



Recent Progress of Photocatalytic Fenton-Like Process for Environmental Remediation

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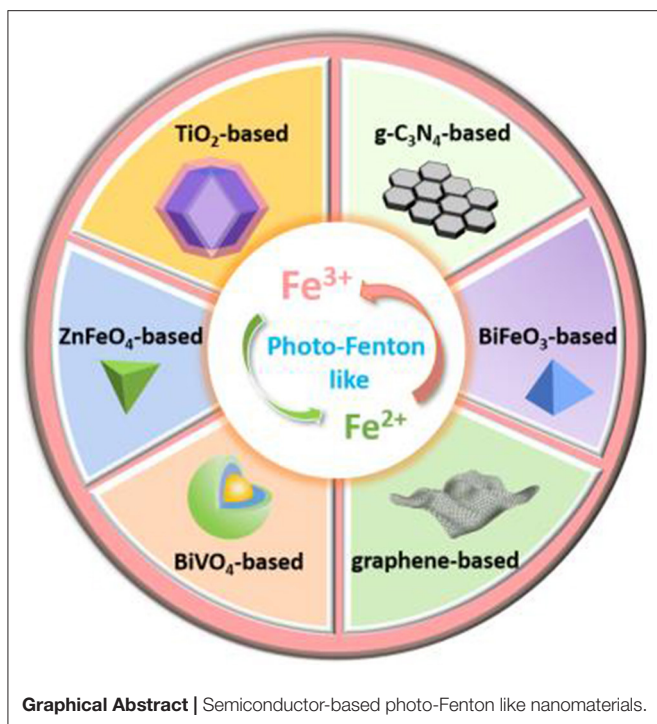
Over the past few decades, Fenton process has been widely studied in environmental remediation. Due to the low efficiency of iron ions recycling, the Fenton efficiency has been seriously impeded for practical application. On this condition, with combination of photocatalysts, it is expected to fully use photo-generated electrons, thus enhancing the photo-Fenton efficiency. This synergistic methodology has assisted many researchers to remove various categories of organic pollutants in discharged wastewater or achieve gas conversion. This comprehensive review describes some significant advances with respect to presentative semiconductors (e.g., TiO₂, g-C₃N₄, graphene, BiVO₄, ZnFeO₄ and BiFeO₃, etc.) including their preparation methods, characterization and applications in environmental remediation (e.g., organic removal, bacteria disinfection, membrane separation, and gas conversion). The mechanism is preferentially discussed. Possibly future development and its correlated potential challenges are specifically proposed and discussed in this review.

Keywords: photocatalytic Fenton reaction, organic pollutant degradation, disinfection, volatile organic compound (VOC), membrane

INTRODUCTION

In recent decades, the aqueous environment arising from a great variety of contaminants, for instance, emerging contaminants (ECs) including pharmaceuticals and personal care products (PPCPs), dyes, endocrine-disrupting compounds (EDCs), flame retardants (FRs), pesticides, and their metabolites pose a major concern to human beings (Esplugas et al., 2007; Klammer et al., 2013). Although their concentration in real sewage is in the $\mu\text{g L}^{-1}$ - ng L^{-1} range, they unconsciously discharge into the environment and biologically accumulate in human body, thus posing a severe threat to receiving waters (e.g., rivers, aquifers and groundwater) (Zhang et al., 2014). To the best of our knowledge, conventional wastewater treatment plants (WWTP) are often unable to entirely degrade persistent organic pollutants (Jelic et al., 2011; Klammer et al., 2013). Consequently, the pollutants and their metabolites accumulate in the aquatic environment, indirectly they may cause ecological risk. As a result, the alternatively advanced technique is of paramount importance to be developed.

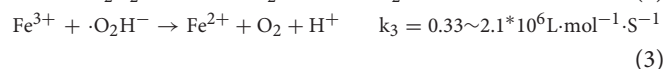
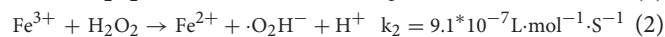
Advanced oxidation processes (AOPs), which have been proposed as replaceable solutions for degrading persistent organic compounds, because the hydroxyl radicals ($\cdot\text{OH}$) are



unselectively promote organic substances oxidation at high reaction rates (Zhang et al., 2009; Sun et al., 2020). Besides this, AOPs are also called as versatile technologies owing to the various alternative ways in generation hydroxyl radicals (Lee and von Gunten, 2010). In comparison with conventional treatment techniques, AOPs are more efficient and capable of degrading recalcitrant pollutants. In AOPs, a variety of oxidants such as hydrogen peroxide (H_2O_2) (Dong C. et al., 2018; Xing et al., 2018a), persulfate (Matzek and Carter, 2016; Wang and Wang, 2018), peroxymonosulfate (Shao et al., 2017; Tan et al., 2017; Duan et al., 2018; Lei et al., 2019; Ma et al., 2019; Shen et al., 2019), permanganate (Guo et al., 2018; Chow and Sze-Yin Leung, 2019; Wang et al., 2019), and ozone (O_3) (Khan et al., 2017; Ikehata and Li, 2018) have been employed to degrade organic matters. Among these oxidants, H_2O_2 has been widely recognized as economically and environmentally friendly oxidant, according to its high efficacy and environmental friendliness.

In short, the combination of Fe^{2+} and H_2O_2 are called conventional Fenton reaction, which belong to a type of classical AOPs. Since 1894, H.J.H Fenton proposed the concept of Fenton process, he found that Fe^{2+} and H_2O_2 could degrade tartaric acid. Thus, it has been widely used in environmental remediation in the following decades (Jain et al., 2018). As the merits of Fenton progress, it is normally operated under ambient temperature and pressure (Qian et al., 2017, 2018a), and generate strongly oxidizing radical species (primarily $\cdot\text{OH}$) for the complete decomposition of organic pollutants into non-toxic products, such as CO_2 , H_2O and inorganic salts (Dong C. et al., 2018). Besides this, the advantages of Fenton process over other WWTPs are extremely superior, including of higher removal efficiency, no residues and wide region for treating substances as well as no need of special equipment. The conventional Fenton

mechanism, which is involved with $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, is exhibited as the following equations:



However, the conventional decomposition efficiency of H_2O_2 in $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system is constrained by the low $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle, owing to the low reaction rate constant of Equation (2). Therefore, the key to enhance the Fenton efficiency is accelerating the reaction constant of Equation (2); meanwhile, the iron sludge will be greatly reduced due to the high efficacy of $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle.

Besides Fenton process, photocatalytic oxidation has been considered as alternative and efficient AOP as well. Photocatalysis based AOPs initiate the complex chain reactions, and it may produce the colorless organic intermediates. Correspondingly, these colorless intermediates maybe more toxic than the parent molecular. Additionally, all of the Fenton reactions including conventional Fenton process and Fenton-like or photo-Fenton-like process easily produce iron mud, and it needs a large amount of manpower and chemicals to treat and remove iron mud. Thus, to achieve a thorough mineralization of organic compound is the main goal of AOPs in environmental remediation. After retrospection of the past few decades, it can be found that many studies have utilized the nano-photocatalysts for the degradation of organic pollutants; however, the utilization efficiency of photo-generated electrons and holes still remains a challenge for researchers in WWTPs. Based on this background information, many researchers have coupled Fenton reaction with photocatalysis as a novel technique to treat wastewater, which can be assigned to novel Fenton-like reaction. By means of this, it is able to realize a win-win situation. To be more specific, it can not only prolong the lifetime of photo-generated carries [i.e., photo electrons (e^-) and hole (h^+)], but also the photo-generated electrons will accelerate the cycle of $\text{Fe}^{3+}/\text{Fe}^{2+}$, leading to higher mineralization of pollutant and the reduction of iron sludge.

In this paper, we mainly review and summary several representative nanomaterials, which have been applied in photocatalytic Fenton reaction, including of TiO_2 -based, $\text{g-C}_3\text{N}_4$ -based, reduced graphene oxide (RGO)-based and other semiconductors-based nanomaterials (e.g., Ag, BiVO_4 , ZnFeO_4 , and BiFeO_3 based nanomaterials). This review mainly aims to review the nanomaterials based AOPs that are used for degradation of different organic pollutants in wastewater or volatile organic compounds (VOCs) removal and provide some effective information for developing latest solution of WWTPs.

TiO_2 -BASED PHOTOCATALYTIC FENTON REACTION

Removing Organic Pollutant

Since 1972, Fujishima and Honda (1972) found that titanium oxide (TiO_2) could split water to produce hydrogen under UV light irradiation, thus opening up a new era of titanium oxide (TiO_2) in photocatalysis. Up to now, TiO_2 has been

TABLE 1 | Summary of TiO₂ based heterogeneous photo-Fenton and photo-Fenton like process under light irradiation.

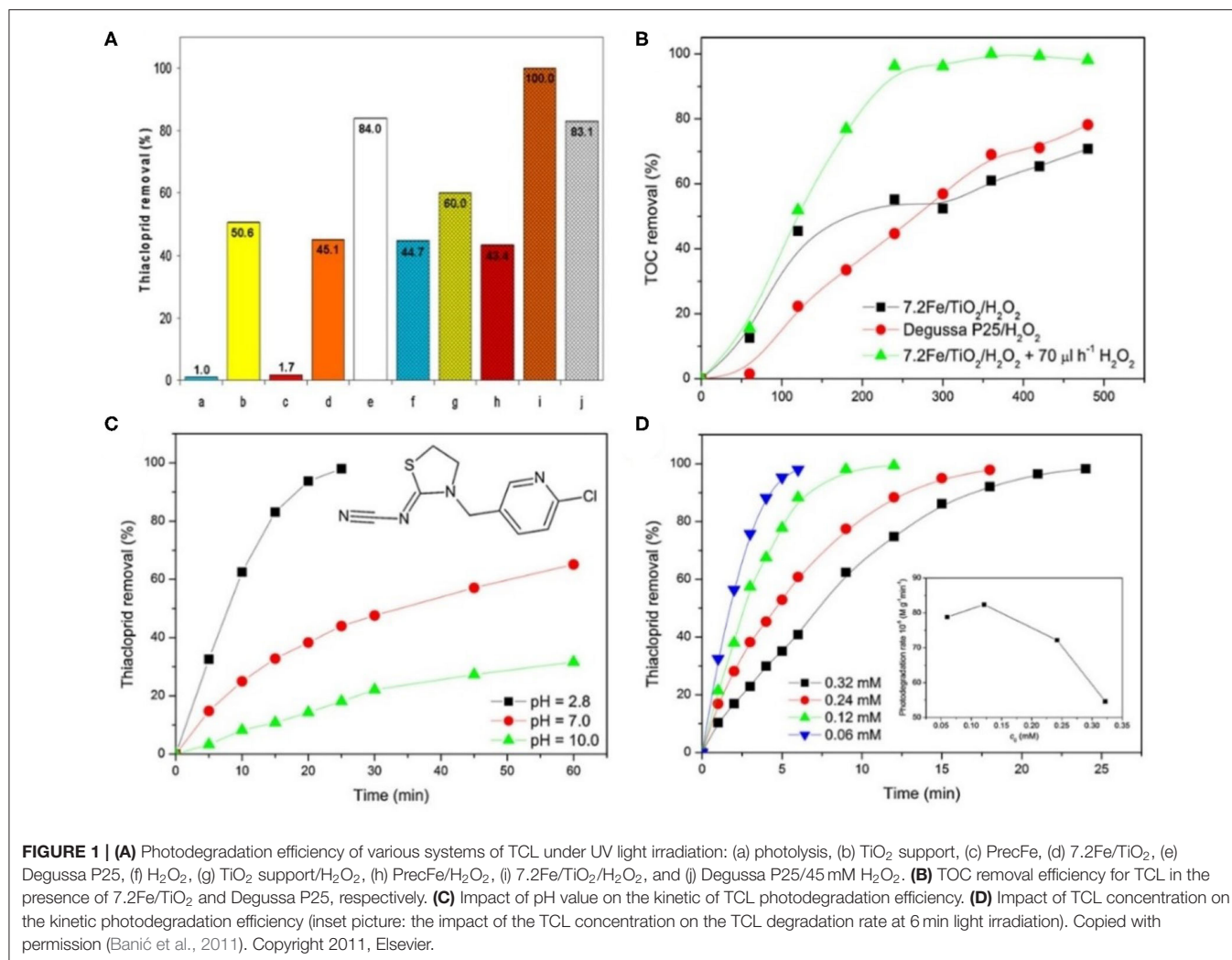
Catalyst	Target pollutant	pH	Catalyst dose	H ₂ O ₂ dose	Reaction time	Light source	Decolorization	References
ZnSe/TiO ₂	10 mg/L pentachlorophenol	5.0	100 μM Fe ³⁺	75 μM	120 min	Solar light	99% discoloration	ThanhThuy et al., 2013
Fe-VT	100 mg/L orange X-GN	3.0	0.5 g/L	3.92 mM	80 min	UV light	98.7% discoloration, 54.4% TOC removal	Chen et al., 2010
TiO ₂	40 ppm 3-chloropyridine	2.8	0.88 mM Fe ²⁺ , 700 mg/L TiO ₂	8.8 mM	60 min	UV light	100% TOC removal	Ortega-Liébana et al., 2012
TiO ₂	0.1 mM phenol and benzoic acid	6.0	0.25 mM Fe (III), 1.0 g/L TiO ₂	10 mM	120 min	UV light	phenol 100%, BA: 96%	Kim et al., 2012
Fe-TiO ₂	2.1 × 10 ⁻⁴ mol L ⁻¹ phenol	6.4	0.2 g/L	0.015 mM	300 min	UV light	20%	Tryba et al., 2006
Fe-C-TiO ₂	2.1 × 10 ⁻⁴ mol L ⁻¹ phenol	2.8	0.2 g/L	0.015 mM	120 min	UV light	98% degradation removal	Tryba et al., 2006
Fe-TiO ₂	0.32 mM thiacloprid	2.8	1.67 g/L	45 mM	500 min	UV light	100% TOC removal	Banić et al., 2011
CdS/MWCNT-TiO ₂	50 mM methylene blue	3.5	0.75 g/L	0.6 mM	120 min	Visible light	98% discoloration and 83% TOC removal	Kim and Kan, 2015

well-applied in the fields of energy and environment, including organic removal (Vaiano et al., 2015; Shayegan et al., 2018; Chen et al., 2019; Dong et al., 2019), hydrogen production (Zhang et al., 2012; Xi et al., 2014; Xing et al., 2015; Zhou Y. et al., 2016), CO₂ reduction (Yu et al., 2014; Dong et al., 2018a; Xing et al., 2018b), nitrogen fixation (Comer and Medford, 2018; Li C. et al., 2018; Zhao et al., 2019), and methane conversion (Wang P. et al., 2017; Yu et al., 2017), etc. Attributed to the sufficiently high reduction potential, low economical cost and high stability, TiO₂ has attracted great attention as one of the most potential and influential photocatalysts (Dong et al., 2018b). In terms of photocatalytic Fenton reaction, especially, TiO₂ based nanomaterials have been developed. Consequently, Photo-Fenton oxidation process employed modified TiO₂, Fe²⁺ or Fe³⁺, and H₂O₂ under light irradiation, leading to significant improved generation of hydroxyl radicals and degradation efficiency of organic pollutants owing to synergy between photocatalysis and Fenton reaction. Some examples have been summarized in **Table 1**.

In **Table 1**, we have listed some representative work in recent years. In 2012, Ortega-Liébana et al. (2012) developed Fe²⁺/TiO₂/H₂O₂/UV system for the degradation of 40 ppm 3-chloropyridine. The results showed that photo-Fenton process is more efficient than sole TiO₂ photocatalysis, which meant that this technique possessed more practical industrialized application than photocatalysis. As to some modified TiO₂ nanomaterials, for instance, Tryba et al. (2006) prepared Fe-TiO₂ and Fe-C-TiO₂ nanomaterials, which could effectively degrade phenol. The highly efficient decomposition of phenol on Fe-C-TiO₂ photocatalysts mainly attributed from several factors: (1) the produced hydroxyl radicals in Fenton process; (2) the reduction of Fe³⁺ back to Fe²⁺ under UV light; (3) the cocatalytic effect of hydroquinone. Additionally, Banić et al. (2011) prepared Fe/TiO₂ materials with various loading amount of Fe₂O₃ nanoparticles. The 7.2Fe/TiO₂/H₂O₂ system

exhibited the highest activity for removing TCL among all the used AOPs (**Figures 1A,B**). In **Figure 1A**, it could be observed that 1.67 g L⁻¹ 7.2Fe/TiO₂/45 H₂O₂ system achieved 100% removal efficiency after 25 min. However, in this case, TiO₂ only acted as a good support, because the degradation efficiency of 7.2Fe/TiO₂ is lower compared to the TiO₂ support, indicating the presence of Fe under UV irradiation did not contribute to the catalytic activity of the material, and not facilitating the cycle of Fe³⁺/Fe²⁺. Moreover, the results indicated that the removal efficiency was influenced by some possible parameters including pH and TCL concentrations (**Figures 1C,D**). In **Figure 1C**, the optimal pH value was fixed at 2.8. As to TCL concentrations, when TCL concentration exceeded 0.12 mM, the reaction rate tended to slow down (**Figure 1D**), ascribed to that most of the 7.2Fe/TiO₂ active sites were occupied, leading to reduced generation of reactive oxygen species.

