Graphene-Based Photo-Fenton Catalysts for Pollutant Control

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Received: 16 October 2020 / Revised: 23 October 2020 / Accepted: 2 November 2020 / Published online: 4 January 2021
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Abstract

Water pollution is a global environmental issue with multi-dimensional influences on human life. Some strategies, such as photo-Fenton reaction, have been employed to remove recalcitrant pollutants. Two-dimensional (2D) graphene and its three-dimensional (3D) configurations have attracted considerable attention as emerging carbon-based catalysts in photo-Fenton fields owing to their alluring properties in electron transfer, reactant adsorption, and light response. This review summarizes the recent developments in 2D and 3D graphene-based catalysts for photo-Fenton reactions. Their structures, characteristics, activity, and mechanisms are discussed. The conclusions and outlooks are proposed for the profound understanding of challenges and future directions.

Keywords Photo-Fenton · Graphene · Pollutant control · Aerogel · Hydrogel

Introduction

With continuous developments of human societies and industries, water pollution is becoming increasingly serious and riveting attention among researchers. Although a small fraction of pollutants is present in aquatic environments, most of them bio-accumulate and resist traditional physical removal methods [1]. Consequently, innovative strategies, such as advanced oxidation processes (AOPs), have been introduced; the Fenton reaction, which was discovered in 1894, is one of the most studied strategies [2–10]. The main reactions stated below [Eqs. (1), (2)] reveal the major oxidation mechanism, where ferrous ions (Fe^{2+}) continuously react with hydrogen peroxide (H_2O_2) to produce hydroxyl radicals ($\cdot\text{OH}$) with strong oxidizing ability, which plays a

vital role in the subsequent degradation of pollutants. The concurrent reduction of ferric ions (Fe^{3+}) to Fe^{2+} realizes the circulation of iron ions. However, Eq. (2) is the rate-determining step, whose rate is approximately 1/6000 that of Eq. (1), which greatly abates the effectiveness of $\text{Fe}^{3+}/\text{Fe}^{2+}$ circulation [11]. The invalidation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ circulation induces not only the insufficient utilization efficiency of H_2O_2 but also the aggregation of Fe^{3+} . It precipitates to form ferric hydroxide ($\text{Fe}(\text{OH})_3$), namely iron sludge, when pH is above 3, leading to thorny secondary pollution [12]. Traditional Fenton reactions possess four major drawbacks: (1) low utilization efficiency of H_2O_2 , (2) narrow pH range, (3) excess iron ion loss and secondary pollution of iron sludge, and (4) difficulties in recycling powder catalysts [13–16].

As a branch of Fenton reactions, the photo-Fenton reaction improves the utilization efficiency of H_2O_2 after the introduction of ultraviolet (UV) or visible light because of the photo-induced reduction of Fe^{3+} to Fe^{2+} [Eq. (3)] and the production of $\cdot\text{OH}$ [Eq. (4)] [11]. In traditional photo-Fenton reactions, ferrous compounds, such as ferrous sulfate (FeSO_4), are added directly into aqueous catalytic systems to react with H_2O_2 in ionic state [17]. Such type of homogeneous reaction exacerbates the formation of iron sludge, resulting in blocked iron recycling and secondary

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pollution [18]. Iron-based catalysts may contribute to interface reactions between iron ions and H_2O_2 , suppressing the formation of iron sludge and waste of iron sources [19]. Various methods to introduce iron-based catalysts have been investigated to ameliorate the application range of pH, formation of iron sludge, and catalyst recycling in photo-Fenton reactions [20, 21].

In photo-Fenton reactions, a myriad of catalysts display their outstanding potential in degrading recalcitrant pollutants. In recent years, graphene-based materials have become promising candidates owing to their unique merits of theoretical specific surface, electron mobility, wide light response, and mechanical strength [22, 23]. Numerous reports have proved the overwhelming benefits of graphene in various AOPs, including photo-Fenton reactions [24]. Early in 2011, Fu and Wang [25] loaded ZnFe_2O_4 on graphene and applied the ZnFe_2O_4 -graphene hybrid catalyst for the photo-Fenton reaction in degrading methylene blue (MB). The salient improvement over pristine ZnFe_2O_4 is ascribed to the enhanced light absorbance of graphene and inherent π -conjunction in graphene, which is conducive for the separation of photo-generated electrons and holes, thus extending the lifetime of photo-generated electrons. Moreover, the introduction of graphene in the photo-Fenton reaction can quickly transfer the electrons to Fe^{3+} , accelerating its reduction to Fe^{2+} and enabling the $\text{Fe}^{3+}/\text{Fe}^{2+}$ circulation in the photo-Fenton reaction. In addition, the large specific surface endows graphene-based catalysts with the preeminent adsorption of pollutants and retards the agglomeration of catalyst nanoparticles [26–28]. Figure 1 illustrates the general photo-Fenton scheme of graphene-based materials.

Fig. 1 General photo-Fenton scheme of graphene-based materials

Given the peculiar properties and alluring prospects of graphene in photo-Fenton reactions, this review summarized the recent advances in graphene-based photo-Fenton catalysts and categorized them into 2D and 3D graphene-based photo-Fenton systems, whose structures, characteristics, activity, and mechanisms were discussed in detail. Moreover, attempts to overcome the four aforementioned drawbacks that hampered the practical application of photo-Fenton reactions were presented. On the basis of the above analysis, a perspective on the direction and emphasis in this field was provided to understand the possible path of photo-Fenton reactions in practical industrial wastewater treatment.

Two-Dimensional Graphene-Based Photo-Fenton Systems

Graphene oxide (GO) obtained by the exfoliation and oxidation of graphite possesses oxygen-containing functional groups on the surface [29, 30]. These functional groups allow GO to chemically bond with various active materials and form highly stable 2D graphene-based photo-Fenton systems. Consequently, the high stability, great dispersity, and rapid reaction of 2D graphene-based photo-Fenton systems triggered a myriad of studies. Iron-based catalysts have been extensively applied in recent research to restrain the formation of iron sludge. As a result, recently developed 2D graphene-based photo-Fenton systems were divided into 2D graphene/iron oxides, 2D graphene/spinel ferrites, and 2D graphene/iron-based metal organic frameworks, whose characteristics, advantages, and mechanisms were introduced specifically.

Two-Dimensional Graphene/Iron Oxides

Multifarious iron oxides with nanostructures have attracted considerable attention because of their natural abundance, environmental friendliness, and efficient production of iron complex and $\cdot\text{OH}$ irradiated by UV light [31]. So far, ferric oxide (Fe_2O_3) [31, 32], ferriferrous oxide (Fe_3O_4) [33, 34], and iron oxyhydroxide (FeOOH) [35] display peculiar properties and compelling catalytic ability with the aid of graphene in photo-Fenton reactions.

