炭材料在过硫酸盐高级氧化技术中的应用进展

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摘 要： 炭材料凭借其拥有独特的纳米结构、优异的导电性、化学稳定性及吸附特性等在催化领域中显示出广阔的应用前景，有望成为新一代绿色非金属催化剂。近年来，国内外在各类炭材料应用于活化过硫酸盐高级氧化技术中的研究发展极其迅速。不同的炭材料具有不同的结构特征和表面性质，其对过硫酸盐的活化机理和对污染物的转化机理也有所不同。到目前为止，各种方法已经被开发并应用于活化过硫酸盐，提高了研究者对各类新型炭材料催化机理的认识。本文对石墨烯、碳纳米管、炭纤维、多孔炭、炭凝胶、炭微球、炭纳米泡、碳量子点等各种新型炭材料作为非均相催化剂或催化剂载体在活化过硫酸盐高级氧化工艺中的理论和应用研究现状进行了总结，并围绕炭材料催化剂的制备方法及结构特性、炭材料催化剂在活化效率中的构效关系、自由基及非自由基产生途径以及在降解环境污染物中的应用效果等方面展开阐述。最后指出了目前炭材料在实际应用中面临稳定性差、环境风险和生产成本高等方面的挑战以及解决方法。

关键词： 高级氧化技术；过硫酸盐；炭材料；催化剂活化；自由基降解
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The use of carbon materials in persulfate-based advanced oxidation processes：A review

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Abstract： With their unique nanostructure，excellent conductivity，chemical stability and adsorption properties，carbon materials have a wide range of application possibilities in the field of catalysis，and are expected to become a new generation of green non-metallic catalysts. In recent years，worldwide research on the applications of various carbon materials in the advanced oxidation technology using activated persulfate（PS）has developed rapidly. Here，theoretical and applied research progress on graphene-based materials，carbon nanotubes，carbon fibers，porous carbons，carbon aerogels，carbon microspheres，carbon nanobubbles and carbon quantum dots as heterogeneous catalysts to activate peroxymonosulfate and peroxydisulfate are reviewed. The preparation methods and structural characteristics of the carbon catalysts，the relationship between their structure and activity in the activation of PS，the paths for the generation of free radicals and non-free radicals，and the uses of carbon materials in the degradation of pollutants by activated PS are summarized. Finally，the challenges of poor stability，environmental risks and high costs of carbon catalysts in practical applications and their solutions are pointed out，with the aim of providing references for the further applications of carbon materials in advanced oxidation technologies.

Key words： Advanced oxidation process；Persulfate；Carbon materials；Catalyst activation；Free radical degradation

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1 Introduction

Currently，environmental pollution caused by some new pollutants（such as drugs，personal care products，endocrine disruptors and other refractory organics）has attracted more and more attention[1]. Activated persulfate（PS）oxidation is a new advanced oxidation technology developed rapidly in recent ten years. The O—O bond in peroxymonosulfate（PMS）or peroxydisulfate（PDS）molecules breaks under the action of activation factors，forming a sulfate radical

($SO_4^{-}\cdot$) with a lone pair of electrons and strong ability to obtain electrons[2]. $SO_4^{-}\cdot$ has higher oxidation potential (E_0 = 2.5-3.1 V) than PS itself, which can form organic free radicals through electron transfer, thus realizing the oxidation and degradation of organic pollutants[3]. In recent years, PS-based advanced oxidation process has been favored by researchers at home and abroad owing to its strong oxidation ability, fast reaction rate and wide applicability to pollutants in waste water.

The activation methods of PS include the use of external energy activators (such as ultrasound, heat and ultraviolet), transition metals (such as iron, cobalt, manganese) and chemical activators (such as alkali, phenol and quinone)[1]. Activation with external energy is an effective process, but has high energy consumption and harsh reaction conditions that hinder its large-scale application. Homogeneous transition metal activation is highly dependent on the solution pH, and there is a risk of metal leaching[4]. In order to overcome these problems, some new activating materials and methods of PS have been developed. Carbon materials include nano carbon materials (such as one-dimensional single-walled carbon nanotubes, two-dimensional graphene and three-dimensional mesoporous carbons) and amorphous carbon materials (activated carbons, biochar and black carbon). Due to the high specific surface area and abundant pores, activated carbons, biochar and other materials are mainly used as adsorbents in environmental applications, while some new carbon materials have attracted more attention owing to their special nanostructures, superior conductivity and electrochemical performance.

Studies have shown that the catalytic performances of carbon materials are related to the pristine carbon configuration, oxygen functional groups, defect degree, and dimensional structure[5]. Carbon-based catalysts can activate PS to remove pollutants through radical and non-radical pathways. For the radical pathway, carbonyl groups may play a role in the decomposition of PS to form $SO_4^{-}\cdot$. For the non-radical pathway, PS can react with the edge sites of carbon materials to form reactive intermediates, while the activated PS complex attacks the organic pollutants through a non-radical process[6]. Meanwhile, more research has been carried out on the correlation between the properties of carbon materials and electron transfer efficiency and its control mechanism. As an electron transfer medium, the relationship between these new carbon materials and various electron donors and electron acceptors in the environment has gradually become a research hotspot in recent years[7].

Because of the advantages of new carbon materials, such as wide sources of raw materials, simple preparation process and environmental friendliness, it has shown great application prospects in the field of environmental pollution control and is gradually becoming a new generation of green catalysts. Since 2014, the research of carbon materials as PS activators to deal with various organic pollutants has developed rapidly at home and abroad. Different carbon materials have different structural characteristics and surface properties, and their activation mechanism for PS and transformation mechanism for different pollutants are also different. It is extremely paramount to study the electron transfer mechanism of various new carbon materials in the catalytic PS process and develop targeted environmental functional materials[7,8]. However, there is no summary of the application of graphene, carbon nanotubes and other new carbon materials in the field of activated PS oxidation. In this paper, the theory and application of different new carbon materials to activate PMS and PDS in the treatment of environmental pollutants at home and abroad in the past five years are systematically reviewed, and the challenges and development directions in this field in the future are put forward, which may provide theoretical guidance for the further application of new carbon materials in the field of catalytic oxidation and environmental remediation.

