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Review

Carbon nanotube-based materials for persulfate activation to degrade organic contaminants: Properties, mechanisms and modification insights

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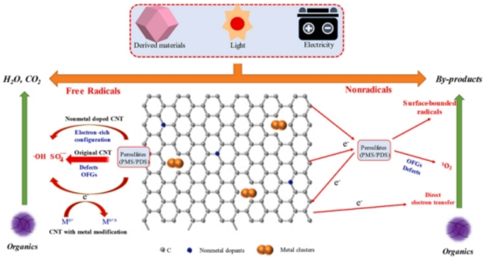
HIGHLIGHTS

- Application of CNT based composites presents great potential in PS activation.
- OFGs, defects and high conductivity are conducive to activation.
- Both radical and nonradical pathways are responsible for the activation.
- Crossover technologies might be future research direction.

GRAPHICAL ABSTRACT



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ABSTRACT

Removal of harmful organic matters from environment has great environmental significance. Carbon nanotube (CNT) materials and their composites have been demonstrated to possess excellent catalytic activity towards persulfate (PS) activation for the degradation of organic contaminants. Herein, detailed information concerning the function, modification methods and relevant mechanisms of CNT in persulfate-based advanced oxidation processes (PS-AOPs) for organic pollutant elimination has been reviewed. The activation mechanism of PS by CNT might include radical and nonradical pathways and their synergistic effects. The common strategies to improve the stability and catalytic capability of CNT-based materials have also been put forward. Furthermore, their practical application potential compared with other catalysts has been described. Finally, the challenges faced by CNT in practical application are clearly highlighted. This review should be of value in promoting the research of PS activation by CNT-based materials for degradation of organic pollutants and the corresponding practical applications.

1. Introduction

Recently, various anthropogenic activities (e.g., agricultural operations, mining, and discharge of industrial wastewaters and sanitary effluents) are accelerating organic pollutants entering the environment such as organochlorine pesticides, organic dyes, polyaromatic hydrocarbons and antibiotics, causing severe environmental concerns (Pan et al., 2020a, 2020b; Wang and Bai, 2017). Harmonious balance

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between nature and survival of livings has been interrupted, and it is urgent to tackle this problem. Well-known treatment methods such as adsorption, microbiological treatment and phytoremediation suffer from inherent drawbacks including secondary pollution, long reaction time and low efficiency (Chen et al., 2021b). In recent years, the advanced oxidation processes (AOPs) have been recognized as a promising technology with the generation of highly active free radicals, which may react with most of organic molecules in water and decompose them into small molecules even CO_2 and H_2O under a mild reaction condition (Zhao et al., 2021).

Compared with the traditional hydroxyl radical (·OH)-based AOPs induced by hydrogen peroxide (H_2O_2), persulfate (PS) mainly containing peroxydisulfate (PDS) and peroxymonosulfate (PMS) species shows greater selectivity and has lower requirements for external reaction conditions (Hu et al., 2017). As a result, persulfate-based advanced oxidation processes (PS-AOPs) have attracted a lot of attention in recent years, and the differences between PMS and PDS are shown in Table 1. Unsymmetrical PMS molecule shows a shorter bond distance compared with that of symmetric PDS molecule (1.460 Å vs 1.497 Å). The breaking of the O-O bond would lead to the generation of long-lasting reactive sulfate radical ($SO_4^{\cdot -}$). Hydroxyl radical is also formed via the following reaction between $SO_4^{\cdot -}$ and H_2O, which serves as ancillary radical during the degradation of pollutants, as shown in Eqs. (1)–(3). In addition, PDS possesses a higher standard redox potential compared with PMS, which indicates the higher oxidation capability of PDS.

$$HSO_5^- + e^- \rightarrow SO_4^{\cdot -} + OH^- \quad (1)$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\cdot -} + SO_4^{2-} \quad (2)$$

$$SO_4^{\cdot -} + H_2O \rightarrow SO_4^{2-} + \cdot OH + H^+ \quad (3)$$

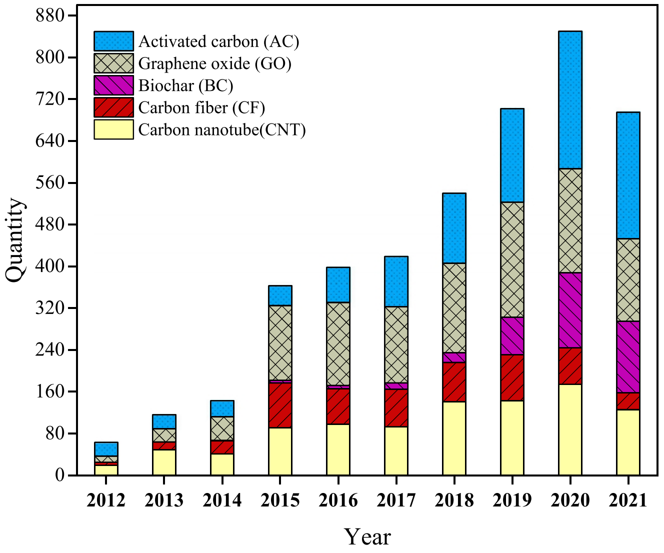
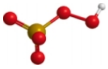
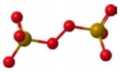


Fig. 1. Reports published during the last decade concerning different carbon-containing catalysts for the activation of PMS/PDS with the keywords of "the chosen materials" + persulfate. The data were obtained from the database of Web of Science.

Up to now, various approaches have been applied to activate PMS and PDS for the generation of reactive species (Oh et al., 2016; Xiao et al., 2018). Specifically, carbon-based materials can act as green and effective catalysts to activate PS for degradation of organic pollutants (Duan et al., 2015d; Guo et al., 2020; Li et al., 2017b; Lu et al., 2020). The number of relevant reports has experienced an upward trend during the last decade (Fig. 1). Bekris et al. (2017) indicated that graphene could be utilized as the PDS activator for the degradation of propyl. Wang et al. (2020) suggested that the sulfurized biochar showed a good performance in PS activation towards bisphenol A (BPA) removal. Among various carbocatalysts, granular carbonaceous materials like activated carbon (AC), biochar and carbon fiber have been applied in AOPs, but they exhibited mediocre performance with limited function and poor anti-interference capability (Duan et al., 2018). On the contrary, part of original nanocarbocatalyst including carbon nanotubes, reduced graphene oxide and mesoporous carbon presents outstanding performance for PS adsorption and activation (Duan et al., 2015d). CNT based materials are more likely to be coupled with another technology when used as electrode, such as photocatalysis or filtration thus improving their practical application potential (Jang et al., 2021; Yin et al., 2021b).

