{Fe}_3\text{O}_4$  NPs inevitably generated interfacial or dissolved  $\text{Fe}^{3+}$  during the Fenton reaction, some electron donors were needed to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . Furthermore,  $\text{Fe}_3\text{O}_4$  NPs were apt to agglomerate during the Fenton reaction.<sup>21</sup> It was proved that loading  $\text{Fe}_3\text{O}_4$  NPs can suppress both agglomeration and the leakage of Fe ions.<sup>22</sup>

Recently, it was found that loading metal oxide NPs onto MOFs could overcome the drawbacks of a single catalyst. Among iron-based MOFs, Materials of Institute Lavoisier-type frameworks (MILs) were proved to be efficient catalysts for Fenton-like reactions. MILs showed many advantages, such as high catalytic activity, adjustable size and shape, well-defined pore architecture, high specific surface area, excellent photoresponsiveness, tailorable chemical composition and high aqueous stability.<sup>23</sup>  $\text{Fe}_3\text{O}_4$  NPs were loaded onto MILs to construct composites, and the individual drawbacks could be improved.<sup>16</sup> The combination of  $\text{Fe}_3\text{O}_4$  NPs and MIL-100(Fe) was a feasible strategy. The composite showed excellent catalytic activity and possessed the advantages of MIL-100(Fe) and  $\text{Fe}_3\text{O}_4$  NPs.<sup>16</sup> Liang *et al.*<sup>24</sup> synthesized magnetic MIL-100(Fe). The

catalyst showed excellent performance for the degradation of oxytetracycline hydrochloride *via* photo-Fenton under visible sunlight. They also constructed a  $\text{CuS}/\text{Fe}_3\text{O}_4@\text{MIL-100}(\text{Fe})/\text{vis}/\text{H}_2\text{O}_2$  system, using which, 95.31% of oxytetracycline hydrochloride could be removed.<sup>25</sup> Gong *et al.*<sup>26</sup> prepared  $\text{Fe}_3\text{O}_4@\text{GO}@\text{MIL-100}(\text{Fe})$ , and nearly 100% of 2,4-dichlorophenol could be removed by  $\text{Fe}_3\text{O}_4@\text{GO}@\text{MIL-100}(\text{Fe})$  in a photo-Fenton reaction.

Although the  $\text{Fe}_3\text{O}_4/\text{MIL-100}(\text{Fe})$  composite showed excellent catalytic activity for a heterogeneous Fenton reaction, the low  $\text{Fe}^{2+}/\text{Fe}^{3+}$  cycle rate limited its extensive application in Fenton processes.<sup>27</sup> Recently, heterogeneous Fenton catalysts were loaded onto various organic or inorganic materials, such as organic membranes, resins, zeolite, silicon, clay, activated carbon and graphene oxide (GO).<sup>23</sup> Catalysts interacting with supports may produce new active sites; the supports could also act as an electron bridge; the electrons could transfer between pollutants; and  $\text{H}_2\text{O}_2$  and Fe species promote  $\text{Fe}^{3+}$  reduction to  $\text{Fe}^{2+}$ .<sup>28</sup> GO is a good conductive material, and  $\text{Fe}_3\text{O}_4$  NPs loaded onto GO were used to overcome the limitations mentioned.<sup>13,29</sup> It acted as a “bridge”, when electrons from organic oxidation were transferred to the  $\equiv\text{Fe}^{3+}$  close to GO. Agglomeration of  $\text{Fe}_3\text{O}_4$  NPs was hindered by loading  $\text{Fe}_3\text{O}_4$  NPs onto GO sheets,<sup>30</sup> and its rich oxygen-containing functional groups were favorable for pollutant adsorption, thus realizing effective degradation of pollutants.<sup>31</sup> It is expected that loading of  $\text{Fe}_3\text{O}_4/\text{MIL-100}(\text{Fe})$  composite onto GO could produce marked changes to its structure, performance and activity in a heterogeneous Fenton reaction.

Enlightened by the above analysis, we synthesized a  $\text{GO}/\text{MIL-100}(\text{Fe})@\text{Fe}_3\text{O}_4$  heterostructure using  $\text{Fe}_3\text{O}_4$  NPs as the active component and GO as an electron bridge to MIL-100(Fe) for the photo-Fenton degradation of ERY. The surface morphology, crystalline structure, elemental composition and optical adsorption properties of the catalyst were characterized. The catalytic performance, the influences of operating parameters (such as pH conditions,  $\text{H}_2\text{O}_2$  concentration and catalyst dosage) on ERY removal, and the stability of the catalyst, were systematically evaluated.  $\text{GO}/\text{MIL-100}(\text{Fe})@\text{Fe}_3\text{O}_4$  showed enhanced photo-Fenton catalytic activity for ERY degradation compared to  $\text{Fe}_3\text{O}_4$  NPs, MIL-100(Fe) or  $\text{MIL-100}(\text{Fe})@\text{Fe}_3\text{O}_4$ , which can be ascribed to the synergistic effects between  $\text{Fe}_3\text{O}_4$  NPs, MIL-100(Fe) and GO. In a  $\text{GO}/\text{MIL-100}(\text{Fe})@\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}_2 + \text{vis}$  system, the electrons from organics and MIL-100(Fe) can be effectively transferred to  $\text{Fe}_3\text{O}_4$  NPs by GO, thus accelerating the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  cycle, and enhancing the catalytic activity.

## 2. Experimental

### 2.1. Materials

All the solvents and reagents were of at least analytical grade and used without purification.  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (99%),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (99%), NaOH (98%), HCl (36–38%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%), silver nitrate ( $\text{AgNO}_3$ , 99.8%), 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ , 98%), ammonium oxalate (AO, 99%), *tert*-butyl alcohol (TBA, 99.8%), *p*-benzoquinone (BQ, 99.5%),  $\text{NaHCO}_3$  (99%),  $\text{NaH}_2\text{PO}_4$  (99%), NaCl (99%),  $\text{Na}_2\text{SO}_4$  (99%),  $\text{NaNO}_3$



(99%) and humic acid (HA, 99%) were obtained from Sino-pharm Chemical Reagent Co., Ltd. Erythromycin (ERY, 85%) was obtained from Aladdin Reagent (Shanghai) Co., Ltd. All solutions were prepared using deionized Milli-Q water (18.2 M $\Omega$ ).

## 2.2. Preparation of samples

**2.2.1. Synthesis of Fe<sub>3</sub>O<sub>4</sub> NPs.** Fe<sub>3</sub>O<sub>4</sub> NPs were prepared by a chemical coprecipitation method.<sup>32</sup> Briefly, FeCl<sub>2</sub>·4H<sub>2</sub>O (2.0 g, 10.1 mmol) and FeCl<sub>3</sub>·6H<sub>2</sub>O (5.2 g, 19.2 mmol) were dissolved in deionized water (25 mL), followed by the addition of 0.85 mL of concentrated hydrochloric acid. The obtained solution was added into a three-necked round flask (500 mL), then 100 mL of NaOH solution (1.2 mol L<sup>-1</sup>) was added dropwise into the above solution under non-magnetic agitation and an N<sub>2</sub> atmosphere at 80 °C. Afterwards, the obtained suspension was aged for 30 min and cooled to room temperature. Finally, the black precipitate was separated from the suspension by magnetic separation and rinsed with deionized water several times until the pH of the scrubbing solution achieved a neutral value, and then dried through freeze drying for 24 h.

**2.2.2. Synthesis of partially reduced GO.** Partially reduced GO was prepared *via* a one-step hydrothermal method.<sup>28</sup> In a typical process, 20 mg of GO powder and 0.08 g of ascorbic acid were added to 10 mL of deionized water. Then, the mixture was treated under ultrasonication for 30 min, transferred to a Teflon-lined autoclave (100 mL), and kept at 180 °C for 16 h. After cooling to 25 °C, a hydrogel was obtained, which was dipped in ethanol solution (15%) for 24 h to remove the remaining precursor. Finally, the sample was treated by freeze drying for 24 h to produce partially reduced GO.

**2.2.3. Synthesis of MIL-100(Fe).** MIL-100(Fe) was prepared by a hydrothermal method.<sup>33</sup> FeCl<sub>3</sub>·6H<sub>2</sub>O (960.1 mg, 3.55 mmol) and benzene-1,3,5-tricarboxylic acid (H<sub>3</sub>BTC, 501.5 mg, 2.39 mmol) were dissolved in deionized water (20 mL). The mixture was stirred for 30 min, then added to a Teflon sealed-autoclave, and heated at 150 °C for 24 h.<sup>33</sup> The obtained red-brown samples were centrifuged, rinsed with deionized water, and dried through freeze drying for 24 h.

**2.2.4. Synthesis of GO/MIL-100(Fe).** GO/MIL-100(Fe) was prepared by a hydrothermal method.<sup>33</sup> A suspension of H<sub>3</sub>BTC (501.5 mg, 2.39 mmol) and obtained GO (15 mg) in deionized water (50 mL) was prepared by stirring for 1 h. Then, FeCl<sub>3</sub>·6H<sub>2</sub>O (960.1 mg, 3.55 mmol) was dissolved in the above H<sub>3</sub>BTC-GO suspension. The mixture was stirred for 30 min, then added to a Teflon sealed autoclave, and heated at 150 °C for 24 h. The obtained samples were centrifuged, rinsed with deionized water, and dried through freeze drying for 24 h.