When it comes to coupled semiconductor, ThanhThuy et al. (2013) prepared ZnSe/TiO₂ nanocomposites. Under simulated solar light, the ZnSe sensitized TiO₂ nanotube arrays exhibited remarkable capability for photocatalytic degradation of pentachlorophenol assisted with photo-Fenton system (i.e., Fe³⁺/H₂O₂/humic acid). The results showed that 99.0% of pentachlorophenol could be degraded in comparison with pure TiO₂ NTAs (64.0%) after 2 h solar light irradiation. Further, Kim and Kan (2015) synthesized CdS/carbon nanotube-TiO₂ (CdS/CNT-TiO₂), which was applied in heterogeneous photo-Fenton process as well. The heterogeneous photo-Fenton oxidation cocatalyzed by CdS/CNT-TiO₂ was mainly engaged in the combination of the photocatalytic, photo-Fenton and photosensitizing oxidation. Consequently, the photo-Fenton process achieved a high decolorization (98%) and mineralization rate (83%). To the best of our knowledge, the concentration of ferrous and ferro ferric ion as well as hydrogen peroxide is of great necessary for enhancing treatment efficiency and minimizing operating costs. In **Figure 2A**, firstly, it was found

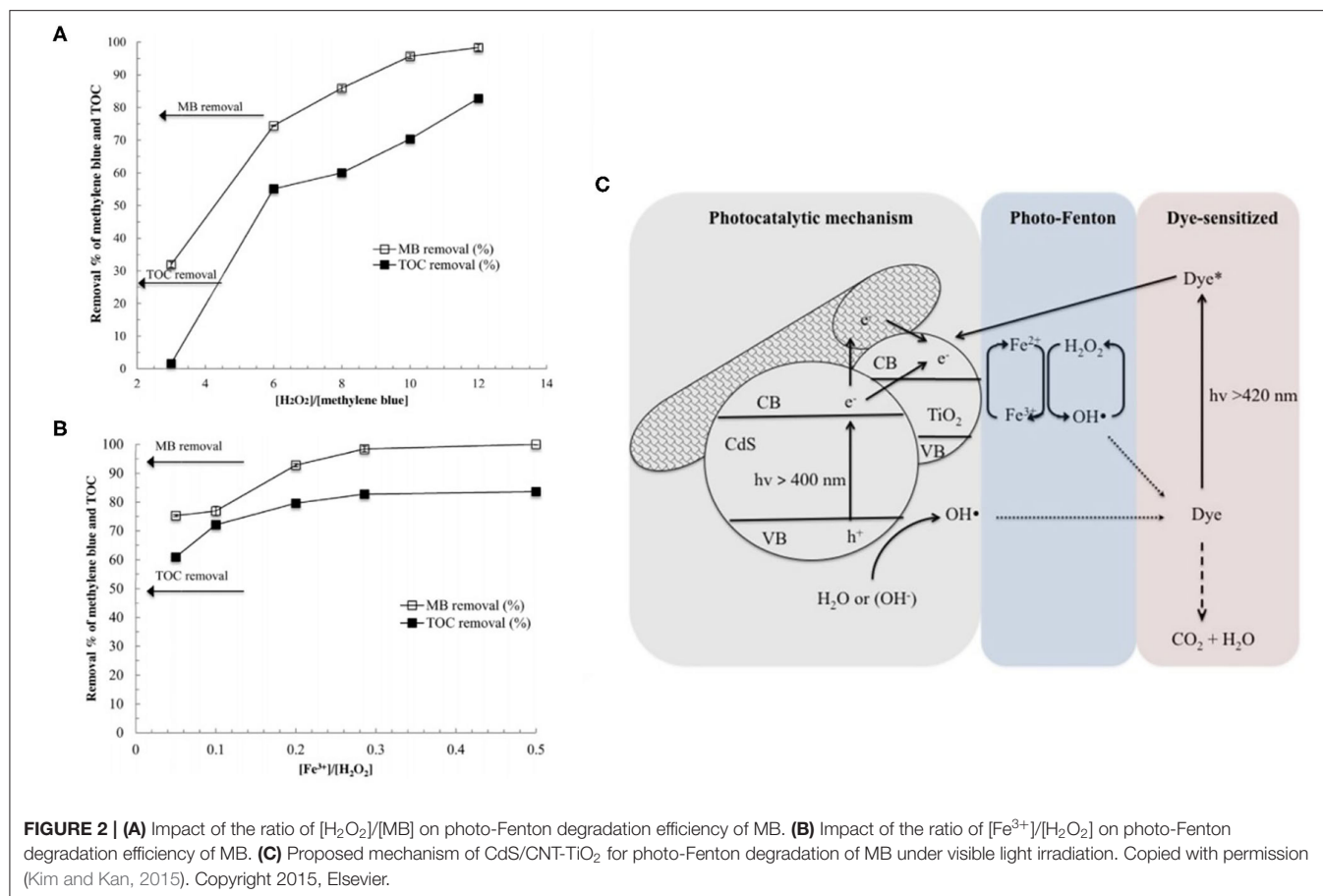


that degradation and TOC removal efficiency of MB can be increased to 99 and 83%, respectively. Secondly, the ratio of $[\text{Fe}^{3+}] : [\text{H}_2\text{O}_2]$ increased from 0.05 to 0.5 led to the MB removal efficiency to 100%; meanwhile, the TOC removal efficiency could be increased from 61 to 84% (**Figure 2B**). The detailed mechanism has been proposed in **Figure 2C**. Specifically, the photo-induced electron (e_{cb}^-) on the surface of TiO₂ can be scavenged by oxygen, whereas the photo-induced hole (h_{vb}^+) can react with OH⁻ or H₂O. Afterwards, the electrons transferred to these adsorb Fe³⁺ ions on TiO₂ surface, leading to the cycle of Fe³⁺/Fe²⁺. Simultaneously, the electron on TiO₂ surface would possibly impede the electron-hole recombination. Lastly, MB molecular acting as photosensitizer would form MB* under visible light irradiation. The electron transfer between the MB* and Fe³⁺ would be beneficial to regenerating Fe²⁺, which accelerated the kinetic rate of the photo-Fenton process.

Disinfection

Apart from the organic pollutant removal, photo-Fenton process serving for water disinfection has emerged in recent decades.

Commonly, according to the rules, two main solutions are able to be adopted if researchers want to employ photo-Fenton process to bacterial inactivation, including of drinking water disinfection and secondary effluent from municipal wastewater treatment plants (MWWTPs) (Giannakis et al., 2016). In terms of the target microorganisms, especially *E. coli* K12, was mostly selected as studied target. Regarding TiO₂ on disinfection, the earliest systematic study was reported mainly based on photocatalytic water disinfection for *E. coli* inactivation (Rincón and Pulgarin, 2004a,b). Afterwards, Rincón and Pulgarin (2006) compared Fe³⁺ and TiO₂ assisted system. Several systems have been established (e.g., UV-vis/TiO₂, UV-vis/TiO₂/H₂O₂, UV-vis/Fe³⁺/H₂O₂, and UV-vis/H₂O₂). It was revealed that the disinfection rate of TiO₂ could be accelerated if H₂O₂ existed. Herein, TiO₂ itself can show disinfection efficiency of *E. coli*, acting as photocatalyst, which can produce hydroxyl radicals under UV-vis irradiation. After addition of H₂O₂, the photoinduced charge transfer will be effectively separated because H₂O₂ acting as electron acceptor, thus preventing the recombination of electron-hole pairs, and generating much



more $\cdot OH$ radicals. In **Figure 3A**, it could be clearly seen that TiO₂/H₂O₂ system is more efficient than Fe³⁺/H₂O₂ system. Compared to the dark controls in **Figure 3B**, the irradiation of solar light could promote the bacterial inactivation. H₂O₂ alone did not obviously impede the *E. coli* survival, whereas TiO₂ could increase its bactericide oxidation ability.

In this section, TiO₂ based nanomaterials have been briefly introduced in the field of organic pollutant removal and disinfection of bacteria in wastewater. Regarding of this, TiO₂ based nanomaterial is expected to perform as well as in actual usage.

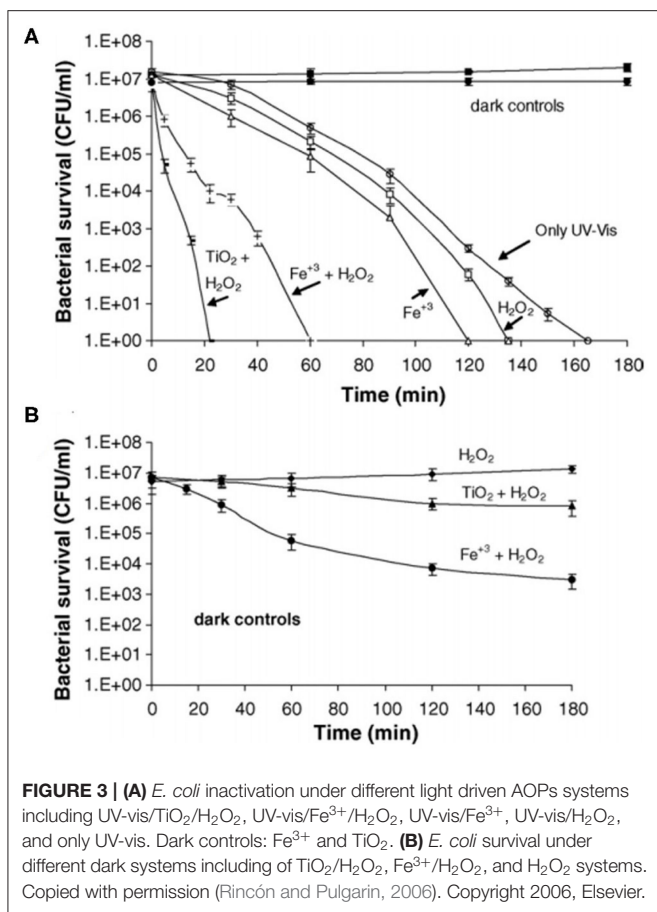
g-C₃N₄-BASED PHOTOCATALYTIC FENTON REACTION

Due to the simple synthesis method, good physical and chemical stability and earth abundant characteristics, graphite carbonitride (g-C₃N₄) has attracted scientists attention in terms of energy conversion and environmental remediation (Lan et al., 2019). As to homogeneous Fe²⁺/H₂O₂ Fenton process, the water-soluble Fe²⁺ catalyzed H₂O₂ to produce hydroxyl radical; however, traditional homogeneous catalysts will be constrained by the following drawbacks: (1) low decomposition efficiency of H₂O₂; (2) sludge residue; (3) limited pH value between 3.0 and 4.0 (Qian et al., 2018b). Overall, iron leaching issue has posed

serious problem in acidic aquatic environment. Additionally, g-C₃N₄ nanomaterials have emerged as a promising visible-light-response photocatalyst in organic removal and water splitting (Dong H. et al., 2018; Safaei-Ghomi et al., 2019). In 2012, Cui et al. (2012) firstly reported that visible light excited of g-C₃N₄ catalyzed H₂O₂ to produce $\cdot OH$ radicals. Successively, g-C₃N₄ coupled with various types of Fe-based materials were explored for removing recalcitrant organic pollutants via photo-Fenton process, including of iron minerals (He et al., 2017), Fe(III) (Hu et al., 2016), single molecule iron complex (Chen et al., 2010; Banić et al., 2011), and iron oxide (Zhou L. et al., 2016; Wang et al., 2018) etc. Moreover, carbon nitride-based nanomaterials could serve as photo-Fenton-like membranes (Yu et al., 2018; Lan et al., 2019). Except of above mentioned, Li et al. (2016) constructed solid-gas-interfacial Fenton reaction over alkalized-C₃N₄ photocatalyst in isopropanol photodegradation. The specific illustration will be revealed in this section.

Removing Organic Pollutant

Regarding photo-Fenton degradation of refractory organic pollutants, notably, Zhou L. et al. (2016) has built a highly efficient visible-light-driven heterogeneous photo-Fenton system (i.e., Fe₂O₃/g-C₃N₄/H₂O₂), which demonstrated that Fe₂O₃ nanoparticles were uniformly dispersed onto the surface of g-C₃N₄ (**Figure 4A**) and formed a heterojunction with g-C₃N₄



to enhance the charge separation. It can be clearly observed that Fe₂O₃ nanoparticles uniformly dispersed onto g-C₃N₄ nanosheets in comparison with pristine g-C₃N₄ (Figure 4B). As to degradation efficiency, the result was clarified in Figure 4C. The photo-Fenton capacity of Fe₂O₃/g-C₃N₄ was investigated for removing MO aided by H₂O₂ under visible-light irradiation. From the figure curves, it can be obtained that all the Fe₂O₃/g-C₃N₄ exhibited superior degradation efficiency than pure Fe₂O₃ and g-C₃N₄ as well as g-C₃N₄+Fe₂O₃. The absorbance intensity of MO decreased gradually with time as shown in Figure 4D. Moreover, the kinetic constant of photo-Fenton degradation efficiency of Fe₂O₃/g-C₃N₄ was determined as shown in Figure 4E. Significantly, the *k*-value of Fe₂O₃/g-C₃N₄ is about 45.4 times higher than that of Fe₂O₃, 8.4 times higher than that of g-C₃N₄ and 7.2 times than that of g-C₃N₄+Fe₂O₃, respectively. Based on experimental analysis, a possible mechanism is proposed in Figure 4F. Once irradiated with visible light, the electron-hole pairs will be produced from both of Fe₂O₃ and g-C₃N₄; meanwhile, the interfacial charge transfer promoted by the contact between Fe₂O₃ and g-C₃N₄ will further enhance the charge separation efficiency. The highly efficient efficiency not only arose from the photo-generated holes reacting with water molecular to produce hydroxyl radicals, but also the photo-induced electrons will be utilized to produce hydroxyl radicals. The generated electrons in the CB of Fe₂O₃ and transferred from

the CB of g-C₃N₄ will contributed the conversion between Fe³⁺ and Fe²⁺. Overall, the generation rate of hydroxyl radicals which produced during Fenton process will be accelerated, thus leading to the enhancement of degradation efficiency. In addition, the fully consumption of photo-induced electrons during Fenton process will ulterior promote the charge separation, introducing more holes devoting to degradation process. Lastly, the catalytic activity can be greatly enhanced if photocatalysis technique joint with Fenton process were employed in one system.

Differentiate with the sole Fe₂O₃ nanoparticles, Guo et al. (2019) constructed a Z-scheme hetero-structured α-Fe₂O₃@g-C₃N₄ catalyst, which was obtained by calcination of melamine and Fe-based MOF. Commonly, MOFs are mainly used to prepare metal oxide nanoparticles, which can inherit the merits of metal oxide acting as sacrifice templates. The morphology characterization has been shown in Figure 5A. Regarding the TC degradation efficiency, by adjusting the addition amount of MIL-53 (Fe), the researchers obtained the optimized composite, which exhibited excellent photo-Fenton performance for the removal of TC (Figure 5B). The corresponding degradation kinetic rate was calculated in Figure 5C, the *k*-value of FOCN-0.45 (0.042 min⁻¹) was 6, 7, and 14 times, compared to that of pristine MIL-53 (Fe) (*k* = 0.007 min⁻¹), α-Fe₂O₃ (*k* = 0.006 min⁻¹), and g-C₃N₄ (*k* = 0.003 min⁻¹), respectively. As to reactive species, the scavenger results in Figure 5D demonstrated that ·OH was the dominant species, accompanied with O₂⁻ and h⁺ co-participating in the degradation of TC. The specific mechanism of photo-Fenton reaction over Z-scheme hetero-structured α-Fe₂O₃@g-C₃N₄ was shown in Figure 5E. Generally, g-C₃N₄ and α-Fe₂O₃ can be both excited under visible light (420 nm) irradiation to produce photo-induced electron (e⁻) and hole (h⁺). Owing to the Z-scheme structure, a proportion of electrons of the CB of α-Fe₂O₃ would be prone to transferring to the VB of g-C₃N₄. The electron of CB for g-C₃N₄ would react with O₂ to produce superoxide radicals to degrade pollutants. Because of the CB position of α-Fe₂O₃ more negative than the standard potential of Fe³⁺/Fe²⁺ (0.77 V vs. NHE), thus the electrons of α-Fe₂O₃ were able to participate in the cycling of Fe³⁺/Fe²⁺, leading to activating H₂O₂ to generate hydroxyl radical. As to the holes in the VB of α-Fe₂O₃, the VB position of α-Fe₂O₃ (1.98 V vs. NHE) was lower than the potential of OH⁻/·OH (1.99 V vs. NHE). Consequently, the accumulated holes in the VB of α-Fe₂O₃ directly degraded the organic pollutants.

