Metal-organic frameworks for highly efficient heterogeneous Fenton-like catalysis

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Contents

1. Introduction	4
2. Fe-based MOFs for heterogeneous Fenton-like catalysis	7
3. Other single metal-based MOFs for heterogeneous Fenton-like catalysis	13
4. Heterobimetallic MOFs for heterogeneous Fenton-like catalysis	17
5. The effects of pH on the performance of MOFs-based Fenton-like catalysis	22
6. Stability and reusability of MOFs-based Fenton-like catalysts	24
7. Concluding remarks and prospects	26
Acknowledgements	29
References	30
Accester	

Abstract

Heterogeneous Fenton-like reaction is an advanced oxidation process which has gained wide spread acceptance for high removal efficiency of recalcitrant organic contaminants. Recently, the use of metal-organic frameworks (MOFs) or MOF composites as catalysts for Fenton-like catalysis has received increasing attention due to their permanent porosity and tunable open metal centers. In this article, we present an overview of the development and progress in synthesis of different types of MOFsbased catalysts and their applications for Fenton-like oxidation of ganic pollutants. Special attention has been paid to the catalytic mechan mely the routes of reactive species production on the surface of catal The representative studies in this area were comprehensively reviewed. Ov rav s concluded that several classes of MOFs materials with fixed metal centres are able to catalytic degradation of eanwhile, the research in this field is at an organic pollutants at a wide pH early stage, many improven ents re required before industrial applications. ameworks; Fenton-like; Wastewater; Organic pollutant; Keywords: Met Catalysis.

1. Introduction

Water is essential for the subsistence of living beings. Unfortunately, water pollution remains a pervasive threat. Huge amounts of synthetic organic contaminants, such as pharmaceuticals and personal care products (PPCPs), pesticides and dves are released daily into different types of wastewaters and ultimately enter into natural water channels [1-6]. It is well known the vast majority of these compounds are resistance to microbial attack and with high stability to sunlight irradiation [7-10]. Many of recalcitrant compounds are able to cause damages to iving organisms including human being [11-14]. Thus, an effective elimination of these compounds from the environment is important and necessary Advanced oxidation processes (AOPs) have been demonstrated to achieve good esuns for the elimination of organic pollutants from wastewater in very show treatment times [15-17]. AOPs are ctrochemical, or photochemical methods environmentally friendly chen sharing the common feature of the in-situ production of highly active hydroxyl radical oxitizin, agent [7]. (•OH) as their man

Fenton process has been attracted considerable attention in the field of environmental remediation [18-21]. In classical Fenton reaction (Eqs. (1)), the ferrous iron (Fe²⁺) catalyzes the decomposition of hydrogen peroxide (H₂O₂), resulting in the generation of •OH [22]. The formed ferric ions (Fe³⁺) can be reduced through Eqs. (2), which is known as Fenton-like reaction [23]. Apart from Fe³⁺, some other transition metal ions (e.g., Co and Cu ions) have also been used as the catalyst in Fenton-like reaction [24]. •OH generated from Fenton reaction is the second most reactive chemical species known next to fluorine atom, they can initiate the decomposition of organic pollutants by hydrogen abstraction (Eqs. (3)) or by hydroxyl addition (Eqs.

(4)

 $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + \bullet OH$ (1) $Fe^{3+} + H_2O_2 \leftrightarrows Fe^{2+} + H^+ + HO_2 \bullet$ (2)

 $RH + \bullet OH \rightarrow H_2O + R \bullet \rightarrow \text{ further oxidations}$ (3)

 $R + \bullet OH \rightarrow \bullet ROH \rightarrow further oxidations$

(4)) [19].

Following the pioneering practical use of Fenton's reaction. the degradation of organic compounds in the 1930s [22], Fenton re and its derivative technologies, such as electro-Fenton [25-28] and poto-Fenton [29-31], have been extensively studied for the decomposition of a tigh number of organic pollutants. Since mass transfer limitations are negligible in homogeneous Fenton oxidation systems, the reaction can work tively during the degradation process [32]. However, the traditional F nton process suffers from some drawbacks, such as, the need for strict pH regulation (pH 2.8-3.5) [33], sludge generation [34], and the loss of the catalyst in the effluent [35], which make this technique complex and uneconomical. In order to overcome these drawbacks, heterogeneous Fenton-like processes using solid catalysts have been developed. In heterogeneous catalysis, iron (or other transition metals) is stabilized on/in the catalyst's structure and thus can reduce the hydroxide precipitation under a wider pH range [36-39]. Several reviews have summarized a wide range of materials that have been used as catalysts or metal supports in heterogeneous Fenton-like process [40-44]. These reviews highlight that the development of new types of heterogeneous catalysts with low cost, high activity, good stability and environmental benignancy is important yet challenging.

Metal-organic frameworks (MOFs), also called porous coordination networks (PCNs) [45, 46], or porous coordination polymers (PCPs) [47, 48], are crystalline inorganic-organic hybrids assembled from organic ligands and metal ions (or clusters) [49]. MOFs not only combine the respective beneficial characteristics of inorganic and organic components but also often exhibit unique properties that exceed the expectations for a simple mixture of the components [50, 5] Besides, MOFs materials can be designed with dimensions, textural c istics and specific structures to meet the need of a specific application [22]. Early efforts in this research area were mainly focused on the synthesis of ter Mors materials [53-55]; however, in recent years there has been more interest in the searching for potential applications 0s [59], MOFs have influenced many fields [52, 56-58]. Since its discovery such as separation [60], ene gy storage [61], sensing [61], and catalysis [62].

The occurrence of MOFs opens up new opportunities for the development of catalysts with excellent characteristic features, such as chemical tenability, well-defined structure, large pore volume and high specific area [52, 63]. To date, various MOFs-derived catalysts have been reported. Moreover, an increasing number of review articles on this topic have appeared in recent years [64-72]. For example, Wen et al. [64] systematically reviewed the recent progress in the design and architecture of MOFs involved H_2 production system. In a more recent one, Zhu et al. [71] summarized the synthesis, structures and photocatalytic applications of

Titanium-based MOFs. MOFs bring a great deal of opportunities for the development of new heterogeneous Fenton-like catalysts. The past few years has witnessed rapid progress in MOFs-derived Fenton-like catalysts. To date, various MOFs-derived Fenton-like catalysts including single metal (e.g., Fe, Co, Cu) and multiple metals (e.g., Fe/Co, Fe/Cu) containing MOFs have been reported. The growing number of publication on this topic suggests that MOFs-based Fenton-like catalysis will play a role in the elimination of organic pollutants. Several review papers [73-76] have summarized some data on the performance of MOFs-based Fenton-like catalysis has not been reported to date. Therefore, a review summizing MOFs-based Fenton-like reactions is highly expected.