As an earth-abundant n-type semiconductor, $\alpha\text{-Fe}_2\text{O}_3$ stands out as the most discussed crystalline polymorph of Fe_2O_3 because of its low cost, heat endurance, and chemical stability. With a relatively narrow band gap of 1.90–2.20 eV, $\alpha\text{-Fe}_2\text{O}_3$ can absorb approximately 43% solar light [32, 36] and releases few iron ions as a heterogeneous Fenton catalyst [31]. Nevertheless, the inherent high recombination rate of photo-generated electrons and holes and inefficient conversion efficiency of Fe^{2+} and Fe^{3+} in $\alpha\text{-Fe}_2\text{O}_3$ hamper the overall catalysis in photo-Fenton reactions [32]. With

its fascinating electron transport property and large specific surface area, graphene is regarded as a promising support to overcome the demerits of $\alpha\text{-Fe}_2\text{O}_3$. Guo et al. [37] first synthesized a GO- Fe_2O_3 composite through a simple impregnation method and used it as the photo-Fenton catalyst in degrading Rhodamine B (RhB). As shown in Fig. 2a, Fourier-transform infrared (FT-IR) spectroscopy was employed to analyze the oxygen-containing functional groups before and after impregnation to identify the chemical structures of GO and GO- Fe_2O_3 . The peaks at 1719, 1621, 1417, 1223, and 1053 cm^{-1} , which were ascribed to C=O, aromatic C=C, carboxyl C-O, epoxy C-O, and alkoxy C-O, respectively, appeared in GO and GO- Fe_2O_3 but were slightly different in their positions and sharpness, suggesting change in coordination environment of these groups. In specific, the peak at 1719 cm^{-1} was weaker in GO- Fe_2O_3 than that in GO because of the formation of -COO^- after loading Fe_2O_3 . In addition, the extra peak at 535 cm^{-1} ascribed to Fe-O in Fe_2O_3 elucidated the connection between Fe_2O_3 and -COO^- on the edge of GO, corroborating that Fe_2O_3 could form bonds with oxygen-containing functional groups on the GO surface and be firmly fixed on GO. Degradation tests revealed that GO- Fe_2O_3 greatly accelerated photo-Fenton reactions (Fig. 2b), where 99% RhB was degraded in 40 min. Removal of 60% RhB in 80 min under dark conditions also demonstrated the preeminent adsorption ability of GO- Fe_2O_3 . Moreover, 90.9% RhB was eliminated in 80 min when pH was up to 10.09, suggesting that the electronegativity and the oxygen-containing functional groups on the GO surface extended the pH application range to some extent.

Liu et al. [31] subsequently investigated the mechanism of degrading different organic pollutants in the $\alpha\text{-Fe}_2\text{O}_3\text{@GO}$ photo-Fenton system. Ultraviolet and visible diffuse reflectance spectroscopy (UV-Vis DRS) (Fig. 2c) revealed that $\alpha\text{-Fe}_2\text{O}_3\text{@GO}$ showed an enhanced light absorption and slight redshift than $\alpha\text{-Fe}_2\text{O}_3$, indicating that the former has greater photo-Fenton efficiency than the latter. Such slight redshift might be credited to the formation of Fe-O-C bond between $\alpha\text{-Fe}_2\text{O}_3$ and GO. The degradation rates of MB at pH 3–12 reached 99% in 80 min, suggesting that π - π stacking and electronegativity of the GO surface allowed $\alpha\text{-Fe}_2\text{O}_3\text{@GO}$ to adsorb MB in large quantities. To validate this theory, the authors conducted degradation and adsorption experiments on different organic pollutants (Fig. 2d). Results showed that the degradation and adsorption of cationic compounds (MB and RhB) were conspicuously quicker than those of anionic compounds (Orange II and Orange G) and neutral compounds (phenol, 2-nitrophenol, and endocrine disrupting compound 17 β -estradiol), proving the aforementioned speculation. Moreover, the degradation rate of MB remained 99% after 10 cycles, and no detectable iron leaching was identified by inductively coupled plasma (ICP)-optical emission spectroscopy, suggesting the outstanding catalytic stability and inhibition of iron sludge formation in this $\alpha\text{-Fe}_2\text{O}_3\text{@GO}$ photo-Fenton system.

Bio-friendly Fe_3O_4 nanoparticles are promising photocatalysts because of their unique magnetic, electronic, and catalytic properties. The coexistence of Fe^{2+} and Fe^{3+} in the octahedral structure endows Fe_3O_4 with the enhanced ability of iron ion cycle [33]. The inherent magnetic property allows

Fig. 2 **a** FT-IR spectra of GO and GO- Fe_2O_3 ; **b** discoloration of RhB under different conditions: (a) RhB/ H_2O_2 /Vis; (b) RhB/ H_2O_2 , in the dark; (c) RhB/GO- Fe_2O_3 , in the dark; (d) RhB/GO- Fe_2O_3 /Vis; (e) RhB/GO- Fe_2O_3 / H_2O_2 , in the dark; (f) RhB/GO- Fe_2O_3 / H_2O_2 /Vis; and (g) RhB/ Fe^{3+} / H_2O_2 /Vis. Reproduced with permission from Ref. [37]. Copyright 2013 Elsevier Ltd. **c** UV-Vis diffuses reflectance spectra of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3\text{@GO}$; **d** degradation of various organics in the $\alpha\text{-Fe}_2\text{O}_3\text{@GO} + \text{H}_2\text{O}_2 + \text{UV}$ system. Reproduced with permission from Ref. [31]. Copyright 2017 Elsevier B.V.

Fe_3O_4 composite catalysts to be separated from wastewater with minor loss in the presence of an external magnetic field, which is a possible solution to the difficulty in recycling photo-Fenton catalysts. However, Fe_3O_4 nanoparticles agglomerate and form large particles, which reduces the specific surface area and solubility, thereby suppressing catalytic activity [27]. To this end, the researchers loaded Fe_3O_4 nanoparticles on the GO surface and employed the composite catalysts in photo-Fenton reactions. Qiu et al. [20] reported a feasible Stöber-like method using Fe(III) acetylacetonate as the precursor to synthesize ultra-dispersed Fe_3O_4 nanoparticles on the surface of reduced graphene oxide (rGO). This method could be applied in large-scale synthesis without the need for reducing agents and organic surfactants. High-resolution transmission electron micrographs (Fig. 3a, b) showed that amorphous Fe_3O_4 nanoparticles (3–4 nm) dispersed uniformly on the surface of almost two layers of GO sheets. No naked GO sheets or scattered Fe_3O_4 nanoparticles were observed. This result manifested that the authors successfully synthesized Fe_3O_4 nanoparticles highly dispersed on the GO surface through the Stöber-like method. The obtained $\text{Fe}_3\text{O}_4/\text{GO}$ catalyst showed a compelling specific surface area ($199.8 \text{ m}^2/\text{g}$). The superior adsorption capability stemming from the large specific surface area greatly contributed to the degradation of 98% methyl orange (MO) in 30 min in photo-Fenton reactions. By virtue of the particular magnetic property of Fe_3O_4 nanoparticles, the catalysts were recovered rapidly without loss and difficulties (Fig. 3c). As displayed in Fig. 3d, the $\text{Fe}_3\text{O}_4/\text{GO}$ catalyst was compared with commercial Fe_3O_4 powders in the photo-Fenton degradation of MO. The degradation rate remained 90% after four cycles with the $\text{Fe}_3\text{O}_4/$

GO catalyst, whereas commercial Fe_3O_4 powders lost the catalytic activity notably in each cycle. It was ascribed to the generation of iron sludge, which covered the surface of Fe_3O_4 and induced inefficient $\text{Fe}^{3+}/\text{Fe}^{2+}$ circulation. In this $\text{Fe}_3\text{O}_4/\text{GO}$ photo-Fenton system, the photo-induced electrons generated from dyes and Fe_3O_4 migrated to GO sheets for the superior conductivity, so that Fe^{3+} could capture electrons and be reduced to Fe^{2+} , thereby continuing to react with H_2O_2 to produce $\cdot\text{OH}$. The proposed mechanism was concordant with the fact that no change in the $\text{Fe}_3\text{O}_4/\text{GO}$ catalyst was observed before and after the photo-Fenton reactions from the transmission electron microscopy (TEM) and field-emission scanning electron microscopy (FESEM) images.