Furthermore, some other novel g-C₃N₄ based nanomaterials have been progressed in photo-Fenton application. For instance, Palanivel et al. (2019) rationally designed an effective heterostructure (ZnFe₂O₄/g-C₃N₄) nanocomposite, which showed good photo-Fenton performance for degradation of 20 mg/L MB. Besides Fe₂O₃ nanoparticles, Sahar et al. (2017) prepared Fe₃O₄/g-C₃N₄ nanoparticles mainly throughout electrostatic self-assembly effect, exhibiting an obviously enhanced Fenton, photo-Fenton and peroxidase-like efficiency. To achieve the goal of easy access of recycling, Wang H. et al. (2017) synthesized magnetic BaFe₁₂O₁₉/g-C₃N₄ nanocomposites, which showed excellent capacity and recyclability for removing RhB. The enhanced photocatalytic performance was mainly attributed to the synergy of BaFe₁₂O₁₉

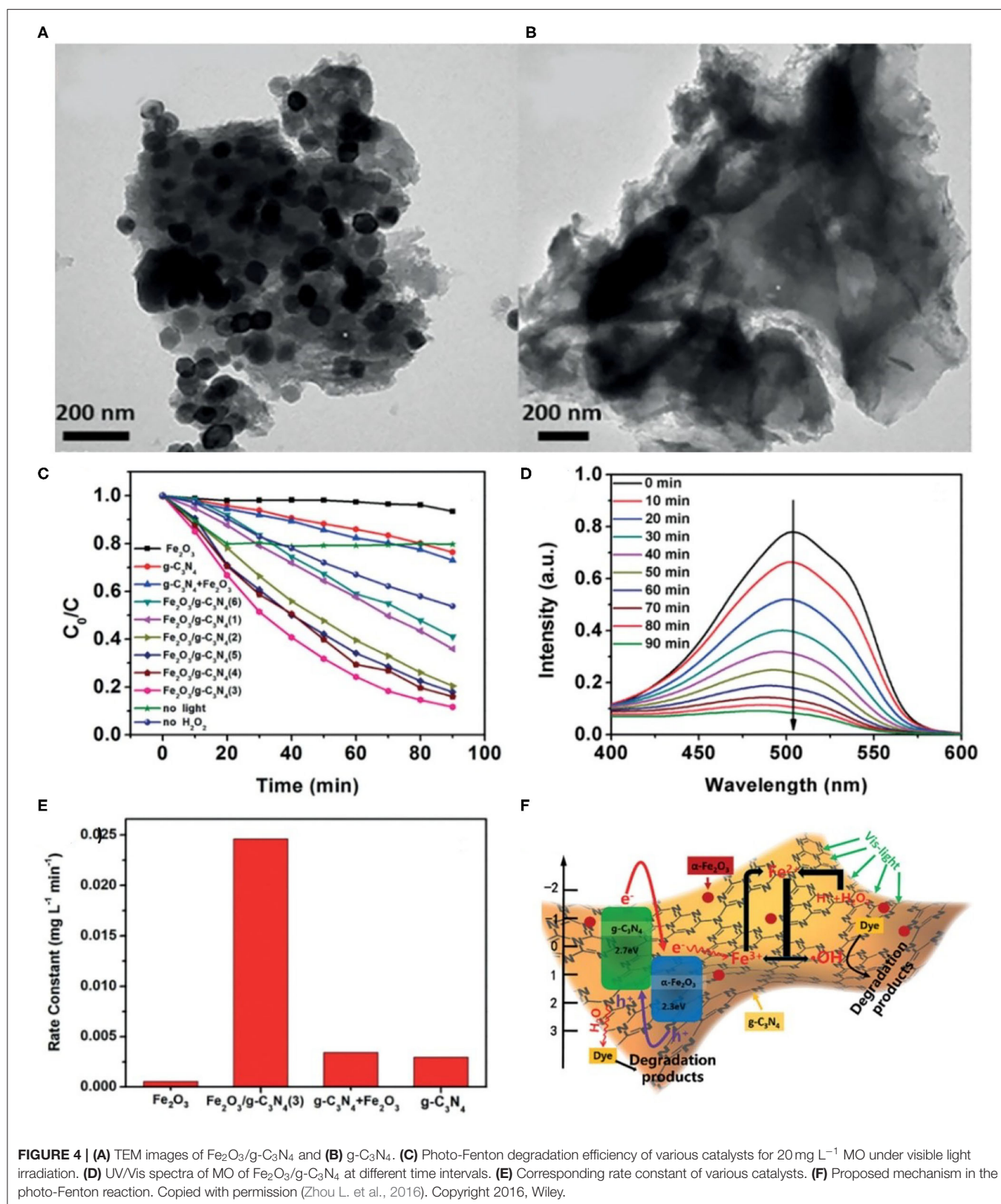


FIGURE 4 | (A) TEM images of $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ and **(B)** $\text{g-C}_3\text{N}_4$. **(C)** Photo-Fenton degradation efficiency of various catalysts for 20 mg L⁻¹ MO under visible light irradiation. **(D)** UV/Vis spectra of MO of $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ at different time intervals. **(E)** Corresponding rate constant of various catalysts. **(F)** Proposed mechanism in the photo-Fenton reaction. Copied with permission (Zhou L. et al., 2016). Copyright 2016, Wiley.

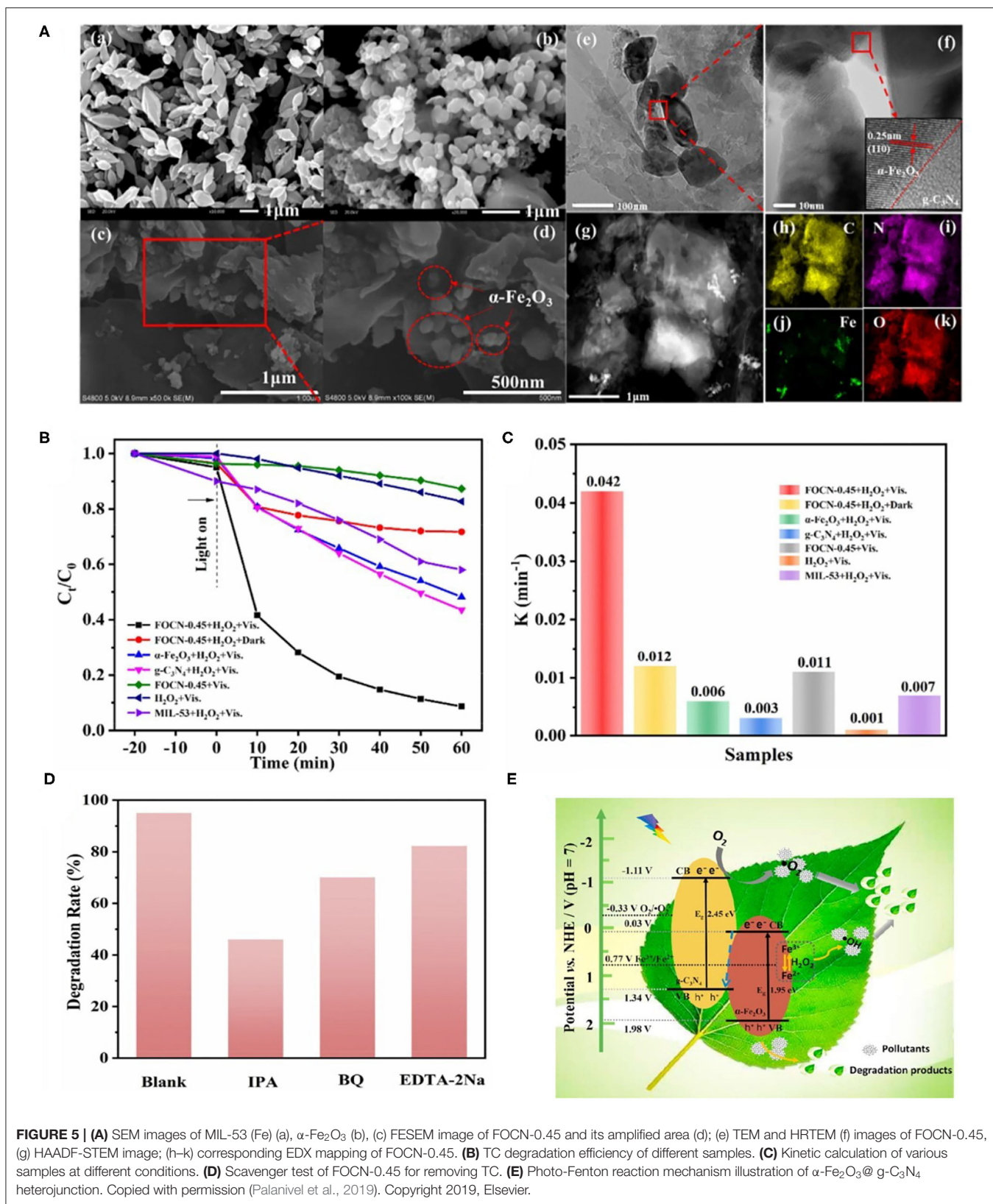


FIGURE 5 | (A) SEM images of MIL-53 (Fe) (a), α - Fe_2O_3 (b), (c) FESEM image of FOCN-0.45 and its amplified area (d); (e) TEM and HRTEM (f) images of FOCN-0.45, (g) HAADF-STEM image; (h–k) corresponding EDX mapping of FOCN-0.45. **(B)** TC degradation efficiency of different samples. **(C)** Kinetic calculation of various samples at different conditions. **(D)** Scavenger test of FOCN-0.45 for removing TC. **(E)** Photo-Fenton reaction mechanism illustration of α - Fe_2O_3 @g- C_3N_4 heterojunction. Copied with permission (Palanivel et al., 2019). Copyright 2019, Elsevier.

TABLE 2 | Summary of C₃N₄ based heterogeneous photo-Fenton like process under visible light irradiation.

Catalyst	Target pollutant	pH	Catalyst dose	H ₂ O ₂ dose	Reaction time	Decolorization	References
g-C ₃ N ₄ /FeOCl	50 mg/L tetracycline 10 mg/L rhodamine B	/	0.2 g/L 0.2 g/L	2 mM	60 min	90%	Zhao et al., 2020
g-C ₃ N ₄ -IMD-FePcCl ₁₆	Carbamazepine (CBZ)	7.0	0.1 g/L	5 mM	100 min	100%	Chen X. et al., 2017
g-C ₃ N ₄ /LaFeO ₃	10 mg/L rhodamine B	/	0.5 g/L	5 mM	120 min	100%	Ye et al., 2018
Fe-doped g-C ₃ N ₄	20 mg/L phenol, bisphenol A, 2, 4dichlorophenol	/	1.0 g/L	8.0 mM	50 min	100%	Hu et al., 2019
Oxygen doping C ₃ N ₄ (HS g-C ₃ N ₄ -O)	Rhodamine B	/	0.5 mg cat, 1.0 mM FeCl ₃	20 mM	50 min	100%	Guo et al., 2016
Cu ₂ (OH)PO ₄ /g-C ₃ N ₄	10 mg L ⁻¹ RhB	/	0.02 g cat	10 mM	40 min	100%	Chen et al., 2015
Zn _{1-1.5x} Fe _x S/g-C ₃ N ₄	10 mg/L p-nitrophenol (PNP)	/	0.8 g/L	1 mM	60 min	96%	Wang et al., 2020
Fe-g-C ₃ N ₄ /GMC	50 mg/L Acid Red 73	/	0.8 g/L	40 mM	40 min	99.2%	Ma et al., 2017

and g-C₃N₄, thus facilitating charge separation, and thereby promoted the photo-Fenton efficiency. For more examples, we have specially summarized many other excellent g-C₃N₄ based nanomaterials in **Table 2**.

Volatile Organic Compounds (VOCs) Removal

Apart from the liquid-phase Fenton reaction, Li et al. (2016) constructed a solid-gas interfacial Fenton system, which is joint with an alkalized g-C₃N₄ based photocatalyst, converting the photogenerated H₂O₂ into reactive oxygen species (ROS). This powerful case contains light acting as driving force, alkalized g-C₃N₄-based photocatalyst as an *in-situ* H₂O₂ collector and surface-coated Fe³⁺ as a trigger for H₂O₂ conversion, thus achieving efficient activity of VOCs photodegradation. For instance, taking the photo-oxidation of isopropyl alcohol as a model. Specifically, **Figure 6A** showed the generation rate and apparent quantum yield (AQY) of acetone and CO₂ at about 420 nm of each CNK-OH&Fe catalyst with various Fe³⁺ loadings. Notably, the CNK-OH&Fe samples exhibited an increasing photocatalytic capacity accounting for the loading amount of Fe³⁺. Consequently, when the loading amount 1.4 wt%, it exhibited the optimal efficiency, signifying the increasing amount of Fe³⁺ loading not only promoting the utilization rate of photoelectron as well as suppressing the light absorption of catalyst. The IPA photooxidation rate of the optimal CNK-OH&Fe sample achieved ca. 270 folds higher than that of pristine C₃N₄ (**Figure 6B**). In **Figure 6C**, the generating H₂O₂ was difficult to be observed over CNK-OH&Fe, attributing to the generated H₂O₂ quickly reacting with Fe²⁺ and the photoelectrons quickly reducing Fe³⁺ to form ·OH radicals. To confirm the truth of H₂O₂ converting into ·OH radicals over CNK-OH&Fe, EPR test were performed. It was found that apart from the direct ·OH formation of surface hydroxyl radicals inducing from holes, the CNK-OH&Fe indeed triggered the Fe²⁺ and H₂O₂ converting into ·OH. On one hand, the enhanced efficiency was arising from the conversion of electrons promoting the generation of reactive radicals (e.g., ·OH and ·O₂⁻ radicals) via the solid-gas interfacial Fenton process. On the

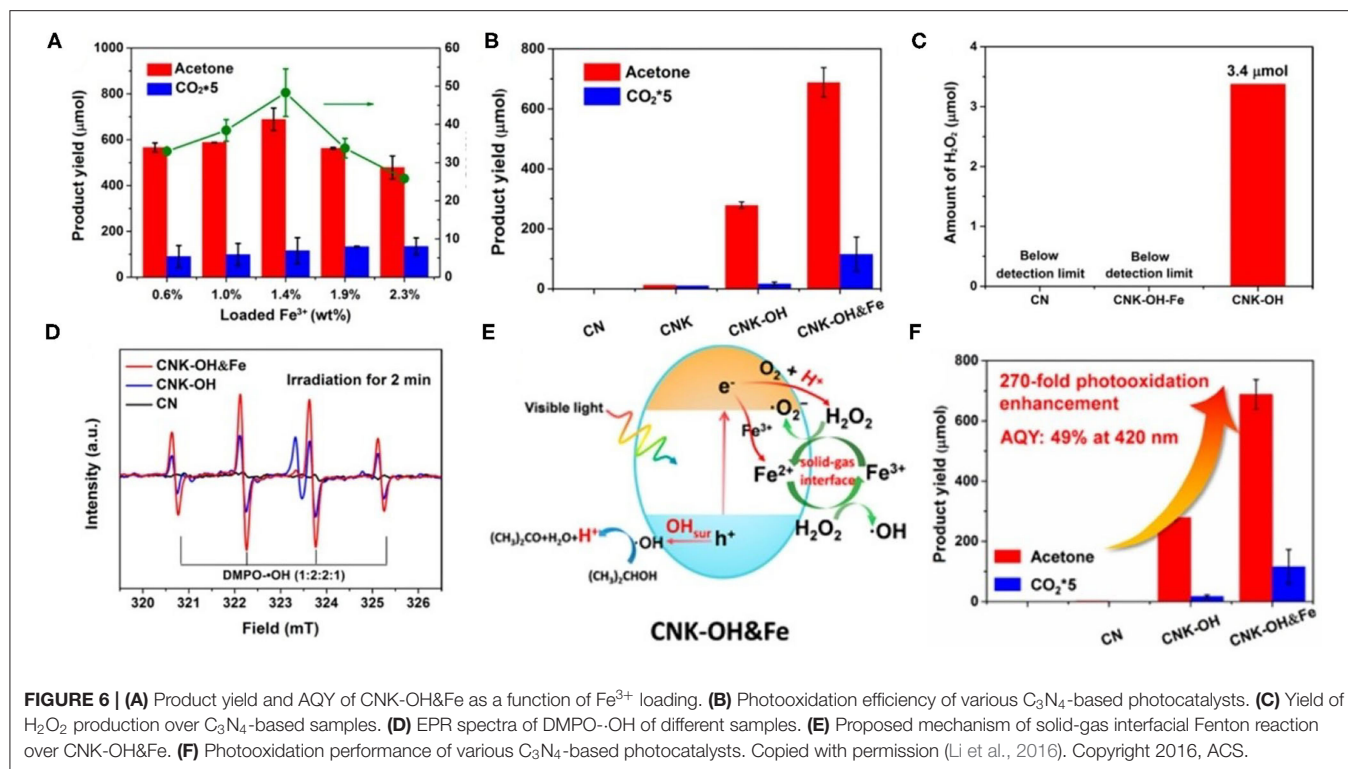
other hand, the hydroxyl and Fe³⁺ species determined the *in-situ* protons production and Fe²⁺/Fe³⁺ formation. In **Figure 6D**, the amount of hydroxyl radicals over CNK-OH&Fe was ca. 4.0 times than that of CNK-OH. **Figure 6E** elaborately illustrated the possible mechanism over CNK-OH&Fe catalyzed isopropanol conversion. As to quantum yield, in **Figure 6F**, compared with the pristine C₃N₄, more than two orders of magnitude of conversion rate were obtained, which is equivalent to AQY of 49% around 420 nm. In addition, it is expected that this discovery is not only unique for C₃N₄-based nanomaterials, but provide a useful guidance for other semiconductors which can be alkalized on surface (e.g., WO₃ and SrTiO₃) should also provide the same light-driven Fenton process. It is expected that this will open a low economic cost and facile way to employ solar energy to effectively eliminate gaseous organic pollutants.