This review aims at giving an account of fundamental aspects of MOFs-based Fenton-like catalysis. Sections **21** liecuss the synthesis of different types of MOFs-derived catalysts and their application for Fenton-like oxidation of organic pollutants. Specific attention has been paid to the catalytic mechanism and the effects of structure on the catalytic activity of MOFs-based catalysts. Section 5 introduces the effects of initial pH on the performance of MOFs-based Fenton-like catalysis. Afterward, the stability and reusability of MOFs-based Fenton-like catalysts are presented. Section 7 provides a conclusion of the review and finally, the outlooks of these emerging technologies are given for plausible research directions.

2. Fe-based MOFs for heterogeneous Fenton-like catalysis

Among various types of reported MOFs, Fe-based MOFs showed great potential

as the heterogeneous Fenton-like catalyst because Fe is nontoxic, abundant in earth crust minerals and Fe-based MOFs show intensive absorption in the visible light region duo to the existence of iron-oxo (Fe-O) clusters [77, 78]. Till now, a vast of Fe-based MOFs have been developed using different types of organic ligands. Bipyridine is one of the most widely used ligands because of its oxidative resistance of pyridine ring to •OH and the strong binding affinity with Fe^{2+} [79, 80]. What's more, recent progress has shown that introduction of carboxyl group to the 2,2'-bipyridine ligand can further stabilize the obtained complex. to the carboxyl group would bind with the Fe³⁺ formed in the cata vcle to avoid its hydrolyzation. As reported by Li et al. [81], a Fe(L MOF material (Fe-bpydc) was successfully synthesized with 2,2'-bipyridin -5) dearboxylate as the ligand and exhibited high catalytic activity for $\underline{H_2O_2}$ bear neutral pH conditions. The total degradation is 23, revealing that its activity turnover number (TON) of a thr and stability are superior to most of the reported MOF catalysts [81]. The ligands can performance of Fe-based MOFs catalysts by affecting the also affect the con olvtn spatial structure of MOFs [77, 82]. For instance, MIL-100(Fe) (Fig.1, 3D, 1,3,5-benzenetricarboxylic acid as the ligand) showed much intensive absorption in the visible light region and higher catalytic ability as compared with those of MIL-68(Fe) (Fig.1, 2D, 1,4-benzenedicarboxylic acid as the ligand) [77]. It was likely because MIL-100(Fe) contains Fe₃O cluster in its framework, thus the formed electron in the Fe₃O cluster could be effectively transferred from the metal center to the substrate. Previous studies have demonstrated μ_3 -O in the catalysts could promote

the formation of a pronounced electronic delocalized state in the μ_3 -O cluster, which could help the electron transfer from metal ion to oxidant to form active species [83, 84]. The results highlight the great potential to find more economical and sustainable MOFs for Fenton-like catalysis due to the fact that the structures of MOFs are highly tunable.

It should be noted that pure MOFs catalyst may exhibit relatively low catalytic activity as compared to iron salts due to the restricted iron sites on MOFs catalyst. The efficiency of the MOFs-catalyzed Fenton-like process ca be enhanced by introduction of additional activity sites to the catalyst. In a work, Lv et al. [85] fabricated a novel Fe^{II}@MIL-100(Fe) Fenton-like talyst (Fig. 2a) and studied its application for degrading high concentration methylene blue (MB) (the detailed information of the mentioned pollutants in t s review are provided in Table 1). After introducing Fe(II) species, F 00(Fe) was more positively charged and $(1228 \text{ m}^2/\text{g})$ compared with that of MIL-100(Fe) (1646 showed lower BET surface ¹@MIL-100(Fe) exhibited lower adsorption ability for MB, m^2/g . Consequent which is believed adversely affect the catalytic degradation process [28, 86]. Nevertheless, the authors found Fe^{II}@MIL-100(Fe) present much higher Fenton-like catalytic ability compared to MIL-100(Fe) catalysts [85]. The possible mechanism as displayed in Fig. 2b, suggested Fe(II) and Fe(III) in Fe^{II}@MIL-100(Fe) have synergistic effect on the generation of •OH [85]. It is noteworthy that Fe(II) loaded on MIL-100(Fe) might dissolve into the solution during Fenton-like reaction. It was found that the leached Fe from Fe^{II} @MIL-100(Fe) reached 7.1 mg L⁻¹, which may cause potential risks to the environment.

The combination of photoenergies (UV-light/visible light) can also largely enhance the efficiency of MOFs-catalyzed Fenton-like process, which is currently active area of interest for this technology. As a matter of fact, numerous research efforts have been devoted to photo-Fenton/like processes over the last two decades [87-89]. And recently, there has been more interest in developing new heterogeneous photo-Fenton/like processes [42, 90, 91]. It is well established that FeOOH could be a promising visible light photocatalyst due to their small band go gy of 2.2-2.5eV [92]. Unfortunately, the fast electron hole recombination the photocatalyst largely limits the efficiency of the oxidation [92]. C. ne researchers have shown this can be overcome by reducing its particle size 93 OFs that contain very small size of Fe(III) oxide clusters (5-8nm) were therefore considered as visible light tkers [94] have synthesized a new group of photocatalyst. In 2013, Laurier Fe(III)-oxo clusters contailing MOFs, and demonstrated their high photocatalytic efficiency in des rhodamine B (RhB). In the following works, several dati groups have found MIL-53(Fe) exhibited high photo-Fenton activity under visible light irradiation [95, 96]. In a resent published work, the MIL-53(Fe)/H₂O₂/vis system shows significantly higher performance for the degradation of two PPCPs (clofibric acid and carbamazepine) than that of MIL-53(Fe)/H₂O₂, Fe(II)/H₂O₂ or TiO₂/vis system [97]. It was concluded that the direct excitation of iron-oxo cluster mainly contribute to the photo-Fenton activity of MIL-53(Fe), which has also been proposed by several previously reported studies [98, 99]. As shown in Fig. 3 [99], in the

presence of H_2O_2 and visible light, the positive synergistic effects could contribute to the catalytic performance of MIL-53(Fe). On the one hand, Fe(III) on the surface of MIL-53(Fe) can catalyze the decomposition of H_2O_2 to produce •OH via Fenton-like reaction (Eqs. (5) and (6)). On the other hand, H_2O_2 as an efficient scavenger could capture the photo-induced electrons in the excited MIL-53(Fe) to form •OH (Eqs. (7) and (8)).