$\beta\text{-FeOOH}$ has also attracted attention because of its natural abundance as a biocompatible catalyst. With the narrow band gap of 2.12 eV, $\beta\text{-FeOOH}$ can effectively absorb visible light. However, $\beta\text{-FeOOH}$ minerals usually exist in the form of very small particles, which tend to agglomerate, thus causing inactivation. In addition, the inherent poor electron–hole separation ability results in the short lifetime of photo-generated electrons and poor catalytic ability in photo-Fenton reactions [35, 38]. To overcome these defects, Su et al. [35] prepared a $\beta\text{-FeOOH}@/\text{GO}$ nanocomposite through moderate hydrolysis for MB degradation. UV–Vis DRS (Fig. 4a) revealed that $\beta\text{-FeOOH}@/\text{GO}$ was more capable than $\beta\text{-FeOOH}$ in absorbing UV and visible light owing to the interface interaction between $\beta\text{-FeOOH}$ and GO sheets. In the photoluminescence (PL) spectra (Fig. 4b), the peak of $\beta\text{-FeOOH}@/\text{GO}$ was lower than that of $\beta\text{-FeOOH}$, suggesting stronger inhibitory effect on the recombination of photo-generated electrons and holes and

Fig. 3 **a, b** HRTEM of the amorphous $\text{Fe}_3\text{O}_4/\text{GO}$ composites; **c** magnetic separation property of the $\text{Fe}_3\text{O}_4/\text{RGO}$ photocatalyst; **d** cycle test (i_1 – i_4 : $\text{Fe}_3\text{O}_4/\text{RGO}$; ii_1 – ii_4 : commercial Fe_3O_4 powders; iii_1 : $\text{Fe}_3\text{O}_4/\text{RGO}$ in the dark) for the solar-driven degradation of MO under simulated solar light irradiation. Reproduced with permission from Ref. [20]. Copyright 2015 Elsevier B.V.

Fig. 4 **a** UV–Vis DRS and **b** PL spectra of β -FeOOH and β -FeOOH@GO; **c** effect of pH on the MB decolorization and **d** durability of the catalyst after six recycles in the β -FeOOH@GO + H_2O_2 + UV system. Reproduced with permission from Ref. [35]. Copyright 2018 Elsevier Ltd.

longer lifetime of photo-generated electrons. As a result, the degradation rate of MB with β -FeOOH@GO reached 99.7% in 60 min, and the calculated pseudo-first-order rate constant was 0.6322 min^{-1} , which was much higher than that of β -FeOOH (0.2148 min^{-1}). Moreover, the pH application range and catalytic stability of β -FeOOH@GO were satisfactory. As shown in Fig. 4c, the degradation of MB with the addition of β -FeOOH@GO remained in a high speed at pH 2.67–12.11. This result can be ascribed to the fact that the point of zero charge of β -FeOOH@GO was 2.25 and the negatively charged surface at higher pH value ($\text{pH} > 2.25$) augmented the adsorption of cationic MB. As illustrated in Fig. 4d, the degradation and adsorption rates of different cycles showed no significant differences. The maximum concentration of dissolved iron was 0.277 mg/L , accounting for only 0.4% of the loaded β -FeOOH. These results indicate that the β -FeOOH@GO catalyst has the potential to overcome the narrow application range of pH and the generation of iron sludge. Basing from the results of X-ray photoelectron spectroscopy and electron spin resonance (ESR) spectroscopy, the authors proposed the degradation mechanism of MB as follows. First, MB was adsorbed on the surface of β -FeOOH@GO through electrostatic interaction and π - π stacking. Second, H_2O_2 reacted with Fe^{2+} generated through the photoreduction of Fe^{3+} on the catalyst surface to generate $\cdot\text{OH}$. Third, GO guaranteed the increase in the active sites and the effective enrichment of MB molecules, which were further attacked by $\cdot\text{OH}$. Fourth, GO effectively

captured the photo-generated electrons from the semiconductor conduction band or the LUMO of the dye and quickly transferred them to the active site of β -FeOOH because of the heterojunction between β -FeOOH and GO. Finally, Fe^{3+} could react with $h\nu$, H_2O_2 , or the transferred electrons and be reduced to Fe^{2+} , facilitating $\text{Fe}^{3+}/\text{Fe}^{2+}$ circulation.

Table 1 summarizes the catalytic performance of some typical photo-Fenton catalysts based on 2D graphene/iron oxides and iron oxides. Obviously, graphene-based catalysts possess an obvious edge over those without graphene owing to the outstanding physical and chemical properties of graphene.

2D Graphene/Spinel Ferrites

Spinel ferrites are face-centered cubic structured oxides (MFe_2O_4 , $\text{M} = \text{Co}$, Cu , Zn , Ni , Mn , etc.) that have been widely applied in magnetic resonance imaging, electronic equipment, processing heavy metal waste and chemical sensors [26]. The properties of spinel ferrites largely depend on the position, nature, and quantity of the metal incorporated in the structure. Apart from thermal and chemical stability, spinel ferrites often possess magnetic properties and superior light absorption. Many spinel ferrites, such as ZnFe_2O_4 and NiFe_2O_4 , have a narrower band gap of 1.90–2.20 eV than traditional photocatalysts, such as CdS (2.40 eV) and WO_3 (2.80 eV), suggesting their wider visible light absorption [39]. Spinel ferrites are effective photocatalysts and

Table 1 Recent studies on 2D graphene/iron oxide-based photo-Fenton systems

Catalyst	Light source	$\text{C}_\text{H}_2\text{O}_2$	C_catalyst (g/L)	pH	Pollutant	Efficiency	Efficiency without graphene	References
GO- Fe_2O_3	300 W Dy lamp, > 420 nm	10 mL/L	1	3.65	RhB (100 mL, 100 mg/L) and 4-nitrophenol (100 mL, 50 mg/L)	99% and 92% in 80 min	–	[37]
$\alpha\text{-Fe}_2\text{O}_3$ @GO	300 W Xe lamp, > 400 nm	10 mL/L	0.2	7.0 ± 0.2	RhB (50 mL, 50 mg/L)	92% in 150 min	~ 32% in 150 min	[59]
Fe_3O_4 @rGO@ TiO_2	300 W Xe lamp, > 400 nm	0.176 mol/L	1.5	Neutral	MB (50 mL, 10 mg/L)	99% in 120 min	–	[60]
Ammonia-modified graphene- Fe_3O_4	Sunlight within 10 am to 2 pm in Jorhat, Assam, India (600–700 W/ m^2)	0.15 mol/L	0.5	7	Phenol, 2-nitrophenol and 2-chlorophenol (30 mL, 0.4 mM)	93.6% in 80 min, 98.8% in 50 min, and 98.1% in 60 min	Phenol: 57% in 120 min	[61]
Fe_3O_4 /GO	300 W Xe lamp, AM 1.5	24.0 mL/L	–	3.5	MO (50 mL, 10 mg/L)	98% in 30 min	82% in 30 min	[20]
Fe_3O_4 @hydrophilic graphene	500 W mercury lamp	24.0 mL/L	0.06	3.5	MO (50 mL, 10 mg/L)	87.7% in 30 min	9.5% in 30 min	[33]
Fe_3O_4 -GO	500 W Xe lamp	20 mg/L	0.25	5.0	Phenol (500 mL, 20 mg/L)	98.8% in 120 min	73.7% in 120 min	[34]
Graphene- Fe_3O_4	90 W UV lamp	10 mL/L	0.2	4	MO (100 mL, 20 mg/L)	99.2% in 30 min	43% in 30 min	[62]
Pyrrolic N-doped GO/ Fe_2O_3	300 W Xe lamp, > 420 nm	–	0.2	–	MB (50 mL, 10 mg/L)	~ 70% in 2 h	~ 48% in 120 min	[32]
$\alpha\text{-Fe}_2\text{O}_3$ @GO	100 W mercury lamp, 365 nm	1.10 mmol/L	0.25	3–12	MO (400 mL, 40 mg/L)	~ 95% in 20 min	~ 78% in 20 min	[31]
ZnO- Fe_3O_4 /rGO	300 W Xe lamp, > 420 nm	30 $\mu\text{mol/L}$	0.4	7	MB (50 mL, 10 mg/L)	~ 97% in 150 min	~ 41% in 150 min	[27]
$\gamma\text{-Fe}_2\text{O}_3$ /GO	250 W mercury lamp	50.0 mL/L	0.2	4.2–10.2	MB (50 mL, 50 mg/L)	99% in 100 min	~ 88% in 120 min	[63]
Au- Fe_3O_4 /graphene	40 W UV-C lamp	40 mL/L	–	7	MB (100 mL, 20 mg/L)	100% in 120 min	–	[64]
$\beta\text{-FeOOH}$ /GO	125 W mercury lamp, 365 nm	1.10 mmol/L	0.25	2.67–12.11	MB (400 mL, 40 mg/L)	99.7% in 60 min	96.1% in 60 min	[35]