**2.2.5. Synthesis of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>.** FeCl<sub>2</sub>·4H<sub>2</sub>O (2.0 g, 10.1 mmol) and FeCl<sub>3</sub>·6H<sub>2</sub>O (5.2 g, 19.2 mmol) were dissolved in deionized water (50 mL), followed by the addition of 0.85 mL of concentrated hydrochloric acid and 0.48 g of obtained GO/MIL-100(Fe), then stirred for 30 min. The obtained suspension was added into a three-necked round flask (500 mL), then 100 mL of NaOH solution (1.2 mol L<sup>-1</sup>) was added dropwise into the above suspension under non-magnetic

agitation and an N<sub>2</sub> atmosphere at 80 °C. Then, the obtained GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> suspension was aged for 30 min and cooled to room temperature. Finally, the black precipitate was separated from the suspension by magnetic separation and rinsed with deionized water several times, and dried through freeze drying for 24 h.

## 2.3. Characterization

The sizes and microstructures of the materials were examined using transmission electron microscopy (TEM, JSM-2200FS, JEOL, Japan) with 200 kV accelerating voltage. The X-ray powder diffraction (XRD) patterns were obtained using an X-ray diffractometer (D8 Focus, Brooke, Germany), where the detection conditions were 40 kV, 40 mA, and a  $2\theta$  range of 5°–80°. Raman spectra were obtained by a confocal Raman spectroscopic system (inVia Qontor, Renishaw, UK) using a 532 nm excitation laser. Information on the surface chemical state of the materials was obtained using X-ray photoelectron spectroscopy (XPS, PHI5300, PerkinElmer, USA). The surface areas and pore structures were analyzed by N<sub>2</sub> adsorption–desorption on an ASAP 2020HD88 (Micromeritics, America) using the BET and BJH methods. The UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained with a Specord 210 Plus UV-visible spectrophotometer (Jena, Germany). Photoluminescence (PL) spectra were obtained *via* a steady-state/transient fluorescence spectrometer (Edinburgh FLS1000, United Kingdom).

## 2.4. Experimental procedures

The experiments were conducted in a photochemical reaction system (BL-GHX-CH500, Xi'an Depai Biotech. Co., Ltd, China). A 300 W xenon lamp (PLS-SXE300/300UV, Perfect Light, China) with a cutoff filter (420 nm) was applied as a visible light source, and the light source was 15 cm above the surface of the solution. The solution pH, H<sub>2</sub>O<sub>2</sub> concentration and catalyst dosage were optimized. A determined amount of catalyst was added uniformly to 100 mL of ERY solution of a certain concentration, and the pH of solution was adjusted by adding 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> or 0.1 mol L<sup>-1</sup> NaOH. The suspension was stirred in the dark for 30 min until adsorption equilibrium, then the xenon lamp was switched on and a determined amount of H<sub>2</sub>O<sub>2</sub> was added to the suspension to start the reaction. Suspension samples were taken at given time intervals using a 4.0 mL syringe, and immediately filtered with 0.22  $\mu$ m drainage syringe filters (Tianjin Branch Billion Lung, China), and a quenching agent (1.0 mL) was rapidly added to the filtrate to quench reactive species. The filtrate was diluted 10 fold and tested with a UV-vis detector (Agilent Cary 300 UV-vis Spectrophotometer, USA) at 583 nm in methyl violet solution. Erythromycin reacted with methyl violet to form a coordination compound, and the concentration of erythromycin was calculated based on the concentration of the coordination compound. The removal efficiency of ERY was calculated as:  $(C_0 - C_t)/C_0 \times 100\%$ , where  $C_0$  is the initial concentration of ERY, and  $C_t$  is the concentration at time  $t$ . The used catalysts were recovered by filtration, and washed with alcohol and deionized water, dried under vacuum, then reused for the next cycle, to evaluate their



reusability. The concentrations of iron ions leaching from the catalysts were measured by ICP-MS (Thermo Fisher iCAP Q, America). To confirm the primary active species in the degradation reaction, scavengers like 20 mmol L<sup>-1</sup> tertiary butanol (TBA), silver nitrate (AgNO<sub>3</sub>), ammonium oxalate (AO), and *p*-benzoquinone (BQ) were added to the solution before adding H<sub>2</sub>O<sub>2</sub>. The active species can be confirmed by the effect of different scavengers on ERY removal.

## 3. Results and discussion

### 3.1. Characterization of catalysts

The surface morphology and structural characteristics of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> were investigated by TEM. As can be seen in Fig. 1a, GO showed a silk-like wrinkled structure, and more active nanoparticles can be anchored onto wrinkled GO. Fe<sub>3</sub>O<sub>4</sub> NPs showed a spherical morphology with a rough surface, and the average diameter was about 12 nm (Fig. 1b). MIL-100(Fe) with a side length of about 40 nm displayed irregular shapes (Fig. 1c). For GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> (Fig. 1d), MIL-100(Fe) and Fe<sub>3</sub>O<sub>4</sub> NPs were uniformly anchored onto the GO surface, suggesting the successful loading of MIL-100(Fe) and Fe<sub>3</sub>O<sub>4</sub> NPs onto the GO surface.

The crystal structures of the catalysts were analyzed by their XRD patterns (Fig. 2). For GO, the peak at  $2\theta = 10.4^\circ$

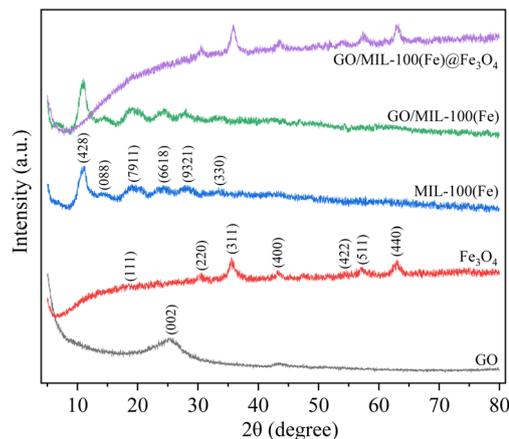


Fig. 2 XRD patterns of GO, Fe<sub>3</sub>O<sub>4</sub> NPs, MIL-100(Fe), GO/MIL-100(Fe) and GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>.

corresponded to the (001) crystal plane. After reduction, the peak at  $2\theta = 10.4^\circ$  disappeared, and a broad reflection peak appeared at  $2\theta = 25.46^\circ$ , which can be ascribed to the (002) crystal plane of reduced GO.<sup>34</sup> For Fe<sub>3</sub>O<sub>4</sub> NPs, the peaks at  $2\theta = 18.51^\circ$  (111),  $30.26^\circ$  (220),  $35.61^\circ$  (311),  $43.26^\circ$  (400),  $54.30^\circ$  (422),  $57.19^\circ$  (511), and  $62.97^\circ$  (440) corresponded to cubic

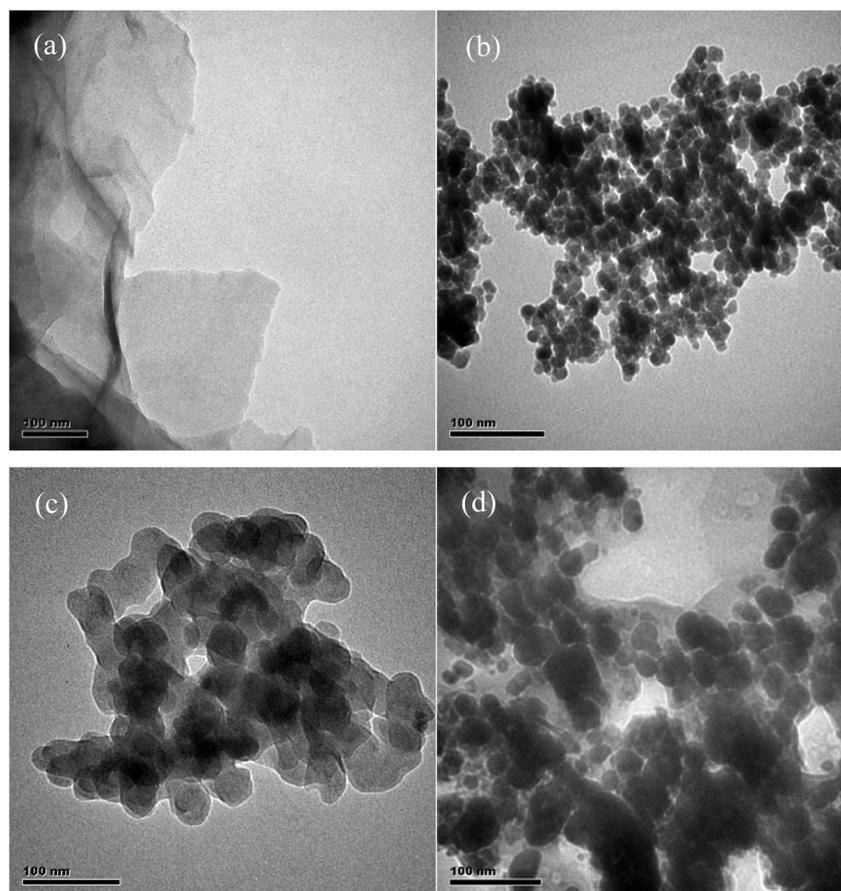


Fig. 1 TEM images of GO (a), Fe<sub>3</sub>O<sub>4</sub> NPs (b), MIL-100(Fe) (c) and GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> (d).