 $Fe(III)species + H_2O_2 \rightarrow Fe(II)species + HO_2 \bullet + H^+$ (5) $Fe(II)species + H_2O_2 \rightarrow Fe(III)species + \bullet OH + OH^-$ (6) $MIL-53(Fe) + hv \rightarrow h^+ + e^-$ (7) $H_2O_2 + e^-(MIL-53(Fe)) \rightarrow \bullet OH + OH^-$ (8)

By composing MOFs with suitable material, the physicochemical properties of the photocatalyst can be further improved [100]. In 2014, the group of Wu and co-workers described the application of eraphene oxide as a support for Fe-MIL-88B [101]. It was reported that RhY degradation efficiency of Fe-MIL-88B/graphene oxide under explore to natural sunlight was significantly improved as compared to that of graphene oxide and Fe-MIL-88B separately. More recently, the group of Vu successfully synthesized a novel Fe-MIL-88B/Graphene oxide composite by solvothermal method [102]. They found that graphene oxide could not only play the role as support, but also lead to the formation of α -FeOOH by the interaction between Fe(III) oxide species and hydroxyl/carboxylic groups in graphene oxide [103].

In practical applications for wastewater treatment, MOFs-based catalysts have difficulties in separating from the reaction solution for recycling due to their highly

dispersive nature. The design novel core-shell structures with Fe₃O₄ as the core and MOFs as the shell could be a feasible solution [104, 105]. Fe₃O₄ nanoparticles have been extensively studied as heterogeneous Fenton-like catalyst due to its low toxicity and good magnetic properties [106], however, Fe₃O₄ is highly susceptible to photodissolution [107]. Interestingly, the exciting radiation can be overcome by using MOFs as the shell. In 2013, Zhang and co-workers [108] successfully fabricated the Fe₃O₄@MIL-100(Fe) catalyst through a simple method (Fig. 4a). The prepared catalyst can be easily separated and recycled without obvious less atalytic activity. More importantly, MB degradation rate of Fe₃O₄@MIL-1 H₂O₂ photo-Fenton system was even higher than those of conventional N_4 and TiO₂ photocatalysis. In the core-shell Fe₃O₄@MOFs/H₂O₂ photo-Fe⁴to tem, H_2O_2 acts as an electron acceptor and reacts with the photo-induced Vectrons on MOFs, which suppresses the recombination of photo-induce -hole pair (Fig. 4b) [109]. Further study revealed that the catalytic erformance of Fe₃O₄@MOFs/H₂O₂ photo-Fenton system thic ness of the MOFs shell. Zhao et al. [109] examined the is closely related the thickness of the shere (25 -250 nm) on the photocatalytic ability of Fe₃O₄@MIL-100, and determined that the optimal thickness of the MOF shell is about 50 nm. It was suggested that when the thickness of the shell is too small, only little amount of electron-hole pairs would be generated; however, when the thickness of the shell is too large, the generated holes localized in the MOFs shell are unable to access the Fe_3O_4 core, which would reduce the photocatalytic ability [109, 110]. Very recently, sulfonated Fe₃O₄@MIL-100 (Fe₃O₄ @MIL-100(Fe)-OSO₃H) has been synthesized by

Moradiet et al. [111] and proved as an efficient Fenton-like catalyst. It was demonstrated that the sulfonate group of the MOFs forms a new trap-state inside the band gap of $Fe_3O_4@MIL-100(Fe)$, which promotes the electron transfer between the sulfonate group and $Fe_3O_4@MIL-100(Fe)$ at the interface.

3. Other single metal-based MOFs for heterogeneous Fenton-like catalysis

Apart from iron-based MOFs, many other metals, such as Cu, Co and Ni, based MOFs have been synthesized and used as heterogeneous Fenton-like catalysts.

Cu-based catalysts have attracted significant attention or to the redox properties of copper are similar to iron [112-115]. In 2015 l co-workers [116] synthesized copper-doped mesoporous silica micropheres (Cu-MSMs) using the a 0.91 wt% of the copper species hydrothermal method. The characterizations s ov was embedded in the framework of the NSMs by chemical binding of Cu-O-Si. rformance for the degradation of phenytoin Cu-MSMs exhibited excellent of e (IP). The possible interaction processes during the (PHT) and diphenhydrami proposed in Fig. 5. On the first step, H_2O_2 was converted to Fenton-like react •OH by the framework \equiv Cu(I) in Cu-MSMs and \equiv Cu(I) was synchronously oxidized to \equiv Cu(II). The generated •OH can then initiate the decomposition of PHT and DP. More importantly, the produced phenolic intermediates can be adsorbed on the surface of Cu-MSMs, complexing with the framework \equiv Cu(II) and forming \equiv Cu-ligands, which can interact with H_2O_2 and facilitate the reduction of $\equiv Cu(II)$. As a result, \equiv Cu-ligands accelerated the Cu(II)/Cu(I) cycles on the Cu-MSMs surface, leading to more efficient •OH generation for the pharmaceuticals oxidation.

Apart from Cu(I), Cu(II) was also used to synthesis MOFs catalyst. For instance, a new five-coordinated copper-MOFs, Cu₂(2,2'-bipyridine)₂(pentafluorobenzoate)₄ (Compound 1), was hydrothermally synthesized by Han et al. in 2016 [117]. As seen from Fig. 7, each Cu(II) center in Compound 1 is five coordinated to two nitrogen atoms and three oxygen atoms, presenting an approximately square-pyramidal coordination geometry. Compound 1 showed no catalytic activity for methyl orange (MO), however, in the presence of H_2O_2 , about 85% of MO can be removed from the solution in 15 min. Besides, the authors found that Fenton like reaction did not change the structure of Compound 1 and UV-vis radiation ad no impact on the catalytic activity of this Fenton process. Based on he above findings, the probable mechanisms for MO degradation were proported (Fig. 7). Firstly, •OH can be generated by Cu(II) catalytic decomposition of H₂O₂ through a Fenton-like reaction. structure, the Cu(II) center of compound 1 Secondly, considering from the trends to have six or seven-oordinated structure according to the valence bond theory; rdinited Cu(II) may coordinate to oxygen atoms from H2O2 therefore, five-con molecules to form transition state I, II and III (Fig. 6). Then Cu-O bonds in transition state III (oxygen atoms belonging to H_2O_2) would be disconnected to produce •OH.