active in neutral and alkaline Fenton systems. Loading spinel ferrites on graphene hampers the agglomeration of spinel ferrite nanoparticles and the leaching of poisonous ions. Given the large specific surface area and robust light absorption of graphene, the graphene/spinel ferrite composites ought to perform enhanced catalytic activity in photo-Fenton reactions.

Zinc ferrite (ZnFe_2O_4) is characterized by visible light response, light stability, and low cost. Owing to the narrow band gap of 1.90 eV, ZnFe_2O_4 is particularly popular in solar energy conversion, photocatalysis, and photochemical hydrogen production. Early in 2011, Fu and Wang [25] synthesized ZnFe_2O_4 -graphene by using a one-step hydrothermal method readily and employed it for the photo-Fenton

degradation of MB with visible light. The FESEM image in Fig. 5a shows that ZnFe_2O_4 nanoparticles (7–10 nm) were uniformly loaded on the surface of exfoliated graphene sheets. The ZnFe_2O_4 -graphene with 20 wt% graphene exhibited greater photo-Fenton activity (99% degradation of MB in 90 min) than pristine ZnFe_2O_4 (20% degradation of MB in 90 min). Probing the cause of the great enhancement, electrochemical impedance spectroscopy measurements were performed to identify the electrical resistivity. As shown in Fig. 5b, the Nyquist curves of ZnFe_2O_4 -graphene possessed a much smaller radius than those of ZnFe_2O_4 and GO, implying lower electrical resistance and higher electronic mobility. In short, graphene is a unique 2D material with zero band gap and π -conjugation structure. On its surface,

Fig. 5 **a** FESEM images of ZnFe₂O₄-G (0.2); **b** EIS of (a) ZnFe₂O₄-G(0.2), (b) pure ZnFe₂O₄, and (c) GO; and **c** images of ZnFe₂O₄-G(0.2) suspension with and without a magnetic field. Reproduced with permission from Ref. [25]. Copyright 2011 American Chemical Society. **d** Photo-Fenton degradation of MB. Initial conditions are as follows: (1) MB + GO-NiFe₂O₄ + 1.0 mmol/L H₂C₂O₄ + visible light; (2) MB + NiFe₂O₄ + 1.0 mmol/L H₂C₂O₄ + visible light; (3) MB + GO-NiFe₂O₄ + H₂C₂O₄ in

the dark; (4) MB + GO-NiFe₂O₄ + visible light; (5) MB + GO-NiFe₂O₄ in the dark; (6) MB + H₂C₂O₄ in the dark; and (7) MB + GO + NiFe₂O₄ + H₂C₂O₄ + visible light; **e** cyclic tests of 0.10 g of GO-NiFe₂O₄ catalyst in 50.0 mL of solution containing 20.0 mg/L MB in the presence of 1.0 mmol/L oxalic acid; **f** photochemical process mediated by graphene in the GO-NiFe₂O₄ hybrid material. Reproduced with permission from Ref. [41]. Copyright 2013 Elsevier Ltd.

the carriers appeared as massless fermions. Thus, the photo-generated electrons produced by ZnFe₂O₄ could quickly transfer from its conduction band to graphene, improving the activity of photo-Fenton reactions. Moreover, the catalysts were easily recovered because of the magnetic property of ZnFe₂O₄ (Fig. 5c). The subsequent unchanged degradation rate of MB for 10 cycles exemplified the catalytic stability of ZnFe₂O₄-graphene.

With a narrow band gap of 2.10 eV, NiFe₂O₄ has the potential to be a photocatalyst because of its stable structure, high electrical resistance, and photochemical stability. The ferromagnetism stemming from its magnetic moment of the antiparallel spin between the Ni²⁺ ion and the Fe³⁺ ion reduces the cost of catalyst recovery [40]. Liu et al. [41] loaded NiFe₂O₄ on GO sheets through a facile hydrothermal method and performed the degradation of MB with the addition of a GO-NiFe₂O₄ composite, visible light, and oxalic acid. The authors selected oxalic acid rather than H₂O₂ for the increased light absorption because of the formation of ferric oxalate and the large rate constant of the rate-determining step of the ferric oxalate-based photo-Fenton system. The photo-Fenton experiment (Fig. 5d) showed that the photo-Fenton degradation rate of MB with GO-NiFe₂O₄ reached 96.2% after 10 h, whereas that of MB with NiFe₂O₄ was 24.6%, which was almost same as the Fenton degradation rate of MB in the dark with GO-NiFe₂O₄. In addition, the mechanical mixture of GO and NiFe₂O₄ demonstrated no obvious catalytic enhancement over NiFe₂O₄. These results suggested that the effective combination of GO and NiFe₂O₄

achieved such an efficient catalytic performance and that GO increased the light absorbance rather than degraded MB by itself. A recycling degradation experiment was also carried out readily because of the ferromagnetism of NiFe₂O₄. Results revealed that the degradation rate remained above 90% even after eight cycles (Fig. 5e). A schematic of the degradation is provided in Fig. 5f.

Researchers have also disclosed the effect of GO on other spinel ferrite-based photo-Fenton systems, such as manganese ferrite (MnFe₂O₄) and cobalt ferrite (CoFe₂O₄). MnFe₂O₄ is also a magnetically separable material. With multiple absorption bands at 295, 430, 576, and 745 nm, MnFe₂O₄ broadly responds to UV and visible light. Unfortunately, MnFe₂O₄ itself does not exhibit photocatalytic activity under visible light excitation [42]. Zhou et al. [42] therefore combined it with graphene for enhanced light absorption. Under visible light irradiation, the degradation rate of NH₃-N solution with graphene-manganese ferrite (rG-MnFe₂O₄) in 10 h was 92%, which was much higher than that with MnFe₂O₄ (51.5%). The ameliorated light absorption caused by the combination of graphene and MnFe₂O₄ and the improved pollutant adsorption resulting from the increase in the specific surface area from 3.99 m²/g of rG to 7.30 m²/g of rG-MnFe₂O₄ contributed to the intriguing photo-Fenton catalytic activity. CoFe₂O₄ is characterized by its narrow band gap, low toxicity, natural abundance, and low cost. He and Lu [43] synthesized rGO/CoFe₂O₄ hybrids through a hydrothermal method, in which CoFe₂O₄ nanoparticles were uniform particles with an average size

of ~ 17 nm loaded on the surface of rGO. Malachite green was taken as the model pollutants for the photo-Fenton reactions at neutral pH. The introduction of rGO improved the degradation rate from ~ 79 to $\sim 99\%$ in 30 min, corresponding to the pseudo-first-order kinetic rate constants of 11.20 and 18.42 h^{-1} . The high valence band of CoFe_2O_4 enabled the photo-generated electrons to transfer spontaneously from CoFe_2O_4 to rGO, thereby increasing photo-Fenton activity.