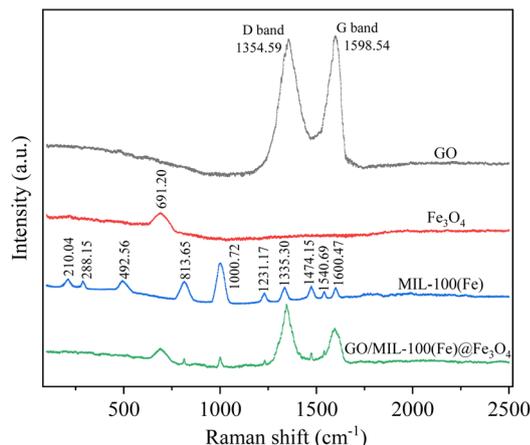


Fig. 3 Raman spectra of GO, Fe<sub>3</sub>O<sub>4</sub> NPs, MIL-100(Fe) and GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>.

Fe<sub>3</sub>O<sub>4</sub> with the inverse spinel structure [JCPDS card no. 19-0629],<sup>35</sup> indicating the successful synthesis of Fe<sub>3</sub>O<sub>4</sub> NPs. The main characteristic peaks for MIL-100(Fe) were in accordance with the simulated ones from crystal data.<sup>33</sup> The diffraction peaks at  $2\theta = 11.16^\circ$  (428),  $13.96^\circ$  (088),  $19.09^\circ$  (7911),  $24.16^\circ$  (6618),  $27.93^\circ$  (9321), and  $33.39^\circ$  (330) were also coincident with those reported for MIL-100(Fe). In the XRD pattern of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>, the diffraction peaks for cubic Fe<sub>3</sub>O<sub>4</sub> and MIL-100(Fe) can be found. However, in neither the XRD pattern of GO/MIL-100(Fe) nor that for GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>, did any distinct peaks of GO appear, which may be ascribed to the small size of GO crystallites. These results suggested the successful synthesis of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>.

To further confirm the existence of GO in GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>, the Raman spectra of GO, Fe<sub>3</sub>O<sub>4</sub> NPs, MIL-100(Fe) and GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> were measured (Fig. 3). The GO spectrum showed two broad peaks at 1354.59 and 1598.54 cm<sup>-1</sup>, which were ascribed to the specific D (1354.59 cm<sup>-1</sup>) and G (1598.54 cm<sup>-1</sup>) bands corresponding to the vibration of sp<sup>3</sup> carbons appearing in the disordered region (or defects) in the graphite lattice and the C=C stretching of sp<sup>2</sup>-hybridized carbon atoms, respectively.<sup>26</sup> Fe<sub>3</sub>O<sub>4</sub> NPs showed a rather simple spectrum, where only one A<sub>1g</sub> vibration peak could be observed at 691.20 cm<sup>-1</sup>.<sup>36</sup> Several peaks could be found in the spectrum of MIL-100(Fe). The peaks at 210.04 cm<sup>-1</sup>, 288.15 cm<sup>-1</sup>, 492.56 cm<sup>-1</sup>, 1474.15 cm<sup>-1</sup> and 1540.69 cm<sup>-1</sup> were characteristic of vibrational modes, which were directly related to Fe<sup>3+</sup> and Fe<sup>2+</sup> in MIL-100(Fe).<sup>37</sup> The peak at 813.65 cm<sup>-1</sup> can be ascribed to -COO- functional group bonding to the benzene ring, while H<sub>3</sub>BTC in-plane vibrations were confirmed by the peaks at 1000.72 cm<sup>-1</sup>, 1231.17 cm<sup>-1</sup>, 1335.30 cm<sup>-1</sup> and 1600.47 cm<sup>-1</sup>.<sup>37</sup> The main peaks for GO, Fe<sub>3</sub>O<sub>4</sub> NPs and MIL-100(Fe) can be found in the spectra of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>. The Raman spectrum of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> also contained D and G bands, confirming the presence of GO and Fe<sub>3</sub>O<sub>4</sub> NPs in the composite.<sup>37</sup> However, partial Raman peaks for MIL-100(Fe) tended to be weak and even disappeared after the introduction of Fe<sub>3</sub>O<sub>4</sub> NPs and GO, which can be ascribed to the

sheltering of MIL-100(Fe) by GO and Fe<sub>3</sub>O<sub>4</sub> NPs. The peak at 1474.15 cm<sup>-1</sup> changed, which was related to the change in organic ligand coordination with Fe<sup>3+</sup> and Fe<sup>2+</sup>, because carboxylate vibrations actually appeared in this region.<sup>38</sup> The above results confirmed that GO and Fe<sub>3</sub>O<sub>4</sub> NPs introduced some distortion into the MIL-100(Fe) structure.<sup>38</sup>

The surface element content and valence states of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> were tested by XPS. Fig. 4a shows the XPS full spectrum, clearly indicating the presence of C, O and Fe in GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> and MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>. The C 1s spectrum in Fig. 4b could be divided into three peaks: 284.63 eV, 285.63 eV and 288.78 eV, corresponding to the characteristic peaks of C-C, C-O-C, and O-C=O.<sup>39</sup> The peaks located at binding energies of 284.63 eV and 288.78 eV were related to the benzene ring and carboxylic functional groups in MIL-100(Fe).<sup>16</sup> For the spectrum of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>, the peak at 285.63 eV was derived from C-O in GO,<sup>27</sup> which cannot be found in MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>. Additionally, the strength of the peaks at 284.63 eV and 288.78 eV increased in GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> compared with those of MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>, suggesting that GO promoted the generation of MIL-100(Fe). The O 1s spectrum can be divided into two peaks at 530.78 eV and 532.83 eV, which can be ascribed to the oxygen element of organic linkers in MIL-100(Fe) and Fe-O bonds respectively.<sup>16</sup> As for GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>, the peaks at 530.78 eV and 532.83 eV shifted to higher binding energy (530.78 eV and 532.76 eV for MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>), which can be ascribed to the C-O functional groups from GO.<sup>26</sup> As can be seen from Fig. 4d, the Fe 2p fitted peaks of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> showed two obvious peaks at 711.58 eV and 725.43 eV (712.48 eV and 725.88 eV for MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>), which were attributed to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> peaks for Fe species. For GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>, the Fe 2p spectra can be divided into four peaks at 711.22 eV, 713.24 eV, 724.57 eV and 726.00 eV, and two peaks at 711.22 eV and 724.57 eV, respectively, corresponding to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> for Fe<sup>2+</sup>, while two peaks at 713.24 eV and 726.00 eV can be ascribed to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> for Fe<sup>3+</sup>, further indicating that Fe species existed as a mixed-valence state (Fe<sup>2+</sup> and Fe<sup>3+</sup>).<sup>39</sup> The ratio of Fe<sup>2+</sup>/Fe<sup>3+</sup> can be calculated according to the peak area of Fe 2p<sub>3/2</sub>, as can be seen from Fig. 4d, after the introduction of GO, the peak area of Fe 2p<sub>3/2</sub> for Fe<sup>2+</sup> increased, which indicated that GO was favorable for the formation of Fe<sup>2+</sup> in GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>. The above analysis indicated that GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> had been successfully synthesized.

N<sub>2</sub> adsorption-desorption isotherms were used to analyze the surface area and pore structure of Fe<sub>3</sub>O<sub>4</sub> NPs, MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> and GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>. As shown in Fig. 5, Fe<sub>3</sub>O<sub>4</sub> NPs showed a type IV isotherm with hysteresis ( $P/P_0 = 0.5-0.9$ ), according to the Brunauer-DeMing-DeMing-Teller (BDDT) classification,<sup>28</sup> which characterize a mesoporous structure. The adsorption and desorption isotherms remained almost horizontal and parallel, indicating a IUPAC type H<sub>4</sub> hysteresis loop. The type IV isotherm with a type H<sub>4</sub> hysteresis loop indicated the existence of narrow lamellar slit-like pores. After loading Fe<sub>3</sub>O<sub>4</sub> NPs onto MIL-100(Fe), MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> showed a type IV isotherm with a type H<sub>3</sub> hysteresis loop, suggesting a mesoporous structure on the outer layer of the catalyst.<sup>16</sup> GO/MIL-