Cobalt ion $[E^{0}(Co^{3+}/Co^{2+}) = +1.92 \text{ V}]$ based Fenton-like process has been investigated with H₂O₂, persulfate (S₂O₈²⁻, PS) or peroxymonosulfate (HSO⁵⁻, PMS) as the oxidant. In recent years, remarkable progress has been made in the synthesis of Co-based MOFs [118-122]. Bis-benzimidazoles derivatives have been often used as N-based ligands in the construction of Co-based MOFs, since their flexible nature

allows them to bend and rotate freely with the metal centers [123]. On the other hand, aromatic dicarboxylates have proved to be excellent organic ligands due to their remarkable coordination ability, high structural stability and versatile coordination modes [120]. To take one step further, some research groups have made their efforts on the fabrications of mixed-ligand MOFs. In a related report, three cobalt(II) based MOFs have been hydrothermally synthesized by self-assembly of cobalt(II) nitrate with three flexible bis(benzimidazole) and tetrabromoterephthalic acid (H₂tbta) (Fig. 7a) [119]. The degradation experiments showed the Comp nd 4 (2D layer structure) can almost completely remove congo red (C ompound 2 only present a 77.3% removal, suggesting the structure of OFs plays an important role on the catalytic activity of the catalysts. The results indicated the subtle difference in organic ligand have a significant influence in the construction of MOFs structures. e results of many other works. In a more These findings are in conscient resent study, a family of o(II) based MOFs has been synthesized using flexible ole) ligands [124]. It can be observed that the spacer of bis(5,6- dimethy nzir the organic ligands and carboxylate anions have a great influence on the construction of different structures in the self-assembly process of bis(5,6-dimethylbenzimidazole) polymers. As shown in Fig. 7b, Compound 5 features a 3-fold interpenetrating dia array with 4-connected networks; Compound 6 exhibits a 3D noninterpenetrated 3-connected framework; while Compound 7 and 8 displays 2D networks. The discrepancy in structures consequently led to the different Fenton-like catalytic ability. The 3D Compounds (5 and 6) exhibited much higher activities than 2D Compounds

(7 and 8) for the activation of H_2O_2 . When Compound 5 or 6 was used as the heterogeneous catalyst, the degradation efficiency of CR ended up to 89 or 98% after 130 min, respectively. However, when Compound 7 and 8 was introduced into the system, only about 56 or 52% of the dye was removed, respectively [124]. The different catalytic activities of the studied Compounds may be due to the distinct coordination environments around the metal centers [122, 125].

Some works have been done on the comparison of catalytic activity of the MOFs with the same organic ligands but different metal irons. Recently two new metalorganic frameworks (MOFs) were obtained from copper (Cu-A) or cobalt acetates (Co-A) and mixed ligands (siloxane dicarbo vlic acid and 4,4 bipyridyne) at room temperature [126]. The scanning electrop ope (SEM) images showed the synthesized Cu-A MOFs are quasi-spherical particles (spherulites) and Co-A MOFs ve the smaller pore size, the higher surface are cubic crystallites. Co-A was gap Consequently, Co-A showed much higher activity area and lower energy ban mid under natural sunlight as compared to Cu catalyst. In a (97% removal in previous work, Yao et al. [127] discovered that using dicyandiamide as a C/N precursor, magnetic metal M (M = Fe, Co, Ni) nanocrystals could be embedded in nitrogen-doped carbon nanotubes (M@N-C) (Fig. 8a). The Fenton-like activity of M@N-C on the degradation of Acid Orange 7 (AO7) was examined using different oxidants (PMS, PS and H₂O₂). Results showed that the catalytic activity abided by the order of Co@N-C > Fe@N-C > Ni@N-C. It was also found that PMS was the most suitable oxidant for these Fenton-like processes under neutral pH. The authors

claimed that the high activation of PMS for AO7 degradation would be ascribed to the unique structural features in two aspects: the radical process and the non-radical process occur upon N doping in nitrogen-doped carbon nanotubes (Fig. 8b).

4. Heterobimetallic MOFs for heterogeneous Fenton-like catalysis

Pristine MOFs incorporated or doped with another one or more metal centers have received increasing attention in recent years, since the combination may enhance their particular activity [128-131].

Prussian blue (PB), a mixed-valence iron(III) hexacyanof I) compound, is considered as the first synthetic MOF [132]. It is well know PB would convert into Fe(OH)₃ in an alkaline solution [133], which will limit their practical use in various catalysis reaction processes [134]. nu co-workers [135] developed another interesting application of PB to evalytic removal organic pollutants from solution. In 2015, they synthe kinds of Fe-Co Prussian blue analogues [135]. The catalysts was constructed by Fe^{2+}/Fe^{3+} (PBAs) as photo-Fenton ca alyst J³⁻ and octahedral [anion groups, exhibiting cubic lattice structure (Fig. 9). These two Fe-Co PBAs showed exceptionally high efficiencies for the decomposition of RhB at pH from 3 to 8.5. The degradation capacity of Fe(II)-Co PBA/H₂O₂/vis system was comparable to that of the homogeneous photo-Fenton process (Fe^{3+}/H_2O_2) under the similar conditions. Apart from the conventional characterization techniques, Mössbauer spectroscopy was used to deeply explore the coordination environment and the oxidation state of iron species in the Fe-Co PBAs during the photo-Fenton process. The whole photo-Fenton reaction mechanism over Fe-Co PBAs was concluded in Fig. 9. In the first step of the photo-Fenton process, the water molecules coordinated to iron sites were replaced by H_2O_2 molecules; the formed Fe(II)-peroxide complexes can then produce •OH via Eq. (9). On the other hand, the Fe(III) in the catalysts could also be reduced by H_2O_2 at a slower rate to produce HOO• (Eq. (10)). In particular, 1O_2 produced from HOO• and •OH (Eq. (11-14)) was proved directly involved in the degradation of RhB.