2D Graphene/Iron-Based Metal Organic Frameworks

Metal organic frameworks (MOFs) are crystalline porous materials composed of multidentate organic ligands and metal ions or clusters. Given their large specific surface area, MOFs have been widely used in gas storage, adsorption, and separation [44, 45]. In addition, MOFs are extensively responsive to UV and visible light owing to their ligand–metal charge transfer (LMCT) property, making them promising candidates as novel photocatalysts. In particular, iron-based MOFs have attracted wide attention because of their $\text{Fe}_3\text{-}\mu_3\text{-oxo}$ clusters and low toxicity [46]. However, the application of MOFs as photo-induced catalysts is limited by the poor separation and migration of photo-induced carriers,

whose common amelioration methods include surface modification and doping [47]. Considering the preeminent visible light absorption and electron mobility of graphene, MOF materials could be loaded on graphene to prepare hybrid photo-Fenton catalysts. The introduction of graphene is also believed to improve structural stability and inhibit photo-corrosion [48].

In 2018, Liu et al. [47] polymerized ultrathin GO on the surface of MIL-88A(Fe) to prepare MIL-88A(Fe)/GO. As shown in the SEM image in Fig. 6a, MIL-88A(Fe) appeared as needle-shaped nanorods $1\text{--}3\text{ }\mu\text{m}$ long with high crystallinity and GO distributed evenly on the surface. UV–Vis DRS (Fig. 6b) revealed that all the samples absorbed light effectively at the wavelength of $200\text{--}600\text{ nm}$. Concerning pristine MIL-88A(Fe), the characteristic absorption peak at about 250 nm was ascribed to the LMCT of O(II) to Fe(III), and the bands at $300\text{--}500\text{ nm}$ were attributed to the d–d transition of Fe(III). The absorption edges of MIL-88A(Fe)/GO and MIL-88A(Fe)/GO were similar, but the introduction of GO considerably increased the absorption intensity, especially that in the visible light area, implying increased photo-Fenton catalytic ability. The results in the photo-Fenton degradation of RhB were consistent with the speculation. The

Fig. 6 **a** SEM image of MIL-88A(Fe)/GO; **b** UV–Vis DRS spectra of MIL-88A(Fe) and MIL-88A(Fe)/GO nanocomposites. Reproduced with permission from Ref. [47]. Copyright 2017 Elsevier B.V. **c–e** Separation of the GO/MIL-88A(Fe) membrane for MB solution; **f–h** photo-Fenton self-cleaning to degrade accumulated MB molecules. Reproduced with permission from Ref. [46]. Copyright 2019 Elsevier B.V.

pseudo-first-order kinetic rate constant of the degradation of RhB with MIL-88A(Fe)/GO was 0.0645 min^{-1} , which was 8.4 times higher than that with MIL-88A(Fe). The composite retained its high photo-Fenton performance in a wide pH range of 1–9 with no significant loss of catalytic ability after five cycles, suggesting the wide pH application range and stable catalytic stability of the composite. Xie et al. [46] reported a facile vacuum filtration strategy to prepare a GO/MIL-88A(Fe) membrane for the separation and degradation of MB. The introduction of GO modulated the 2D nanochannel in the membrane, enabling high flux and efficient separation to be mutually compatible. Concomitant light absorption enhancement contributed to the photo-Fenton reaction for the removal of contaminants clogging the interior of the membrane. The degradation of MB could be intuitively observed in Fig. 6c–h. After the separation (Fig. 6c–e), the residue of MB inside the membrane (Fig. 6f) was completely eliminated after the photo-Fenton process with visible light irradiation in 30 min (Fig. 6g, h). The mechanism conjectured from the results of ESR spectra is as follows. First, GO/MIL-88A(Fe) membrane generated electron–hole pairs when irradiated by visible light, in which holes directly oxidized organic pollutants and electrons migrating onto the GO surface promoted the decomposition of H_2O_2 into $\cdot\text{OH}$. Meanwhile, electrons could also be captured by oxygen to form superoxide radicals ($\text{O}_2^{\cdot-}$) on the membrane surface, and the generated $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ completely degraded organic pollutants. Within the catalyst, Fe–O clusters also facilitated the decomposition of H_2O_2 through Fenton-like reactions, and active sites provided by GO nanosheets enhanced the photo-Fenton catalytic ability.

Gong et al. [44] used MIL-100(Fe) to synthesize an $\text{Fe}_3\text{O}_4@\text{GO}@\text{MIL-100(Fe)}$ magnetic catalyst with a core–shell structure for the degradation of 2,4-dichlorophenol (2,4-DCP). Figure 7a–c displays the microstructures of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{GO}$, and $\text{Fe}_3\text{O}_4@\text{GO}@\text{MIL-100(Fe)}$, respectively. Fe_3O_4 is spherical with a rough surface whose diameter is 300–350 nm. After loading GO, a rugate surface texture appeared on $\text{Fe}_3\text{O}_4@\text{GO}$ because of the GO shell. Further wrapped with MIL-100(Fe), the surface became rougher with the MIL-100(Fe) shell, contributing to the spectacular specific surface area of $1048.1 \text{ m}^2/\text{g}$, which was much larger than that of $\text{Fe}_3\text{O}_4@\text{GO}$ ($79.4 \text{ m}^2/\text{g}$). The degradation rates of 2,4-DCP in the photo-Fenton system with $\text{Fe}_3\text{O}_4@\text{GO}@\text{MIL-100(Fe)}$ exceeded 90%, and the total organic carbon (TOC) removal rates reached 50% in four cycles. Coupled with the inherent magnetism, the $\text{Fe}_3\text{O}_4@\text{GO}@\text{MIL-100(Fe)}$ hybrid catalyst displayed its great potential for practical recycling. Analysis of the ESR spectra (Fig. 7d, e) revealed that the peaks of DMPO- $\text{HO}\cdot$ with an intensity ratio of 1:2:2:1 and the peaks of DMPO- $\text{O}_2^{\cdot-}$ with an intensity ratio of 1:1:1:1 were strong, suggesting that more $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ radicals were generated in the system. Combining additional PL spectra and photocurrent response measurements, the authors proposed the possible mechanism. When irradiated by visible light, photo-generated electrons were generated in MIL-100(Fe), captured by GO rapidly, and transferred to Fe_3O_4 and Fe^{3+} in MIL-100(Fe), promoting the reduction of Fe^{3+} to Fe^{2+} . The increased $\text{O}_2^{\cdot-}$ from the dissolved oxygen and $\cdot\text{OH}$ promoted the degradation of 2,4-DCP.

Fig. 7 TEM images of **a** Fe_3O_4 , **b** $\text{Fe}_3\text{O}_4@\text{GO}$, and **c** $\text{Fe}_3\text{O}_4@\text{GO}@\text{MIL-100(Fe)}$; ESR spectra of **d** DMPO- $\text{HO}\cdot$ adducts and **e** DMPO- $\text{O}_2^{\cdot-}$ adducts in the photo-Fenton system with Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{GO}$, MIL-100(Fe), $\text{Fe}_3\text{O}_4@\text{MIL-100(Fe)}$ and $\text{Fe}_3\text{O}_4@\text{GO}@\text{MIL-100(Fe)}$ under visible light irradiation. Reproduced with permission from Ref. [44]. Copyright 2019 Elsevier B.V.