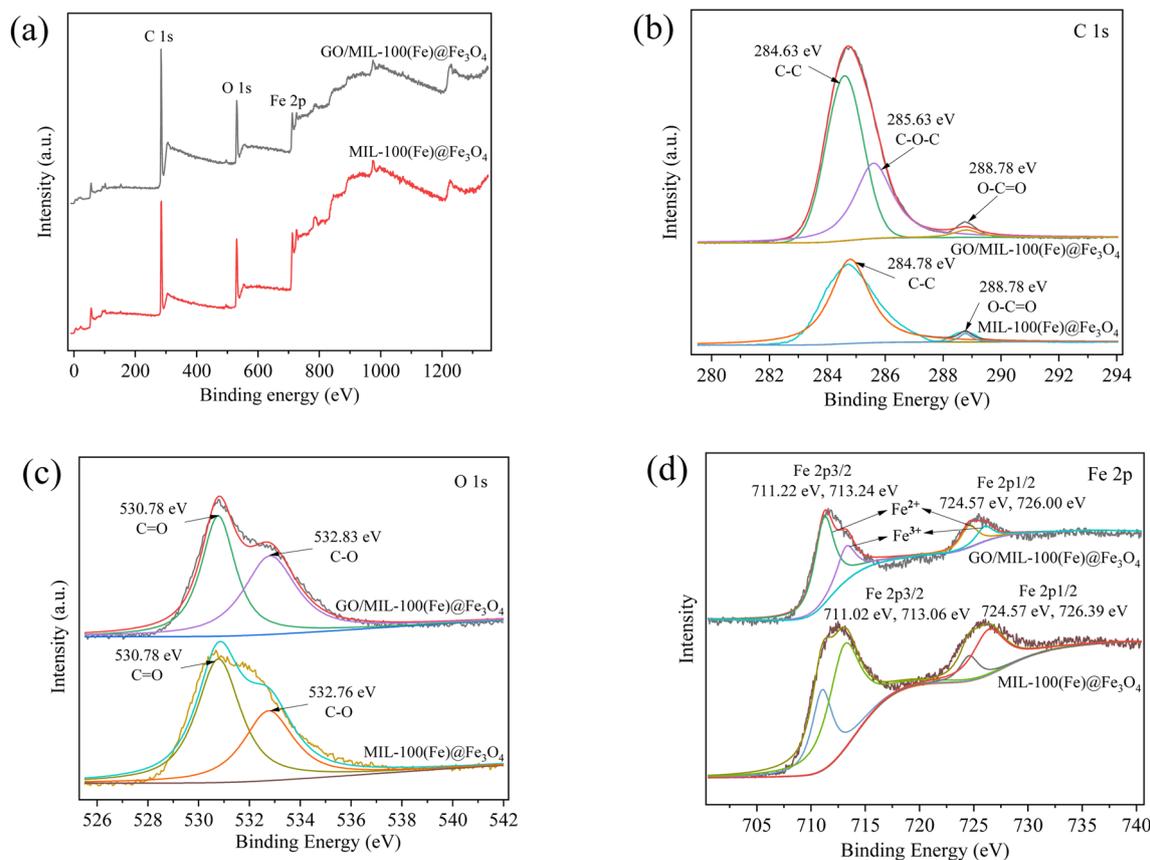


Fig. 4 XPS analysis of the catalysts: full-scan spectrum (a), C 1s (b), O 1s (c) and Fe 2p (d).

100(Fe)@Fe<sub>3</sub>O<sub>4</sub> showed the same type of isotherm and hysteresis as MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>, but the hysteresis loop was larger, suggesting an increase in pore diameter.

The specific surface areas of Fe<sub>3</sub>O<sub>4</sub> NPs, MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> and GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> by BET measurement, were 54.25 m<sup>2</sup> g<sup>-1</sup>, 684.53 m<sup>2</sup> g<sup>-1</sup> and 841.46 m<sup>2</sup> g<sup>-1</sup>, respectively, suggesting that MIL-100(Fe) and GO can significantly increase the specific surface area of the catalyst. Additionally, the pore size distribution centers for GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> were around 3.98 nm and 19.35 nm, which were larger than those of Fe<sub>3</sub>O<sub>4</sub>

NPs or MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>. These properties promoted the adequate contact of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> with pollutants. The high surface area and porosity of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> would promote the adsorption and diffusion of pollutants to the active sites during degradation, endowing the catalyst with high catalytic activity.

UV-vis DRS spectroscopy was used to analyze the optical response of the catalyst. As can be seen in Fig. 6a, MIL-100(Fe) showed wide and intense absorption capacity for UV and visible light in the range 250–600 nm. The absorption of ultraviolet

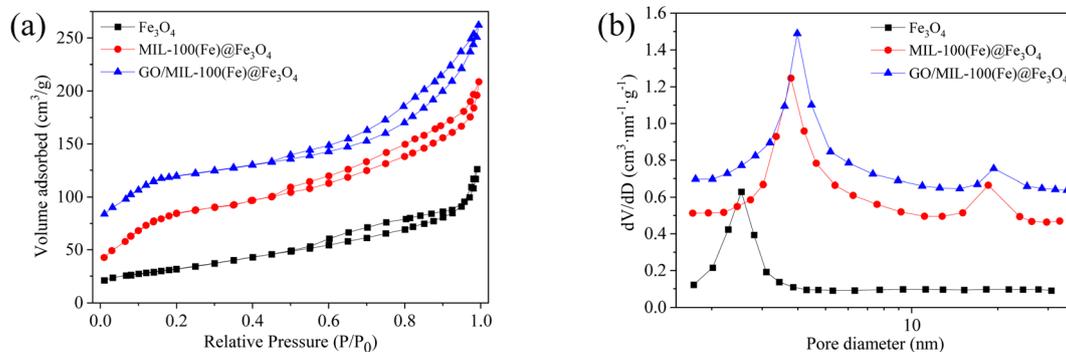


Fig. 5 N<sub>2</sub> adsorption-desorption isotherms of Fe<sub>3</sub>O<sub>4</sub> NPs, MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> and GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> (a), and the corresponding BJH pore size distributions (b).



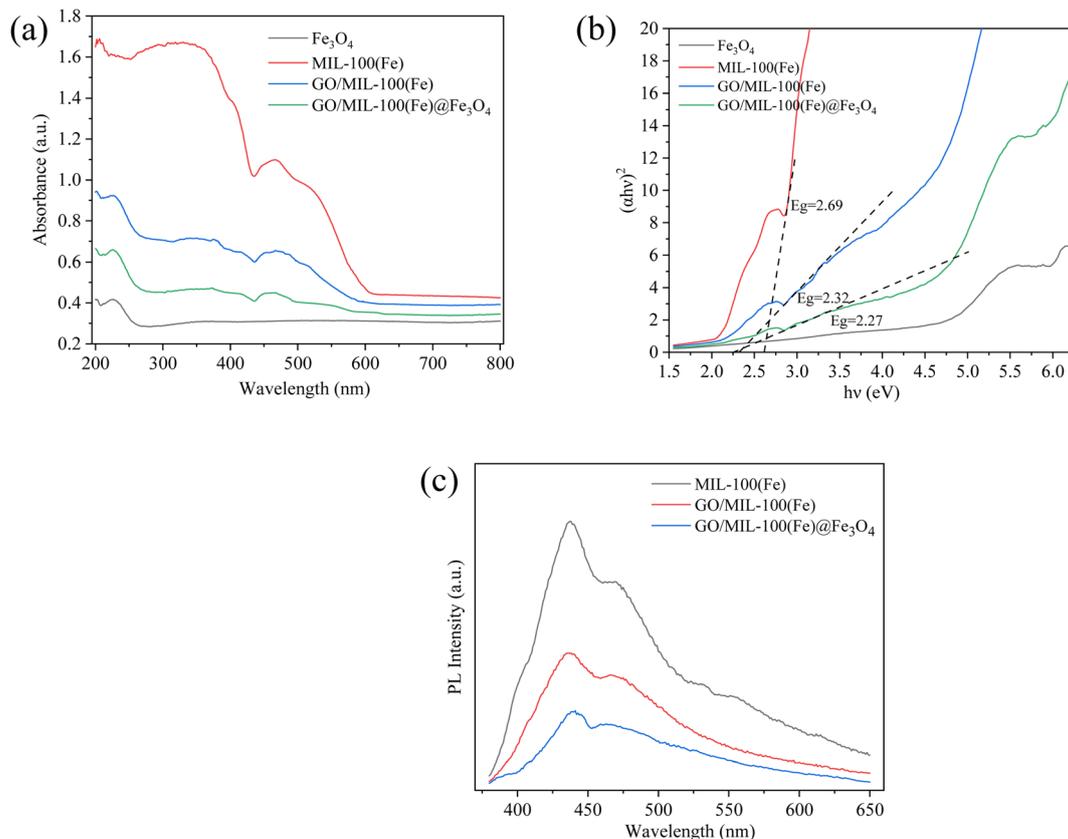


Fig. 6 UV-vis diffuse reflection spectra of catalysts (a), the corresponding plots of  $(\alpha h\nu)^2$  vs. photon energy ( $h\nu$ ) (b), and photoluminescence (PL) spectra (c).

light can be ascribed to ligand-to-metal charge transfer,<sup>40</sup> while the strong ability to absorb visible light was attributed to the  $\text{Fe}_3\text{-}\mu_3\text{-oxo}$  cluster in MIL-100(Fe).<sup>16</sup> After the introduction of  $\text{Fe}_3\text{O}_4$  NPs and GO, the composite showed a similar absorption edge to MIL-100(Fe) in the range 250–600 nm, indicating that the inherent band gap of  $\text{GO/MIL-100(Fe)@Fe}_3\text{O}_4$  was derived mainly from electron transfer from the valence band (VB) to the conduction band (CB) of MIL-100(Fe).<sup>16</sup> This suggested that  $\text{GO/MIL-100(Fe)@Fe}_3\text{O}_4$  may commendably utilize incident light to generate more active species.<sup>16</sup> Meanwhile, the band gap energies can be calculated with Tauc plots ( $(\alpha h\nu)^n = A(h\nu - E_g)$ ), where  $\alpha$ ,  $h$ ,  $\nu$ ,  $A$  and  $E_g$  are the absorption coefficient, Planck constant, light frequency, proportionality constant and band gap, respectively (for a direct band gap semiconductor,  $n = 2$ ).<sup>16</sup> The calculated band-gap values were 2.69 eV, 2.32 eV and 2.27 eV for MIL-100(Fe), GO/MIL-100(Fe) and GO/MIL-100(Fe)@ $\text{Fe}_3\text{O}_4$ , respectively (Fig. 6b). With improved absorption of visible light, GO/MIL-100(Fe)@ $\text{Fe}_3\text{O}_4$  may produce more electrons to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and generate more reactive oxidation species under light radiation.