Table 1
Comparison between PMS and PDS.

	PMS	PDS
Molecular formula	$KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$	$Na_2S_2O_8/K_2S_2O_8$
Molecular configuration[a]		
Distance of O-O bond structure (Å) (Chen et al., 2018)	1.453	1.497
Bond energy (kJ/mol) (Chen et al., 2018)	377	92
Solubility in water (mg/L at 20 °C) (Yang et al., 2010)	250,000	730,000
Standard redox potential (Ren et al., 2020a)	1.75 – 1.82 V_{NHE}	2.01 – 2.12 V_{NHE}
Price	$2.2 per kilogram	$0.74 per kilogram

[a] The red dot represents oxygen atom, the white dot represents hydrogen atom and the yellow dot represents sulfur atom.

Except for catalytic properties, the superior chemical, electronic and mechanical properties of CNT render it excellent engineering materials. Consequently, CNT materials are applied in various fields including sensors, chemical probes, energy storage, field emission display, solar panels and healthcare (Bera et al., 2016; Dai et al., 1996; He et al., 2013; Martin et al., 2005). Three primary ways are commonly used to prepare this pristine CNT, i.e., arc-discharge method, chemical vapor deposition and laser ablation method (Omoriyekomwan et al., 2021). When applied as catalyst, many studies concentrate on the functionalization or modification of CNT to improve its affinity towards specific organic molecules (Cheng et al., 2017). For example, surface functionalization can transform or introduce more activated functional groups and increase the number of active sites on the surface of CNT. Also, heteroatom-doping including both nonmetal and metal doping to create CNT hybrids offers another choice to activate PS on CNT materials (Jiao et al., 2016). Doping heteroatom on CNT could excite unreactable carbon (C) atoms on surface of CNT and increase electron transfer capability (Peng et al., 2020). N doping could offer regulated active sites and properties, which can improve PS activation efficiency greatly (Liang et al., 2017; Sun et al., 2014). For metal modified CNT, the confined metal on CNT could inhibit its oxidation and agglomeration and prolong reactivity of the material (Jiao et al., 2016). In recent years, multiple modification of CNT has attracted a lot of attention. The co-doping of metal or nonmetal or their combination has showed a high reactivity for activating PS to degrade organics (Fu et al., 2021; Zhu et al., 2020).

Considering that the research field of PS activation for degradation of organic pollutants catalyzed by CNT-based materials is rapidly growing and evolving, a timely and comprehensive review summarizing the recent advances is of great necessity. To the best of our knowledge, review focusing on such aspect is rare. A previous review called "Heteroatom doping in metal-free carbonaceous materials for the enhancement of persulfate activation" has been published (Liu et al., 2022), however, it focused on metal-free carbonaceous materials instead of CNT-based materials. In this review, we explore the PS activation mechanism in different CNT/persulfates systems. Meanwhile, the relationship between properties of carbon nanotubes and their catalytic activation capability is also described in detail. Finally, we propose some research prospects in the field of practical application of CNT based PS-AOPs system.

2. Mechanisms of PS activation with different CNT structures

Basically, the interaction between carbon nanotubes and PS involves both free radical pathway which produces free radicals ($SO_4^{\cdot-}$ and·OH) to degrade organic substrates and nonradical pathway which extracts the electron from organic substrates directly (Fig. 2). In many cases, these two situations co-exist due to their different type and number of active sites.

2.1. Production and reaction mechanism of free radicals

Free radical pathways mean that organic pollutants are degraded via the direct attack of free radicals ($SO_4^{\cdot-}$ and·OH). Sun et al. (2014) prepared pristine carbon nanotubes to activate PMS and PDS, and the $SO_4^{\cdot-}$ was regarded as the main active species. Fig. 2 describes the PS activation via radical pathway through the electron conduction mechanisms. The adsorbed PMS on CNT tends to accept the electrons from active sites (defects at the edge sides or vacancies, unpaired electrons at Lewis basic sites, the original electrons activated with the external energy input, and one-pair electrons formed by doping other atom species) to dissociate the O-O bond electronically, and generate one molecule of $SO_4^{\cdot-}$. For symmetrical PDS, it's harder to induce the dissociation of O-O bond compared with PMS. Attack from electrons can only lead to unsymmetrical cleavage of the PDS and also generate one molecule of $SO_4^{\cdot-}$ and sulfate ion (SO_4^{2-}). Then part of $SO_4^{\cdot-}$ further reacts with H_2O or OH^- and generates·OH. During this process, CNT is regarded as an electron donor to provide the electrons for PMS/PDS activation and a supporter for reaction. Compared to·OH with short lifetime ($t_{1/2} \leq 1$ μs), limited-range transport and strong pH dependency (normally existing in the pH range from 7 to 10), $SO_4^{\cdot-}$ is easier to transport in long distance and contact with organic pollutants continuously under different water conditions (Olmez-Hanci and Arslan-Alaton, 2013; Yu et al., 2020). These radicals can react with micromolecule organics through hydrogen extraction or other means, and trigger electron transfer when attacking macromolecule organics.

2.2. Production and reaction mechanism of nonradical pathways

Recent studies have put forward another possibility that organic pollutants initiate oxidation reaction through self-decomposition via a nonradical process, not via sulfate free radicals. Three other hypotheses, including formation of surface-bounded reactive species, singlet oxygen ($^1O_2$) and direct electron transfer, have been assumed to activate PS. PS in aqueous environment may be activated to produce surface-bounded $SO_4^{\cdot-}$ and·OH, generate $^1O_2$ to degrade organic substance, or form a metastable complex structure (CNT-PS) (Huang et al., 2021).

The formation of surface-bounded reactive species means that the aforementioned generated radicals cannot transport to liquid solution, but rather on the boundary layer or surface of CNT particles (Su et al., 2019). PS molecules could be directly bound with the surface of CNT to form metastable reactive complexes with high oxidation capacities. Different from surface persistent free radicals, the generated metastable reactive complexes accompany with adsorbed radicals decaying in the absence of organic compounds. PDS was reported to generate surface-bounded sulfate radicals to degrade 2,4-DCP in the sp^2-hybridized system of CNT (Cheng et al., 2016). Chen et al. (2021a) found that both surface-bound $SO_4^{\cdot-}$ and·OH played a role in activation of PDS by multi-walled carbon nanotube (MWCNT). Unlike the attack by radical species, the organic pollutants are preferentially degraded by direct electron abstraction. Up to now, these surface-bounded radicals are reported to be only generated in PDS activation process, where the defects and delocalized π electrons at curvature sheet are responsible for weakening the O-O bond of PS.