In the following yer, this group reported that hydrazine (Hz) could significantly promote the degradation performance of Fe-Co PBAs based Fenton-like process [136]. Hz increased the activity of Fe(III)-Co PBA for bisphenol A (BPA) degradation by over two orders of magnitude at pH = 4.0. It was suggested that two mechanisms could be account for this dramatic enhancement in BPA degradation. Firstly, the Hz coordinated iron sites in the catalyst were identified more active than the original ones. Secondly, the addition of Hz could enhance the dissolution of Fe(III)-Co PBA which largely increased the reaction rate. In the same year, this group has successfully synthesized porous $Fe_xCo_{3-x}O_4$ nanocages based on the Fe-Co PBAs [137]. It was reported that the CN– in Fe-Co PBAs can be removed by heating at 500 °C for 1 h. Interestingly, with the increase of Fe doping amount, the morphology of $Fe_xCo_{3-x}O_4$ nanocages became more and more uniform and the particle size of them increased from about 80 to 160 nm. The obtained $Fe_xCo_{3-x}O_4$ nanocages showed much higher catalytic activity compared with Co_3O_4 and Fe_3O_4 , which was believed mainly due to the presence of octahedral (B-site) Co(II) on the catalyst surface. B-site Co(II) could provide the electrons and lead to the increase of Co(III) in B-site D ite Co(III) would then accept the electrons from the system to keep the characteristic on the catalyst surface, which suggested the Co(II)-Co(III)-Co(II) priox cycles were involved during the catalytic oxidation reaction [138].

In 2005, F'erey et al [139] reported the discovery of the mesoporous Cr-MIL-101 which exhibited him provinc surface area, incredibly larger pore size (2.9–3.4 nm), significantly highly dro- and thermal- stability. Following this work, extensive attempt have been made to incorporate metals nanoparticles into MIL-101 (Cr) frameworks to produce new types of catalysts. In 2014, Vu's group published the incorporation of Fe (an amount of ca. 25% of Cr atoms) into Cr-MIL-101 by conventional solvo thermal method [140]. In this case, Fe–Cr-MIL-101 showed high photo-Fenton activity and high stability, whereas Cr-MIL-101 exhibited almost no Fenton catalytic activities. This results suggested that Fe(III) sites in Fe-Cr-MIL-101 is mainly responsible for the decomposition of H_2O_2 . In the following year, Qin and co-works [141] present an organic acid (citric acid, CA) cooperative strategy to

assemble Fe-C oxides on the coordinatively unsaturated Cr sites of MIL-101 (Cr). This method can prevent the nanoparticles aggregated on the outer surface of host matrix. Different with conventional solution impregnation, the adding of citric acid can remarkably enhance the binding between metal ions and secondary building units of MOFs, which is very useful in metal loading control (Fig. 10a). In this report, the property-dependence of MOFs materials on the photo-Fenton catalytic activity was also investigated by comparing Fe³⁺-CA/MIL-101(Cr) with Fe³⁺-CA/MIL-53(Cr). The results revealed that the former one exhibited 10 times more as ity than the later one, in terms of decoloration and TOC removal. This sugg that the structure and properties of the support had a significant effect on activity of the catalysts for the 00, the grafting of Fe-C oxide decomposition of H₂O₂. As illustrated in 19 nanoparticles dispersed on outer surface and into cavities of MIL-53 led to a loss of between the nanoparticles and support [142. activity due to the detrimental in er excitation and ligand-to-metal charge transfer were 143]. The metal-oxo clus tant role in the photocatalytic properties of MOFs [144-146]. known to play at mpo In this regard, it was reasonable to believe that the unexceptionable catalytic activity of Fe³⁺-CA/MIL-101(Cr) were derived from the direct excitation of Cr-oxo cluster and interfacial photo-generated charge transfer between [Fe-O-C] sites and Cr node [145].

To improve the catalytic performances of MOFs, some researchers focus their efforts on the introduction of noble-metal nanoparticles into such materials. To date, a number of methods, including incipient wetness impregnation, colloidal synthesis and

chemical vapor deposition, have been studied for the fabrication of noble-metal doped MOF nanocomposites [145, 147-150]. However, many of these techniques result in high energy consumption or insufficient interfacial contact between the noble-metal nanoparticles and the MOFs [151]. In 2015, Liang et al. [151] successfully fabricated Pd@MIL-100(Fe) using a facile alcohol reduction method at 90 °C for the degradation of MO. It was demonstrated that Pd on the surface of Pd@MIL-100(Fe) can reduce the recombination of photogenerated electron-hole pairs and thereby improve the photocatalytic performance of the original-MIL 100 E. In the same year, a series of M@MIL-100(Fe) (M = Au, Pd, and Pt) w esized by the same group fabricated though a photodeposition technique at room-temperature [152]. The photocatalytic activities of the prepared catal sta found in the following order: Pt@MIL-100(Fe) > Pd@MIL-100(Fe) $\underline{ua}MIL-100(Fe) > MIL-100(Fe)$. The higher photoactivity of M@MII M = Au, Pd, and Pt) can be attributed to the synergistic effect between metal nanoparticles and MIL-100(Fe), the efficient and enhanced visible-light absorption [153, 154]. In the both charge-carrier set atio cases, •OH can be generated though the decomposition of H₂O on the photogenerated holes and the reactions of H₂O₂ with photogenerated electrons/Fe(III)-O clusters as shown in Fig. 11 [152].

The utilization of MOFs materials as the precursor or template to produce porous Fenton-like catalysts has also been demonstrated [155, 156]. In a previous work, Bao and co-works [157] present a solvothermal method to synthesize CuFe₂O₄/Cu@C composite materials derived from 1,3,5-benzenetricarboxylic ([Cu/Fe]-BTC) MOFs.