Charge transfer influenced the photocatalytic reaction. The influence of GO and  $\text{Fe}_3\text{O}_4$  in  $\text{GO/MIL-100(Fe)@Fe}_3\text{O}_4$  on the separation of photogenerated electrons and holes can be clarified using photoluminescence emission spectra. Basically, lower PL emission peaks suggested more efficient separation of photogenerated electrons and holes.<sup>16</sup> As shown in Fig. 6c,

a broad PL peak can be seen at around 437 nm, and this could be due to the recombination of self-trapped excitation. The intensity of PL emission peaks decreased in sequence: MIL-100(Fe) > GO/MIL-100(Fe) > GO/MIL-100(Fe)@ $\text{Fe}_3\text{O}_4$ , suggesting that GO/MIL-100(Fe)@ $\text{Fe}_3\text{O}_4$  may show the best photo-Fenton activity, revealing that the recombination of photogenerated electron-hole pairs can be largely inhibited by the introduction of GO and  $\text{Fe}_3\text{O}_4$  into GO/MIL-100(Fe)@ $\text{Fe}_3\text{O}_4$ .

### 3.2. Catalytic performance

The catalytic performance of  $\text{GO/MIL-100(Fe)@Fe}_3\text{O}_4$  was evaluated by ERY removal. As can be seen from Fig. 7a, in the absence of catalysts, the concentration of ERY remained almost unchanged under visible-light irradiation. 41.7% of ERY in the  $\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}_2 + \text{vis}$  system was removed within 60 min. The removal efficiency for ERY in the  $\text{GO@Fe}_3\text{O}_4 + \text{H}_2\text{O}_2 + \text{vis}$  system increased to 68.7%, indicating that GO played an important role in the photo-Fenton reaction. Additionally, in the MIL-100(Fe) +  $\text{H}_2\text{O}_2 + \text{vis}$  and MIL-100(Fe)@ $\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}_2 + \text{vis}$  systems, ERY removal efficiencies were 74.4% and 86.8%, respectively, suggesting that the catalytic activity of MIL-100(Fe)@ $\text{Fe}_3\text{O}_4$ , combining  $\text{Fe}_3\text{O}_4$  NPs with MIL-100(Fe), needed to be improved. Nevertheless, under the same experimental conditions, 97.3% of ERY was removed in the  $\text{GO/MIL-100(Fe)@Fe}_3\text{O}_4 + \text{H}_2\text{O}_2 + \text{vis}$  system, achieving the maximum value. In the GO/MIL-100(Fe)



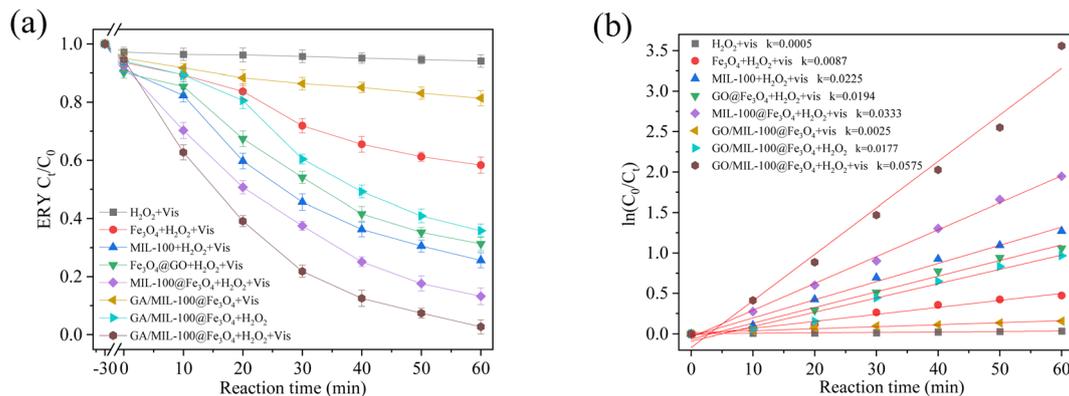
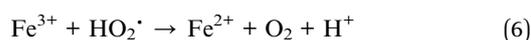


Fig. 7 Degradation curves in different reaction systems (a), and the corresponding degradation kinetics of the degradation curves (pseudo-first-order kinetics model) (b). pH = 4.03,  $[H_2O_2]_0 = 10 \text{ mmol L}^{-1}$ ,  $[catalyst]_0 = 0.1 \text{ g L}^{-1}$ ,  $[ERY]_0 = 0.1 \text{ mmol L}^{-1}$ ,  $T = 30 \text{ }^\circ\text{C}$ .

@ $Fe_3O_4$ /dark system, only a Fenton-like reaction took place for the degradation of ERY. Therefore, the increased removal of ERY in the GO/MIL-100( $Fe$ )@ $Fe_3O_4$ /vis system was ascribed to the photo-Fenton-like reaction. Thus  $H_2O_2$  and visible-light irradiation were sufficient, and more  $\cdot OH$  and  $HO_2\cdot$  were generated for ERY degradation.

The kinetics of the reactions were analyzed and the reaction processes followed the pseudo-first-order kinetic equation ( $K_{app}t = -\ln(C/C_0)$ ), where  $K_{app}$  is the first-order kinetic constant ( $\text{min}^{-1}$ ),  $t$  is the reaction time (min),  $C_0$  is the original concentration of ERY solution ( $\text{mmol L}^{-1}$ ), and  $C$  is the concentration of ERY solution after reaction for a period ( $\text{mmol L}^{-1}$ ). As shown in Fig. 7b, under dark conditions, the apparent rate constant of the GO/MIL-100( $Fe$ )@ $Fe_3O_4 + H_2O_2$  system was  $0.0177 \text{ min}^{-1}$ . After introducing light, the apparent rate constant increased to  $0.0575 \text{ min}^{-1}$ . This suggested that visible light can promote the decomposition of  $H_2O_2$  into more  $\cdot OH$ , thus enhancing removal efficiency for ERY. The apparent rate constant of the GO/MIL-100( $Fe$ )@ $Fe_3O_4 + H_2O_2 + vis$  system was 2.96 times that of the GO@ $Fe_3O_4 + H_2O_2 + vis$  system and 2.56 times that of the MIL-100( $Fe$ ) +  $H_2O_2 + vis$  system, suggesting a probable synergistic effect among  $Fe_3O_4$ , GO and MIL-100( $Fe$ ). The synergistic effect was evaluated by calculating the synergistic factor ( $F > 1$ ) ( $F = K_{GO/MIL-100(Fe)@Fe_3O_4} / (K_{Fe_3O_4@GO} + K_{MIL-100(Fe)})$ ), where  $K_{GO/MIL-100(Fe)@Fe_3O_4}$ ,  $K_{Fe_3O_4@GO}$  and  $K_{MIL-100(Fe)}$  are the apparent rate constants of GO/MIL-100( $Fe$ )@ $Fe_3O_4$ , GO@ $Fe_3O_4$  and MIL-100( $Fe$ ), respectively.<sup>39</sup> After calculation,  $F = 1.37$ , confirming the synergistic effect among  $Fe_3O_4$ , GO and MIL-100( $Fe$ ). The enhanced ERY removal efficiency in the GO/MIL-100( $Fe$ )@ $Fe_3O_4 + H_2O_2 + vis$  system can be ascribed to: (1) light-induced  $H_2O_2$  generated more  $\cdot OH$  (eqn (5)) and accelerated the  $Fe^{2+}/Fe^{3+}$  cycle (eqn (1), (2) and (6)); (2) GO as an electron transfer channel immediately transferred electrons from the conduction band of MIL-100( $Fe$ ) to the surface of the  $Fe_3O_4$  NPs, hindering recombination of  $e^- - h^+$  pairs; (3) GO combined with  $Fe_3O_4$  NPs and MIL-100( $Fe$ ) greatly promoted the contact of ERY and active sites in the composite.



### 3.3. Effects of solution pH, $H_2O_2$ concentration and catalyst dosage

The initial solution pH directly influenced active species generation, and it was an important influencing factor for ERY degradation. When the initial solution pH increased from 3.02 to 4.03, the ERY degradation efficiency increased from 93.8% to 97.3% (Fig. 8a), and the apparent rate constant increased from  $0.0446 \text{ min}^{-1}$  to  $0.0575 \text{ min}^{-1}$  (Fig. 8b). This was because acidic conditions were favorable for the reaction between  $Fe^{2+}$  and  $H_2O_2$  to produce  $\cdot OH$ . However, under acidic conditions,  $\cdot O_2^-$  was consumed and inhibited, so too low a pH may decrease ERY removal efficiency and reaction rate. When the pH further increased from 4.03 to 8.98, the degradation efficiency decreased from 97.3% to 52.2%. The decreased degradation efficiency can be ascribed to: (1) increased pH may lead to aggregation of  $Fe_3O_4$  NPs; (2) alkaline conditions may lead to the direct decomposition of  $H_2O_2$  into inactive species; (3) increased pH results in negative charge over the catalyst surface and ERY deprotonation, causing mutual repulsion between ERY and the catalyst.<sup>39</sup> Overall, ERY degradation efficiencies were above 50% in the pH range of 3.02–8.98, indicating the excellent catalytic activity of the catalyst under a wide pH range.