The aforementioned papers on 2D graphene/iron oxides, 2D graphene/spinel ferrites, and 2D graphene/iron-based MOFs suggested the following common points: (1) graphene materials exhibit excellent light absorption, pollutants adsorption, and electron transport capabilities, thus improving the efficiency of photo-Fenton systems; (2) graphene is competent for the firm support of photo-Fenton catalysts that effectively inhibit the agglomeration of active components; (3) researchers tend to prepare iron-containing catalysts and increase the reaction pH, thus broadening the pH conditions of the reaction and hampering the formation of iron sludge; and (4) magnetic materials are becoming popular in photo-Fenton systems because of easy recycling. However, even magnetic 2D graphene-based materials are difficult to be separated from the sewage sludge under the actual scenario. The incidental agglomeration of 2D graphene-based composite catalysts after the reaction and the dissolution of active substances also leads to irreversible deactivation. Consequently, researchers have focused on using 3D graphene-based materials.

Three-Dimensional Graphene-Based Photo-Fenton Systems

Although 2D graphene-based materials have many advantages, their lamellar structures easily agglomerate, which reduces the specific surface area and active sites. Small 2D graphene-based catalysts may enter the aquatic environment, leading to potential pollution [38]. Fortunately, 3D graphene aerogel and hydrogel materials obtained by the self-assembly of 2D graphene materials not only inherit the intriguing properties of 2D graphene-based materials but also are easily separated from the aqueous solution. The special 3D porous structure also provides a myriad of channels for the transport and diffusion of reactants. Accordingly, 3D graphene materials have been widely applied in sensors [49], energy storage [50], and pollutant control [21].

Three-Dimensional Graphene-Based Aerogels

As a novel carrier, the graphene aerogel is characterized by a porous 3D framework, large specific surface area, excellent electron mobility, mechanism stability, and great adsorption [51]. After the self-assembly of 2D graphene materials, the original contact resistance between graphene sheets disappears, accelerating the electron transport. In addition, the intricate and conductive graphene network renders a multitude of paths for transport and diffusion [38]. Consequently, graphene aerogels have been widely investigated in sensors, oil absorption, energy storage, and catalysis [52]. As early as 2015, Qiu et al. [21] applied graphene aerogels in photon-Fenton reactions and laid a solid foundation for subsequent

research in the synthetic method. In general, metallic oxide nanoparticles, conductive polymers, or other carbon materials are introduced to effectively regulate the nanostructure and function of graphene aerogels [51], which are discussed as follows.

The metallic oxide nanoparticles on graphene aerogels function as the active sites in photo-Fenton reactions. In addition, graphene aerogels offer 3D support for the high dispersion of metallic oxide nanoparticles on the graphene surface. Qiu et al. [21] first reported the application of Fe_2O_3 on graphene aerogels ($\text{Fe}_2\text{O}_3/\text{GAs}$) in photo-Fenton in 2015. The Stöber-like method was adopted to grow Fe_2O_3 nanocrystals in situ on graphene aerogels. Figure 8a displays the macroscopic structure of $\text{Fe}_2\text{O}_3/\text{GAs}$ after a hydrothermal process, whose size could be easily modulated by altering the vessel. The $\text{Fe}_2\text{O}_3/\text{GA}$ material possessed ultra-light mass characteristics and very low density (8 mg/cm^3) despite containing 18.3 wt% Fe_2O_3 nanocrystals. Figure 8b shows that $\text{Fe}_2\text{O}_3/\text{GAs}$ had a 3D hierarchical macroporous structure, where granular Fe_2O_3 nanocrystals were inserted into the graphene skeleton without any observable agglomeration. The TEM image in Fig. 8c demonstrates that Fe_2O_3 nanoparticles, mostly in the size of 25 nm, were highly dispersed on the graphene surface. The consistent absence of agglomeration suggested that the Stöber-like approach was particularly conducive for the in situ growth of highly dispersed Fe_2O_3 nanocrystals on graphene aerogels. In addition, the mechanical strength of $\text{Fe}_2\text{O}_3/\text{GAs}$ was proved preeminent, as shown in Fig. 8d. It could withstand continuous compression for dozens of times, after which $\text{Fe}_2\text{O}_3/\text{GAs}$ was almost completely expanded, indicating the great elasticity and preeminent mechanical strength. The stress-strain curve also indicated the same conclusion, and the diagrams of the sandwich biscuit-like structure are shown in Fig. 8e. The catalytic property of $\text{Fe}_2\text{O}_3/\text{GAs}$ in photo-Fenton reactions was also satisfying. Comparison of the photo-Fenton degradation of MO (Fig. 9a) showed that Fe_2O_3 and $\text{Fe}_2\text{O}_3/2\text{D-graphene}$ ($\text{Fe}_2\text{O}_3/\text{GR}$) suffered rapid deactivation after the two cycles of degradation owing to iron leaching. Although the amounts and particle sizes of Fe_2O_3 in $\text{Fe}_2\text{O}_3/\text{GR}$ and $\text{Fe}_2\text{O}_3/\text{GAs}$ were highly similar, the degradation rate in the $\text{Fe}_2\text{O}_3/\text{GAs}$ photo-Fenton system did not change appreciably even after 10 cycles because of its tough 3D network structure, which precluded iron leaching. This proposed reason was validated by Fe^{2+} capture experiments, where 1,10-phenanthroline monohydrate (Phen) was employed to capture the dissolved Fe^{2+} ions after degradation (Fig. 9b). The dissolution of Fe^{2+} in Fe_2O_3 was much higher than that in $\text{Fe}_2\text{O}_3/\text{GAs}$, which reacted with OH^- to form $\text{Fe}(\text{OH})_3$ and impeded the $\text{Fe}^{3+}/\text{Fe}^{2+}$ circulation. Moreover, $\text{Fe}_2\text{O}_3/\text{GAs}$ exhibited excellent photo-Fenton activity in a wide pH range of 3.5–9.0 (Fig. 9c), but pristine Fe_2O_3 was gradually deactivated under neutral conditions with the

Fig. 8 **a** $\text{Fe}_2\text{O}_3/\text{GAs}$ with variable shapes prepared by changing the reaction vessel (reaction vessel increases from right to left); **b** FESEM and **c** TEM images of $\text{Fe}_2\text{O}_3/\text{GAs}$; **d** compression test of $\text{Fe}_2\text{O}_3/\text{GAs}$; and **e** structure of $\text{Fe}_2\text{O}_3/\text{GAs}$ during the compression test. Reproduced with permission from Ref. [21]. Copyright 2015 The Royal Society of Chemistry

increase in the number of cycles because of the iron sludge covered on the surface (Fig. 9d). Figure 9e illustrates the proposed mechanism, which is similar to that in 2D graphene-based photo-Fenton systems.