Ketonic, carbonyl groups and defects on CNT are identified to be the primary active sites for the generation of $^1O_2$ (Cheng et al., 2019, 2017). It is generally convinced that $^1O_2$ is generated by PS self-decomposition. Besides, CNT based catalysts could serve as electron acceptors to induce the generation of $^1O_2$. The generation of $^1O_2$ via carbonyl groups is shown in Fig. 3(a) (Cheng et al., 2017). The carbonyl on the surface of CNT is attacked by one molecule of $S_2O_8^{2-}$ or HSO_5^-, resulting in formation of PS adducts (Reaction 1). With the loss of a hydrogen ion (H^+) in the presence of OH^- ions, persulfate adducts are decomposed into a dioxirane intermediate (Reaction 2) via intramolecular nucleophilic displacement reaction (one molecule of SO_4^{2-} is generated when PDS is activated). Finally, a molecule of $S_2O_8^{2-}$ or HSO_5^- attacks the dioxirane part of adduct thus forming a $^1O_2$ molecule (Reaction 3). As for the whole process during PS activation, PS absorbed on the sp^2-hybridized carbon lattice contributes to the formation of SO_4^{2-} and $^1O_2$. Afterwards,

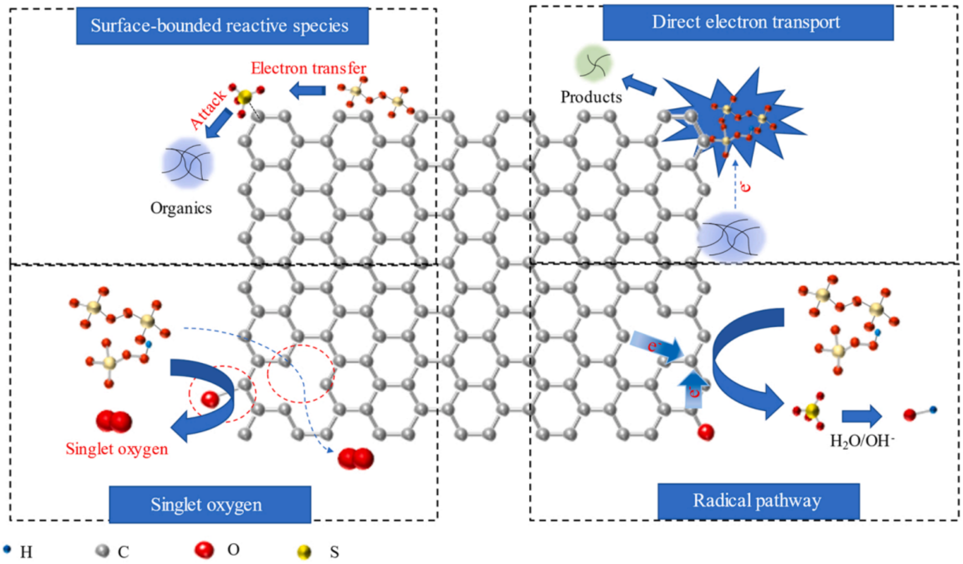


Fig. 2. Radical and nonradical pathways for PS activation with original CNT applied.

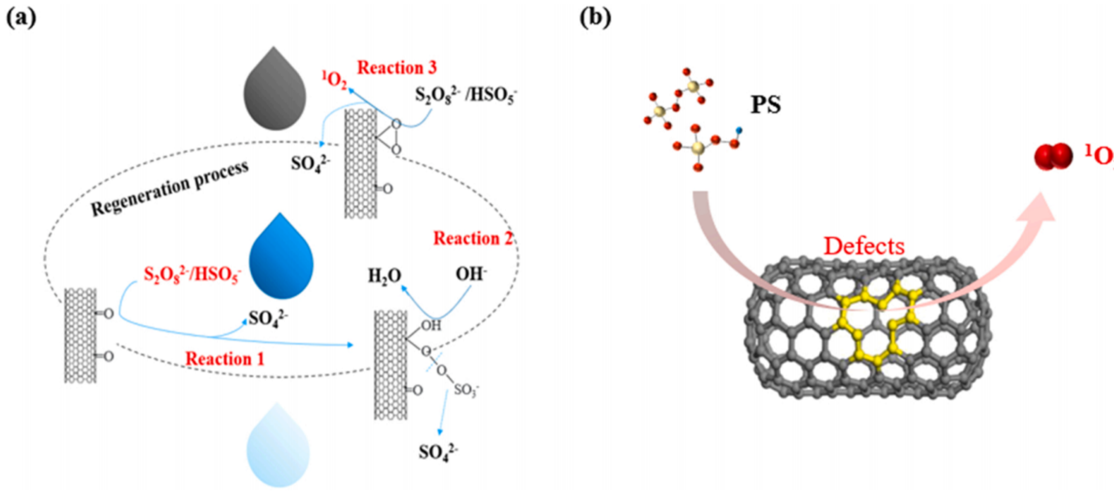


Fig. 3. The generation of $^1O_2$ via (a) carbonyl groups and (b) defects in CNT based AOPs system.

the generated $^1O_2$ could oxidize organic matters via electrophilic addition or extracting the electrons from organic compounds directly (Lee et al., 2020). However, some studies claim that the formed oxidative persulfate adducts preferentially abstract H atom in pollutants directly as a surface-bonded species because this process is more thermodynamically favorable than Reaction 3. Hence, other active sites instead of $C{=}O$ are engaged in the formation of $^1O_2$ (Liu et al., 2021c). Discovered active sites include defects inducing $^1O_2$ generation in CNT composites (Fig. 3(b)). Unsaturated active C atoms in defects promote the dissociation the O-O bond of oxidants and generate $^1O_2$ (Cheng et al., 2019). Then $^1O_2$ can achieve the elimination of most unsaturated organic compounds via electron abstraction and electrophilic addition. However, the researches on PS activation via defects are still in its infancy. More reliable researches are needed on the pathway of $^1O_2$ generation via vacancy defects.