2 Activation of PMS by new carbon materials

Under the action of various activation factors such as carbon materials, both PMS and PDS will produce $SO_4^{-}\cdot$. However, the microstructure and properties of PMS and PDS are different, so it is not accurate to explain the activation and oxidation mechanism of PS only according to the observation results of PMS and PDS[9]. The differences between the reactivity of PMS and PDS mostly stem from the fact that the peroxide bond in PMS is asymmetrical with a partial positive charge induced on the peroxide oxygen attached to the hydrogen, while the peroxide bond in PDS is symmetrical in charge distribution. Therefore, the nonpolar PMS is more prone to nucleophilic attack by various nucleophiles. In addition, the steric hindrance due to the presence of two SO_3 moieties on both sides of the peroxide linker also makes PDS less reactive to select organic compounds than PMS[9]. The above differences in microstructure and properties

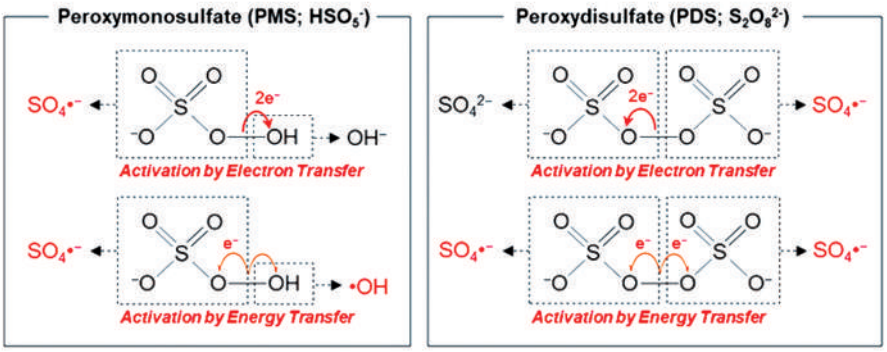

Fig. 1　Activation of PMS and PDS through electron- and energy-transferring processes[9]. Reprinted with permission.

between PMS and PDS lead to the differences in specific activation process. PMS with an asymmetric molecular structure is more likely to be activated by carbonaceous materials and noble metal catalysts through a mediated electron transfer mechanism, while PDS is more likely to be activated by energy (light, ultrasound and heat), which homolytically break the peroxide bond due to lower bond dissociation energy (Fig. 1).

2.1　Graphene materials

Graphene is a new two-dimensional nanomaterial, which has an excellent conductivity, chemical stability and high adsorption performance. It can not only be used as a catalyst to degrade organic pollutants, but also as a dopant and support of metal catalysts to improve the performance of the metal catalysts. At present, graphene has become an ideal green substitute of metals/oxides for environmental catalysis.

2.1.1 Reduced graphene oxide

Compared with one-dimensional CNTs, two-dimensional reduced graphene oxide (rGO) shows better catalytic activity due to the increase of surface defects, structural defects and vacancies[6]. Theoretical and experimental analysis shows that the defects such as vacancies and zigzag/armchair edges of rGO interface act as the active sites for cleaving O—O bond in PMS, which improves the adsorption energy, elongates O—O bond and increases the electron transfer efficiency. It is established that the reaction rate constant in degradation pollutants is closely related to the I_D/I_G value that indicates the degree of graphene disorientation caused by structural defects of thermally annealed rGO[10]. Among the three kinds of rGO with a similar oxygen content, the one with the highest ketone group (C═O) has the best activation efficiency, which indicates that the electron rich ketone group is the main active species in the oxygen functional groups and promotes the adsorption of PMS molecules in the defect center. Although graphene, as the parent material of other graphite materials, has opened up a new prospect for the application of two-dimensional materials, the characteristics of the original graphene, such as zero band gap, limit functional groups and high chemical potential, also hinder the application of the original graphene as a catalyst to some extent[11]. Olmez et al. found that rGO could be used as an activator of PMS to effectively degrade the endocrine disruptor bisphenol A (BPA) in different water bodies, but the catalyst was seriously inactivated after the second use, so further research was needed to improve the catalytic stability of rGO[11].

2.1.2 Heteroatom-doped graphene

The adsorption capacity of rGO is significantly improved by nitrogen modification. There are at least two possible reasons for this enhancement effect. The presence of ammonia and nitrogen functional groups reduces the aggregation of rGO and the introduction of N not only binds to acidic BPA molecules as Lewis-base sites, but also increases the reduction degree of rGO, activates the spontaneous free-flowing π electron of graphene, thus increasing the π -π interaction between aromatics and rGO as reported previously[12]. In the N-rGO/PMS system, an adsorption-degradation cycle is started again and repeated until all BPA is degraded (Fig. 2)[12]. In the process of PMS activation, N-rGO plays a dual role of a PMS activator and an electron transfer medium. Density functional theory (DFT) calculations demonstrate that N doping improves the charge density of net positive carbon atom, reduces the energy gap, and enhances the activation of PMS[13]. While metal organic frameworks (MOFs) have been extensively explored as a platform for developing porous metal oxides, another intriguing direction is to use MOFs as precursors to prepare carbonaceous materials. A N-doped GO, which is prepared by simple pyrolysis of MOFs and dicyandiamide, shows better performance than graphene, iron oxide, manganese oxide and cobalt oxide

in PMS activation, and the main active species are singlet oxygen ($^1O_2$)[14]. During the preparation of N—GO, the contents of reactive functional groups (graphitic N, pyrrolic N, pyridinic N, nitric oxide and C ═O) in N—GO are delicately controlled by adjusting the annealing temperature, so as to enhance the performance of PMS, and the N—GO prepared at 600 ℃ has a high N-doping content, the most suitable reactive functional groups, and manifestes the most perfect catalytic performance[15].

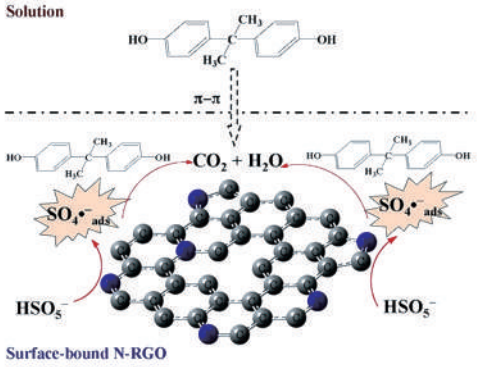

Fig. 2 Degradation mechanism of BPA by N-rGO/PMS system[12]. Reprinted with permission.

Polyatomic co-doping can generate many kinds of functional groups on the surface of GO and plays a better role in improving the catalytic performance of composites. Sun et al. doped N and S into industrial rGO, the composite catalyst revealed a high activity of activating PMS for catalytic oxidation of endocrine disruptor under various conditions[16]. When N and boron-co-doped graphene (NBG) is used as a PMS activator to degrade sulfacetamide, the concentration of main functional groups as well as catalytic activity of NBG can be delicately controlled by adjusting the temperature of thermal annealing. Among them, the NBG synthesized at 800 ℃ has not only the highest level of total N and B, the highest content of pyridine N and BC3, but also the best efficiency of activating PMS[17]. It has been conclusively proved that the introduction of B can promote the transition from non-free radical oxidation dominated by NG/PMS system to non-free radical and free radical co-oxidation in NBG/PMS system. The synergistic coupling effect between pyridine N and BC3 is the main reason for improving the catalytic activity of NBG800[18].

2.1.3 Metal-catalysts supported on graphene

Loading metal particles with a special catalytic activity on carbon materials with a high conductivity and strength will help to enhance the fixation and dispersion of metal particles, solve the problem of easy agglomeration in the catalytic process, improve the catalytic activity and service life of the catalyst, and avoid the release of free metal ions in the treatment process[19]. In particular, carbon-metal composites can form new atomic configuration, which may reduce the local function of carbon surface, and reduce the resistance PS activation by electrostatic or covalent interactions[20]. And M-C bond is beneficial for the transfer of electrons from metal to PS as compared with M-O bond[6]. Therefore, the development of carbon-based magnetic nanocomposites is a win-win strategy for both carbon catalysts and magnetic nanoparticles, which can be easily realized by external magnetic field. It has been confirmed that the catalytic activity of rGO-based magnetic nanocomposites for PS is better than that of CNTs-based magnetic catalysts.