$H_2O_2$  concentration also greatly influenced the photo-Fenton reaction, because it greatly influenced the generation and amount of active species. As shown in Fig. 9a, when the concentration of  $H_2O_2$  increased from  $5.0 \text{ mmol L}^{-1}$  to  $20.0 \text{ mmol L}^{-1}$ , the removal efficiency increased from 74.4% to 97.9% (within 60 min of reaction), and the related reaction rate constant increased from  $0.0216 \text{ min}^{-1}$  to  $0.0622 \text{ min}^{-1}$ . The degradation efficiency and related rate constant achieved their maximum values when the concentration of  $H_2O_2$  was  $20.0 \text{ mmol L}^{-1}$ , because the increased  $H_2O_2$  concentration promoted more production of  $\cdot OH$ . But as the concentration of  $H_2O_2$  further increased to  $50.0 \text{ mmol L}^{-1}$ , ERY removal efficiency decreased gradually. The probable reasons for these results were: (1) limited surface active sites on the catalyst limited the degradation efficiency; (2) excessive  $H_2O_2$  would capture  $\cdot OH$  and quench  $\cdot OH$  (eqn (7)); (3)  $\cdot OOH$  competing with  $\cdot OH$  leads to the useless consumption of reactive species (eqn (8)).



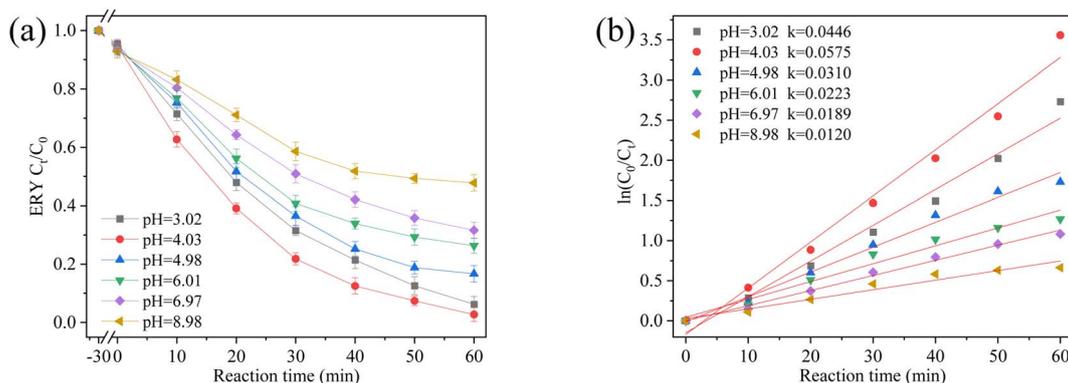


Fig. 8 The effect of the initial pH on the photo-Fenton degradation of ERY (a), and kinetic analysis of the degradation of ERY at different initial pH levels (pseudo-first-order kinetics model) (b).  $[\text{H}_2\text{O}_2]_0 = 10 \text{ mmol L}^{-1}$ ,  $[\text{catalyst}]_0 = 0.1 \text{ g L}^{-1}$ ,  $[\text{ERY}]_0 = 0.1 \text{ mmol L}^{-1}$ ,  $T = 30 \text{ }^\circ\text{C}$ .

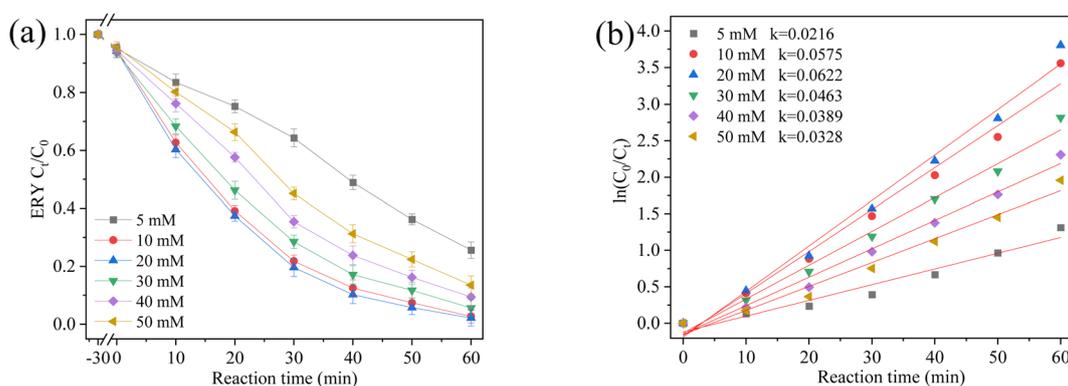
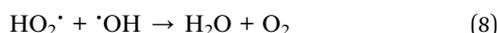
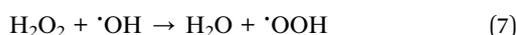


Fig. 9 Effect of the initial  $\text{H}_2\text{O}_2$  concentration on the photo-Fenton degradation of ERY (a), and kinetic analysis of the degradation of ERY at different initial  $\text{H}_2\text{O}_2$  concentrations (pseudo-first-order kinetics model) (b).  $\text{pH} = 4.03$ ,  $[\text{catalyst}]_0 = 0.1 \text{ g L}^{-1}$ ,  $[\text{ERY}]_0 = 0.1 \text{ mmol L}^{-1}$ ,  $T = 30 \text{ }^\circ\text{C}$ .



Catalyst dosage played a crucial role in ERY degradation. As depicted in Fig. 10a, when the dosage of  $\text{GO}/\text{MIL-100}(\text{Fe})@\text{Fe}_3\text{O}_4$  increased from  $0.05 \text{ g L}^{-1}$  to  $0.1 \text{ g L}^{-1}$ , ERY degradation efficiency

increased, and the kinetic constant increased from  $0.0302 \text{ min}^{-1}$  to  $0.0575 \text{ min}^{-1}$ . This was attributed to the fact that the appropriate amount of catalyst provided sufficient active sites, which was favorable for ERY degradation. However, when the catalyst dosage continued to increase to  $0.4 \text{ g L}^{-1}$ , the ERY degradation efficiency decreased, and the related kinetic constant decreased to  $0.0325 \text{ min}^{-1}$ . Excessive catalyst increased the turbidity of the

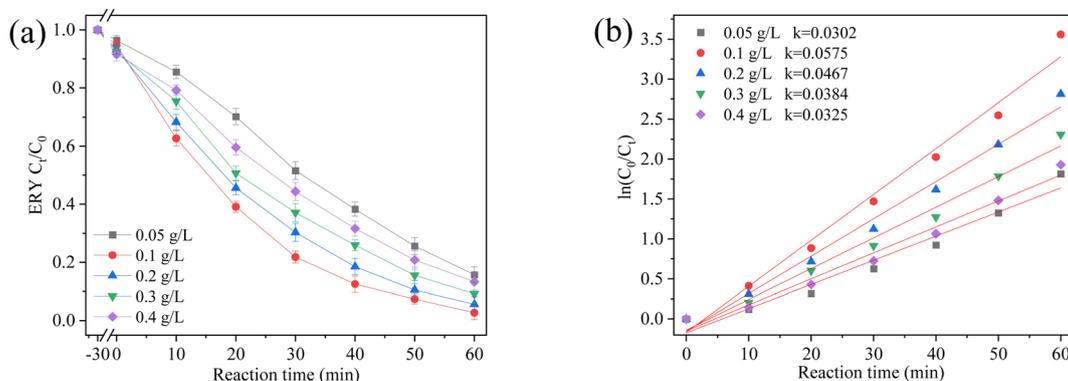


Fig. 10 Effect of the catalyst dosage on the photo-Fenton degradation of ERY (a), and kinetic analysis of the degradation of ERY at different catalyst dosages (pseudo-first-order kinetics model) (b).  $\text{pH} = 4.03$ ,  $[\text{H}_2\text{O}_2]_0 = 10 \text{ mmol L}^{-1}$ ,  $[\text{ERY}]_0 = 0.1 \text{ mmol L}^{-1}$ ,  $T = 30 \text{ }^\circ\text{C}$ .



ERY suspension, leading to decreased transparency of the solution, influencing the light absorption by the catalyst, and thus hindering the photo-Fenton reaction process.<sup>41</sup>

In natural water, the coexisting natural organic matter (e.g., humic acid, HA) and inorganic anions ( $\text{HCO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) could influence interfacial reactions related to reactive radicals. The influences of HA and common anions on the degradation of ERY were analyzed using simulated wastewater (Fig. 11a and b). The ERY degradation efficiency decreased from 97.3% to 76.5%, and the related kinetic constant ( $k$ ) decreased from  $0.0575 \text{ min}^{-1}$  to  $0.0240 \text{ min}^{-1}$ . HA inhibited degradation by complexing iron species, scavenging radicals and competing with ERY molecules for adsorption sites.<sup>42</sup>  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  had little influence on ERY degradation.  $\text{Cl}^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HCO}_3^-$  showed obvious inhibition of ERY degradation, because  $\text{Cl}^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HCO}_3^-$  in solution can react with free radicals. Notably,  $\text{HCO}_3^-$  can react with Fe species. It can also act as a scavenger for reactive oxygen species, generating less reactive species, such as  $\text{HCO}_3^\cdot$  and  $\text{CO}_3^{\cdot-}$ .<sup>43</sup> The removal efficiency decreased from 97.3% to 63.9%, and the related kinetic constant ( $k$ ) decreased from  $0.0575 \text{ min}^{-1}$  to  $0.0174 \text{ min}^{-1}$ .  $\text{H}_2\text{PO}_4^-$  led to a reduction in ERY removal efficiency, from 97.3% to 72.4%, and the related kinetic constant ( $k$ ) decreased from  $0.0575 \text{ min}^{-1}$  to  $0.0198 \text{ min}^{-1}$ .  $\text{H}_2\text{PO}_4^-$  may react with highly reactive free radicals to generate less oxidative  $\text{H}_2\text{PO}_4^\cdot$ , and Fe–O may also accumulate on the catalyst surface and react with free  $\text{H}^+$  to generate Fe–OH, which can react with  $\text{H}_2\text{PO}_4^-$  to form inner complexes (such as  $\text{FeH}_2\text{PO}_4^+/\text{FeHPO}_4$ ), thus covering surface active sites.<sup>43</sup>  $\text{Cl}^-$  led to a reduction in ERY degradation efficiency, from 97.3% to 76.5%, and the kinetic constant ( $k$ ) decreased from  $0.0575 \text{ min}^{-1}$  to  $0.0216 \text{ min}^{-1}$ .  $\text{Cl}^-$  can scavenge highly reactive free radicals to generate less reactive radicals (such as  $\text{Cl}^\cdot$  and  $\text{Cl}_2^{\cdot-}$ ).<sup>42</sup>  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  showed minimal interaction with electrons, ROS and Fe species. The slight negative influence of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  on ERY degradation may be due to competition for reaction sites, but it was negligible.<sup>43</sup>