Photo-Fenton-Like Membranes for Wastewater Treatment

Membrane separation, a potential water treatment technology that has caused global attention to energy shortages and environmental pollution crises. In the last few decades, a vast amount of polymer and inorganic membranes have been deeply developed. Particularly, reverse osmosis (RO), plays a pivotal role in the generation of high-standard purified water, and simultaneously removes a vast number of contaminants (e.g., total dissolved solids, pathogens and organic pollutants).

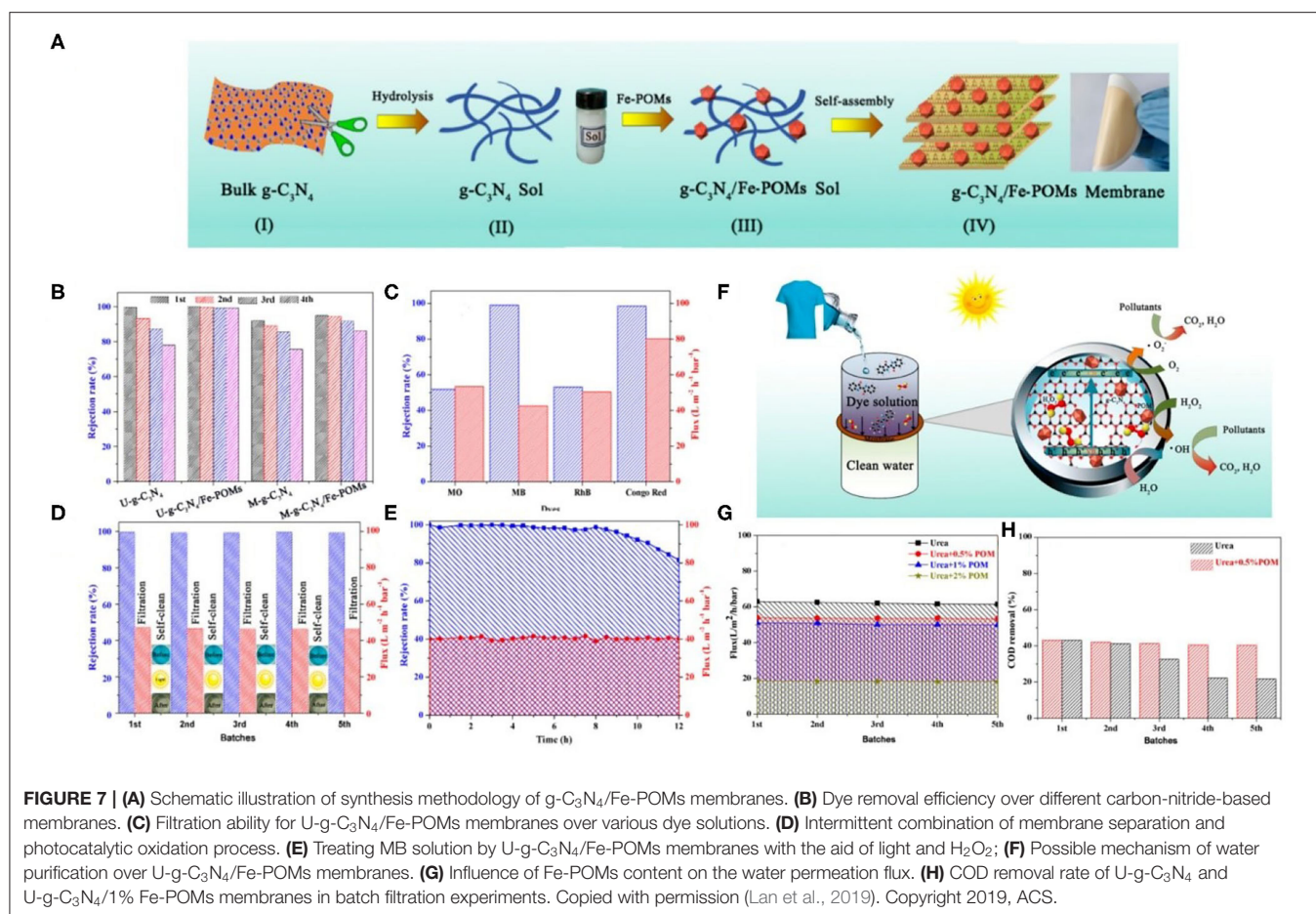
In membrane development history, the thin film composite (TFC) polyamide membranes, thin film nanocomposite (TFN) membranes, molecular layer-by-layer (mLBL) membranes and self-assembled artificial water channels, carbon nanotubes (CNTs), microporous metal-organic frameworks (MOFs), graphene, graphene oxide, and MoS₂ incorporated membranes have been deeply developed and studied; however, to meet all the demands of high-quality membranes including high selectivity, evitable stability and anti-fouling capabilities as well as high permeation flux, is still a huge challenge (Yang et al., 2016, 2018; Tang et al., 2018).

Interestingly, carbonaceous materials are gradually recognized as promising candidates for designing high-performance membranes, including of 1D carbon nanotubes,



2D graphene as well as its derivatives. However, for the practical application of carbon materials, it is limited by the difficulty of manufacturing densely arranged nanostructures. In addition, as to graphene-based membranes, it is necessary to greatly enhance the permeability and structural stability of the membrane. Therefore, it is of paramount importance to constructing membranes with feasible mass transfer resistance and water permeation flux. It is worth noting that graphite carbon nitride (g-C₃N₄) is expected to establish a new platform for the development of innovative membranes with excellent separation and self-cleaning properties, especially ultra-thin g-C₃N₄ nanosheets. On this condition, for the first time, Lan et al. (2019) innovatively manufactured g-C₃N₄-based catalytic membrane by soft self-assembly method for water purification. This membrane is mainly based on the nanochannels in g-C₃N₄ nanosheets and heterogeneous catalysis engaging in Fe-containing polyoxometalates. As shown in **Figure 7A**, the synthetic method of photo-Fenton-like membrane has been briefly described. Continuous modification of large amounts of g-C₃N₄ is beneficial to forming g-C₃N₄ sol (step II). Afterwards, customized g-C₃N₄ sol molecules with abundant amino and hydroxyl functional groups, provide enough active sites for Fe-POM nucleation (step III). After that, the self-assembly of the dispersion is filtered through a polycarbonate filter membrane to perform a carbonitride-based membrane treatment (Step IV). As shown in **Figures 7B–E**, the performance of POM incorporated into a g-C₃N₄ membrane was evaluated by pumping wastewater into membrane. First, the effect of carbon nitride microstructure was studied. As shown in **Figure 7B**, MB

molecules can be completely removed from the water by g-C₃N₄ membrane. Compared with the melamine-derived membrane, the urea-derived sample showed much better removal efficiency. Moreover, the versatility of Ug-C₃N₄/Fe-POMs membranes in water purification was tested by filtering various dye molecules, as shown in **Figure 7C**. The results indicated that the synthesized membranes are capable of intercepting methyl blue (MB), Congo red (CR), methyl orange (MO), and rhodamine B (RhB) is extremely effective. In **Figure 7D**, the unique nanochannels in Ug-C₃N₄/Fe-POM ensured that contaminant molecules are completely removed through each filtration process. Therefore, if coupled with light irradiation and H₂O₂, this membrane exhibited stable water flux and good repelling ability (**Figure 7E**). In addition, a possible mechanism was proposed in **Figure 7F**. It was revealed that periodic atomic vacancies and structural defects in tri-s-triazine are conducive to the nanopores on the surface of the g-C₃N₄ layer. It is convinced that the gap between layers of carbon nitride provided a shortcut to dyes molecular diffusion. The modification of Fe-POMs significantly improved the separation performance of carbon nitride. In actual sewage treatment, the membranes were verified by pumping actual textile wastewater (initial COD: 290 mg L⁻¹) over Ug-C₃N₄/Fe-POMs membranes. Generally, the greater the amount of Fe-POM in the membrane, the higher the rejection rate, and the smaller the permeation flux of water (**Figure 7G**). As can be seen from **Figure 7H** that the addition of Fe-POMs posed a significant impact on the COD removal performance. Therefore, the Ug-C₃N₄/Fe-POMs membrane maintained the same COD rejection rate and permeable flux after five



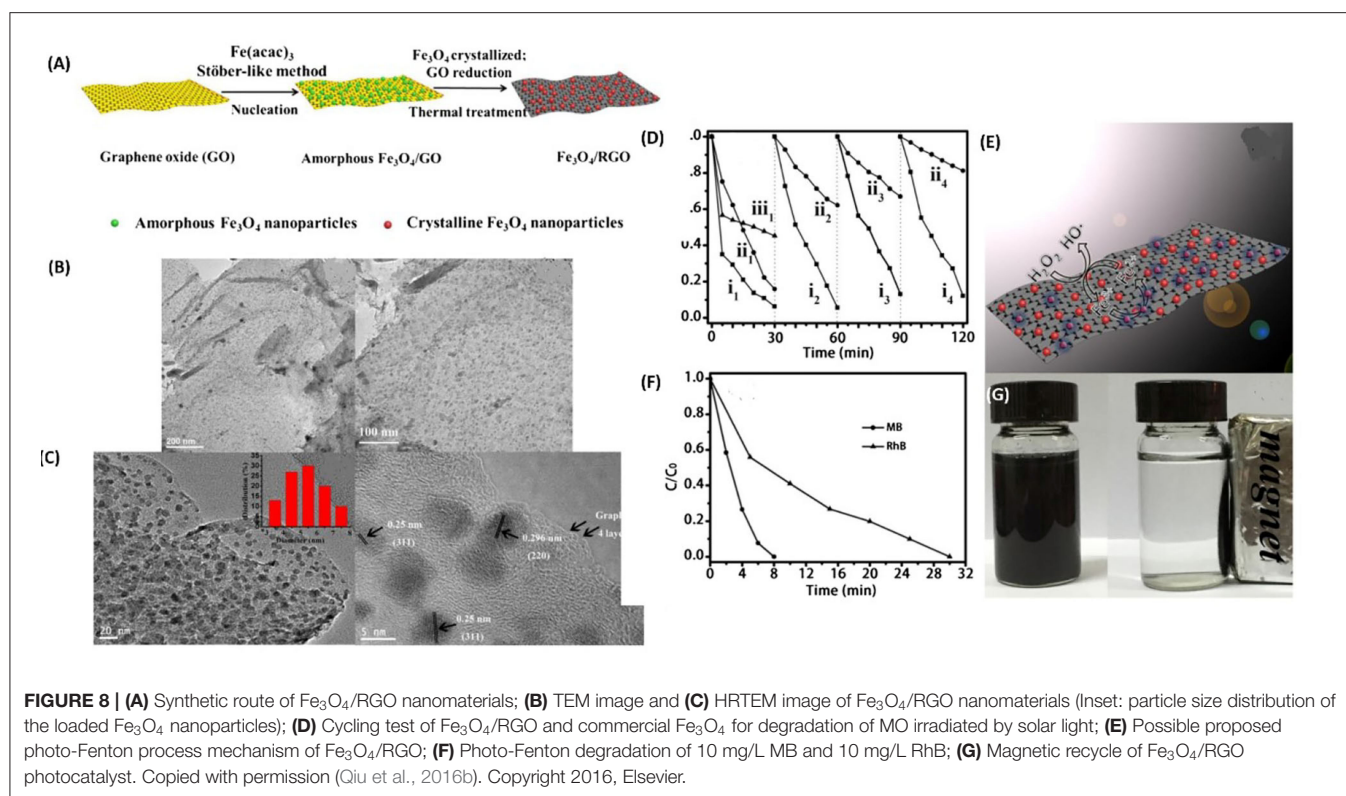
batches of treatment. It well reveals the merits of self-assembled photo-Fenton membrane based on Fe-POM. Overall, this work provides a viable way to develop catalytic carbonitride-based membranes for water purification.

In this section, graphite carbon nitride ($g\text{-C}_3\text{N}_4$) nanomaterials were reviewed for the application of photo-Fenton process in removing organic pollutant, volatile organic compounds (VOCs) removal and membrane separation for wastewater. If irradiated by visible light or solar light, the photo-generated electrons facilitated the cycle of $\text{Fe}^{3+}/\text{Fe}^{2+}$, leading to the enhanced efficiency of organic pollutant and VOCs removal, which is attributed to the simultaneous photocatalytic effect as well as photo-Fenton oxidation process. According to this line of thought, $g\text{-C}_3\text{N}_4$ can be a promising candidate not only in organic pollutant removal but also assist in membrane separation and self-cleaning.

REDUCED GRAPHENE OXIDE (RGO)-BASED PHOTOCATALYTIC FENTON REACTION

Graphene has been recognized as an excellent candidate supporting material owing to its unique physical properties,

such as a high electric potential density, electron mobility, and optical absorption (Nair et al., 2008; Mayorov et al., 2011). In the field of environmental remediation, for instance, graphene is usually employed as a good support for loading nanomaterials, such as TiO_2 , ZnO , Fe_2O_3 , CdS , Co_3O_4 , and CdSe , etc. (Xiang et al., 2012; Guo et al., 2013) With the assistance of graphene, these nanocomposites can be uniformly dispersed onto graphene nanosheets and suppress aggregation, thus enhancing the catalytic efficiency because of excellent specific area and electrical conductivity (Wang et al., 2016). In the broad sense of Fenton process, two-dimensional graphene nanosheets and three-dimensional graphene hydrogel or aerogel have been deeply investigated. In the last decade, graphene-based nanocomposites, such as $\text{Fe}_2\text{O}_3/\text{graphene oxide}$ and $\text{Fe}_3\text{O}_4/\text{RGO}$ composites have been widely studied in removing organic pollutants (Xiang et al., 2012; Qiu et al., 2016b). These reported graphene-based photocatalysts show excellent photocatalytic activity, which is due to the transfer of photogenerated charge from the NPs surface to the graphene surface, thereby promoting the separation of electron-hole pairs and the generation of additional $\cdot\text{OH}$ radicals. In addition, the combination of the aromatic ring of rGO and organic pollutants mainly comes into being $\pi\text{-}\pi$ interaction and electrostatic interaction, which is conducive to the degradation process (Zhang et al., 2009; Sun



et al., 2020). Especially, Fe_2O_3 , FeOOH , and Fe_3O_4 have been reported effective in Fenton reaction. Additionally, the three-dimensional graphene-based hydrogels, as well as aerogels have been investigated a lot in photo-Fenton like reaction. In this section, we will clarify them gradually.