The as-synthesized CuFe₂O₄/Cu@C composite showed excellent degradation compared with Fe₃O₄@C, which is believed due to the synergistic effect of Cu⁰ in the generation of •OH [157]. In a recent study, series of graphene-encapsulated transition-metal nitrides (Fe_xMn_{6-x}Co₄-N@C; 0 < x < 6) with well-controlled morphology have been synthesized through thermal decomposition of MOFs (Mn_vFe_{1-v}-Co PBAs) at 650 °C in N₂ atmosphere (Fig. 12a) [158]. Under such conditions, the CN- group of PBAs will serve as nitrogen and carbon sources to form nitrogendoped graphene layers [159-162]. Meanwhile, Co and Fe toms will form a Fe-Co alloy, while Mn atoms will form Mn₄N nanocrysta e. The Fenton-like degradation of BPA showed Fe_xMn_{6-x}Co₄-N@C are eachly efficient catalysts for PMS activation, which was mainly attributed to the convisionce of Fe, Mn, and Co species in catalyst [158]. As illustrated in Fig.12b, = $\frac{12}{10}$ /Fe⁰/Co⁰ in Fe_xMn_{6-x}Co₄-N@C could radicals with itself oxidized to activate PMS to produce $SO_4^ \equiv Mn^{2+}/Fe^{2+}/Co^{2+}$ $/{\rm Co}^{3+}$. On the other hand, the formed and ould be further reduced to $\equiv Mn^{2+}/Fe^{2+}/Co^{2+}$ by PMS and thus $\equiv Mn^{3+}/Fe^{3+}/Co^{3+}$ makes the reaction proceed cyclically until PMS was completely consumed [163-165]. Besides, the authors found that the increasing in Mn content could largely enhance the catalytic performance, due to the fact that Mn₄N can facilitate the electron transfer for PMS activation.

5. The effects of pH on the performance of MOFs-based Fenton-like catalysis

It is very useful to understand the effect of the initial pH on the catalytic activity of MOFs-based catalysts since the actual wastewater always has variable pH values

[166-170]. Several works have suggested that MOFs-based Fenton-like catalysis could work over a wide pH range [85, 99, 135, 157, 171]. For example, Ai et al. [99] reported that H_2O_2 can be decomposed on the reactive metals sites on MIL-53(Fe) catalyst over a wide pH range from 3.0 to 9.0. However, it was worth notice that the degradation rate of RhB in that work decreased with the increase of initial pH values. Similar result was reported in a recent study [97], in which the degradation performance of MIL-53(Fe)/H₂O₂/vis was found closely dependent on the initial solution pH. The apparent rate constant of carbamazepine degradate at pH 3 is over 6 times faster than that at pH 7. High pollutant removal at low pH values can be explained by the fact that Fenton/Fenton-like actions between H₂O₂ and Fe in the catalysts preferred acidic conditions [1 sides, for some catalysts (e.g., Fe₃O₄/C/Cu), higher concentration of men Lions would dissolved at lower pH, enhancing the generation of •O homogeneous Fenton/Fenton-like reactions [171]. It is also reported that increase of pH from acidic (pH 3.0) to neutral (pH 6.5) tal tic performance of Fe₃O₄@MIL-100 in the photo-Fenton has little impact the process [109]. A possible explanation for this observation is the reaction between photoinduced electrons and H₂O₂ takes an important part in •OH generation. The combination of Fe and other metal (Cu/Co) allows the Fenton-like process to be conducted at even broader pH range. For example, Bao et al. [157] reported that nearly complete removal of MB was achieved in 15 min at pH 3.02, 5.12, and 8.14 by a CuFe₂O₄/Cu@C catalyzed Fenton-like reaction, but the removal efficiency would dramatically decrease as the pH further increase to 10.0 or higher. This is because in alkali media, H_2O_2 loses its oxidizing ability due to its decomposition to H_2O and O_2 [111, 173]. Base on the results obtained from the lab-scale experiments (Table 2), it is reasonable to conclude that MOFs-based Fenton-like catalysis is generally effective at pH 3.0-6.0. It well known that the traditional homogeneous Fenton process requires to be operated at the pH of 2.8-3.5 [7], which is actually the primary drawback of this technique. Promising results have been obtained using MOFs-based Fenton-like catalysis, showing that these technologies may help to solve this problem in the near future.

6. Stability and reusability of MOFs-based Fenton-like converse

The stability of the MOFs-based catalysts a key issue that should be considered, especially from the view of actual arpheatons. Firstly, it is important to know whether the MOFs-based Fenton-Insecatalysts could maintain their initial ao et al. [97] studied the Fourier transform structures during the oxidation infrared spectroscopy (F) spectra and X-ray diffraction (XRD) patterns of the reactions, finding that the crystal and chemical structure samples before an the afte of MIL-53(Fe) after four cycles are almost unchanged. Similar results were published in many other works [81, 85, 99, 135], suggesting that Fenton-like process has little impact on the main structure of the MOFs catalysts. On the other hand, leaching metal ions from MOFs catalysts was monitored to get a better understanding of sample stability (Table 2). It is well known that the traditional heterogeneous Fenton-like catalyst, such as iron oxides, would undoubtedly result in leaching of metal ions, giving rise to high risks to human beings [127]. Due to their special structure,

MOFs-based Fenton-like catalysts generally exhibited higher stability than the traditional heterogeneous Fenton-like catalyst. For instance, Lv et al. [85] found the leaching Fe from MIL-100(Fe) after 240 min reaction was only 14% of Fe₂O₃ catalyst. In another study, MIL-100(Fe) layer was found could reduce the leaching of Fe from the Fe₃O₄ core [109]. For Fe₃O₄@MIL-100 with 10, 20, or 40 layers of MIL-100, the iron leaching was 2.93, 0.86, 0.41 mg/L after a reaction time of 3 h, respectively. According to the scientific results, the amount of leached metals was largely depended on the chemical structure of the catalysts. For example, et al. [85] found that the leached Fe from Fe^{II}@MIL-100(Fe) reached , however, other researchers reported the leached Fe from Fe_xCo- Q_4 nanocages [137] and their predecessor Fe-Co PBA [135] was only abou 0 ¹. The addition of chelating agent, such as organic acid, can remarkably whance the stability of the MOFs-based the leached Fe from Fe³⁺-CA/MIL-101 was catalysts. As reported by Qin et below 0.08 mg/L, which wa much lower than that leached from Fe-MIL-101(Cr) (1.5 lieved that a stable bridge of CA molecule was established mg/L) [140]. It between Fe³⁺ and the secondary building units of MOFs so that they can be protected from leaching in the solution [141]. As shown in Table 2, the concentrations of leached metals in most cases are below the environmental standard (2 mg/L) imposed by the European Union [82]. Interestingly, the catalytic performance of the leached metal iron was investigated in a recent published work [82]. In the experiment, the catalyst (MIL-88B-Fe) was dispersed into the phenol solution by sonication, and then the suspension was stirred for 30 min. After MIL-88B-Fe was removed by filtration,

 H_2O_2 solution was added to the solution to initiate the homogeneous catalysis. It was found the phenol degradation catalyzed by the leached iron ions was negligible. The results suggested that the catalytic activity of MIL-88B-Fe was dominated by heterogeneous catalysis rather than homogeneous catalysis resulting from the leached iron. This result is in consistent with the findings by Hu et al. [174], who proposed that Fenton-like oxidation mainly occurs at the solid–liquid interface.