#### 3.4. Stability of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>

The stability of a catalyst is crucial for the practical application of photo-Fenton. The stability of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> was

estimated using recycling experiments. As can be seen in Fig. 12, after four cycles of reactions, the ERY and corresponding TOC removal efficiencies were 90.8% and 25.9%, respectively, suggesting that ERY was partially decomposed into smaller molecules by photo-Fenton degradation. ERY was not completely mineralized into CO<sub>2</sub>. According to previous studies, heterocyclic by-products, aromatic methyl ester derivatives and tertiary aliphatic amines have been detected during ERY Fenton degradation. The by-products are generated by the cleavage of multiple C–C bonds of ERY, followed by internal cyclization to generate a heterocyclic and aromatic structure.<sup>44</sup> Some short-chain aliphatic carboxylic acids, such as maleic, fumaric, oxamic, oxalic and formic acids, have also been detected.<sup>44</sup> Further research is required to analyze the harmlessness of the remaining TOC to living beings. After four cycles, an insignificant decrease in ERY degradation efficiency and TOC removal was found (Fig. 12a); the iron leaching was at a low level (Fig. 12b); and the magnetic properties (Fig. 12c) and crystal structure (Fig. 12d) of the catalyst had not changed very much, indicating the good stability of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> and that it would be an excellent photo-Fenton catalyst for ERY treatment in water.

#### 3.5. Analyses of reactive oxidizing species

To further verify the main active species in the reactions, free radical capture experiments were performed using 20 mmol L<sup>-1</sup> tertiary butanol (TBA), silver nitrate (AgNO<sub>3</sub>), ammonium oxalate (AO), and *p*-benzoquinone (BQ), as capture agents for  $\cdot\text{OH}$ ,  $\text{e}^-$ ,  $\text{h}^+$  and  $\cdot\text{O}_2^-$ , respectively. Fig. 13a obviously indicates that after adding TBA and AO, ERY removal efficiency decreased from 97.3% to 18.4% and 10.6%, respectively, and the related kinetic constants also decreased significantly (Fig. 13b), indicating that  $\cdot\text{OH}$  and  $\text{h}^+$  played a dominant role in the removal of ERY. After adding AgNO<sub>3</sub> and BQ, the interference effect on ERY removal was very low, suggesting that  $\cdot\text{O}_2^-$  was a minor active species for ERY degradation, while  $\text{e}^-$  made the weakest contribution to ERY degradation.

#### 3.6. Possible degradation mechanism

Based on ERY degradation experiments, the degradation efficiency of different systems ranked from highest to lowest was:

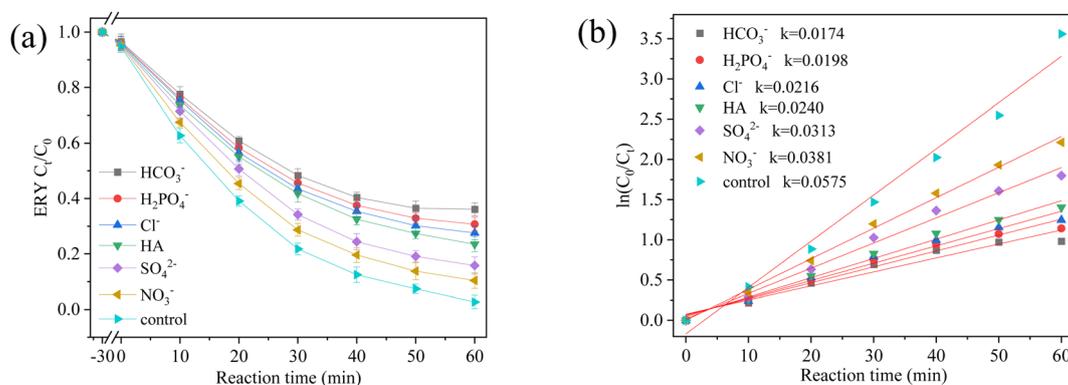


Fig. 11 Effect of coexisting HA and anions on the photo-Fenton degradation of ERY (a), and kinetic analysis of the degradation of ERY with coexisting HA and anions (pseudo-first-order kinetics model) (b). pH = 4.03,  $[\text{catalyst}]_0 = 0.1 \text{ g L}^{-1}$ ,  $[\text{H}_2\text{O}_2]_0 = 10 \text{ mmol L}^{-1}$ ,  $[\text{ERY}]_0 = 0.1 \text{ mmol L}^{-1}$ ,  $[\text{HA}] = 10 \text{ mg L}^{-1}$ ,  $[\text{anion}] = 10 \text{ mg L}^{-1}$ ,  $T = 30 \text{ }^\circ\text{C}$ .



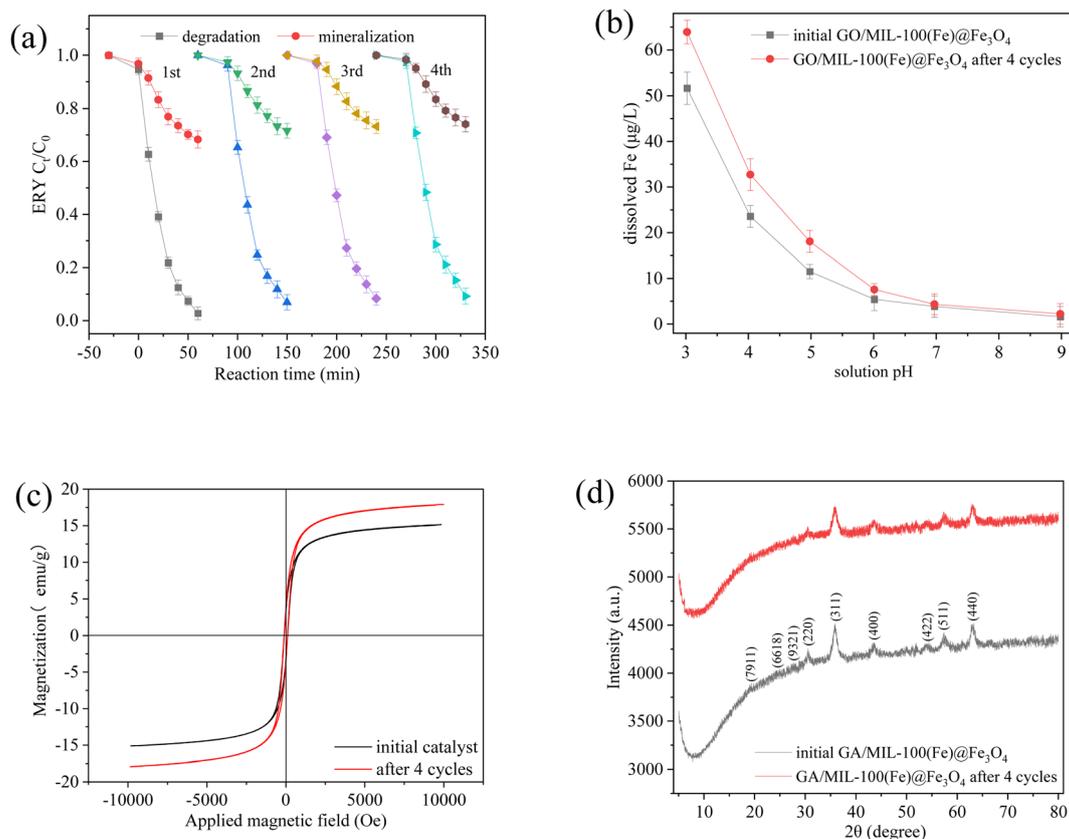


Fig. 12 Cycles of ERY degradation in the photo-Fenton system (a), leaching of Fe during the 1st cycle and 4th cycle (b), magnetic hysteresis loop at 298 K (c) and XRD patterns (d) of initial GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> and a sample after 4 cycles under the optimum conditions. pH = 4.03, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 10 mmol L<sup>-1</sup>, [catalyst]<sub>0</sub> = 0.1 g L<sup>-1</sup>, [ERY]<sub>0</sub> = 0.1 mmol L<sup>-1</sup>, T = 30 °C.

GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> + vis > MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> + vis > MIL-100(Fe) + H<sub>2</sub>O<sub>2</sub> + vis > GO@Fe<sub>3</sub>O<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> + vis > GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> > Fe<sub>3</sub>O<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> + vis > GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> + vis. GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> showed the highest degradation efficiency under the same initial conditions. Visible light significantly promoted the degradation of ERY, suggesting the synergistic effect of the visible-light-induced reaction and the Fenton reaction. A possible

mechanism for photo-Fenton degradation of ERY by GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> was proposed (Fig. 14), and the reaction equations can be seen in the following equations.<sup>45</sup>

In the visible-light-induced reaction, the Fe–O cluster in MIL-100(Fe) was excited by visible light,<sup>45</sup> and photogenerated electrons (e<sup>-</sup>) and photogenerated holes (h<sup>+</sup>) were generated over the MIL-100(Fe) surface (eqn (9)). Subsequently, as the level of the CB of Fe<sub>3</sub>O<sub>4</sub> NPs was lower than that of MIL-

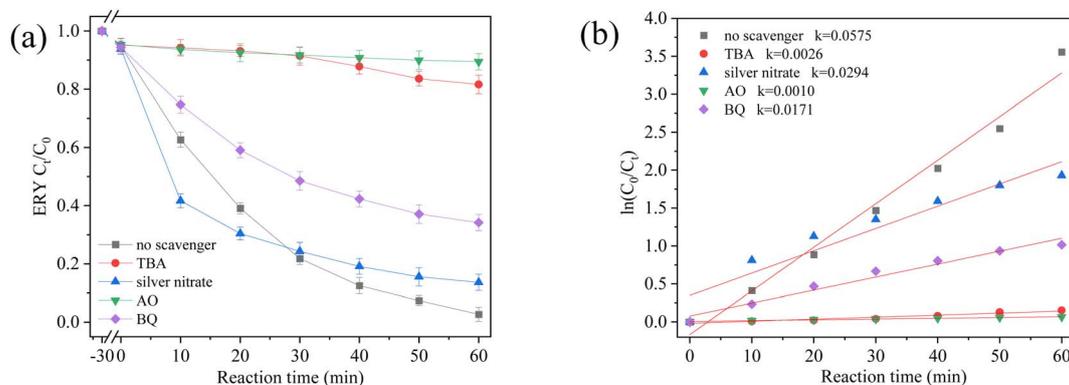


Fig. 13 Effect of radical scavengers on the photo-Fenton degradation of ERY (a), and kinetic analysis of the degradation of ERY with different radical scavengers (pseudo-first-order kinetics model) (b). pH = 4.03, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 10 mmol L<sup>-1</sup>, [catalyst]<sub>0</sub> = 0.1 g L<sup>-1</sup>, [ERY]<sub>0</sub> = 0.1 mmol L<sup>-1</sup>, T = 30 °C.



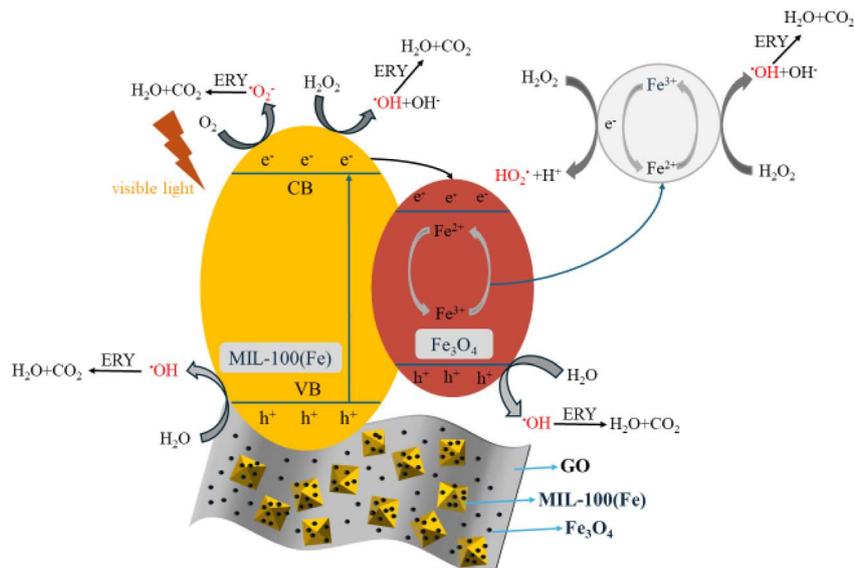
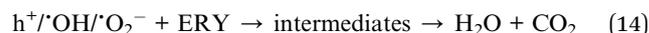
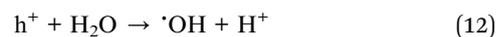
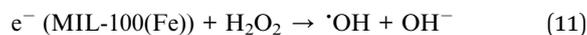
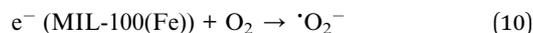
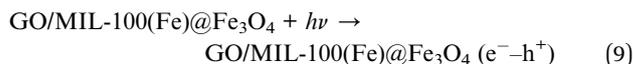


Fig. 14 The proposed degradation mechanism of ERY in the photo-Fenton system over GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub>.

100(Fe), the photogenerated electrons from MIL-100(Fe) were transferred to the surface of the Fe<sub>3</sub>O<sub>4</sub> NPs, hindering the recombination of photogenerated e<sup>-</sup>-h<sup>+</sup> pairs.<sup>45</sup> Then photogenerated electrons and holes could be delivered to H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> NPs, where the electrons reacted with H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> to form ·OH and ·O<sub>2</sub><sup>-</sup> (eqn (10) and (11)),<sup>46</sup> and the holes reacted with H<sub>2</sub>O to form ·OH (eqn (12)), while H<sub>2</sub>O<sub>2</sub> can also form ·OH under light irradiation (eqn (5)). GO may act as a charge transfer bridge, facilitating the separation of e<sup>-</sup>-h<sup>+</sup> and the migration of photogenerated electrons from MIL-100(Fe) to Fe<sub>3</sub>O<sub>4</sub> NPs. The migration of electrons was in the opposite direction to that of holes, which was favorable for hindering e<sup>-</sup>-h<sup>+</sup> recombination, thus improving the utilization efficiency of e<sup>-</sup> and h<sup>+</sup>. Furthermore, holes with strong oxidation capacity could also attack ERY, and ERY could be decomposed into small molecules.

In the Fenton reaction, Fe<sub>3</sub>O<sub>4</sub> NPs acted as nuclei to provide Fe<sup>2+</sup>, which reacted with H<sub>2</sub>O<sub>2</sub> to produce ·OH and Fe<sup>3+</sup>, and Fe<sup>3+</sup> was also slowly reduced to Fe<sup>2+</sup>, which could continuously generate ·OH. When Fe<sub>3</sub>O<sub>4</sub> NPs were bound to MIL-100(Fe), Fe<sub>3</sub>O<sub>4</sub> NPs acted as electron acceptors, promoting the Fe<sup>2+</sup>/Fe<sup>3+</sup> cycle (eqn (13)). GO acted as an electron transfer channel, where photogenerated electrons were immediately transferred to the surface of Fe<sub>3</sub>O<sub>4</sub> NPs through GO, thus accelerating Fe<sup>3+</sup> in GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> being converted to Fe<sup>2+</sup> (eqn (13)). Meanwhile, the added H<sub>2</sub>O<sub>2</sub> could capture electrons from the visible-light-induced reaction to produce ·OH, and Fe<sup>3+</sup> in Fe<sub>3</sub>O<sub>4</sub> NPs could also be converted to Fe<sup>2+</sup> by the electrons. The generated Fe<sup>2+</sup> react with H<sub>2</sub>O<sub>2</sub> in the Fenton reaction, accelerating the Fe<sup>2+</sup>/Fe<sup>3+</sup> cycle (eqn (1) and (2)). Finally, the generated h<sup>+</sup>, ·OH and ·O<sub>2</sub><sup>-</sup> participated as active species in the degradation of ERY (eqn (14)). In this way, MIL-100(Fe), Fe<sub>3</sub>O<sub>4</sub> NPs and GO in GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> showed synergistic effects, exhibiting excellent catalytic activity for the degradation of ERY.



## 4. Conclusions

In this study, GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> was synthesized *via* an *in situ* growth method and showed excellent photo-Fenton catalytic performance for ERY degradation over a wide pH range. ERY degradation was conducted under different reaction conditions. The degradation efficiency of ERY in the GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> + vis system achieved 97.3% within 60 min. Free radical quenching experiments indicated that various active species, such as h<sup>+</sup>, ·OH, ·O<sub>2</sub><sup>-</sup> and e<sup>-</sup>, participated in ERY degradation, but h<sup>+</sup> and ·OH played a dominant role. GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> not only showed excellent catalytic activity, but also showed good stability: after four cycles, the degradation efficiency for ERY still remained above 85%. The excellent catalytic activity of GO/MIL-100(Fe)@Fe<sub>3</sub>O<sub>4</sub> could be ascribed mainly to the following: (1) an improvement in charge distribution and acceleration of the Fe<sup>3+</sup>/Fe<sup>2+</sup> cycle derived from the synergistic effects between Fe<sub>3</sub>O<sub>4</sub> NPs and MIL-100(Fe); (2) GO acting as an electron transfer channel facilitated the transfer of photogenerated electrons over MIL-100(Fe), hindered the recombination of photogenerated carriers, and accelerated the Fe<sup>3+</sup>/Fe<sup>2+</sup> cycle; and (3) multiple



active species participated in ERY degradation. The results indicated that GO/MIL-100(Fe)<sub>3</sub>O<sub>4</sub> would be an excellent heterogeneous photo-Fenton catalyst for wastewater treatment.

## Author contributions

Lian Yu: writing – original draft, methodology, investigation, formal analysis. Baozi Lu: methodology, investigation. Zhen Liang: writing – review and editing, methodology, formal analysis. Dabin Wang: writing – review and editing, investigation. Jiarui Lu: data curation, methodology. Fengyi Wei: methodology, formal analysis. Cunzhen Liang: project administration, funding acquisition, conceptualization.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

All data supporting the findings of this study are included in the main manuscript.

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d5ra06917c>.

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