Direct electron transfer is another possible catalytic pathway. As shown in Fig. 2, the electrons abstract from organic pollutants transport to CNT composites directly. This special electron transfer process has been proved to be dominated by the potential difference between the highest occupied molecular orbital (HOMO) of organic compounds and the lowest unoccupied molecular orbital (LUMO) of used CNT. A metastable composite structure CNT-PDS* /PMS* is formed with elevated oxidation capacity compared with the pristine CNT, which promotes the direct or indirect electron transfer from organic pollutants to CNT-PDS* /PMS* to fulfill the redox cycle. CNT serves as the mediator to transfer electrons from organic compounds (electron donors) to adsorbed PS (electron acceptors). Reactions only occur in the presence of electron donors, mediators and acceptors. Organic pollutants are converted into small molecules. Noteworthily, electron-rich organic substances are more likely to drive electron transfer process and achieve their self-elimination (Ren et al., 2022).

In general, both free radical pathway and nonradical pathway are important procedures during PS activation in CNT based AOPs system. The type of PS and surface-active sites could lead to the changes of pollutant degradation pathways and removal rates (Ushani et al., 2020). PDS is mainly activated through nonradical pathway while PMS is proved to produce both free and nonradical species in CNT catalyst (Guan et al., 2018). Moreover, the carbon matrix with sp^2 hybridized orbitals and strong electron donating sites could serve as electron transfer tunnels towards PS for the generation of $SO_4^{\cdot-}$ and •OH, whereas the redistribution of local electrons of CNT materials and high graphitization degree caused by defects or other functional groups could promote nonradical pathway. In free radical pathways, the high redox potential of generated free radicals enables the complete removal of pollutants and oxidizes them into CO_2 and H_2O, which is hard to achieve in nonradical pathway (Gao et al., 2022). However, the nonradical pathway can be applied in a more complex water matrix (with a wider pH range and more impurities). In this case, the removal process is more likely to be used in practice with less chemical consumption (Duan et al., 2018b; Lee et al., 2020). The desired catalytic performance can be adjusted by appropriately changing the aforementioned properties of CNT, therefore achieving a better application prospect in practical use.

2.3. *Active sites determination*

It has been known that determination of active sites is the key to study CNT/PS system. The occurrence of free radicals can be identified through a common procedure: the first step is to test the inhibitory impacts with different quenchers. The removal efficiency of organics decreased with the addition of different scavengers. Alcohols including methanol, ethanol or isopropanol are expected to consume the produced free radicals such as $SO_4^{\cdot-}$ and·OH. Nitrobenzene, 4-nitrobenzoateion tertiary butanol alcohol (·OH scavengers) can be further applied to distinguish the main active radicals. Sometimes alcohols cover carbon surface, kinetically retarding organic degradation. The dosage of alcohols should be carefully arranged. For reactive agents or surface-adsorbed radicals that cannot be identified precisely, a further electron paramagnetic resonance (EPR) with specific spin trapping agent could be useful (Yun et al., 2018; Zhou et al., 2015). Finally, the reaction products and relevant substrates in pollutant degradation process should be in accordance with the reactivity of generated reactive species (Sun et al., 2014). On the contrary, for the direct electron transfer that does not involve the generation of aforementioned transient species, the detection is indirect and requires to be confirmed by electrochemical characteristics including cyclic voltammetry (CV) and linear sweep voltammetry (LSV), chronoamperometric measurements, and ESI analysis (Ho et al., 2019; Zhu et al., 2018). Distinctly, LSV measurement is a key step to verify direct electron transfer with electric current shifting suddenly through CNT electrode in the co-presence of pollutants and persulfates, while other technologies are employed as an accessory to confirm the electron transfer process. The common ways to identify $^1O_2$ include using sodium azide (NaN_3) as the scavenger and following by spin trapping by 2,2,6,6-tetramethyl-4-piperidone (TMP) with the detection of characteristic triplet peaks in EPR spectrum. However, such techniques are not favorable for detection of $^1O_2$ exclusively. Firstly, NaN_3 (as a strong reducing scavenger) or furfuryl alcohol (FFA) and diphenylanthracene (DPA) (as chemical probes) can further react with hydroxyl radical and sulfate radical. Moreover, there are other methods to detect $^1O_2$ and/or its possible intermediate in addition to EPR trapping technique. In order to exclude possible interference of other reactive species, multi-strategies are recommended with the assistance of fluorescent probes or photosensitizers (Duan et al., 2018b). Since the detection of reactive species seems to be ambiguous, a more systematic and efficient detection procedure is encouraged to trace their occurrence and determine their particular role.

Accompanied with characterization techniques, the relationship between the possible active sites of materials and their performance can be understood. The main characterization techniques for CNT materials are focused on morphological features, elemental composition and surface chemistry. Morphology analysis based on scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and scanning tunneling microscopy (STM) are good means to obtain the information on size and morphology, micro pore structure, thickness and heteroatom distribution in atomic-scale of materials, respectively. Then, energy dispersive X-ray spectrometer (EDX) and X-ray photoelectron spectroscopy (XPS) are usually employed to test the purity or successful preparation of materials. Noteworthily, structural composition and surface chemistry will help to speculate and determine the active sites. In general, the defect level obtained by Raman spectroscopy is a vital parameter for evaluating the contribution of defects. XPS is an important tool to analyze the role of a certain element composition and chemical state of catalyst samples. Fourier transform infrared spectroscopy (FTIR) before and after tests contributes to reflect the importance of functional groups to PS activation.

3. The roles of CNT properties

The cleavage of O–O bond and charge transfer between the PS and CNT to generate reactive species are the key to PS activation efficiency. Herein, investigation of properties of CNT including carbon configurations, defect degree, and surface chemistry (mainly oxygen-containing functional groups) within a porous framework is critical for improved PS activation effeciency by CNT.

3.1. Carbon configurations

Generally, PS activation is largely dependent on the electrical conductivity. The high degree of sp^2 hybridization endows CNT with delocalized π electrons and a high density, consequently leading to the high electrical conductivity. CNT contributes to a closer contact between electron donor and acceptor, thereby promoting electron transfer efficiency. In this case, the degradation of organic pollutants becomes easier (Cheng et al., 2019). In the nonradical process, the excellent conductivity of CNTs contributes to the stabilization of active species as well as the catalytic process involving electron transfer from contaminants (acting as electron donors) to PS (acting as electron acceptor) (Duan et al., 2016). In free radical process, CNT is used as an electron donor and medium to transform electrons to PS. As both PS activation and organic degradation process involve electron transfer, the participation of CNT as electron transfer medium is of great importance.