Cobalt and its oxides are the most effective metal catalysts for activating PS. In order to reduce the leaching of Co in the catalytic process, many researchers have loaded Co on GO to improve its practicability in the treatment of wastewater by activated PMS[18,21-26]. In a short period of time, organic pollutants are completely removed by PMS and Co_3O_4-GO composite catalysts, which is synthesized by connecting and dispersing the Co_3O_4 nanocrystals on GO nanosheets, which reveals higher catalytic activity than pure Co_3O_4[18,21].

Magnetic cobalt ferrite ($CoFe_2O_4$) is extensively investigated for the activation of PS to generate $SO_4^{-}\cdot$. A $CoFe_2O_4$-GO composite with magnetic recyclability and reusability, which has been prepared by uniformly modifying $CoFe_2O_4$ nanoparticles on GO nanosheets, has a larger specific surface area and more active oxygen species than $CoFe_2O_4$, less metal ions are released, thus it shows better efficiency in catalyzing the formation of $SO_4^{-}\cdot$ from PMS (Fig. 3)[19,22]. Nevertheless, the excessive content of GO in $CoFe_2O_4$-GO will also lead to excessive adsorption and incomplete degradation of pollutants. The composite material with a 22% GO content has the best effect to activate PMS[23]. The role of GO in the hybrid catalyst is

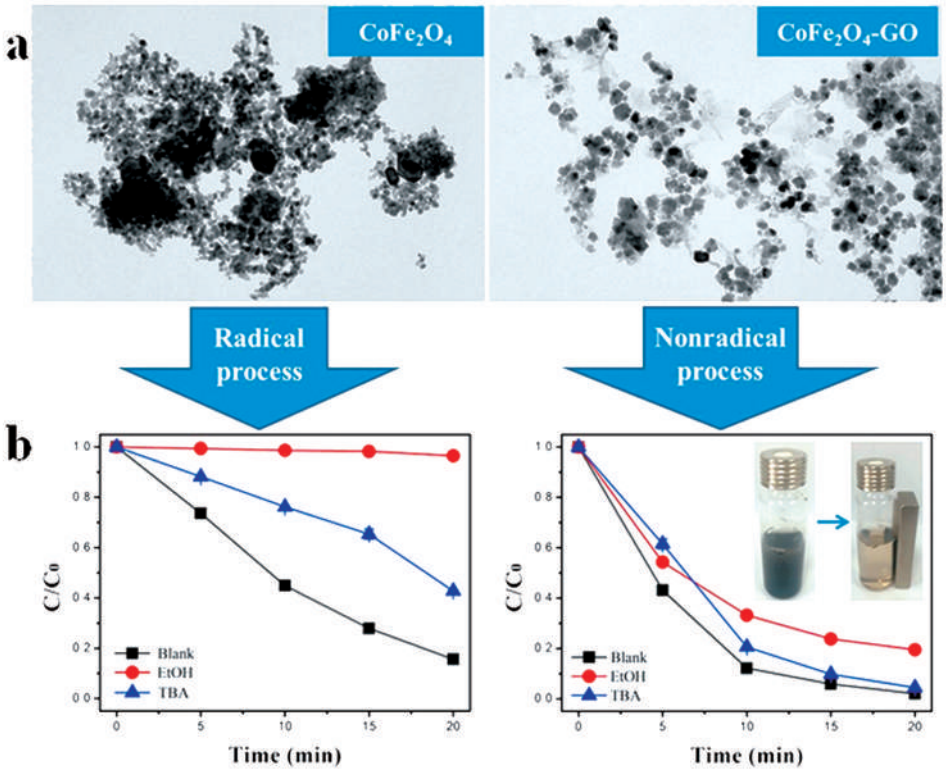

Fig. 3 (a) Typical TEM images of $CoFe_2O_4$ nanoparticles and $CoFe_2O_4$-GO composite and (b) Effects of the radical scavengers on the NOR degradation in $CoFe_2O_4$/PMS and $CoFe_2O_4$-GO/PMS systems[22]. Reprinted with permission.

found to serve as a matrix rather than a catalyst, and the adsorption of pollutants molecules induced by the presence of GO could be desorbed again by the participation of PMS ions[23].

By simple one-step carbonization, MOFs can be turned into carbon-based composites with task-specific functionality rather than the precursors. This strategy is adopted to prepare a magnetic cobalt-graphene (MCG) nanocomposite from carbonizing a self-assembly of a cobalt-based MOF, ZIF-67 and GO, and MCG exhibits an enhanced catalytic activity to activate PMS compared to the carbonized ZIF-67 because rGO also activates PMS and improves electron transport ability[20]. Pi et al synthesized magnetically separable Co-Fe-PBAs@ rGO nanocomposites from Co-Fe Prussian blue analogue, $Co_3[Fe(CN)_6]_2$ and GO through a simple two-step hydrothermal method, and suggested that the synergistic interaction between Co-Fe-PBAs and rGO prevented the aggregation of Co-Fe-PBAs nanoparticles, which enhanced the efficiency for activation of PMS[24]. As a highly efficient heterogeneous catalyst for PMS, GO loaded with cobalt phthalocyanine can effectively reduce the leaching of cobalt ions. The delocalized π electron in GO has the ability to activate PMS to produce $SO_4^{\cdot-}$, and the removal rate is still as high as 100% after 11 times of recycling[25-26]. Transition metal iron, manganese and their compounds can also be loaded onto GO material to prepare PMS activators[27-30]. In a highly active mediator (Fe@ N-doped graphene-like carbon) for PMS activation prepared by MOFs and g-C_3N_4, the variable chemical valences of iron nanoparticles, N functional groups and C═O groups in the support contribute to improve the catalytic activity. In this hybrid catalyst, sp^2 hybridized carbon and electron-rich sp^2 sites of the graphitic domain activate PMS through electron transfer[29].

As has been demonstrated by previous studies, the composite composed of magnetic nanoparticles and carbon materials generally showed excellent performance for activate PS, which exhibited a synergetic effect between carbon materials and magnetic nanoparticles. This was mainly due to the following several reasons. From the aspect of carbon material, it firstly acted as a carrier to disperse magnetic nanoparticles, which avoided the aggregation of nanoparticles, and increased the effective specific surface area and active sites[19]. Additionally, the electron transfer between PS and catalyst could be effectively promoted by the carbon material. Due to the protection of magnetic nanoparticles, the stability of carbon materials became better[20]. In addition, metal doping in car-

bon materials would increase surface defects or become new active centers, which was conducive to the activation properties of the materials[6]. It should be noted that the synergetic effect largely depends on the mass ratio and combination mode between carbon materials and magnetic nanoparticles. Therefore, it is necessary to optimize the preparation method to synthesize the catalyst with an excellent activity.