From the view of long-term industrial applications, the reusability of the MOFs-based catalysts is another important issue to be considered In most cases, as summarized in Table 2, the prepared MOFs catalysts wer table and could be used for repeated treatment of organic pollutants. e catalytic performance of the MIL-53(Fe) [97, 99], Fe–Cr-MiL-101 [140], He3 viiL-100 [109], CuFe₂O₄/Cu@C [157] and MOF(2Fe/Co)/CA [175] catalyst and maintain at the level of fresh sample hand, there are also observations that the after three or more recycles. Or catalytic activities of the MDFs atalysts decreases as with increasing multiple use of lockage of the active sites by degradation intermediates the catalysts, ma [81, 127, 137].

7. Concluding remarks and prospects

As has been stated in this review, the application of MOFs based catalysts represents a promising alternative to homogeneous Fenton processes as well as to the use of conventional catalysts in Fenton-like oxidation. The high specific area, large pore volume and chemical tenability of MOFs minerals make them attractive for that purpose. Particularly promising are the most recent results reported with the heterobimetallic MOFs catalysts, which allows achieving the high rates of the homogeneous Fenton-like process. The conclusions derived from the various literature sources can be stated as follows:

1. MOFs materials with fixed metal centers are able to catalyze H_2O_2 to generate •OH at a wide pH range, even in neutral/alkaline conditions in heterogeneous reaction conditions.

2. Amongst various preparation methods, solvothermal method has been used as a common technique for the production of MOFs catalysts. Amorg various MOFs, iron-based materials of MILs have gained particular atendios in homogeneous Fenton-like catalysis.

3. Changes in flexibility, spacer length and simpletry of the ligands can result in a wide range of MOFs materials bearing diverse architectures and functions. And their chemical structure was closely record to the catalytic performance of the homogeneous Fenton-like citalysis.

4. The efficiency of the MOFs catalyzed Fenton-like catalysis can be enhanced by combining this process with photoenergies or by introducing additional activity sites, such as noble-metal nanoparticles, into the MOFs materials.

5. There was growing interest in using heterobimetallic MOFs for heterogeneous Fenton-like catalysis. The incorporated or doped new metals can effectively enhance the catalytic performance of the pristine MOFs.

6. The recycle time and water stability are essential for the actual working place. Under the tested conditions, most MOFs catalysts have shown to be stable, with limited metal ions leaching. However, the capacity of some highly efficient MOFs would gradually decrease in the cycling runs mainly due to the blockage of the active sites by degradation intermediates.

Note that, research in this field is at an early stage. Many improvements are required before the technology can be scaled up to bench and pilot plant levels.

1. Their potential application is still limited by a number of shortcomings such as aggregation, consequent loss of dipersibility, and iron leaching. Moreover, they can be entrained during supernatants discharge. Their immobilization ortha support or a magnetic core could be potential solutions; however, the attempts reported so far showed that metals leaching cannot be completely applied. Therefore, there is room for considerable improvements in this field.

2. Another important consideration is that most studies have been conducted with simulated wastewater; few studies have been conducted with actual polluted water. Recall that huge differences could be obtained between pollutants removal efficiencies in a simulated wastewater and an actual polluted wastewater. A good example can be found in a recent study by Gao and co-workers [97] in which the Fenton-like process using MIL-53(Fe) yielded more than 94% removal in river water and 71% removal in municipal wastewater. Therefore, significant effort is required to assess these technologies for use with real wastewater.

3. Most studies to date have been conducted at the lab-scale using small reactor. To meet the commercial demonstrations, more attention should be devoted in the future to investigate their economic and operational feasibility, and the problems arising from the scale-up.

4. Many issues still need to be investigated at the lab-scale, especially in terms of obtaining a fundamental understanding of these processes. For example, metal-ligand complexes-associated mechanism needs further in-depth study, these results are encouraging for the rational design of new MOFs Fenton-like catalysts and the application of MOFs Fenton-like process under neutral condition.

5. Systematic research is still required to examine the stability of MOFs catalysts for wider range of operational conditions to avoid the leaching of these metals into reaction solution.

6. The removal of pollutants in MOFs systems are very efficient, while the mineralization are somewhat lower, therefore in the treatment of actual waste water, combining this technology with other complementary treatments, such as conventional bio-oxidation could be one an active research area.

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Pollutant	Abbrev-	Chemical	Molar mass	Structure
	iation	formula	g/mol	
Acid orange 7	AO7	$C_{16}H_{11}N_2NaO_4S$	350.32	Not of other
Bisphenol A	BPA	$C_{15}H_{16}O_2$	228.29	HO OH H ₃ C CH ₃
Carbamazepine	-	$C_{15}H_{12}N_2O$	236.27	
Clofibric acid	-	$C_{10}H_{11}ClO_3$	214.65	а
Congo red	CR	C ₃₂ H ₂₂ N ₆ Na ₂ O ₆ S ₂	96.0	
Diphenhydra- mine	DP	C ₁₇ H ₂ NO	255.36	
Methyl orange	MC	C14H14N3NaO3S	327.33	
Methylene blue	MB	$C_{16}H_{18}ClN_3S$	319.85	
Rhodamine B	RhB	C ₂₈ H ₃₁ ClN ₂ O ₃	479.02	
Phenol	-	C ₆ H ₆ O	94.11	ОН
Phenytoin	PHT	$C_{15}H_{12}N_2O_2$	252.27	°H° H°

Table 1. The detailed information of the mentioned pollutants in this review.