The wall number (single wall or multiple wall) and graphitic degree determine the electronic conductivity and catalytic potential of CNT (Duan et al., 2018c). The conductivity of CNT could be improved via the following methods：1) purification of CNT. CNT has the quality of metal and semiconductor. Multi-walled CNT (MWCNT) is generally metallic. Single-walled CNT (SWCNT) with both semiconductive and metallic properties can be improved by separating metals from carbon nanotubes via physical, biological and chemical methods (Rezaei et al., 2021). 2) annealing is also a feasible strategy to improve the graphitic degree, which promotes the flow of delocalized electrons in the entire flat layer of the CNT to drive the redox process (Han et al., 2019).

3.2. Defective structures of CNT

Structural defects may be considered as important sites for the activation of PS. Defects on the surface of CNT are proved to serve as potential adsorption and catalytic active sites towards PS. The presence of these defective structures can modify the energy band structure and electronic structure thus increasing spin densities of carbon atoms. Also, the adsorption and electron transfer ability of carbon materials themselves are improved (Zhang et al., 2015). According to the structure of formed defects, it can be divided into (Rezaei et al., 2021): 1) structure defects: non-six-membered ring structures are formed surrounding the six-membered carbon structure. 2) bond rotation or particle boundary: Bond rotation defects are usually found on the surface of the graphene layer, forming the Stone-Wales defect structure. 3) doping defects: nitrogen (N) or boron (B) atoms can replace C atoms in the six-membered ring to improve the chemical activity of carbon surface. This type of defect could regulate the electronic structure and change the conduction characteristics of carbon nanomaterials. 4) non-sp^2 carbon defects: non-sp^2 carbon defects include suspension bonds, carbon chains, interstitial atoms, edges, adsorption atoms and vacancies and 5) high strain folding of graphite layer: during the stage of multi-wall nanotube formation, it is easy to form interlayer trap centers to capture various defects. As a result, the walls of multi-walled tubes are often filled with perforated defects. Various defective structures have been reported to play catalytic role in PS activation. Double-vacancy defect, a type of structure defects, has been reported to predominate the reactivity of CNTs among various defect configurations (Shao et al., 2020). Cumulative electrons in structural defect tend to lower the electron density of neighboring carbon atoms, which are more likely to be transferred in CNT compared with intact CNT with even-distributed electrons (Fig. 4). In addition, the reduced HOMO–LOMO gap contributes to an easier transport of electrons on CNT-PS structure. Influenced by improved electrophilic attack toward O–O bond, the nonradical activation of PS can be greatly promoted. However, there is still a lack of valid experiments to confirm activation degree of different defective structures towards PS. One important problem lies in the difficulty in separation and purification of defects in CNT. Hence, oxidative nano-cutting to open CNT seems to be a topic in further research.

The pretreatment of CNT by different acid etching, potassium permanganate oxidation and thermal energy can regulate the quantity of structural defects of CNT. In this process, annealing is a key step affecting defective degree. Part of carbon matrixes are oxidized and converted into saturated bonds or other inorganic small molecules, resulting in the increase of defects (Yang et al., 2019). Up to now, the role of defective structures in PS activation seems to be versatile. On the one hand, the long-pair electrons in defective structure seem to attack PS directly and generate free radicals. On the other hand, as confirmed by control tests and Raman spectra data, the defects also take part in the electron transfer process of nonradical mechanism (Cheng et al., 2019). Yang et al. (2020) further confirmed that the defects in boundary of CNT were able to activate PDS and followed a nonradical pathway to degrade pollutant. Undoubtedly, there are no systematic researches on the role of different defects on PS activation on CNT and more studies are required concentrating on the reason why defects leading to different PS activation pathway.

3.3. Abundant oxygen-containing compounds

The localized electrons in unsaturated carbon atoms at the edge or defects endow CNT with a strong ability to bond with O, H and other heteroatoms, consequently leading to the formation of different types of oxygen-containing functional groups (OFGs) including ketones (C═O), carboxyl (O-C═O), phenols and ethers (C-O), and hydroxyl (-OH). Some OFGs such as -COOH and -OH are important sites to introduce other functional groups like $-NH_2$ and -S due to their hydrophilic and cation-exchanging properties while C═O can be regarded as an important active site. OFGs terminated at defects could directly participate in the catalytic reactions in PS-AOPs system (Duan et al., 2018c), especially for C═O bond. C═O functional group presents high chemical potential, which can play a significant part in the origin of redox process thus