2.2 Carbon nanotubes

Carbon nanotube (CNT) is a hollow tube with a one-dimensional tubular structure, which is made of single or multi-layer graphite sheets. It is a new type of carbon materials with a diameter of nanometer and a length of tens of nanometers to several millimeters. CNT has a unique cavity structure, adsorption and electrical characteristics. Guan et al found that both CNT/PMS and CNT/PDS systems could effectively remove bromophenol, but the latter only oxidized via non-free radical way, while the former produced free radical and non-free radical species at the same time, which had more advantages in treating wastewater containing multiple pollutants[31]. In the CNT activated PMS system, the decolorization of AO7 mainly occurs on the CNT surface, not in the solution, and the decolorization is mainly completed by free radicals[32].

N doping can change the density of electron cloud around C atom in CNT, which makes it possess outstanding electronic conductivity, and its electronic effect also demonstrates unique performance in catalysis. Ma et al successfully prepared a series of N doped CNT frameworks (NCNTFs) with a distinguishable N content and graphitization degree through in-situ transformation of ZIF-67 in N_2/H_2 atmosphere at different pyrolysis temperatures[33]. The formation of intertwined CNT harvests a desirable mesoporous structure that is favorable for the mass transfer and diffusion of reaction substances, compared with conventional N-doped carbon materials derived from MOFs (Fig. 4). When they are applied for catalytic degradation of BPA in the presence of PMS, NCNTFs-800 shows a higher removal efficiency than NCNTFs obtained at the other pyrolysis temperatures[33].

Existing research has been recognized the critical role played by CNT on oxidation of activated PS. Duan et al. thought that the activation of PMS by N-decorated single-walled CNT (N-SWCNT) was a temperature dependent process[34]. High temperature would change the catalytic process of PMS by N-SWCNT from non-free radical oxidation to free radical pathway, that is, coupling heat with the carbon catalyst could significantly reduce the activation energy. In the N-doped CNTs encapsulating bimetallic Fe/Mn nanoparticles (FeMn@NCNT), encapsulated Fe/Mn were protected by both NCNT and the clingy graphite structure. The redox cycle between Mn and Fe in the multivalent state ensured the high-efficiency catalytic activity of FeMn@NCNT to PMS, which was mostly recovered after heat regeneration[35]. In the Fe_3C@N-doped CNT/graphene nanocomposites synthesized by direct high-temperature pyrolysis with commercial $K_4Fe(CN)_6$ as the precursor, the relatively high graphitization degree and rich N-doping amount make the hybrid material had a promising catalytic activity in PMS activation for powerful removal BPA (Fig. 5)[36].

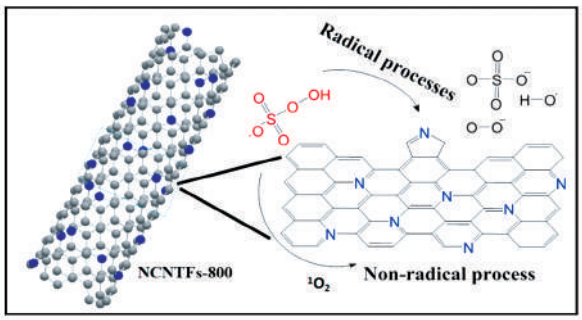

Fig. 4 The radical and non-radical processes in PMS activationby NCNTFs-800[33]. Reprinted with permission.

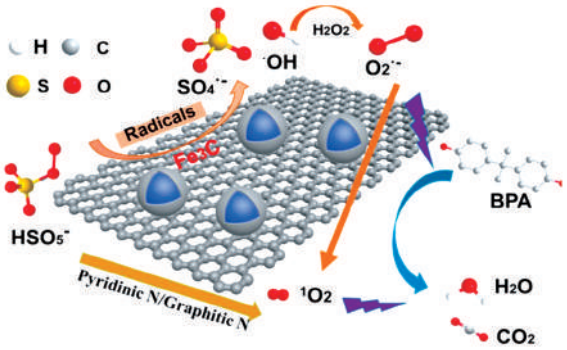

Fig. 5 Activation mechanism of PMS by Fe_3C@NCNTs/GO[36]. Reprinted with permission.

2.3 Carbon fibers

Yang et al carried out a series of studies on the performance of activated carbon fiber (ACF) as a catalyst to activate PMS for dye degradation, and thought that the basic sites on ACF surface were likely to be the active sites that induced the decomposition of PMS and the generation of radicals[37-39]. Recently, investigators examined the effects of N-containing functional groups on the ACF surface, and argued that π-π, pyridine and amine had promoting effects on the catalytic oxidation while the —NO_2 had an inhibitory effect in the ACF/PMS systems[38].

Subsequently, they investigated the conceivable deactivation reasons of ACF in PMS activation, and found that the original organic compounds or intermediate products adsorbed by ACF would be possibly responsible for the deactivation. As one of the solutions, the fact that PMS oxidation on ACF would retard ACF deactivation to a large extent has been proved by pre-oxidation experiments[39]. Beyond that, iodine doped CF also exhibited an extra-high catalytic activity to activate PMS for the removal of dyes over a wide pH range of 3-10, with a remarkably pH-tolerant performance[40].

Cobalt carbon nanofiber composite (Co-CNFs) synthesized by electrospinning and carbonization has a large aspect ratio to avoid aggregation and large specific surface area to provide more reaction sites for improving the catalytic activity of PMS. In this composite, zero valent cobalt was proved to be the main cobalt species of axis or core of the fiber, which might account for its promising magnetic response and recovery performance (Fig. 6)[41]. More importantly, Co@ ACFs presented an enhanced catalytic performance over most reported heterogeneous Co catalysts due to the significant role of ACFs: (1) high adsorption capacity in favor of the enhanced catalytic activity and (2) ACFs as an electron donor to accelerate Co^{2+}/Co^{3+} cycle thereby speeding up degradation[42].

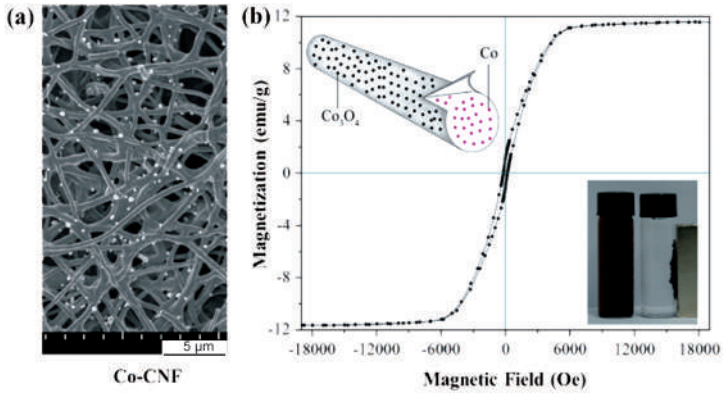

Fig. 6　(a) Typical SEM image of Co-CNFs and (b) Magnetic hysteresis loop of Co-CNFs[41]. Reprinted with permission.