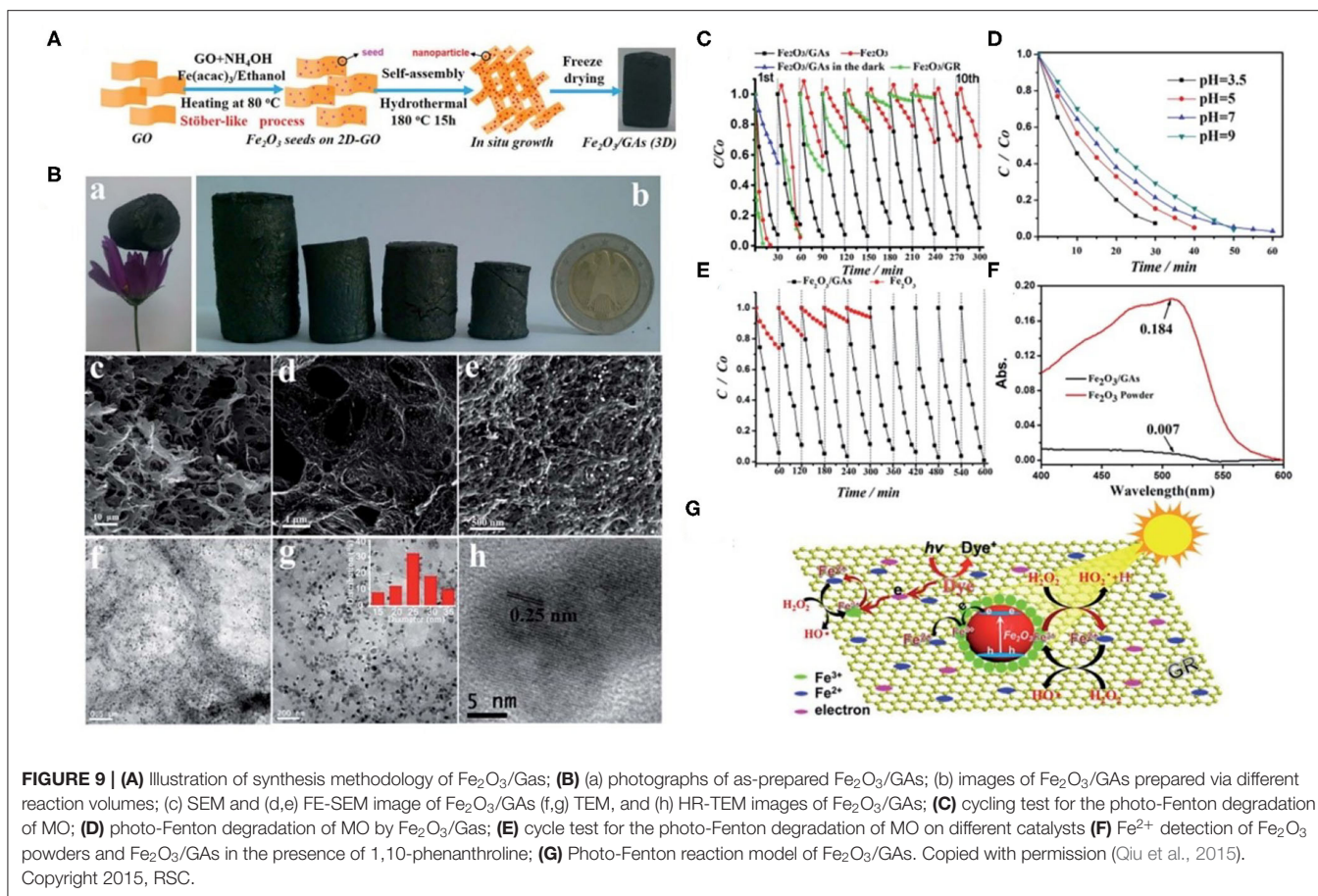
Two-Dimensional Graphene-Based Nanomaterials

In 2016, Wang et al. (2016) prepared $\text{Fe}_3\text{O}_4/\text{HG}$ with hydrophilic graphene (HG) and Fe_3O_4 , which presented high removal efficiency of methyl orange (MO), owing to the rapid transference of photo-generated electrons on the surface of HG to promote the conversion efficiency of $\text{Fe}^{3+}/\text{Fe}^{2+}$. Further, Liu et al. (2017a) developed $\alpha\text{-Fe}_2\text{O}_3$ loaded graphene oxide (GO) nanosheets through a facile hydrolysis process, which showed good Fenton-degradation efficiency for MB as well as rhodamine B, Orange II and Orange G, phenol, 2-nitrophenol and 17-estradiol (E2). An et al. (2013a) synthesized graphene- BiFeO_3 composite for the photo-Fenton degradation of tetrabromobisphenol A. Moreover, Qiu et al. (2016b) innovatively adopted a Stöber-like method to synthesize ultra-dispersed Fe_3O_4 nanoparticles onto graphene, which was applied in photo-Fenton reaction and lithium-battery. As presented in **Figure 8A**, the *in-situ* grown Fe_3O_4 particles were uniformly dispersed on graphene layers via a Stöber-like method. The morphology and structure of the $\text{Fe}_3\text{O}_4/\text{RGO}$ composites have been characterized by TEM and HRTEM, as shown in **Figures 8B,C**, respectively. TEM images showed that the thickness of the RGO plate with highly dispersed Fe_3O_4

nanoparticles is ultrathin (**Figure 8B**). The HRTEM image of the $\text{Fe}_3\text{O}_4/\text{RGO}$ composite (**Figure 8C**) showed that all nanoparticles are well-dispersed on graphene, and the size distribution shows an average size of 3–8 nm. HRTEM images show clear crystal lattices with a pitch of 0.250 and 0.296 nm, corresponding to the (311) and (220) planes, respectively. The photo-Fenton ability was conducted in the presence of H_2O_2 under the irradiation of solar light. Correspondingly, the result showed that the $\text{Fe}_3\text{O}_4/\text{RGO}$ catalyst possessed superior photo-Fenton activity (98%) (**Figure 8D**). The possible mechanism has been illustrated in **Figure 8E**. Once irradiated by solar light, these electrons generating from dyes and Fe_3O_4 NPs transferred to the graphene; meanwhile, Fe^{3+} ions can easily be reduced by photo-electrons back to Fe^{2+} . Consequently, Fe^{2+} continue to react with H_2O_2 to produce more $\cdot\text{OH}$ radicals on the surface of graphene (**Figure 8E**). As a result, the $\text{Fe}_3\text{O}_4/\text{RGO}$ composites possessed an excellent photo-Fenton capacity for degradation of organic dyes (**Figure 8F**), which can be recycled by an extra magnetic (**Figure 8G**).

Three-Dimensional Graphene-Based Hydrogel or Aerogel

Besides the two-dimensional (2D) graphene-based heterogenous catalysts, to achieve the facile recycle of catalysts, three-dimensional (3D) graphene hydrogel or aerogel has been developed by many researchers, such as cobalt ferrite nanoparticles related graphene aerogel (Qiu et al., 2016a), graphene oxide (GO)-carbon nanotubes (CNTs)- FeOOH aerogel (Liu et al., 2017b), stretchable $\text{Fe}_2\text{O}_3/\text{graphene}$ aerogels (Qiu



et al., 2015), reduced graphene oxide nanosheet/ Fe_xO_y /nitrogen-doped carbon layer aerogel (Yao et al., 2019), $\text{Fe}_3\text{O}_4/\text{RGO}/\text{PAM}$ hydrogel (Dong et al., 2018c), etc.

Among these 3D graphene-based materials, especially, the graphene oxide aerogels have attracted tremendous attention in recent years, which is a new category of porous 3D framework, owing to its large surface-to-volume ratio, good electron mobility and conductivity, superior mechanical stability, and good adsorption capacity (Leary and Westwood, 2011). In a broad sense, 2D layered structures equipped with sp^2 - and sp^3 -hybridized carbon atoms are assembled in hexagonal rings, making graphene a useful building block for matrix self-assembly, whereas graphene aerogel can be effectively prevent graphene sheets from stacking. Generally, doping a metal oxide into porous 3D structure can effectively suppress stacking; meanwhile, these 3D aerogels possess huge surface area, fast mass and electron transfer kinetics, short diffusion paths in the matrix and good mechanical strength (Sui et al., 2012).

In addition, some previous studies have reported that nanoscale iron oxide in graphene aerogels, which possessed few defects, are especially effective for photo-Fenton degradation of phenols and more complex benzene ring compounds. For example, Qiu et al. (2015) reported three-dimensional (3D) Fe_2O_3 *in-situ* grown on graphene aerogels via Stöber-like method, as shown in **Figure 9A**. The obtained $\text{Fe}_2\text{O}_3/\text{GAS}$

exhibited a 3D macroscopic appearance (**Figure 9B**, inset a) and an ultralight materials property. With the reaction volume increasing, the obtained $\text{Fe}_2\text{O}_3/\text{GAS}$ increase in size (**Figure 9B**, inset b). The SEM image of $\text{Fe}_2\text{O}_3/\text{GAS}$ indicated that the $\text{Fe}_2\text{O}_3/\text{GAS}$ possessed a 3D macroporous structure (**Figure 9B**, inset c, d). Fe_2O_3 nanocrystals are well-embedded into graphene sheets (**Figure 9B**, inset e). TEM results further confirmed the highly dispersed Fe_2O_3 nanocrystals on the surface of graphene (**Figure 9B**, inset f, g). HRTEM image of $\text{Fe}_2\text{O}_3/\text{GAS}$ revealed that d-spacing lattice fringes is ca. 0.25 nm, which corresponded to the (110) planes of Fe_2O_3 (**Figure 9B**, inset h). Subsequently, $\text{Fe}_2\text{O}_3/\text{GAS}$ was investigated for the solar-light-driven Fenton reaction in the presence of H_2O_2 for the degradation of 10 mg/L MO solution (**Figures 9C–E**). The highly photo-Fenton reaction activity was mainly caused by the conversion of $\text{Fe}^{3+}/\text{Fe}^{2+}$ instead of the adsorption. Unlike $\text{Fe}_2\text{O}_3/\text{GR}$, the 3D-GAS can prevent the Fe^{2+} from dissolving in the solution owing to its channels and confinement effect. Besides the acidic conditions, the pH value can be adapted to neutral condition at 7.0, and the corresponding Fenton efficiency of $\text{Fe}_2\text{O}_3/\text{GAS}$ still keeps at a high level, which is much higher than pristine Fe_2O_3 (**Figures 9D, E**). It is well-known that $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle plays a crucial role in Fenton reaction. The excessive Fe^{3+} ions easily produce iron sludge in the aqueous solution, thus deactivating and poisoning the catalyst. In Fenton process, Fe^{3+} ions can

capture the photo-induced electrons and be reduced to Fe^{2+} , thus a high concentration of Fe^{2+} ions, which is complexed with phenanthroline can be detected in the solution (**Figure 9F**). The three-dimensional frame can effectively prevent the dissolution of iron. Once irradiated by solar light, the electrons can be both excited from dyes and Fe_2O_3 nanocrystals, which will transfer to the graphene (**Figure 9G**), leading to positive ions (e.g., Fe^{2+} and Fe^{3+}) adsorbed onto the negative-charge graphene. These Fe^{3+} ions will subsequently capture photo-induced electrons and react with H_2O_2 to produce Fe^{2+} ions again.

Additionally, Liu et al. (2018) used non-toxic sodium ascorbate as reductant to synthesize $\text{FeO}(\text{OH})$ /reduced graphene oxide aerogel ($\text{FeO}(\text{OH})$ -rGA) by means of facile and green-chemistry approach. The stable anchorage can ensure the circulation rate and reduce the leaching of iron, thereby ensuring the effective degradation of toxic phenolic compounds under visible light irradiation. Overall, the aerogel obtained not only has a stable structure, but also has significant catalytic activity for the degradation of phenolic organics at neutral pH. Besides this, Dong et al. (2018c) also developed a functional graphene hydrogel equipped with simultaneous photocatalytic Fenton reaction activity for the degradation of organic pollutants and adsorption for the heavy metal ions. These above-mentioned 3D graphene-based hydrogels or aerogels provide researchers a new pathway to process the wastewater treatment.

In a summary, reduced graphene oxide (RGO) based nanomaterials have been extensively employed in photocatalytic Fenton reaction, varying from two-dimensional (2D) nanosheets to three-dimensional (3D) hydrogels or aerogels. Especially, the 2D graphene nanosheets blocked the aggregation of iron oxide nanoparticles, benefiting the electron transferring on graphene and impeding the generation of iron sludge during photo-Fenton process. As to 3D graphene hydrogels and aerogels, it can effectively prevent the stacking of 2D graphene nanosheets by doping of metal ions. Moreover, its 3D-structured shape is suitable for multiple and simple recycling. It is expected that reduced graphene oxide will build a new platform for environmental remediation.

OTHER SEMICONDUCTORS-BASED PHOTOCATALYTIC FENTON REACTION

Except of the TiO_2 -based, graphitic carbon nitride-based and graphene-based nanomaterials, some other semiconductor-based nanomaterials can work as effectively as well in photo-Fenton process, such as Ag (Chen et al., 2016; Zhu et al., 2018a,b), BiVO_4 (Xu et al., 2017; Li X. et al., 2018; Gao et al., 2019), ZnO (Choi et al., 2015; Ojha et al., 2017; Saleh and Taufik, 2019), ZnFeO_4 (Khadgi and Upreti, 2019; Palanivel et al., 2019), and BiFeO_3 (Luo et al., 2010; An et al., 2013b; Jia et al., 2018), etc. In this section, we will make a brief description, including of Ag-based nanomaterials, BiVO_4 -based nanomaterials, ZnFeO_4 and BiFeO_3 based nanomaterials, which all perform well as photo-Fenton like catalysts.

Ag-Based Photo-Fenton Catalysts

In the past few decades, people have paid great attention to the research on the heterogeneous photo-Fenton process for the degradation of organic pollutants. As far as known, the high combination rate of photo-generated carriers will impede its photocatalytic efficiency. Thus, an idea is proposed that the joint of photo-Fenton catalysts with plasmonic materials, this issue might be solved.

Some researchers have reported that Ag/AgCl/Fe-S plasmonic catalyst could effectively degrade bisphenol A in photo-Fenton system under visible light irradiation (Liu et al., 2017c). Further, Zhu et al. (2018b) reported that a novel photo-Fenton catalyst of Ag/AgCl/ferrihydrate could degrade bisphenol A as well, which revealed that the loading of Ag/AgCl could accelerate the conversion of $\text{Fe}^{3+}/\text{Fe}^{2+}$ by the photo-generated electrons transferring from Ag nanoparticles owing to the surface plasmon resonance (SPR) effect. Moreover, Chen et al. (2016) prepared Ag/hematite mesocrystal, which displayed a high photo-Fenton activity in the oxidation of RhB, MO and glyphosate under visible light irradiation.

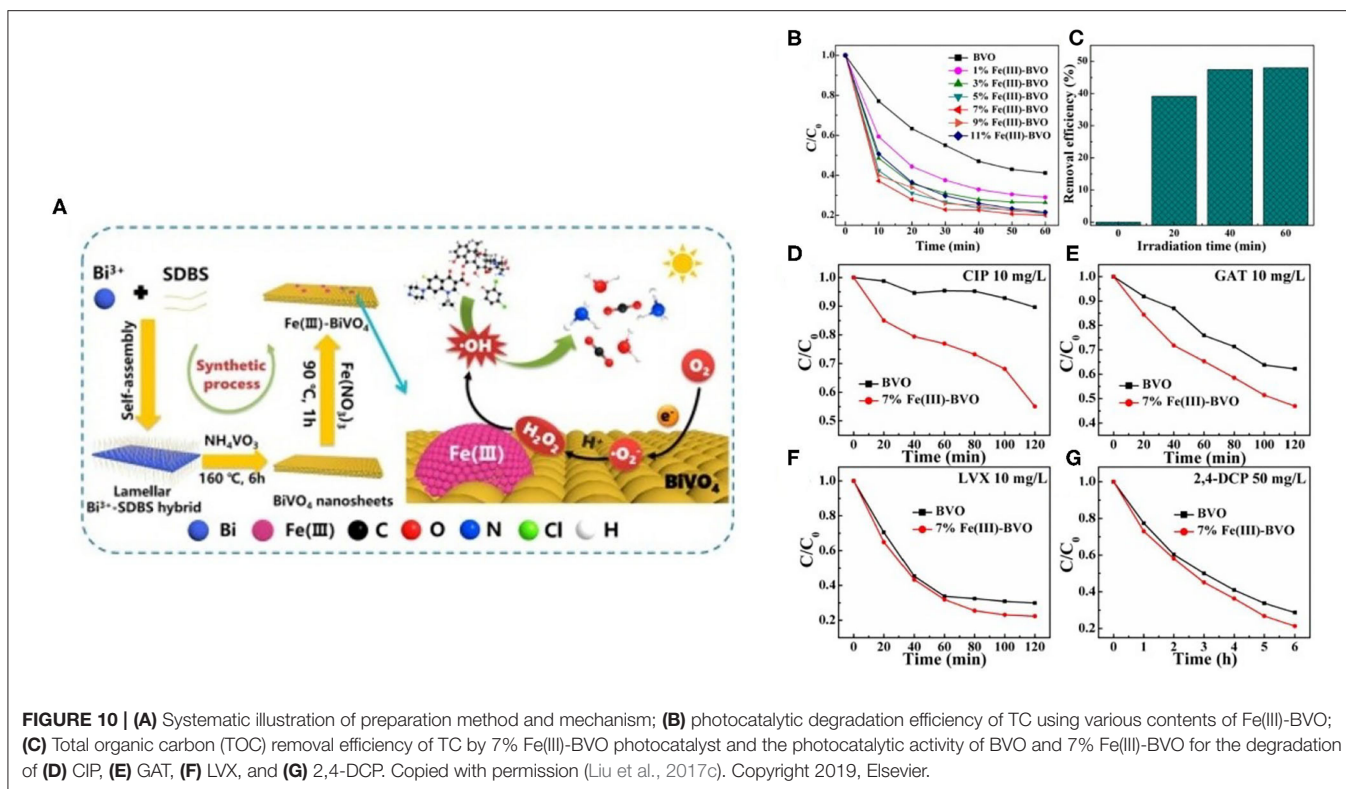
BiVO_4 -Based Photo-Fenton Catalysts

In recent years, BiVO_4 has been well-considered as a typical photocatalyst with narrow band gap. Due to its non-toxicity, good stability and photochemical properties, it has been extensively studied in the treatment of photocatalytic wastewater. In addition, BiVO_4 is a good candidate cocatalyst in photo-Fenton process; however, pure BiVO_4 is constrained by several drawbacks, such as a narrow visible light response range, low specific surface area, and rapid recombination of charged charges. Thus, various modification strategies have been adopted to investigate its potential application including doping ions, heterostructure fabrication, and precious metal deposition.