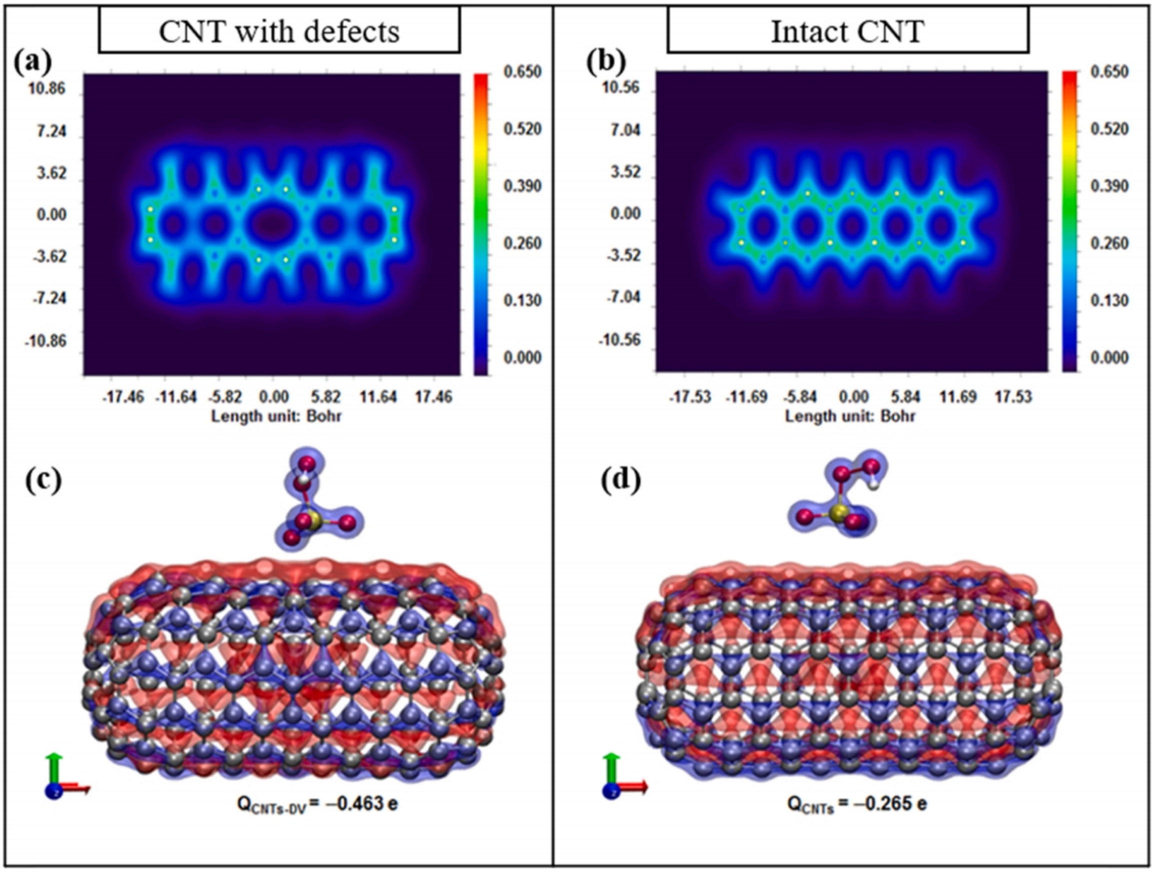


Fig. 4. Effect of defects on the distribution of valence electron density maps in (a) CNT with defects and (b) original CNT; the number of electron transfer and electron density difference between (c) CNT with defects, (d) original CNT and PMS. Blue contours represent electron accumulation and red contours indicate electron deletion. Copyright 2020, ACS publications.
Reproduced with permission from Shao et al. (2020).

inducing the removal of organic pollutants (Cheng et al., 2016). Yang et al. (2019) prepared MWCNT with the post treatment including nitric acid modification and annealing to induce PDS activation for the removal of phenol. The sample of MWCNT with the highest intensity of C═O exhibited the highest activation efficiency. Similar result was also reported by Cheng et al. (2016) that CNT modified with glutaraldehyde achieved a 95% removal of 2,4-dichlorophenol (2.4-DCP) over 5 min (Cheng et al., 2016). The role of OFGs varied at different activation processes. It has been hypothetically proposed that PS activation by the OFGs at the defective edges of CNT-based catalyst undergoes the processes of Eqs. (4)–(8) (Chen et al., 2021c; Cheng et al., 2019; Xiao et al., 2018). However, carbonyl groups on CNT have also been reported to be unfavorable for PS adsorption and restrain electron transportation in the CNT based AOPs system (Ren et al., 2020b). One possible explanation might lie in the polarity of C═O, which contains two reaction centers including a positive C atom center and a negative O atom center. For radical activation process and singlet oxygen formation process, negative PS could be attached on C atom and receive the electron from negative O atom apart from original active sites. As a result, the generation rate of reactive species has been greatly promoted. On the contrary, for direct electron transfer process that involves the electron transfer from organics to CNT-PDS* /PMS* , negative O atom might be unfavorable for electron transport when organics were adsorbed on C atom surrounding by O atom. However, this hypothesis lacks valid data support, which might become a future research direction.

$$\mathrm{CNT=C=O+HSO_5^-\rightarrow SO_4^{\cdot -}+CNT=C-O^{\cdot}+OH^-} \tag{4}$$

$$\mathrm{CNT=C-O^+ +HSO_5^-\rightarrow SO_5^{\cdot -}+CNT=C=O^{\cdot}+H^+} \tag{5}$$

$$\mathrm{CNT=C=O+S_2O_8^{2-}\rightarrow 2SO_4^- +C=C-O} \tag{6}$$

$$\mathrm{CNT=COOH+S_2O_8^{2-}\rightarrow SO_4^{\cdot -}+C=C-OO^{\cdot}+HSO_4^-} \tag{7}$$

$$\mathrm{CNT-OH+S_2O_8^{2-}\rightarrow SO_4^{\cdot -}+C=C-O^{\cdot}+HSO_4^-} \tag{8}$$

Pre-oxidation treatment is utilized to increase these electron-donating groups in CNT (Lavagna et al., 2021). Air oxidation is a weak method which employs gas-phase oxidants such as oxygen, ozone, air or nitric oxides to form surface-bounded groups. Post-treatment method in liquid phase like acidification (HSO_4, HNO_4 and or their mixture) or oxidation (e.g., H_2O_2 and K_2MnO_4) is another effective and robust way to elevate the density of certain OFGs at the defective edges of CNT. The choice of annealing temperature could greatly influence the density of OFGs. Most of OFGs on the surface of CNT are thermally unstable, which makes them easy to be adjusted on the surface of CNT, especially for C═O (Duan et al., 2016; Yang et al., 2019).

It is noteworthy that the excessive OFGs at the surface of CNT might lead to the suppression of its catalytic activity. The excessive OFGs might destroy the C═C bond including aromaticity and conjugated double bonds. Finally, it adversely influences the electron transfer on the carbon units in a graphene sheet, electron cloud density of connected carbon atoms at the edge of carbon network, and the oxidation capability of ketones groups (Chen et al., 2018). At the same time, with excessive vacant sites occupied, CNT might be substantially deactivated as the physical accessibility of persulfates to the active sites is hindered due to the electrostatic repulsion interactions.

Apart from OFGs, the electrophilic oxygen is also proved to be a PS activator. The role of electrophilic peroxide (O_2^{2-}) and superoxide ($O_2^{\cdot -}$)

species on the edges of CNT has been proved by the selective deactivation of CNT with iodometric oxidation. It is known that the electrophilic oxygen tends to attack PS molecules and generate reactive radicals through electron transfer (Li et al., 2020).

4. Modification ways and activation mechanisms of CNT

Based on above analysis, the appropriate modification is essential to improve electron transfer ability and adjust reaction sites in CNT based PS system.

4.1. Heteroatom doping in CNT

Heteroatom such as nitrogen (N) and boron (B) doping in CNT has been proved to be an effective way to enhance the catalytic performance of CNT. For CNT materials with highly-conjugated π electron system and good electron transfer ability, advantages of heteroatom doping include (Chen et al., 2018): 1) changing electron density in part of doped position, 2) breaking the inertia of conjugate electron system and 3) introducing structure defects and new active sites into the pristine hexatomic ring. Table 2 lists common agents for heteroatom doping of CNT and their application performance.