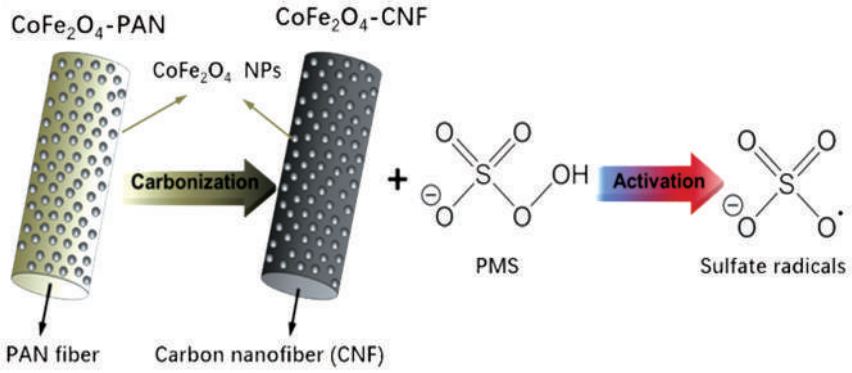

Fig. 7　Preparation of $CoFe_2O_4$@CNF and the formation of radicals form activation of PMS[43]. Reprinted with permission.

As cobalt ferrite nanoparticle (CFNPs) in water are prone to agglomerate, a few attempts have been made to immobilize CFNPs on CNF to prepare a composite, which contains well distributed CFNPs, high magnetism and stable carbon support, making the CF@CNF composite a highly promising catalyst for activating PMS (Fig. 7)[43]. Furthermore, in the photoelectrocatalysis system consisting of a γ-Bi_2MoO_6 anode and a Co_3O_4 loaded ACF paper cathode, PMS is activated by Co_3O_4 on the ACF paper to generate $SO_4^{-}\cdot$, in which photogenerated-electrons accelerate the cobalt cycle process on the cathode, resulting in strong inhibition of CO leaching[44].

2.4　Porous carbons

N-doped porous carbons (NPCs) have emerged as promising metal-free catalysts towards PMS activation for environmental remediation. In general, NPCs prepared at 800 ℃-1 000 ℃ have the highest graphite

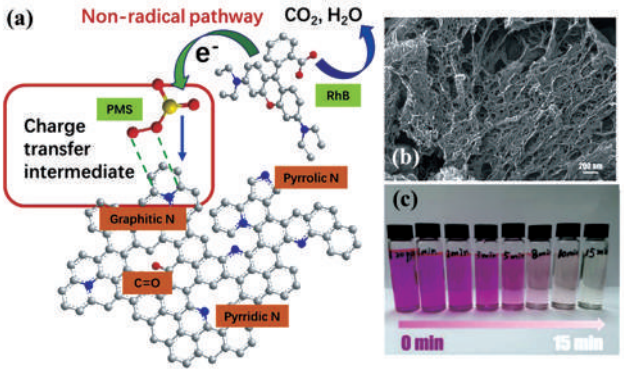

Fig. 8 (a) Mechanism of PMS activation by NHPC-800, (b) SEM images of NHPC-800 and (c) RhB degradation by NHPC-800/PMS system[47]. Reprinted with permission.

edges and folds, which provides sufficient exposed catalytic active centers and fast electron transportation for rapidly activation of PMS (Fig. 8)[45-48].

Co-doping of Co and N into carbon may synergistically modify the electronic structure of carbon and enhance its catalytic activity towards PMS[49]. Moreover, the catalytic activity of Co-N-PC is significantly enhanced with the increase of Co-N coordination sites ($Co\text{-}N_x$), which could also inhibit Co leaching due to its strong binding. The synergism of Co and N is ascribed to the combination of their different roles. The N doping mainly produces the charged carbon sites for PMS adsorption, while the Co doping mainly facilitates the electron transfer from carbon to PMS for its dissociation into $SO_4^{-}\cdot$[49]. Liu et al. discussed the role of NH_2-group incorporation on the development of microstructure and physical-chemical properties of obtained Fe@PC, and reaction mechanism for PMS activation, and it was assumed that the addition of N in PC and the rigid encapsulation structure reduced the defects of the Fe@PC, which were favorable for the enhancement of the catalytic activity and stability of the obtained Fe@PC in the activation of PMS[50]. Zeng et al subtly integrated eco-friendly and cost-effective Fe-based nanoparticles (Fe/Fe_3C) within NPC to effectively activate PMS[51]. Benefiting from the promising enrichment ability of NPC matrix and abundant accessible sites arising from NPC and the catalyst, Fe/Fe_3C@NPC outperformed common oxides for PMS activation and organic compound degradation[51].

Among porous carbon materials, mesoporous carbon (MC) display marked advantages owing to their high surface area and ordered mesoporous structure, capable of providing a large amount of active sites for PMS activation and enhancing reactant diffusion. Comparing different nanocarbon materials, it is found that the 3D hexagonal OMC has the advantages of higher surface area and edge defects with a higher density of electronic states than other nanocarbon materials with different structural dimensions (such as 0D fullerene, 1D single-walled CNTs, 2D graphene nanoplate, and cubically-OMC), which are the key factors affecting the electron transfer reactions, and the ketonic moiety (C═O) is highly responsible for the high performance of 3D hexagonally-OMC[52].

Notably, heteroatom – doped MC exhibited remarkable advantages over MC when used as catalysts and supports. In comparison with the MC obtained from ethylenediamine (EDA) and dicyandiamide, N-doped MC prepared using EDA and carbon tetrachloride as the precursors displayed a higher activity for PMS activation and toxic o-phenylphenol degradation[53]. Compared with the pristine ordered mesoporous carbon (OMC), the catalytic activity of boron-doped OMC was greatly increased, which was resulted from the enhanced adsorption capacity and the increased catalytic activity for PMS activation[54]. On the one hand, boron doping increased the BET surface area and pore size of OMC. On the other hand, Lewis acid sites were introduced on the surface of OMC that acted as catalytic sites for PMS activation[54]. In addition, CoO_x-doped OMC combined with PMS could completely degrade 20 mg/L phenol in 60 min. The catalytic activity of CoOx-doped OMC for PMS activation was much higher than that of Co_3O_4, $CoFe_2O_4$ and OMC, and was not affected by HCO_3- and humic acid[55].

2.5 Carbon aerogels

As emerging carbonaceous materials, carbon aerogels revealed a great potential in environmental purification. Hu et al used the GO sheets and resorcinol formaldehyde resin in the presence of cobalt ions to prepare macroscopic three-dimensional Co-doped carbon aerogels (Co-CA)[56]. Cobalt ions were introduced as a polymerization catalyst to bridge the organogel framework, and finally were retained as both

metallic cobalt and Co_3O_4, which were wrapped by graphitized carbon layers[56]. Although Co-CA showed a lower cobalt loading and higher mass transfer resistance than traditional powder catalysts, it could activate PMS with a lower activation energy and efficiently eliminated organic contaminants[56]. In the 3D porous Co_3O_4/N doped graphene aerogel (Co_3O_4/NGA) hybrid prepared by a combined feasible hydrothermal and freeze-drying method, Co_3O_4 nanocrystals and the new active sites created by N doping into the graphene honeycomb network should synergistically contribute to the high activating PMS and degradation efficiency[57].