Table 2. The suitable operation pH, reusability and leaching ions of some studiedMOFs Fenton-like catalyst.

Catalyst	Suitable pH	Reusability	Leached ions	refs
MIL-100(Fe):	NA	No obvious loss of catalytic	No detectable	[77]
2500 mg/L		activity after 3 cycles.	Fe	
MIL-100(Fe):	3.0 - 8.0	NA	Fe: 2.2 mg/L	[85]
1000 mg/L			~	
MIL-88B-Fe:	4.0 - 5.0	Catalytic performance almost	Fe: 082 mg/L	[82]
100 mg/L		unchanged after 4 recycles.		
MIL-53(Fe):	3.0 - 5.0	4 successive r ns vithout	NA	[97]
100 mg/L		obvious loss vaci vity.		
MIL-53(Fe):	3.0 - 9.0.	Catnytic performance almost	NA	[99]
400 mg/L	C	wichanged after 3 recycles.		
Fe ^{II} @MIL-100(3.0 - 2.0	NA	Fe: 7.1 mg/L	[85]
Fe): 1000 mg/L	\sim			
Fe-bpydc:	3.0 - 6.0	Catalytic activity decreased	NA	[81]
10 mg/L		after 2nd and 3rd runs.		
Fe ₃ O ₄ @MIL-	3.0 - 6.5	4 successive runs without	Fe: 0.86 mg/L	[109]
100: 100 mg/L		obvious loss of activity.		
Fe–	3.2 - 5.5.	Catalytic activity almost	Fe: 1.5 mg/L	[140]
Cr-MIL-101:		unchanged after 3 recycles.		
300 mg/L				

Fe ³⁺ -CA/MIL-	NA	4 successive runs without $Fe < 0.08 \text{ mg/L}$	[141]
101: 100 mg/L		obvious loss of activity. $Cr < 0.01 mg/L$	
Co@N-C:	NA	Catalytic activities slightly No detectable	[127]
20 mg/L		decreased after 5 recycles. Co	
CuFe ₂ O ₄ /Cu@C	3.02 - 8.14	Retained its original activity NA	[157]
: 500 mg/L		after 10 runs.	
Fe ₃ O ₄ /C/Cu:	3.0 - 9.0	5 successive runs without NA	[171]
500 mg/L		obvious loss of activity.	
Fe ^{III} –Co PBA:	3.0 - 8.5	Good performance in the Xe< 0.15 mg/L	[135]
200 mg/L		subsequent 4-cycle wis. $Co < 0.15 \text{ mg/L}$	
Fe _{0.8} Co _{2.2} O ₄ :	NA	Good performance even after Fe: 0.11 mg/L	[137]
100 mg/L		4-cycle run Co: 0.36 mg/L	
Pd@MIL-100	4.0 - 6.0	No chous loss of catalytic Almost no ions	[152]
(Fe): 125 mg/L		activity after 4 cycles. leaching.	
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Fig. 1. (a) Topological view of MIL-100 with MTN-type zeolitic architecture. (b) View of the structure of MIL-68 involving two types (hexagonal and trigonal) of channels running through the c-axis. Reproduced with perdistion from ref [77]. Copyright 2015 American Chemical Society.

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Fig. 2. (a) An electrostatic interaction between dye MB and MOF-based materials, (b) proposed catalytic mechanism for the activation of H₂O₂ by Fe^{II}@MIL-100(Fe). Reproduced with permission from ref [85]. Copyright 2015 Fls.vie



Fig. 3. Proposed mechanism for the activation of H_2O_2 by MIL-53(Fe) under visible light irradiation. Reproduced with permission from ref [99]. Copyright 2014 Elsevier.

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Fig. 4. (a) Fe₃O₄@MIL-100(Fe) first proposed for the activation of H O₂. Reproduced with permission from ref [108]. Copyright 2016 The Royal believe of Chemistry. (b) Illustration the possible mechanism behind the endnced photocatalytic ability of Fe₃O₄@MIL-100(Fe) with tunable thickness. Reproduced with permission from ref [109]. Copyright 2016 The Royal Society of Chemistry.





Fig. 5. A possible interaction process among the framework copper species of Cu-MSMs and H_2O_2 . Reproduced with permission from ref [116]. Copyright 2015 Elsevier.

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Fig. 6. The speculative mechanism of degrading MO. Reproduced with permission from ref [117]. Copyright 2014 The Royal Society of Chemist

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Fig. 7. (a) The synthetic routes and structures of Compound 2, 3 and 4 based on flexible bis(benzimidazole) and tetrabromoterephthalic acid [110] (b) The synthetic routes and structures of Compound 5, 6, 7 and 6 base on flexible bis(5,6-dimethylbenzimidazole) ligands. Reproduced with permission from ref [124]. Copyright 2014 The Royal Society of Chemistry.

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Fig. 8. (a) Schematic diagram for the syntheses of M@N-C catalysts (M = Ni, Fe, Co).(b) Mechanisms for dye degradation by Co@N-C/PMS system Peproduced with permission from ref [127]. Copyright 2016 Elsevier.

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Fig. 9. Proposed photo-Fenton reaction mechanism over cubic lattice structure of Fe–Co PBAs Reproduced with permission from ref [135]. Copyright 2015 Elsevier.

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Fig. 10. (a) Preparation of MIL-101(Cr) supporting with Fe–carbon oxides through cooperative organic-acid-directed method with thermal treatment. Without CA, most of Fe₂O₃ aggregated on out surface of MOFs due to externa diffusion of precursor during heating process. (b) Schematic diagram of MIL-104(Cr) and MIL-53(Cr) supported catalysts for activation of H₂O₂ on the catalyte oxidation. Reproduced with permission from ref [141]. Copyright 2015/Elsevier

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Fig. 11. Proposed mechanism for the photocatalytic degradation of PPCPs over Pd@MIL-100(Fe) under visible light irradiation. Reproduced with permission from ref [152]. Copyright 2015 Elsevier.

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Fig. 12. (a) Preparation Route and Model of the Graphene Encapsulated TMNs $(FexMn_6-xCo_4-N@C)$ with Well Controlled Morphology. (b) Proposed mechanism for PMS activation over $FexMn_6-xCo_4-N@C$ nanodnes. Reproduced with permission from ref [158]. Copyright 2015 American Chemical Society.