4.1.1. Synthesis of heteroatom doping CNT

At present, the preparation methods of doped CNT can be divided into three kinds: 1) direct doping, which is carried out during the growth process of CNT. Commonly-used doping methods include arc discharge method, chemical vapor deposition (CVD) and laser evaporation method; 2) direct carbonization of nonmetal-containing materials, and 3) post-treatment. Synthesized CNT is treated with nonmetal precursors followed by a subsequent process including plasma, ball milling, hydrothermal or other methods under nitrogen atmosphere. The synthesis approaches should be selected according to the actual application situation. Direct doping is to induce heteroatom during the shaping of carbon skeleton, which possesses the merits of even distribution and high doping degree. Thus, direct doping is easy to conduct but it also can be somewhat expensive with high energy consumption. Sometimes the used metal catalyst residuals might also affect the formation of doped CNT in CVD process. Direct carbonization of nonmetal-containing materials is a cheap and simple method for synthesis of doping CNTs with controllable shape on the surface of CNT, but it does not show a fine control on doping amounts. Post-treatment is mostly used among other

Table 2
Different agents as doping materials on CNT for persulfate activation.

Doping agents	Procedure	Experimental conditions	Removal ratio	Ref.
N				
N doped CNT	Precursors: pristine CNT, melamine and urea. Thermal-annealed temperature: 700 °C for 1 h	Phenol concentration = 20 mg/L; Catalyst dosage = 100 mg/L; [PMS] = 6.5 mM; T = 25 °C.	100% t = 20 min	(Duan et al., 2015e)
N doped CNT	Precursors: pristine CNT, nitrogen precursor. Thermal-annealed temperature: 750 °C for 1 h	[Phenol] = 0.1 mM; Catalyst dosage = 100 mg/L; [PMS] = 0.2 mM; T = 25 °C	95.6% t = 10 min	(Ren et al., 2020a)
N decorated CNT	Precursors: SWCNT, urea Thermal-annealed temperature: 700 °C for 30 min	Nitrobenzene concentration = 20 mg/L; Catalyst dosage = 200 mg/L; PMS concentration = 2000 mg/L; T = 35 °C	79.4% t = 180 min	(Duan et al., 2018a)
N doped CNT-35	Precursors: MWCNT, ammonium nitrate. Thermal-annealed temperature: 350 °C for 1 h	Phenol concentration = 20 mg/L; Catalyst dosage = 200 mg/L; PMS concentration = 2000 mg/L; PDS concentration = 1480 mg/L; T = 25 °C	100% t_{PMS} = 60 min t_{PDS} = 120 min	(Sun et al., 2014)
N doped CNT	Precursors: CNT, melamine. Thermal-annealed temperature: 700 °C	Phenol concentration = 20 mg/L; Catalyst dosage = 100 mg/L; [PMS] = 6.5 mM; [PDS] = 6.5 mM; T = 25 °C	100% t_{PMS} = 45 min t_{PDS} = 180 min	(Duan et al., 2015a)
Polyimide modified CNT	Precursors: MA, PMDA and CNT powders. Thermal-annealed temperature: 325 °C	Orange G concentration = 50 mg/L; Catalyst dosage = 200 mg/L; PMS concentration = 200 mg/L; T = 25 °C	98.9% t = 15 min	(Wei et al., 2020)
B				
B doped CNT	Precursors: CNT, boric acid	Phenol concentration = 10 mg/L; Catalyst dosage = 200 mg/L; PMS concentration = 1000 mg/L; T = 25 °C	99.4% t = 60 min	(Li et al., 2021)
Co-doped materials				
B-N co-doped CNT	Precursors: melamine, boric acid and CNT. Thermal-annealed temperature: 650 °C for 30 min	[2,4-dichlorophenoxyacetic acid] = 0.1 mM; Catalyst dosage = 200 mg/L; [PMS]= 2.0 mM; T = 25 °C	68% t = 240 min	(Luo et al., 2021)
N-S co-doped CNT-COOH	Precursors: CNT and thiourea Thermal-annealed temperature: 600 °C for 1 h	Benzophenone-4 concentration = 10 mg/L; Catalyst dosage = 100 mg/L; PMS concentration = 1000 mg/L; PDS concentration = 1000 mg/L; T = 25 °C	100% (PMS) 22% (PDS) t_{PMS} = 30 min t_{PDS} = 30 min	(Liu et al., 2016)
Edge-enriched N, S doping CNT	Precursors: MWCNT and thiourea Thermal-annealed temperature: 900 °C for 2 h	BPA concentration = 20 mg/L; Catalyst dosage = 100 mg/L; [PDS] = 1.5 mM; T = 25 °C	100% t = 30 min	(Yang et al., 2020)

methods, the main advantages of which is the well-regulated doping amount and large-scale production (Liu et al., 2022).

The post-treatment of CNT is to mix prepared CNT with chemical precursor powders and pyrolyze them under the protection of nitrogen. Both an agitating mortar under a solvent-free environment and magnetic stirring in ethanol solution can ensure the powders mixing homogenously. During the preparation process, precursor type plays an important role in formation of CNT. N precursors contain organic (urea, polyaniline, indole, melamine, diethyldithiocarbamate) and inorganic compounds (ammonia, ammonia nitrate). Whether N dopants affect final catalytic performance of CNT is still in debate. Ren et al. (2020a) prepared N doped CNT via an easy-to-operate process using melamine and urea powders as N sources. Compared with urea, the use of melamine introduced more pyridinic N, pyrrolic N, and graphitic N and showed better activation effect on PMS. However, Pan et al. (2018a) demonstrated that there is no proportional relationship between N precursors and pollutant removal efficiency because the actual doping level of N is much lower than C and O. As for commonly-used B-containing dopants, they mainly include organic compounds (e.g., 1,4-phenylenebisboronic acid, 3-aminophenylboronic acid, triethylborane and borane tetrahydrofuran) and inorganic substances (e.g., boric acid, sodium borohydride and boron oxide). 1, 4-phenylenebisboronic acid might be the best catalytic precursor due to its higher B mass fraction. The pollutant removal rate with its usage is far beyond than that by using another precursor (Li et al., 2021). Multiple doped CNT shares a similar preparation procedure. One or more precursors are mixed with CNT or C precursor (polyethylene glycol or other organics) together and followed by the pyrolysis of prepared agents. In order to save reagent cost, precursor with multiple heteroatoms is more popular than that containing one. For example, thiourea is usually chosen for the easy preparation of N, S co-doped CNT (Pan et al., 2018a). During the pyrolysis process, operational parameters including pyrolysis temperature, reaction residence time are decisive factors affecting doping level of CNT. The rise of temperature (to about 800 °C) would result in graphitization, and the graphitic carbon lattice produced at high temperature is conducive to the transportation of π electron (Jiang et al., 2020). In addition, part of acidic OFGs would be consumed to generate vacancies, defects and Lewis basic sites. When the temperature increases to a higher level (about 900 °C), the activation efficiency decreases dramatically with the decreased dopants on CNT and collapse of carbon framework (Peng et al., 2021). It is worth noting that reaction residence time might influence both graphitization degree and yield of CNT (Zhao et al., 2021). The effect of operating parameters on formation of CNT has been explored a lot, and more evidence should be found to build bridges between operating parameters and final CNT catalytic capability.