Specifically, Liu et al. (2017c) synthesized Fe(III) grafted BiVO_4 nanosheets, which was employed for the photodegradation of 2,4-dichlorophenol and antibiotics. The results showed that the Fe^{3+} species not only served as efficient electron scavengers, but also provided more active reaction sites. The detailed mechanism is briefly contained in **Figure 10A**. In **Figure 10B**, pure BiVO_4 merely could degrade ca. 60% of TC under visible-light irradiation. When the mass content of Fe(III) was 7%, the degradation efficiency can be up to 80%. Correspondingly, in **Figure 10C**, the TOC removal efficiency for 7% Fe(III)-BVO could be up to 48% after 60 min. Moreover, quinolones antibiotics, including CIP, GAT, and LVX were selected to be degraded. As shown in **Figures 10D–G**, the photocatalytic degradation efficiency of three antibiotics for Fe(III)-BVO is higher than that of pure BVO. Meanwhile, as an intermediate for the synthesis of pesticides and typical toxic organic compounds, photocatalytic degradation of 2,4-DCP possessed important practical significance for the treatment of wastewater.

ZnFeO_4 and BiFeO_3 Based Fenton Catalysts

ZnFe_2O_4 is a novel semiconductor, which possesses a band gap of about 1.9 eV, showing a visible light response, thus becoming



attractive in the field of visible light-driven photocatalysis (Sun et al., 2013; Zhu et al., 2016). Accordingly, both ZnFe_2O_4 and ZnFe_2O_4 -based composites can act as photo Fenton-like catalysts to improve the degradation rate of organic pollutants in the presence of H_2O_2 (Su et al., 2012; Yao et al., 2014). For instance, Su et al. (2012) reported mesoporous ZnFe_2O_4 (meso- ZnFe_2O_4) prepared by a hydrothermal process. As to photocatalytic degradation of AOII, it showed that AOII almost completely removed in H_2O_2 /visible light system after 2 h. It was revealed that high efficiency for AOII degradation was mainly attributed to the strong absorption of ZnFe_2O_4 in visible-light region and more generation amount of $\cdot\text{OH}$ by H_2O_2 . Further, Fu and Wang (2011) reported that they employed a feasible and facile one-step hydrothermal route to fabricate magnetic ZnFe_2O_4 graphene nanocomposites. The results showed that as prepared photocatalysts could serve as the photoelectrochemical catalysts for organic pollutants removal and the generator of hydroxyl radicals via the decomposition of H_2O_2 under visible light irradiation. Moreover, Chen H. et al. (2017) synthesized $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ nanocomposite to degrade organic dye in the presence of H_2O_2 under near-infrared (NIR) irradiation. It was reported that $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ nanocomposite performed well for the degradation of methyl orange under either UV, visible or NIR irradiation.

Besides ZnFe_2O_4 -based nanocomposites, it is also discovered that BiFeO_3 perform as well in photo-Fenton like process. Generally, BiFeO_3 is recognized as one of the important semiconductors, which possess the ability for visible light response. Additionally, BiFeO_3 is widely accepted to be

a promising visible-light-response photocatalyst for organic pollutant removal and hydrogen production (Bharathkumar et al., 2016). In Fenton-like process, Di et al. (2019) constructed Z-scheme heterojunction $\text{Ag}_2\text{S}/\text{BiFeO}_3$. The morphology of $\text{Ag}_2\text{S}/\text{BiFeO}_3$ was characterized by DF-STEM (Figure 11A). The corresponding elemental maps displayed as well. It showed a uniform elemental distribution of Bi, Fe, O and elements Ag and S. The result suggested that the Ag_2S nanoparticles have been successfully loaded onto the surface of BiFeO_3 . Further, the photocatalytic and photo-Fenton efficiency was tested in Figures 11B,C, respectively. It was found that MO degradation was significantly enhanced with the addition of catalysts and H_2O_2 . The specific mechanism of photocatalytic process and photo-Fenton process have been explained in Figures 11D,E. As far as known, the improved efficiency by photo-Fenton process mainly originated from the reduction of Fe^{3+} ions by photo-generated electrons, thus promoting the decomposition rate of H_2O_2 . In addition, An et al. (2013a) prepared a nanoscale composite of BiFeO_3 and graphene, and used this composite to degrade tetrabromobisphenol A by photo-Fenton-like process, which showed that the graphene- BiFeO_3 composite exhibiting higher catalytic ability. Moreover, some researchers have found that BiFeO_3 -based nanomaterials not only work on photo-Fenton process, but also perform well in sulfate radical based Advanced Oxidation Process (SR-AOP), revealing its vast potential in the field of wastewater treatment.

As above mentioned, some other novel Ag-based nanomaterials, BiVO_4 -based nanomaterials, ZnFeO_4 and BiFeO_3 based nanocomposites were elucidated that effectively

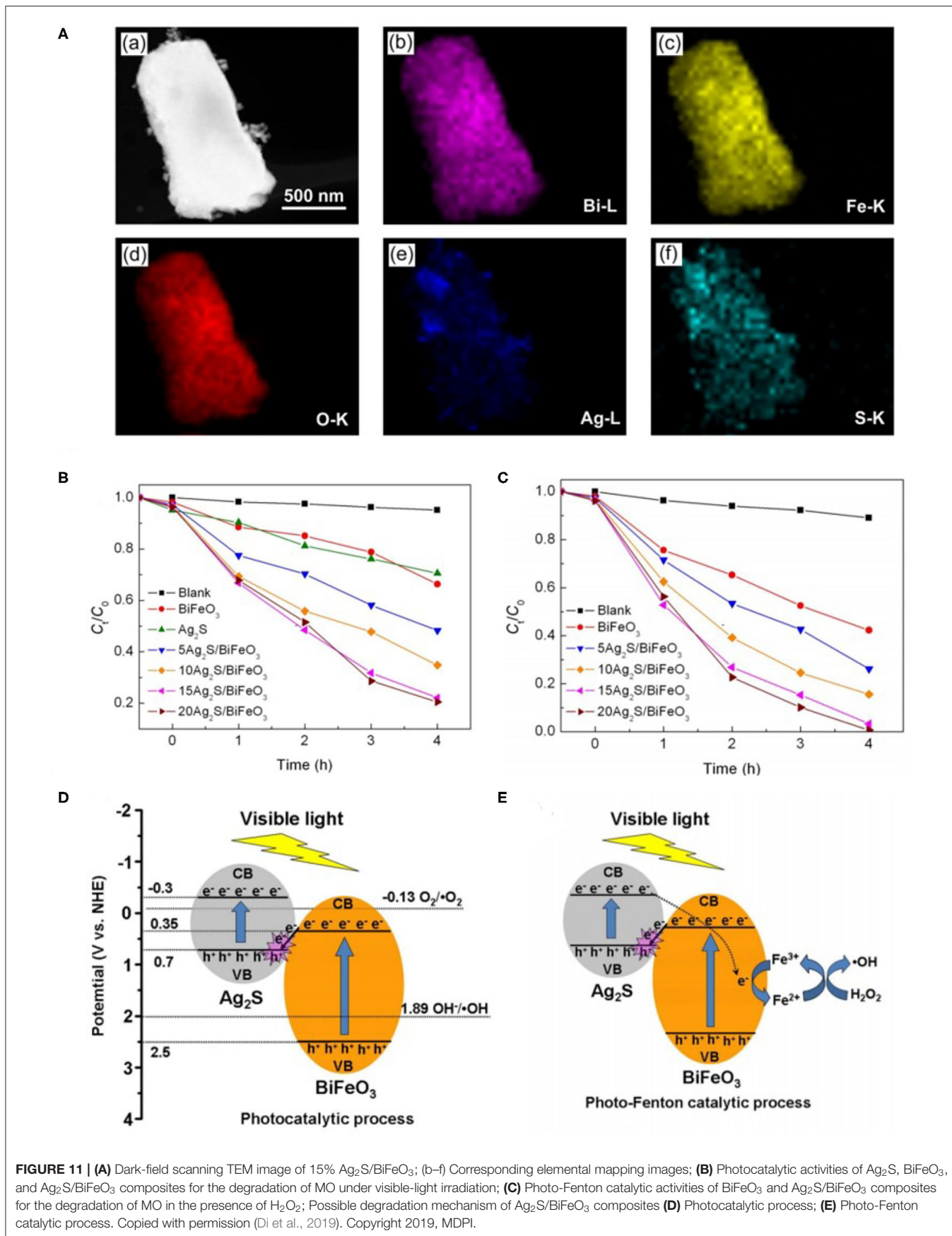


FIGURE 11 | (A) Dark-field scanning TEM image of 15% Ag₂S/BiFeO₃; (b–f) Corresponding elemental mapping images; **(B)** Photocatalytic activities of Ag₂S, BiFeO₃, and Ag₂S/BiFeO₃ composites for the degradation of MO under visible-light irradiation; **(C)** Photo-Fenton catalytic activities of BiFeO₃ and Ag₂S/BiFeO₃ composites for the degradation of MO in the presence of H₂O₂; Possible degradation mechanism of Ag₂S/BiFeO₃ composites **(D)** Photocatalytic process; **(E)** Photo-Fenton catalytic process. Copied with permission (Di et al., 2019). Copyright 2019, MDPI.

work on photo-Fenton reaction, stemming for their property acting as photocatalysts providing photo-electrons, which was involved in the transformation of $\text{Fe}^{3+}/\text{Fe}^{2+}$. On condition of this, there is no doubt that many other novel semiconductor photocatalyst can synergistically improve efficiency of the Fenton process if acting as the dual catalysts.

CONCLUSIONS AND OUTLOOK

In the last few decades, the photo-Fenton and photo-Fenton like process have been progressed a lot. The new developed photo-Fenton or photo-Fenton like process present higher efficiency than that of conventional ones. The key to solve the drawbacks of Fenton process is accelerating the transformation of $\text{Fe}^{3+}/\text{Fe}^{2+}$. Facing with this issue, the worldwide scientists have looked for many methodologies. Firstly, the TiO_2 and modified TiO_2 nanocomposites are able to perform as homogenous or heterogenous photo-Fenton cocatalysts, which focus on speeding up the cycle of $\text{Fe}^{3+}/\text{Fe}^{2+}$, leading to less iron sludge and higher removal efficiency for organic pollutant or bacteria. Secondly, to our best knowledge, graphitic carbon nitride is a new promising candidate in photocatalysis. Various types of iron oxide coupled g- C_3N_4 nanocomposites have been employed in wastewater treatment, VOCs removal and photo-Fenton like membrane separation. Thirdly, graphene is another excellent two-dimensional nanomaterial acting as good support for its good electron transferring capacity and large surface area. On premise that of good activity for 2D structure, three-dimensional graphene-based hydrogel or aerogel have been attempted in photo-Fenton and photo-Fenton like process. As to most of the 3D structural materials, the water-soluble Fe^{2+} ions can be easily anchored onto graphene, which explains why the photo-Fenton efficiency presents so good. In addition, some other semiconductors, such as Ag, BiVO_4 , ZnFeO_4 , and BiFeO_3 based nanomaterials have been reviewed briefly as well. In summary, the existing semiconductors, which are equipped with suitable band gap, large surface area, well-separated photo-generated carriers, which no doubt can be promising candidates in photo-Fenton process. Moreover, in recent years, some other alternative nanomaterials, such as metal disulfides, metal carbides, perovskites, etc. are all expected to provide good reference and efficacy in AOPs. However, facing the actual usage

in industrial treatment, the sophisticated engineers usually focus more on the nanomaterials whether can be applied in actual sewage treatment on a large scale. Hence, the economic cost, recycling issues and stability need to be paid much attention to in the future development. In the field of actual wastewater treatment, the input energy and economic cost are both factors that we should consider in advance. Due to the injurious to human body and limited wavelength region of UV light, developing visible-light-response photocatalysts is a promising way to rationally treat wastewater, so as it can run at ambient temperature and pressure, utilizing atmospheric oxygen or H_2O_2 as oxidant. So far, synthesizing nanomaterials is of high cost, it is of great necessary to synthesize and adopt magnetic nanocomposites, such as Fe_3O_4 -based and cobalt ferrite-based nanocomposites etc. Moreover, catalyst immobilization, which is closely associated with catalyst recovery and agglomeration, as well as the design of photocatalytic reactor are both key research points in the coming years. One possible strategy is heterogenous photo-Fenton like process with membrane processes (PMRs), and the other one is trying to prolong the contact time between solution and immobilized photocatalyst. Many efforts still need to be made to actual application of photo-Fenton-like process in the future development. If feasible, the nanomaterials in photo-Fenton-like process is expected to make a huge progress in environmental remediation.

AUTHOR CONTRIBUTIONS

CD and MX conceived the proposal of this manuscript. CD wrote the paper. MX and JZ gave suggestions on the writing. All authors contributed to the article and approved the submitted version.

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REFERENCES

- An, J., Zhu, L., Wang, N., Song, Z., Yang, Z., Du, D., et al. (2013a). Photo-Fenton like degradation of tetrabromobisphenol A with graphene/ BiFeO_3 composite as a catalyst. *Chem. Eng. J.* 219, 225–237. doi: 10.1016/j.cej.2013.01.013
- An, J., Zhu, L., Zhang, Y., and Tang, H. (2013b). Efficient visible light photo-fenton-like degradation of organic pollutants using *in situ* surface-modified BiFeO_3 as a catalyst. *J. Environ. Sci.* 25, 1213–1225. doi: 10.1016/S1001-0742(12)60172-7
- Banić, N., Abramović, B., Krstić, J., Šojić, D., Lončarević, D., Guzsányi, V., et al. (2011). Photodegradation of thiacloprid using Fe/TiO_2 as a heterogeneous photo-Fenton catalyst. *Appl. Catal. B Environ.* 107, 363–371. doi: 10.1016/j.apcatb.2011.07.037
- Bharathkumar, S., Sakar, M., and Balakumar, S. (2016). Experimental evidence for the carrier transportation enhanced visible light driven photocatalytic process in bismuth ferrite (BiFeO_3) one-dimensional fiber nanostructures. *J. Phys. Chem. C* 120, 18811–18821. doi: 10.1021/acs.jpcc.6b04344
- Chen, C., Zhou, Y., Wang, N., Cheng, L., and Ding, H. (2015). $\text{Cu}_2(\text{OH})\text{PO}_4/\text{g-C}_3\text{N}_4$ composite as an efficient visible light-activated photo-Fenton photocatalyst. *RSC Adv.* 5, 95523–95531. doi: 10.1039/C5RA15965B
- Chen, H., Liu, W., and Qin, Z. (2017). $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ nanocomposite as a broad-spectrum photo-Fenton-like photocatalyst with near-infrared activity. *Catal. Sci. Technol.* 7, 2236–2244. doi: 10.1039/C7CY00308K
- Chen, Q., Chen, L., Qi, J., Tong, Y., Lv, Y., Xu, C., et al. (2019). Photocatalytic degradation of amoxicillin by carbon quantum dots modified $\text{K}_2\text{Ti}_6\text{O}_{13}$ nanotubes: effect of light wavelength. *Chin. Chem. Lett.* 30, 1214–1218. doi: 10.1016/j.ccl.2019.03.002
- Chen, Q., Wu, P., Dang, Z., Zhu, N., Li, P., Wu, J., et al. (2010). Iron pillared vermiculite as a heterogeneous photo-Fenton catalyst for photocatalytic