2.6 Carbon microspheres

Zn-Co Prussian blue analogues (Zn-Co-PBAs) can be used as raw materials to prepare porous N doped carbon (PNC) microspheres, which are used as heterogeneous catalysts for the activation of PMS[58]. The unique configuration of the metal centers/clusters bound by cyanide groups of Zn-Co PBAs offers the PNC microspheres with abundant porosity, a high graphitization degree, and rich N substitution, which improve the catalytic performance of PMS. Notably, methylene blue degradation over PNC-800 is almost completely insusceptible to common ions and natural organic matter, and maintains its catalytic efficiency under the background conditions of several real water samples[58]. Zhou et al prepared carbon microspheres supported cobalt catalysts (Co/CS) by a one-pot hydrothermal method. Cobalt would distribute three-dimensionally in the spheres. The catalytic efficiencies of Co/CS prepared at different calcination temperatures were different, among which Co/CS-400 could activate PMS to completely remove 20 mg/L phenol in 5 min[59].

2.7 Carbon nanobubbles

In the report published by Wang et al., N-doped carbon nanocages-encapsulated carbon nanobubbles (CBs@NCCs) were feasibly fabricated by in situ thermal conversion of Co-Fe-Prussian blue analogues coated with polydopamineshells[60]. Compared with those carbon cavities without the protection of carbon nanocages, CBs@NCCs possessed a higher specific surface area and pore volume[60]. The contribution of unique configuration and proper N modification were believed to be indubitable for improving activation performance of CBs@NCCs to PMS.

3 Activation of PDS by new carbon materials

3.1 Graphene materials

Although it has been reported that graphene itself can activate PDS[61], more researchers use N = doped graphene or graphene supported with metals as catalysts to improve the degradation efficiency. Recent reports confirmed that N-doped graphene and aminated graphene could effectively activate PDS to remove sulfamethoxazole, but the PDS activation by GO was not observed[62]. There is a novel idea, that is, a metal-free catalytic membrane fabricated with a N-GO catalyst prepared with melamine is applied in filtration experiments for the removal of pollutions (Fig. 9)[63]. A crucial advantage associated with the application of this catalytic membrane, instead of a catalyst in powder form, is to avoid the final catalyst separation step after PDS oxidation process. Moreover, many researches have loaded nZVI on graphene materials, which can efficient activate PDS to remove organic pollutants including landfill leachate, trichloroethylene and atrazine[64-66].

Furthermore, dispersion of metal oxide nanoparticles on the rGO surface can prevent agglomeration of nanoparticles and disrupt aggregation of rGO sheets. Redox effect coupled in metal oxide and electron transfer by oxygen-containing functional groups on the rGO surface can promote the formation of $SO_4^{-}\cdot$[67]. Recent evidence suggested that the hybrid materials

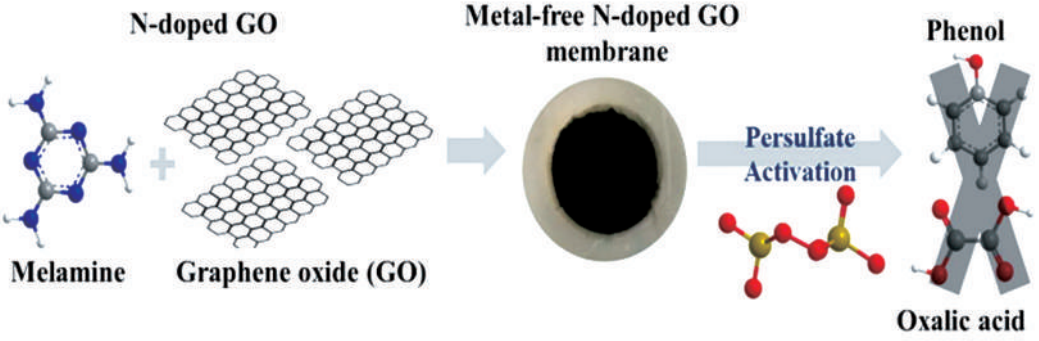

Fig. 9　Preparation of N-GO catalytic membrane and activation of PDS[63]. Reprinted with permission.

prepared by loading CuO or Fe_3O_4 nanoparticles on GO sheets could achieve the effect of complete degradation of pollutants in a short time when coexisting with PDS, and its stability and reusability were better than those of the unloaded oxides[68-69]. When Ag^0 and Fe_3O_4 were co-loaed in the rGO sheets (0.1 g/L) as an heterogeneous activator of PDS, 99% acetaminophen and β-estradiol were removed[70]. In a recent report, Yang et al. combined Ti^{3+} and oxygen vacancy self-doped TiO_2 coupled with rGO to develop a catalyst with a high activity for PDS activation under visible-light irradiation[71]. In another study, in order to solve the problem that application of Schiff base metal complexes was limited by their effectiveness and stability, a novel graphene-based Schiff base copper complex was developed to effectively activate PDS for the oxidation of triclosan. The point was also been put forward that the role of graphene played in catalysis was not only as a carrier but also to build hydrophobic microdomains for the stabilization of the catalytic active sites in the reaction[72].

Several studies have shown that the performance of carbon-based catalysts is significantly reduced after the first use. For example, the removal efficiency of N-doped rGO decreased from 100% to 31% in 45 min, while the removal efficiency decreased from 100% to 20% for N, B-codoped rGO[73,74]. In addition, the cannibalistic reaction after one-time use also means that the generated radicals are not fully utilized for pollutant degradation. Therefore, improving the durability of the carbon-based catalysts is expected to have a positive effect on the improvement of pollutant removal.

3.2 Carbon nanotubes

Generally, compared to other materials, the surfaces of purified or modified of CNTs have significant adsorption capability toward organic compounds, halogen ions and heavy metals[75]. At present, PS activation by CNTs has shown excellent activity towards organic chemical destruction. Many studies have confirmed that activation of PDS by CNTs is mainly through non-free radical pathways[76]. The analysis of the intrinsic mechanism of PDS activation by CNTs manifests that direct CNT mediated electron transfer and the formation of $^1O_2$ are considered to be the two major pathways for oxidation of 2,4-DCP by PDS. The C═O group is determined to be the main active sites contributing to the direct electron transfer oxidation, while $^1O_2$ is generated at surface defects of CNTs[77]. Moreover, the generation of the superoxide radical as a precursor of the singlet oxygen is also confirmed in the process of 2,4-DCP degradation by CNT-activated PDS[78].