Polymers, such as polypyrrole, cellulose, and polyvinyl alcohol, have been exploited as cross-linkers for the self-assembly of GO nanosheets, modulating the structures and properties of graphene aerogels. Tong et al. [53] prepared a reduced graphene oxide/Prussian blue/polypyrrole aerogel (rGO/PB/PPy) hybrid catalyst for photo-Fenton reactions, where rGO, PB, and PPy functioned as the skeleton, the active site, and the cross-linker, respectively. As illustrated in Fig. 10a, the pyrrole monomer was oxidized and polymerized on the surface of GO nanosheets during the synthetic process. The obtained PPy wrapped the surface of GO nanosheets and adhered the adjacent GO layers by the π - π

interaction and hydrogen bond interaction, promoting the self-assembly of 2D GO nanosheets to aerogels. In addition, some oxygenated groups on the GO surface were reduced by the reductive pyrrole monomer. The structural impact brought by the cross-linker is shown in Fig. 10b. The rGO/PB/PPy aerogel presented a 3D framework with a myriad of interconnected holes, and the plane size of its rGO skeleton could reach hundreds of microns. The red arrows marked the PPy in the shape of cauliflowers, which acted as the cross-linker inside. The specific surface area and the pore size distribution reckoned by BET measurements were $70 \text{ m}^2/\text{g}$ and 5.0–50 nm, respectively. Such a large surface area and mesoporous channels promoted the adsorption and diffusion of pollutants, improving the degradation efficiency. Under the optimal conditions of photo-Fenton reactions with visible light irradiation, the RhB degradation rate in 30 min with

Fig. 9 **a** Cycle test for the solar-driven degradation of methyl orange (75 mL MO, 10 mg/L) under different reaction systems (1.2 mL H_2O_2 (30 wt%), initial pH was 3.5); **b** absorption spectra of the MO filter liquor photodegraded by the Fe_2O_3 powders and $\text{Fe}_2\text{O}_3/\text{GAs}$ in the presence of 1,10-phenanthroline monohydrate (initial pH was 3.5); **c** solar-driven degradation of MO on $\text{Fe}_2\text{O}_3/\text{GAs}$ (1.2 mL H_2O_2 (30 wt%), the initial pH was adjusted from 3.5 to 9.0 by adding 0.1 mol/L HCl); **d** cycle test for the solar-driven degradation of MO on different catalysts with the initial pH of 7.0; and **e** photo-Fenton reaction model of $\text{Fe}_2\text{O}_3/\text{GAs}$ in the system containing dye pollutants and H_2O_2 . Reproduced with permission from Ref. [21]. Copyright 2015 The Royal Society of Chemistry

the addition of rGO/PB/PPy was 95.2%, and the calculated pseudo-first-order rate constant was 0.0766 min^{-1} , which were greatly larger than those (5.5% and 0.00337 min^{-1} , respectively) with PB nanoparticles. This great improvement can be ascribed to the fact that rGO and PPy are highly capable of adsorbing organic dyes, resulting in a high concentration of RhB near PB nanoparticles. The other reason lays on the outstanding electrical conductivity of rGO and PPy, which accelerated $\text{Fe}^{3+}/\text{Fe}^{2+}$ circulation.

Other carbon materials further improve graphene aerogels-based photo-Fenton systems by providing additional channels and averting the agglomeration or dissolution of the active sites. Yao et al. [54] employed a two-step synthesis method to sandwich Fe_xO_y between the reduced GO nanosheet (rGS) and the nitrogen-doped carbon layer (NCL) to prepare the rGS/ Fe_xO_y /NCL composite. As shown in Fig. 10c, thin folds with blue marks indicate the rGSs, and the irregular bulges pointed by red arrows represent NCLs.

rGSs were interconnected to form a consecutive framework because of the adhesion brought by the insertion of NCLs. In a study on the photo-Fenton activity of rGS/ Fe_xO_y /NCL aerogels, RhB completely disappeared within 150 min. According to the pseudo-first-order equation, the calculated rate constant K was 0.0237 min^{-1} . A TOC removal experiment indicated a mineralization efficiency of 76.1% in 150 min. Coupled with the high degradation rate maintained in the pH range of 2.1–10.1, the overall excellent photo-Fenton catalytic performance of the rGS/ Fe_xO_y /NCL aerogel was exemplified. To disclose the reason, rGS/ Fe_xO_y aerogel was taken as the control group. The degradation rate obtained under the same conditions (66.7%) was lower than that with the rGS/ Fe_xO_y /NCL aerogel, which was credited to the π - π interaction and the formation of hydrogen bonds. Moreover, the superior conductivity of rGSs and NCLs accelerated the electron transfer between Fe^{3+} and Fe^{2+} , which was supported by the increased reduction current in

Fig. 10 **a** Preparation and **b** SEM image of rGO/PB/PPy aerogel. Reproduced with permission from Ref. [53]. Copyright 2019 Elsevier B.V. **c** SEM image of rGS/Fe_xO_y/NCL aerogel; **d** cyclic voltammetry (CV) scans of rGS/Fe_xO_y/NCL aerogel and γ -Fe₂O₃ NPs. Reproduced with permission from Ref. [54]. Copyright 2018 Elsevier B.V.

Fig. 10d. Importantly, the degradation rate of RhB with rGS/Fe_xO_y/NCL aerogels remained 94.6% after five cycles. No aggregation or loss of Fe_xO_y was found in the TEM images of the recovered sample. ICP atomic spectroscopy also proved that only 3.3 wt% of iron was dissolved after the five cycles, indicating the protective effect of NCLs and rGSs on Fe_xO_y nanoparticles. In general, this sandwich structure not only provided multiple channels for the rapid diffusion and adsorption of reactants but also averted the leaching of Fe_xO_y, thus achieving the preminent catalytic ability, stability, and reusability of the structure. A comparison of catalytic performances between non-graphene catalysts and 3D graphene-based catalysts is provided in Table 2 to highlight the significance of the 3D graphene in photo-Fenton reaction.

Three-Dimensional Graphene-Based Hydrogels

Composed of a porous framework, hydrogels are popular soft materials in electrochemistry, catalysis, sensors, drug delivery, and water treatment [55]. Different from hydrophobic aerogels, hydrogels can absorb large volumes of water in the expanded state because of the abundant hydrophilic groups on their polymeric networks. This extraordinary water-absorbing capability directly results in the adsorptive ability to remove or recycle organic pollutants and heavy metals from aqueous systems, which are not only adsorbed on the surface but also trapped in the inflated 3D framework [56]. Hitherto, many studies have unraveled that graphene-based hydrogels are free from the disadvantages of

traditional hydrogels in mechanical properties and adept at the adsorption of organic pollutants. However, few researchers adopted graphene hydrogels in photo-Fenton reactions to degrade the adsorbed pollutants completely [57, 58]. To our knowledge, Dong et al. [57] reported the only study on the use of graphene-based hydrogels in photo-Fenton systems, demonstrating the feasibility of this direction.