- degradation of azo dye reactive brilliant orange X-GN. *Sep. Purif. Technol.* 71, 315–323. doi: 10.1016/j.seppur.2009.12.017
- Chen, X., Chen, F., Liu, F., Yan, X., Hu, W., Zhang, G., et al. (2016). Ag nanoparticles/hematite mesocrystals superstructure composite: a facile synthesis and enhanced heterogeneous photo-Fenton activity. *Catal. Sci. Technol.* 6, 4184–4191. doi: 10.1039/C6CY00080K
- Chen, X., Lu, W., Xu, T., Li, N., Zhu, Z., Wang, G., et al. (2017). Visible-light-assisted generation of high-valent iron-oxo species anchored axially on g-C₃N₄ for efficient degradation of organic pollutants. *Chem. Eng. J.* 328, 853–861. doi: 10.1016/j.cej.2017.07.110
- Choi, Y. I., Jung, H. J., Shin, W. G., and Sohn, Y. (2015). Band gap-engineered ZnO and Ag/ZnO by ball-milling method and their photocatalytic and Fenton-like photocatalytic activities. *Appl. Surf. Sci.* 356, 615–625. doi: 10.1016/j.apsusc.2015.08.118
- Chow, C.-H., and Sze-Yin Leung, K. (2019). Transformations of organic micropollutants undergoing permanganate/bisulfite treatment: kinetics, pathways and toxicity. *Chemosphere* 237:124524. doi: 10.1016/j.chemosphere.2019.124524
- Comer, B. M., and Medford, A. J. (2018). Analysis of photocatalytic nitrogen fixation on rutile TiO₂(110). *ACS Sustain. Chem. Eng.* 6, 4648–4660. doi: 10.1021/acssuschemeng.7b03652
- Cui, Y., Ding, Z., Liu, P., Antonietti, M., Fu, X., and Wang, X. (2012). Metal-free activation of H₂O₂ by g-C₃N₄ under visible light irradiation for the degradation of organic pollutants. *Phys. Chem. Chem. Phys.* 14, 1455–1462. doi: 10.1039/C1CP22820J
- Di, L., Yang, H., Xian, T., Liu, X., and Chen, X. J. N. (2019). Photocatalytic and photo-Fenton catalytic degradation activities of Z-scheme Ag₂S/BiFeO₃ heterojunction composites under visible-light irradiation. *Nanomater* 9:399. doi: 10.3390/nano9030399
- Dong, C., Ji, J., Shen, B., Xing, M., and Zhang, J. (2018). Enhancement of H₂O₂ decomposition by the co-catalytic effect of WS₂ on the Fenton reaction for the synchronous reduction of Cr(VI) and remediation of phenol. *Environ. Sci. Technol.* 52, 11297–11308. doi: 10.1021/acs.est.8b02403
- Dong, C., Ji, J., Yang, Z., Xiao, Y., Xing, M., and Zhang, J. (2019). Research progress of photocatalysis based on highly dispersed titanium in mesoporous SiO₂. *Chin. Chem. Lett.* 30, 853–862. doi: 10.1016/j.ccl.2019.03.020
- Dong, C., Lian, C., Hu, S., Deng, Z., Gong, J., Li, M., et al. (2018a). Size-dependent activity and selectivity of carbon dioxide photocatalytic reduction over platinum nanoparticles. *Nat. Commun.* 9:1252. doi: 10.1038/s41467-018-03666-2
- Dong, C., Liu, J., Xing, M., and Zhang, J. (2018b). Development of titanium oxide-based mesoporous materials in photocatalysis. *Res. Chem. Intermediate* 44, 7079–7091. doi: 10.1007/s11164-018-3543-5
- Dong, C., Lu, J., Qiu, B., Shen, B., Xing, M., and Zhang, J. (2018c). Developing stretchable and graphene-oxide-based hydrogel for the removal of organic pollutants and metal ions. *Appl. Catal. B Environ.* 222, 146–156. doi: 10.1016/j.apcatb.2017.10.011
- Dong, H., Guo, X., and Yin, Y. (2018). A facile synthesis of goethite-modified g-C₃N₄ composite for photocatalytic degradation of tylosin in an aqueous solution. *Res. Chem. Intermediate* 44, 3151–3167. doi: 10.1007/s11164-018-3298-z
- Duan, X., Su, C., Miao, J., Zhong, Y., Shao, Z., Wang, S., et al. (2018). Insights into perovskite-catalyzed peroxymonosulfate activation: maneuverable cobalt sites for promoted evolution of sulfate radicals. *Appl. Catal. B Environ.* 220, 626–634. doi: 10.1016/j.apcatb.2017.08.088
- Espuglas, S., Bila, D. M., Krause, L. G. T., and Dezotti, M. (2007). Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. *J. Hazard. Mater.* 149, 631–642. doi: 10.1016/j.jhazmat.2007.07.073
- Fu, Y., and Wang, X. (2011). Magnetically separable ZnFe₂O₄-graphene catalyst and its high photocatalytic performance under visible light irradiation. *Ind. Eng. Chem. Res.* 50, 7210–7218. doi: 10.1021/ie200162a
- Fujishima, A., and Honda, K. J. N. (1972). Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238, 37–38. doi: 10.1038/238037a0
- Gao, X., Ma, C., Liu, Y., Xing, L., and Yan, Y. (2019). Self-induced Fenton reaction constructed by Fe(III) grafted BiVO₄ nanosheets with improved photocatalytic performance and mechanism insight. *Appl. Surf. Sci.* 467–468, 673–683. doi: 10.1016/j.apsusc.2018.10.172
- Giannakis, S., López, M. I. P., Spuhler, D., Pérez, J. A. S., Ibáñez, P. F., and Pulgarin, C. (2016). Solar disinfection is an augmentable, *in situ*-generated photo-Fenton reaction-part 2: a review of the applications for drinking water and wastewater disinfection. *Appl. Catal. B Environ.* 198, 431–446. doi: 10.1016/j.apcatb.2016.06.007
- Guo, K., Zhang, J., Li, A., Xie, R., Liang, Z., Wang, A., et al. (2018). Ultraviolet irradiation of permanganate enhanced the oxidation of micropollutants by producing HO• and reactive manganese species. *Environ. Sci. Technol. Lett.* 5, 750–756. doi: 10.1021/acs.estlett.8b00402
- Guo, S., Zhang, G., Guo, Y., and Yu, J. C. (2013). Graphene oxide-Fe₂O₃ hybrid material as highly efficient heterogeneous catalyst for degradation of organic contaminants. *Carbon* 60, 437–444. doi: 10.1016/j.carbon.2013.04.058
- Guo, S., Zhu, Y., Yan, Y., Min, Y., Fan, J., and Xu, Q. (2016). Holey structured graphitic carbon nitride thin sheets with edge oxygen doping via photo-Fenton reaction with enhanced photocatalytic activity. *Appl. Catal. B Environ.* 185, 315–321. doi: 10.1016/j.apcatb.2015.11.030
- Guo, T., Wang, K., Zhang, G., and Wu, X. (2019). A novel α-Fe₂O₃@g-C₃N₄ catalyst: synthesis derived from Fe-based MOF and its superior photo-Fenton performance. *Appl. Surf. Sci.* 469, 331–339. doi: 10.1016/j.apsusc.2018.10.183
- He, D., Chen, Y., Situ, Y., Zhong, L., and Huang, H. (2017). Synthesis of ternary g-C₃N₄/Ag/γ-FeOOH photocatalyst: an integrated heterogeneous Fenton-like system for effectively degradation of azo dye methyl orange under visible light. *Appl. Surf. Sci.* 425, 862–872. doi: 10.1016/j.apsusc.2017.06.124
- Hu, J., Zhang, P., An, W., Liu, L., Liang, Y., and Cui, W. (2019). In-situ Fe-doped g-C₃N₄ heterogeneous catalyst via photocatalysis-Fenton reaction with enriched photocatalytic performance for removal of complex wastewater. *Appl. Catal. B Environ.* 245, 130–142. doi: 10.1016/j.apcatb.2018.12.029
- Hu, J.-Y., Tian, K., and Jiang, H. (2016). Improvement of phenol photodegradation efficiency by a combined g-C₃N₄/Fe(III)/persulfate system. *Chemosphere* 148, 34–40. doi: 10.1016/j.chemosphere.2016.01.002
- Ikehata, K., and Li, Y. (2018). “Chapter 5-ozone-based processes,” in *Advanced Oxidation Processes for Waste Water Treatment*, eds S. C. Ameta and R. Ameta (Fountain Valley, CA: Academic Press), 115–134.
- Jain, B., Singh, A. K., Kim, H., Lichtfouse, E., Sharma, V. K. (2018). Treatment of organic pollutants by homogeneous and heterogeneous Fenton reaction processes. *Environ. Chem. Lett.* 16, 947–967. doi: 10.1007/s10311-018-0738-3
- Jelic, A., Gros, M., Ginebreda, A., Cespedes-Sánchez, R., Ventura, F., Petrovic, M., et al. (2011). Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. *Water Res.* 45, 1165–1176. doi: 10.1016/j.watres.2010.11.010
- Jia, Y., Wu, C., Kim, D.-H., Lee, B. W., Rhee, S. J., Park, Y. C., et al. (2018). Nitrogen doped BiFeO₃ with enhanced magnetic properties and photo-Fenton catalytic activity for degradation of bisphenol A under visible light. *Chem. Eng. J.* 337, 709–721. doi: 10.1016/j.cej.2017.12.137
- Khadgi, N., and Upreti, A. R. (2019). Photocatalytic degradation of microcystin-LR by visible light active and magnetic, ZnFe₂O₄-Ag/rGO nanocomposite and toxicity assessment of the intermediates. *Chemosphere* 221, 441–451. doi: 10.1016/j.chemosphere.2019.01.046
- Khan, A. H., Kim, J., Sumarah, M., Macfie, S. M., and Ray, M. B. (2017). Toxicity reduction and improved biodegradability of benzalkonium chlorides by ozone/hydrogen peroxide advanced oxidation process. *Sep. Purif. Technol.* 185, 72–82. doi: 10.1016/j.seppur.2017.05.010
- Kim, H.-E., Lee, J., Lee, H., and Lee, C. (2012). Synergistic effects of TiO₂ photocatalysis in combination with Fenton-like reactions on oxidation of organic compounds at circumneutral pH. *Appl. Catal. B Environ.* 115–116, 219–224. doi: 10.1016/j.apcatb.2011.12.027
- Kim, J. R., and Kan, E. (2015). Heterogeneous photo-Fenton oxidation of methylene blue using CdS-carbon nanotube/TiO₂ under visible light. *J. Ind. Eng. Chem.* 21, 644–652. doi: 10.1016/j.jiec.2014.03.032
- Klamerth, N., Malato, S., Agüera, A., and Fernández-Alba, A. (2013). Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: a comparison. *Water Res.* 47, 833–840. doi: 10.1016/j.watres.2012.11.008

- Lan, H., Wang, F., Lan, M., An, X., Liu, H., and Qu, J. (2019). Hydrogen-bond-mediated self-assembly of carbon-nitride-based photo-Fenton-like membranes for wastewater treatment. *Environ. Sci. Technol.* 53, 6981–6988. doi: 10.1021/acs.est.9b00790
- Leary, R., and Westwood, A. (2011). Carbonaceous nanomaterials for the enhancement of TiO₂ photocatalysis. *Carbon* 49, 741–772. doi: 10.1016/j.carbon.2010.10.010
- Lee, Y., and von Gunten, U. (2010). Oxidative transformation of micropollutants during municipal wastewater treatment: comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrateVI, and ozone) and non-selective oxidants (hydroxyl radical). *Water Res.* 44, 555–566. doi: 10.1016/j.watres.2009.11.045
- Lei, X., You, M., Pan, F., Liu, M., Yang, P., Xia, D., et al. (2019). CuFe₂O₄@GO nanocomposite as an effective and recoverable catalyst of peroxymonosulfate activation for degradation of aqueous dye pollutants. *Chin. Chem. Lett.* 30, 2216–2220. doi: 10.1016/j.ccl.2019.05.039
- Li, C., Wang, T., Zhao, Z.-J., Yang, W., Li, J.-F., Li, A., et al. (2018). Promoted fixation of molecular nitrogen with surface oxygen vacancies on plasmon-enhanced TiO₂ photoelectrodes. *Angew. Chem. Int. Ed.* 57, 5278–5282. doi: 10.1002/anie.201713229
- Li, X., Liu, S., Cao, D., Mao, R., and Zhao, X. (2018). Synergetic activation of H₂O₂ by photo-generated electrons and cathodic Fenton reaction for enhanced self-driven photoelectrocatalytic degradation of organic pollutants. *Appl. Catal. B Environ.* 235, 1–8. doi: 10.1016/j.apcatb.2018.04.042
- Li, Y., Ouyang, S., Xu, H., Wang, X., Bi, Y., Zhang, Y., et al. (2016). Constructing solid-gas-interfacial Fenton reaction over alkalized-C₃N₄ photocatalyst to achieve apparent quantum yield of 49% at 420 nm. *J. Am. Chem. Soc.* 138, 13289–13297. doi: 10.1021/jacs.6b07272
- Liu, R., Xu, Y., and Chen, B. (2018). Self-assembled nano-FeO(OH)/reduced graphene oxide aerogel as a reusable catalyst for photo-fenton degradation of phenolic organics. *Environ. Sci. Technol.* 52, 7043–7053. doi: 10.1021/acs.est.8b01043
- Liu, Y., Jin, W., Zhao, Y., Zhang, G., and Zhang, W. (2017a). Enhanced catalytic degradation of methylene blue by α -Fe₂O₃/graphene oxide via heterogeneous photo-Fenton reactions. *Appl. Catal. B Environ.* 206, 642–652. doi: 10.1016/j.apcatb.2017.01.075
- Liu, Y., Liu, X., Zhao, Y., and Dionysiou, D. D. (2017b). Aligned α -FeOOH nanorods anchored on a graphene oxide-carbon nanotubes aerogel can serve as an effective Fenton-like oxidation catalyst. *Appl. Catal. B Environ.* 213, 74–86. doi: 10.1016/j.apcatb.2017.05.019
- Liu, Y., Mao, Y., Tang, X., Xu, Y., Li, C., and Li, F. (2017c). Synthesis of Ag/AgCl/Fe-S plasmonic catalyst for bisphenol A degradation in heterogeneous photo-Fenton system under visible light irradiation. *Chin. J. Catal.* 38, 1726–1735. doi: 10.1016/S1872-2067(17)62902-4
- Luo, W., Zhu, L., Wang, N., Tang, H., Cao, M., She, Y. J. E., et al. (2010). Efficient removal of organic pollutants with magnetic nanoscaled BiFeO₃ as a reusable heterogeneous Fenton-like catalyst. *Environ. Sci. Technol.* 44, 1786–1791. doi: 10.1021/es903390g
- Ma, J., Yang, Q., Wen, Y., and Liu, W. (2017). Fe-g-C₃N₄/graphitized mesoporous carbon composite as an effective Fenton-like catalyst in a wide pH range. *Appl. Catal. B Environ.* 201, 232–240. doi: 10.1016/j.apcatb.2016.08.048
- Ma, M., Chen, L., Zhao, J., Liu, W., and Ji, H. (2019). Efficient activation of peroxymonosulfate by hollow cobalt hydroxide for degradation of ibuprofen and theoretical study. *Chin. Chem. Lett.* 30, 2191–2195. doi: 10.1016/j.ccl.2019.09.031
- Matzek, L. W., and Carter, K. E. (2016). Activated persulfate for organic chemical degradation: a review. *Chemosphere* 151, 178–188. doi: 10.1016/j.chemosphere.2016.02.055
- Mayorov, A. S., Gorbachev, R. V., Morozov, S. V., Britnell, L., Jalil, R., Ponomarenko, L. A., et al. (2011). Micrometer-scale ballistic transport in encapsulated graphene at room temperature. *Nano. Lett.* 11, 2396–2399. doi: 10.1021/nl200758b
- Nair, R. R., Blake, P., Grigorenko, A. N., Novoselov, K. S., Booth, T. J., Stauber, T., et al. (2008). Fine structure constant defines visual transparency of graphene. *Science* 320:1308. doi: 10.1126/science.1156965
- Ojha, D. P., Joshi, M. K., and Kim, H. J. (2017). Photo-Fenton degradation of organic pollutants using a zinc oxide decorated iron oxide/reduced graphene oxide nanocomposite. *Ceram. Int.* 43, 1290–1297. doi: 10.1016/j.ceramint.2016.10.079
- Ortega-Liébana, M. C., Sánchez-López, E., Hidalgo-Carrillo, J., Marinas, A., Marinas, J. M., Urbano, F. J. (2012). A comparative study of photocatalytic degradation of 3-chloropyridine under UV and solar light by homogeneous (photo-Fenton) and heterogeneous (TiO₂) photocatalysis. *Appl. Catal. B Environ.* 127, 316–322. doi: 10.1016/j.apcatb.2012.08.036
- Palanivel, B., Mudisoodum perumal, S. d., Maiyalagan, T., Jayarman, V., Ayyappan, C., and Alagiri, M. (2019). Rational design of ZnFe₂O₄/g-C₃N₄ nanocomposite for enhanced photo-Fenton reaction and supercapacitor performance. *Appl. Surf. Sci.* 498:143807. doi: 10.1016/j.apsusc.2019.143807
- Qian, X., Ren, M., Fang, M., Kan, M., Yue, D., Bian, Z., et al. (2018a). Hydrophilic mesoporous carbon as iron(III)/(II) electron shuttle for visible light enhanced Fenton-like degradation of organic pollutants. *Appl. Catal. B Environ.* 231, 108–114. doi: 10.1016/j.apcatb.2018.03.016
- Qian, X., Ren, M., Zhu, Y., Yue, D., Han, Y., Jia, J., et al. (2017). Visible light assisted heterogeneous Fenton-Like degradation of organic pollutant via α -FeOOH/mesoporous carbon composites. *Environ. Sci. Technol.* 51, 3993–4000. doi: 10.1021/acs.est.6b06429
- Qian, X., Wu, Y., Kan, M., Fang, M., Yue, D., Zeng, J., et al. (2018b). FeOOH quantum dots coupled g-C₃N₄ for visible light driving photo-Fenton degradation of organic pollutants. *Appl. Catal. B Environ.* 237, 513–520. doi: 10.1016/j.apcatb.2018.05.074
- Qiu, B., Deng, Y., Du, M., Xing, M., and Zhang, J. (2016a). Ultradispersed cobalt ferrite nanoparticles assembled in graphene aerogel for continuous photo-Fenton reaction and enhanced lithium storage performance. *Sci. Rep.* 6:29099. doi: 10.1038/srep29099
- Qiu, B., Li, Q., Shen, B., Xing, M., and Zhang, J. (2016b). Stöber-like method to synthesize ultradispersed Fe₃O₄ nanoparticles on graphene with excellent photo-Fenton reaction and high-performance lithium storage. *Appl. Catal. B Environ.* 183, 216–223. doi: 10.1016/j.apcatb.2015.10.053
- Qiu, B., Xing, M., and Zhang, J. (2015). Stöber-like method to synthesize ultralight, porous, stretchable Fe₂O₃/graphene aerogels for excellent performance in photo-Fenton reaction and electrochemical capacitors. *J. Mater. Chem. A* 3, 12820–12827. doi: 10.1039/C5TA02675J
- Rincón, A.-G., and Pulgarin, C. (2004a). Bactericidal action of illuminated TiO₂ on pure *Escherichia coli* and natural bacterial consortia: post-irradiation events in the dark and assessment of the effective disinfection time. *Appl. Catal. B Environ.* 49, 99–112. doi: 10.1016/j.apcatb.2003.11.013
- Rincón, A.-G., and Pulgarin, C. (2004b). Effect of pH, inorganic ions, organic matter and H₂O₂ on *E. coli* K12 photocatalytic inactivation by TiO₂: implications in solar water disinfection. *Appl. Catal. B Environ.* 51, 283–302. doi: 10.1016/j.apcatb.2004.03.007
- Rincón, A.-G., and Pulgarin, C. (2006). Comparative evaluation of Fe³⁺ and TiO₂ photoassisted processes in solar photocatalytic disinfection of water. *Appl. Catal. B Environ.* 63, 222–231. doi: 10.1016/j.apcatb.2005.10.009
- Safaei-Ghomi, J., Akbarzadeh, Z., and Teymuri, R. (2019). ZnS nanoparticles immobilized on graphitic carbon nitride as a recyclable and environmentally friendly catalyst for synthesis of 3-cinnamoyl coumarins. *Res. Chem. Intermediate* 45, 3425–3439. doi: 10.1007/s11164-019-03800-9
- Sahar, S., Zeb, A., Liu, Y., Ullah, N., and Xu, A. (2017). Enhanced Fenton, photo-Fenton and peroxidase-like activity and stability over Fe₃O₄/g-C₃N₄ nanocomposites. *Chin. J. Catal.* 38, 2110–2119. doi: 10.1016/S1872-2067(17)62957-7
- Saleh, R., and Taufik, A. (2019). Degradation of methylene blue and congo-red dyes using Fenton, photo-Fenton, sono-Fenton, and sonophoto-Fenton methods in the presence of iron(II,III) oxide/zinc oxide/graphene (Fe₃O₄/ZnO/graphene) composites. *Sep. Purif. Technol.* 210, 563–573. doi: 10.1016/j.seppur.2018.08.030
- Shao, P., Duan, X., Xu, J., Tian, J., Shi, W., Gao, S., et al. (2017). Heterogeneous activation of peroxymonosulfate by amorphous boron for degradation of bisphenol S. *J. Hazard. Mater.* 322, 532–539. doi: 10.1016/j.jhazmat.2016.10.020
- Shayegan, Z., Lee, C.-S., and Haghight, F. (2018). TiO₂ photocatalyst for removal of volatile organic compounds in gas phase - a review. *Chem. Eng. J.* 334, 2408–2439. doi: 10.1016/j.cej.2017.09.153