In the presence of single- or multi-walled CNTs, persulfates bind onto the surface of CNTs, forming reactive complexes that are immediately decomposed upon reaction with organic compounds[79]. Some studies reported that in the PDS/CNT system, PDS was catalyzed initially by CNTs to form a CNT surface-confined and CNT-activated PDS (CNT-PDS*) complex with a high redox potential. Then, the CNT-PDS* complex selectively abstracted electrons from the co-adsorbed phenolic compounds to initiate the oxidation[80-81]. The mechanism of enhanced PDS activation by the nitric acid/annealing modified CNTs was proposed that the nitric acid modification resulted in more defective edges and oxygen-containing groups, and subsequent annealing at high temperate facilitated the conversion of sp^3 to sp^2 carbon, then the catalytic activity for PS activation was enhanced by the active sites of C═O group and sp^2-hybridized carbon at the defective edges[82].

Multi element co-modified CNTs, such as Fe/S doping, Fe/Cu doping and Ni/N doping CNT catalysts can significantly accelerate the PDS activation, and become a common method to improve the stability and oxidation resistance of catalyst[83-85]. For example, copper ferrite decorated multi-walled CNT magnetic nanoparticles show a high catalytic activity, stability and recyclability in diethyl phthalate removal[83]. Especially, leaching of metal ions from the reused catalyst is negligible. In the Fe/S-CNT/PDS system, PDS is first bonded with the sp^2-hybridized system and activated by iron oxide particles and iron-sulfur complexes, then reacts rapidly with the adsorbed 2,4-DCP (Fig. 10)[84]. Interestingly, polyhydroquinone -coated magnetite/multi-walled CNTs can be used as a novel heterogeneous catalyst for PDS oxidation flumequine[86].

It has to be noted that the weight ratio of CNTs to magnetic nanoparticles is critical to maintain a balance between catalysis and adsorption, as well as keep the stable catalytic performance of the nanocomposite. When there are too many magnetic nanoparticles, the catalyst is inclined to aggregate and reduce the specific surface area, which results in the decrease of catalytic activity, and the contact between the functional groups on CNTs and PS is also hindered[83]. On the other hand, if the proportion of CNTs in the nanocomposite is unreasonable, the electron transfer ability of CNTs will not be fully utilized, and the magnetic strength of the composite will decrease, which will bring difficulties for the degradation of pollutant and recovery of the catalyst[6].

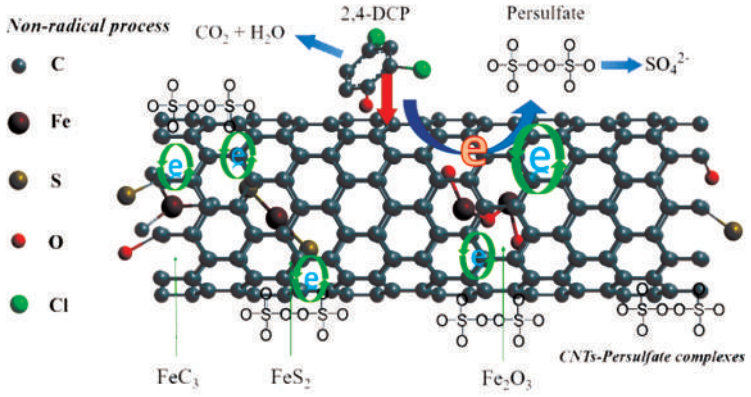

Fig. 10　Oxidation of 2,4-DCP by non-radical mechanism using PDS activated by Fe/S-CNTs[84]. Reprinted with permission.

3.3　Activated carbon fibers

Activated carbon fibers (ACFs) are demonstrated a higher activity than activated carbon (AC) to activate PDS to decolorize Orange G (OG), and the addition of Cl^- and SO_4^{2-} can increase the adsorption of OG on ACF surface, which is thus favorable for decolorization caused by the surface-bound $SO_4^{\cdot-}$ and HO·[87]. The PDS activation efficiency increases with the increase of the ACF content and ultrasonic power, which can generate free radicals and decolorize OG on the ACF surface[88]. On the other hand, the removal efficiency of carbamazepine in electro-ACF activated PDS systems is significantly higher than that of other combined processes, because of the synergistic effect of electrolysis and oxidation[89]. Most strikingly, the ACF can maintain the original features in electro-ACF/PDS process even after 100 cycles, while the ACF alone is seriously damaged in ACF-PDS process after 50 cycles[89].

3.4　Mesoporous carbon

Recently, investigators have examined the influence of MC on PS activation process. The catalytic efficiency of MC was closely related to its specific surface area, defect sites and functional groups[90]. A nonradical pathway was unveiled in the metal – free PDS activation by 3D cubic MC materials for catalytic oxidation in which PDS was activated on the carbon lattice and oxidized the adsorbed phenol molecules via a rapid electron transfer[91]. Meanwhile, the edge sites and kenotic groups of carbon materials would also mediate PDS to produce $SO_4^{\cdot-}$.

A composite nZVI/MC prepared by a chelation-assisted co-assembly and carbothermal reduction strategy was reported by Wu et al[92]. The nZVI particles with surface iron oxide were wrapped with graphitic layers which were uniformly dispersed in MC frameworks (Fig. 11). When nZVI/MC was used as an activator of PDS, the degradation efficiency of 2,4,6-trichlorophenol was nearly three times higher than Fe-SO_4 and $Fe_2O_3 \cdot FeO$, and nearly two times higher than commercial nZVI[92]. Jiang et al found that the removal efficiency of tetracycline hydrochloride by the combination of MC and PDS loaded with nZVI was much higher than that by MC-PDS and nZVI-PDS, indicating that nZVI and MC had a synergistic effect on the activation of PDS[93].

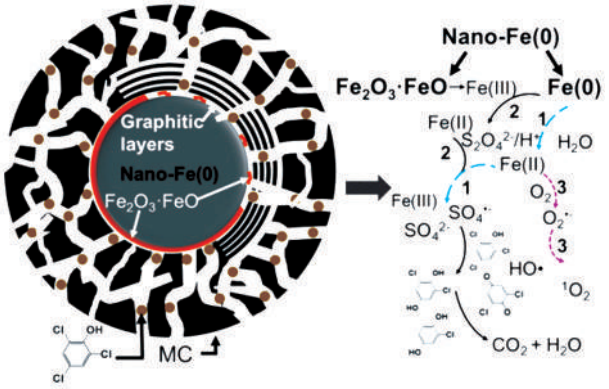

Fig. 11　NZVI wrapped with iron oxide and graphitic layers embedded in MC frameworks and the PDS activation process[92]. Reprinted with permission.

3.5　Carbon gels

The catalytic activity of carbon cryogels prepared by hydrothermal carbonization of glucose directed by polyaniline is positively correlated with its meso-/macropore volume and negatively correlated with its particle size of carbon cryogels. At a higher polymerization temperature, the prepared carbon cryogels exhibit a higher pore volume and smaller particle size, which further enhances its adsorption and catalytic activity for PS activation[94]. An attempt has been made to synthesize porous carbon aerogels from D-glucose, ammonium persulfate and aniline by hydrothermal carbonization. In the sp^2 hybridized system, PDS-bonded with C ═C can directly degrade RhB by a way of non-free radicals. The defective edges of the carbon aerogels in boundary are also conducive to the removal of RhB[95]. Outsiou et al further used carbon

microspheres embedded with iron and cobalt particles as raw materials to prepare magnetic carbon xerogels that could activate PDS to degrade BPA in various water bodies[96]. In addition, the synergistic effect in was found between ferromagnetic carbon xerogels and ultrasound for PDS activation[97].