In that report, Fe₃O₄, rGO, and polyacrylamide (PAM) were employed to prepare Fe₃O₄/rGO/PAM hydrogels by using a two-step chemical synthesis method. The results of a series of experiments proved that this 3D graphene-based hydrogel has excellent mechanical strength, photo-Fenton activity, stability, and potential for practical applications. The SEM image of the Fe₃O₄/rGO/PAM hydrogel is shown in Fig. 11a. Fe₃O₄ nanoparticles were evenly distributed on the surface where PAM chains were wrapped by rGO, forming many small protuberances. The Fe₃O₄/rGO/PAM hydrogel possessed novel mechanical strength. As shown in the compress stress (σ)–compress strain (ε) plot (Fig. 11b), the Fe₃O₄/rGO/PAM hydrogel had higher compress strain than the PAM hydrogel, suggesting the greater anti-compression property of the former than that of the latter. The excellent tensile property of the Fe₃O₄/rGO/PAM hydrogel is displayed in Fig. 11c. Unlike the fragile PAM hydrogel, the Fe₃O₄/rGO/PAM hydrogel was not damaged after the tensile experiment, suggesting its great mechanical strength. In the photo-Fenton reactions, the degradation rate of RhB with the Fe₃O₄/rGO/PAM hydrogel reached 90% under the optimal conditions within 60 min. The high degradation rate was maintained

Table 2 Recent studies on 3D graphene aerogel-based photo-Fenton systems

Catalyst	Light source	$C_{H_2O_2}$	$C_{catalyst}$	pH	Pollutant	Efficiency	Efficiency without graphene	References
Fe_2O_3 /GAs	300 W Xe lamp, AM 1.5	16 mL/L	–	3.5	MO (75 mL, 10 mg/L)	~93% in 30 min in the 4th cycle	~22% in 30 min in the 4th cycle	[21]
$CoFe_2O_4$ /GAs	300 W Xe lamp, AM 1.5	150 mmol/L	–	3.5	MO (75 mL, 10 mg/L)	~100% in 30 min in the 5th cycle	~40% in 30 min in the 5th cycle	[52]
GO-carbon nanotubes- α -FeOOH aerogel	125 W mercury lamp, 365 nm	0.55 mmol/L	125 mg/L	3.18–9	Orange II (400 mL, 40 mg/L)	~99% in 60 min	60.7% in 60 min	[51]
Nano-FeO(OH)/rGO aerogel	500 W Xe lamp, > 420 nm	20 mmol/L	–	3.00	4-chlorophenol (50 mL, 10 mg/L)	100% in 80 min	–	[38]
Fe_2O_3 /rGO aerogel	300 W Xe lamp, > 400 nm	16.67 mL/L	83.33 mg/L	6.5	RhB (60 mL, 15 mg/L)	100% in 120 min	~40% in 120 min	[65]
rGO/Prussian blue/polypyrrole aerogel	300 W Xe lamp, > 420 nm	2 mL/L	0.2 g/L	6.18	RhB (50 mL, 10 mg/L)	95.2% in 30 min	5.5% in 30 min	[53]
rGO nanosheet/ Fe_3O_4 /nitrogen-doped carbon layer aerogel	Xe lamp, > 420 nm	16.67 mL/L	0.5 g/L	6.5	RhB (60 mL, 10 mg/L)	> 99.0% in 150 min	~32% in 150 min	[54]

Fig. 11 **a** SEM image of 0.2Fe/RGO/PAM hydrogel; **b** compress stress (σ)–compress strain (ε) plot of PAM hydrogel and 0.2Fe/RGO/PAM hydrogel; **c** stretchable tests of PAM hydrogel and 0.2Fe/RGO/PAM hydrogel; and **d** photo-Fenton-reaction for the degradation of fine chemical wastewater over 0.2Fe/RGO/PAM (benzenoid wastewater, pH=4.5, visible light: $\lambda > 420$ nm). Reproduced with permission from Ref. [57]. Copyright 2017 Elsevier B.V.

in the pH range of 3.5–6.5, suggesting that the Fe_3O_4 /rGO/PAM hydrogel is an excellent photo-Fenton catalyst under multiple conditions. Meanwhile, the catalytic stability was ascertained by over 90% removal of RhB after 10 cycles. The concentration of Fe^{2+} in aqueous solutions of the ground and unground Fe_3O_4 /rGO/PAM hydrogels was measured using Phen as the chromogenic agent to investigate the stability of the hydrogels. The intensity of

the peak ascribed to the ground Fe_3O_4 /rGO/PAM hydrogel (1.357) was much higher than that of the unground one (0.298), which manifested that the hybrid hydrogel greatly retarded the iron leaching and deactivation of catalysts. Original fine chemical wastewater was also chosen as the model of actual water pollution to test the practical application potential of the Fe_3O_4 /rGO/PAM hydrogel (Fig. 11d). The initial chemical oxygen demand (COD) of

the sewage was 10,400 mg/L, and it dropped to 2840 mg/L after 1 h of visible light irradiation, proving the potential for actual wastewater treatment.

Compared with the 2D graphene-based materials, the novel 3D graphene-based materials are equipped with more practical advantages. Graphene-based aerogels are characterized by low density and high mechanical strength, and the super adsorption capacity of hydrogels is also alluring. The enhanced adsorption and diffusion of pollutants brought by internal multi-channels, the inhibitory effect on agglomeration or dissolution of active sites, and the convenience for recycling as 3D macroscopic catalysts endow 3D graphene-based materials with great value in practical application. Thus, researchers tend to focus on the stability of the material and the trial for degrading actual sewage to lay a solid foundation for the possible application in industrial wastewater treatment in the future. In general, many problems remain to be solved before the practical application of 3D graphene-based materials, including but not limited to the high cost of synthesis and difficulties in catalyst regeneration. Nevertheless, 3D graphene-based materials are the general directions of future graphene-based systems, at least in the photo-Fenton degradation of pollutants.

Conclusions and Outlooks

In this study, the advances of graphene-based photo-Fenton systems were briefly introduced according to the classification of 2D and 3D graphene-based catalysts and discussed in terms of their special morphologic structures, great enhancements brought by graphene, the efficiency of treating pollutants, and practical application potential. Iron compounds have been selected as the active sites and anchored to the surface of graphene in 2D graphene-based photo-Fenton systems to mitigate the inevitable iron leaching in traditional photo-Fenton reactions. The consequent heterogeneous catalysis hampers the loss of catalytic activity and secondary pollution caused by iron sludge. The excellent light absorption, pollutant adsorption, and electron mobility of graphene materials are on full display in 2D graphene-based photo-Fenton systems. Fe^{3+} reduction and $\text{Fe}^{3+}/\text{Fe}^{2+}$ circulation can be carried out efficiently through rapid electron transfer among various active components, thus achieving alluring performance in the degradation of organic pollutants. In addition, many magnetic materials, such as Fe_3O_4 and ZnFe_2O_4 , which can be quickly separated from aqueous solutions by an external magnetic field, were employed to prepare 2D graphene-based magnetically separable catalysts to overcome the difficulty in 2D catalyst recovery to some extent.

Three-dimensional graphene-based materials, including graphene aerogels and graphene hydrogels, inherit the

aforementioned advantages of 2D graphene-based materials and are equipped with additional porous 3D macroscopic structures. The structures not only provide a large number of internal channels for the diffusion and aggregation of pollutants and H_2O_2 but also effectively encapsulate the active sites, preventing their agglomeration or dissolution to form iron sludge. Such 3D macroscopic structures render the convenience in recycling. In addition, aerogels and hydrogels are characterized by their own properties. The former has extremely low density and high mechanical strength, whereas the latter possesses an excellent adsorption capacity for organic pollutants and heavy metals in aqueous solution. In general, 3D graphene-based composite catalysts are the future directions of graphene-based photo-Fenton systems.

Loading active components on 2D/3D graphene is challenging, considering its large surface that is prone to fold. In addition, the traditional synthetic method of GO is complex and not eco-friendly. Thus, researchers should still pursue the synthesis of highly active graphene-based composites with stably and evenly loaded active substances by using simple, low-cost, and eco-friendly methods. Moreover, 3D graphene-based materials do not necessarily have to be in the form of aerogels or hydrogels because both forms lack robustness and are costly in synthesis and reactivation. For example, recent studies have used sponge as a cheap and robust support of graphene-based Fenton catalysts for the treatment of actual wastewater. The synthesis was simpler and cheaper than traditional methods. It provided excellent inspiration for the future preparation of 3D graphene-based materials. In sum, graphene materials still have promising application potential in photo-Fenton reactions and industrial water treatment.

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