- Shen, B., Dong, C., Ji, J., Xing, M., and Zhang, J. (2019). Efficient Fe(III)/Fe(II) cycling triggered by MoO₂ in Fenton reaction for the degradation of dye molecules and the reduction of Cr(VI). *Chin. Chem. Lett.* 30, 2205–2210. doi: 10.1016/j.ccl.2019.09.052
- Su, M., He, C., Sharma, V. K., Abou Asi, M., Xia, D., Li, X. Z., et al. (2012). Mesoporous zinc ferrite: synthesis, characterization, and photocatalytic activity with H₂O₂/visible light. *J. Hazard. Mater.* 211, 95–103. doi: 10.1016/j.jhazmat.2011.10.006
- Sui, Z., Meng, Q., Zhang, X., Ma, R., and Cao, B. (2012). Green synthesis of carbon nanotube-graphene hybrid aerogels and their use as versatile agents for water purification. *J. Mater. Chem.* 22, 8767–8771. doi: 10.1039/c2jm00055e
- Sun, T., Gong, M., Cai, Y., Zhang, L., Xu, Z., Zhang, D., et al. (2020). MCM-41-supported Fe(Mn)/Cu bimetallic heterogeneous catalysis for enhanced and recyclable photo-Fenton degradation of methylene blue. *Res. Chem. Intermed.* 46, 459–474. doi: 10.1007/s11164-019-03960-8
- Sun, Y., Wang, W., Zhang, L., Sun, S., and Gao, E. (2013). Magnetic ZnFe₂O₄ octahedra: synthesis and visible light induced photocatalytic activities. *Mater. Lett.* 98, 124–127. doi: 10.1016/j.matlet.2013.02.014
- Tan, C., Gao, N., Fu, D., Deng, J., and Deng, L. (2017). Efficient degradation of paracetamol with nanoscaled magnetic CoFe₂O₄ and MnFe₂O₄ as a heterogeneous catalyst of peroxymonosulfate. *Sep. Purif. Technol.* 175, 47–57. doi: 10.1016/j.seppur.2016.11.016
- Tang, C. Y., Yang, Z., Guo, H., Wen, J. J., Nghiem, L. D., and Cornelissen, E. (2018). Potable water reuse through advanced membrane technology. *Environ. Sci. Technol.* 52, 10215–10223. doi: 10.1021/acs.est.8b00562
- ThanhThuy, T. T., Feng, H., and Cai, Q. (2013). Photocatalytic degradation of pentachlorophenol on ZnSe/TiO₂ supported by photo-Fenton system. *Chem. Eng. J.* 223, 379–387. doi: 10.1016/j.cej.2013.03.025
- Tryba, B., Morawski, A. W., Inagaki, M., and Toyoda, M. (2006). Mechanism of phenol decomposition on FeC TiO₂ and Fe TiO₂ photocatalysts via photo-Fenton process. *J. Photochem. Photobio. A Chem.* 179, 224–228. doi: 10.1016/j.jphotochem.2005.08.019
- Vaiano, V., Sacco, O., Sannino, D., and Ciambelli, P. (2015). Nanostructured N-doped TiO₂ coated on glass spheres for the photocatalytic removal of organic dyes under UV or visible light irradiation. *Appl. Catal. B Environ.* 170–171, 153–161. doi: 10.1016/j.apcatb.2015.01.039
- Wang, H., Xu, Y., Jing, L., Huang, S., Zhao, Y., He, M., et al. (2017). Novel magnetic BaFe₁₂O₁₉/g-C₃N₄ composites with enhanced thermocatalytic and photo-Fenton activity under visible-light. *J. Alloy. Compd.* 710, 510–518. doi: 10.1016/j.jallcom.2017.03.144
- Wang, J., and Wang, S. (2018). Activation of persulfate (PS) and application for the degradation of emerging contaminants. *Chem. Eng. J.* 334, 1502–1517. doi: 10.1016/j.cej.2017.11.059
- Wang, L., Jiang, J., Pang, S.-Y., Gao, Y., Zhou, Y., Li, J., et al. (2019). Further insights into the combination of permanganate and peroxymonosulfate as an advanced oxidation process for destruction of aqueous organic contaminants. *Chemosphere* 228, 602–610. doi: 10.1016/j.chemosphere.2019.04.149
- Wang, P., Wang, L., Sun, Q., Qiu, S., Liu, Y., Zhang, X., et al. (2016). Preparation and performance of Fe₃O₄@hydrophilic graphene composites with excellent Photo-Fenton activity for photocatalysis. *Mater. Lett.* 183, 61–64. doi: 10.1016/j.matlet.2016.07.080
- Wang, P., Zhao, G., Wang, Y., and Lu, Y. (2017). MnTiO₃-driven low-temperature oxidative coupling of methane over TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst. *Sci. Adv.* 3:e1603180. doi: 10.1126/sciadv.1603180
- Wang, Q., Wang, P., Xu, P., Li, Y., Duan, J., Zhang, G., et al. (2020). Visible-light-driven photo-Fenton reactions using Zn1-1.5xFexS/g-C₃N₄ photocatalyst: degradation kinetics and mechanisms analysis. *Appl. Catal. B Environ.* 266:118653. doi: 10.1016/j.apcatb.2020.118653
- Wang, Z., Fan, Y., Wu, R., Huo, Y., Wu, H., Wang, F., et al. (2018). Novel magnetic g-C₃N₄/α-Fe₂O₃/Fe₃O₄ composite for the very effective visible-light-Fenton degradation of orange II. *RSC Adv.* 8, 5180–5188. doi: 10.1039/C7RA13291C
- Xi, Z., Li, C., Zhang, L., Xing, M., and Zhang, J. (2014). Synergistic effect of Cu₂O/TiO₂ heterostructure nanoparticle and its high H₂ evolution activity. *Int. J. Hydrogen Energ.* 39, 6345–6353. doi: 10.1016/j.ijhydene.2014.01.209
- Xiang, Q., Yu, J., and Jaroniec, M. (2012). Graphene-based semiconductor photocatalysts. *Chem. Soc. Rev.* 41, 782–796. doi: 10.1039/C1CS15172J
- Xing, M., Xu, W., Dong, C., Bai, Y., Zeng, J., Zhou, Y., et al. (2018a). Metal sulfides as excellent co-catalysts for H₂O₂ decomposition in advanced oxidation processes. *Chem* 4, 1359–1372. doi: 10.1016/j.chempr.2018.03.002
- Xing, M., Zhang, J., Qiu, B., Tian, B., Anpo, M., and Che, M. (2015). A brown mesoporous TiO₂-x/MCF composite with an extremely high quantum yield of solar energy photocatalysis for H₂ evolution. *Small* 11, 1920–1929. doi: 10.1002/smll.201403056
- Xing, M., Zhou, Y., Dong, C., Cai, L., Zeng, L., Shen, B., et al. (2018b). Modulation of the reduction potential of TiO₂-x by fluorination for efficient and selective CH₄ generation from CO₂ photoreduction. *Nano. Lett.* 18, 3384–3390. doi: 10.1021/acs.nanolett.8b00197
- Xu, T., Zhu, R., Zhu, G., Zhu, J., Liang, X., Zhu, Y., et al. (2017). Mechanisms for the enhanced photo-Fenton activity of ferrihydrite modified with BiVO₄ at neutral pH. *Appl. Catal. B Environ.* 212, 50–58. doi: 10.1016/j.apcatb.2017.04.064
- Yang, Z., Ma, X.-H., and Tang, C. Y. (2018). Recent development of novel membranes for desalination. *Desalination* 434, 37–59. doi: 10.1016/j.desal.2017.11.046
- Yang, Z., Wu, Y., Wang, J., Cao, B., and Tang, C. Y. (2016). *In situ* reduction of silver by polydopamine: a novel antimicrobial modification of a thin-film composite polyamide membrane. *Environ. Sci. Technol.* 50, 9543–9550. doi: 10.1021/acs.est.6b01867
- Yao, T., Jia, W., Feng, Y., Zhang, J., Lian, Y., Wu, J., et al. (2019). Preparation of reduced graphene oxide nanosheet/Fe_xO_y/nitrogen-doped carbon layer aerogel as photo-Fenton catalyst with enhanced degradation activity and reusability. *J. Hazard. Mater.* 362, 62–71. doi: 10.1016/j.jhazmat.2018.08.084
- Yao, Y., Qin, J., Cai, Y., Wei, F., Lu, F., and Wang, S. (2014). Facile synthesis of magnetic ZnFe₂O₄-reduced graphene oxide hybrid and its photo-Fenton-like behavior under visible irradiation. *Environ. Sci. Pollut. Res.* 21, 7296–7306. doi: 10.1007/s11356-014-2645-x
- Ye, Y., Yang, H., Wang, X., and Feng, W. (2018). Photocatalytic, Fenton and photo-Fenton degradation of RhB over Z-scheme g-C₃N₄/LaFeO₃ heterojunction photocatalysts. *Mater. Sci. Semicon. Proc.* 82, 14–24. doi: 10.1016/j.mssp.2018.03.033
- Yu, J., Low, J., Xiao, W., Zhou, P., and Jaroniec, M. (2014). Enhanced photocatalytic CO₂-reduction activity of anatase TiO₂ by coexposed {001} and {101} Facets. *J. Am. Chem. Soc.* 136, 8839–8842. doi: 10.1021/ja5044787
- Yu, L., Shao, Y., and Li, D. (2017). Direct combination of hydrogen evolution from water and methane conversion in a photocatalytic system over Pt/TiO₂. *Appl. Catal. B Environ.* 204, 216–223. doi: 10.1016/j.apcatb.2016.11.039
- Yu, S., Wang, Y., Sun, F., Wang, R., and Zhou, Y. (2018). Novel mpg-C₃N₄/TiO₂ nanocomposite photocatalytic membrane reactor for sulfamethoxazole photodegradation. *Chem. Eng. J.* 337, 183–192. doi: 10.1016/j.cej.2017.12.093
- Zhang, D., Gersberg, R. M., Ng, W. J., and Tan, S. K. (2014). Removal of pharmaceuticals and personal care products in aquatic plant-based systems: a review. *Environ. Pollut.* 184, 620–639. doi: 10.1016/j.envpol.2013.09.009
- Zhang, L., Tian, B., Chen, F., and Zhang, J. (2012). Nickel sulfide as co-catalyst on nanostructured TiO₂ for photocatalytic hydrogen evolution. *Int. J. Hydrogen Energ.* 37, 17060–17067. doi: 10.1016/j.ijhydene.2012.08.120
- Zhang, Y.-Y., He, C., Deng, J.-H., Tu, Y.-T., Liu, J.-K., and Xiong, Y. (2009). Photo-Fenton-like catalytic activity of nano-lamellar Fe₂V₄O₁₃ in the degradation of organic pollutants. *Res. Chem. Intermed.* 35:727. doi: 10.1007/s11164-009-0090-0
- Zhao, J., Ji, M., Di, J., Zhang, Y., He, M., Li, H., et al. (2020). Novel Z-scheme heterogeneous photo-Fenton-like g-C₃N₄/FeOCl for the pollutants degradation under visible light irradiation. *J. Photochem. Photobio. A Chem.* 391:112343. doi: 10.1016/j.jphotochem.2019.112343
- Zhao, Y., Zhao, Y., Shi, R., Wang, B., Waterhouse, G. I. N., Wu, L.-Z., et al. (2019). Tuning oxygen vacancies in ultrathin TiO₂ nanosheets to boost photocatalytic nitrogen fixation up to 700 nm. *Adv. Mater.* 31:1806482. doi: 10.1002/adma.201806482

- Zhou, L., Wang, L., Zhang, J., Lei, J., and Liu, Y. (2016). Well-dispersed Fe₂O₃ nanoparticles on g-C₃N₄ for efficient and stable Photo-Fenton photocatalysis under visible-light irradiation. *Eur. J. Inorg. Chem.* 34, 5387–5392. doi: 10.1002/ejic.201600959
- Zhou, Y., Yi, Q., Xing, M., Shang, L., Zhang, T., and Zhang, J. (2016). Graphene modified mesoporous titania single crystals with controlled and selective photoredox surfaces. *Chem. Commun.* 52, 1689–1692. doi: 10.1039/C5CC07567J
- Zhu, K., Wang, J., Wang, Y., Jin, C., and Ganeshraja, A. S. (2016). Visible-light-induced photocatalysis and peroxymonosulfate activation over ZnFe₂O₄ fine nanoparticles for degradation of orange II. *Catal. Sci. Technol.* 6, 2296–2304. doi: 10.1039/C5CY01735A
- Zhu, Y., Zhu, R., Xi, Y., Xu, T., Yan, L., Zhu, J., et al. (2018a). Heterogeneous photo-Fenton degradation of bisphenol A over Ag/AgCl/ferrihydrite catalysts under visible light. *Chem. Eng. J.* 346, 567–577. doi: 10.1016/j.cj.2018.04.073
- Zhu, Y., Zhu, R., Yan, L., Fu, H., Xi, Y., Zhou, H., et al. (2018b). Visible-light Ag/AgBr/ferrihydrite catalyst with enhanced heterogeneous photo-Fenton reactivity via electron transfer from Ag/AgBr to ferrihydrite. *Appl. Catal. B Environ.* 239, 280–289. doi: 10.1016/j.apcatb.2018.08.025

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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