3.6 Carbon microspheres

Readily available mesophase carbon microspheres (CMs) are produced as a carbon-rich product by the thermal processing of coal- or petroleum-derived pitch, and they bear highly aromatic constituents with a lamellar structure on their surfaces, which is beneficial for the introduction of desirable functional groups, and can be used as a precursor for high-performance carbon-based materials, such as the super active carbon and catalytic supports, due to their high mechanical strength[98]. Recently, Dong et al investigated the ability of magnetic CM-based composite catalyst (Fe_3O_4-CM) to activate PDS for the remediation of polycyclic aromatic hydrocarbons (PAHs) contaminated marine sediments. Fortunately, PAHs was removed by 87% in Fe_3O_4-CM/PDS system within 24 h, more than twice of that in CM/PDS system. The uniform graphitic structure of Fe_3O_4-CM catalyst was an important mechanism to promote the production of $SO_4^{\cdot-}$ and degradation of PAHs by providing additional active sites[98].

3.7 Carbon quantum dots

Hou et al creatively prepared N-doped carbon quantum dots (NCQDs) supported on three supports (SiO_2, $CeZrO_2$ and Al_2O_3)[99]. Due to the different electrostatic attractions between NCQDs and the supports, NCQDs were highly dispersed on the surface of Al_2O_3 and $CeZrO_2$, while agglomeration of NCQDs was found on surface of SiO_2. Among them, NCQD/Al_2O_3 had a high dispersion and strong adsorption, showing the best activated PDS performance, while NCQD/SiO_2 had a poor effect. Additionally, a volcano type dependence of bisphenol F degradation efficiency on the NCQD loading amount over Al_2O_3 was identified[99].

4 Summary and outlook

From zero-dimensional CQDs, one－dimensional CNTs, two-dimensional GO, to three-dimensional OMCs, various new carbon materials, with their excellent properties and unique structural characteristics, have broadened the application prospects in the field of catalysis, whether as a catalyst or a carrier. Compared with the traditional carbon materials, new carbon materials generally have larger specific surface area and electron mobility, more edge defects and higher plasticity, and are rich in functional groups, such as hydroxyl, carboxyl and ketone group. Based on the current research on the surface modification of carbon-based materials, pyridine N, pyrrole N, graphite N and other nitrogen-containing basic groups can be used as Lewis basic sites to promote electron transfer, while electron rich ketone groups are easier to adsorb PMS on the catalyst surface for catalytic oxidation reaction and the surface structural defects are easier to elongate the O—O bond of PMS, which is conducive to activation of PS. The increase of electron density and the existence of delocalized π electrons are conducive to the electron transfer between carbon-based catalysts and oxidants.

However, the surface mechanism of PS activated by carbon-based catalysts for degradation of organic pollutants is not completely clear, and there are still many key problems to be further explored. So far, various methods have been applied to improve our understanding for oxidation mechanisms involved in PS activation by carbon-based catalysts. Numerous researchers have demonstrated that most of the oxidation process is ascribed to $SO_4^{\cdot-}$ formation. In contrast, some studies propose that carbon-based catalysts act as an electronic mediator to effectively degrade organic pollutions through an electron transfer between electron donor phenols and electron acceptor PS (involving no radical attack). Alternatively, PS activation by carbon nanomaterials leads to another debate that $^1O_2$ can be primarily responsible for the degradation of organic compounds.

Meanwhile, the maturity of material preparation technology and the complexity of application environment put forward higher requirements for the performance of carbon materials, and the further application of new carbon materials in this field will also face more challenges. For the practical applications of carbon-based catalysts, 3 key problems of low catalytic stability, high environmental risk and high production cost must be solved[4]. In the oxidation process, the attack of free radicals on carbon materials will lead to the decline of the catalyst stability and even decomposition. In order to improve the stability of the carbon-based catalysts, the future research should focus on: (1) reasonable designing (with the assistance of computational method) and synthesizing (election of suitable synthesis methods, such as thermal annealing or hydrothermal method) of solid nanocarbon-based materials, which are composed of anti-oxidant surface functional groups (such as graphitic N) and are conducive to oxidation reaction; and (2) to control or optimize the reaction conditions.

The probable environmental risks caused by car-

bon-based catalysts are: (1) the catalyst in the treated suspension is accidentally released to the environment; (2) the generated free radicals such as $SO_4^{-}\cdot$ may react with Cl^- and Br^- in water through single electron oxidation, resulting in the formation of toxic and potentially carcinogenic oxygen anion (ClO_3^- and BrO_3^-)[100]. In order to solve the first problem, it is necessary to develop or improve the appropriate reaction process or reactor to limit the risk of catalyst release. As an example, catalytic oxidation and membrane separation processes are combined to reduce the release of undesirable carbon nanomaterials into the environment. In view of the second problem, the carbon catalyst can induce the occurrence of non-free radical pathway, which has a higher substrate specificity and milder redox potential. It is worth noting that the non-free radical reaction is based on the surface of carbon materials. Therefore, in order to improve the role of non-free radical pathway in the degradation of organic pollutants, it is of great significance to design and synthesize catalysts with both adsorption and catalytic capacity, which are not available for metal oxides and other inorganic catalysts. In addition, a suitable synthesis method should be selected to functionalize the surface of the carbon materials, so as to give the catalysts ideal surface affinity, complexation activity and electrostatic charge. This will help to promote better contact between PS/organics and the surface of carbon catalysts, and promote electron transfer for non-free radical reaction. The design and preparation of carbon materials with a controllable structure and better performance will become a research hotspot in the future.

As for the high cost of catalyst production, it can be solved by using agricultural wastes as raw materials or by using energy-saving and green synthesis methods. Recent studies have shown that waste materials such as lignocellulose and waste graphite can be developed as precursors to produce efficient carbon catalysts[101]. Due to the different characteristics of different precursors, it is necessary to optimize the synthesis process to give different precursor oxidation active functional groups.

At present, it is difficult to quantify the contribution of free radical and non-free radical pathway in the activation of PS by various carbon materials, especially the mechanism of non-free radical pathway is not completely clear. It is indispensable to select the appropriate free radical scavengers to identify the reactive oxygen species, but it must be noted that: (1) a free radical scavenger is only highly reactive to the target reactive oxygen species, but has no significant reaction with other active species or oxidants; (2) it will not affect the catalytic function of carbon materials (e. g. deposition/adsorption onto the surface of carbon materials to passivate the active sites or react with target organic substrates, etc.). Moreover, due to the difference in microstructure and properties between PDS and PMS, it is to be considered to further clarify the catalytic mechanism of new carbon materials in two different systems. In addition, the investigation using real waste water should also be strengthened to reflect the feasibility of activated PS oxidation process in practical applications.

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