In short, preparation method is a key step to change the catalytic performance of CNT composite. More efficient, simple and inexpensive methods should be tested for synthesizing doped CNT in the future.

4.1.2. *Single heteroatom doping*

Single nitrogen (N) doping has been extensively applied to strengthen catalytic activity towards persulfates. N doping can change the electronic cloud density surrounding connected carbon atoms in CNT, which is conducive to the increase in the electrical conductivity of CNT, and its long-pair electron also shows a unique performance during catalysis. N dopants also lead to distortion of C-C bond and lattice, which could elevate chemical potential during PS activation process (Lee et al., 2016). XPS spectra analysis are employed to confirm N species in doped CNT. According to position of nitrogen atoms on the graphite sheet, it can be divided into pyrrolic N, pyridinic N, graphitic N, and other C-N grafted structures (Wang et al., 2012). Various molecular structures of N species endow them with different functions in PS activation process as

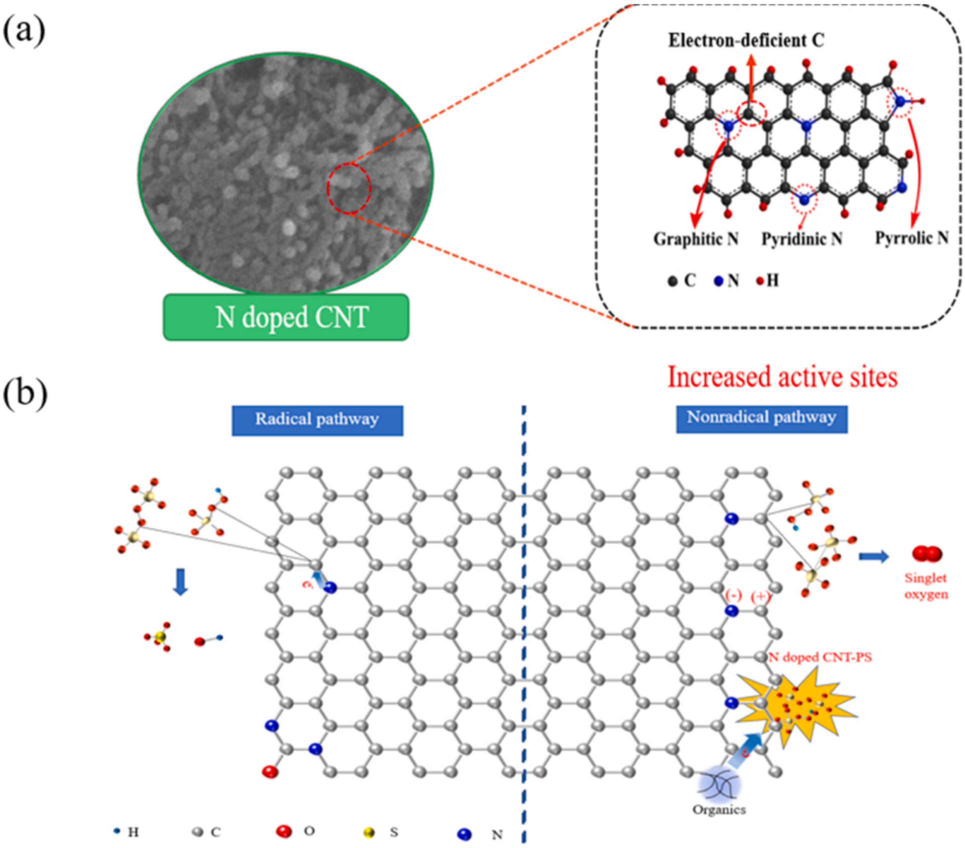


Fig. 5. Copyright 2019, Elsevier. and (b) possible pathways for PMS and PDS activation with N doped CNT.
(a) Increased active sites, adapted from Zheng et al. (2019).

shown in Fig. 5(a). N in Graphitic N has one more outermost electron than the pristine carbon atom which makes it easy to bond with negatively charged oxygen in PS (Schiros et al., 2012). Graphitic N with rich electrons has also been reported to play a significant part in PS activation (Fig. 5(b)). The electron transport to PS can be utilized to break O-O bond of PMS and PDS directly and generate free radicals. This catalytic pathway has been employed in the removal of organics and achieved a satisfactory performance. It has been reported that N doped CNT catalyst can achieve the complete removal of 2,4,4-trihydroxybenzophenone through generated hydroxyl radical and sulfate radical (Pan et al., 2018a). CNT there serves as electron shuttle and provide reaction sites needed for catalytic reaction. Moreover, graphitic N on CNT also exhibits its role in degrading organics via nonradical pathway (Ma et al., 2018; Ren et al., 2020a). During this process, the active sites and pathway in N doped CNT have been changed compared with original CNT. According to DFT computations, graphitic N might promote the charge transfer from neighboring C atom due to their greater electronegativity. Formed positively charged C can reinforce the interaction between PS (PMS or PDS) and N-doped CNT then contributes to weakening the O–O bond of PS to generate $SO_5^{\cdot-}$ and then $^1O_2$ (Duan et al., 2015e; Wang et al., 2017b). During this process, graphitic N is not regarded as active center but an effective way to induce the formation of positively charged carbon center (Cheng et al., 2017; Gao et al., 2020). Moreover, direct electron transfer induced by N doped CNT has also been exploited (Ren et al., 2020a). In PMS activation induced by N doped CNT, graphitic N can elevate the adsorption rate of PMS, thus improving redox potential of N doped CNT–PMS* complexes. However, due to the restriction from limited PDS adsorption amount, N doped CNT–PMS* complexes can only show a moderate degradation rate even with a higher redox potential (Li et al., 2017a). Therefore, more strategies should be put forward to overcome this problem and gain improved removal efficiency towards organics. Except for graphitic N, other fraction of N species in CNT also plays a role in PS activation process. Charge is expected to transfer from the electron-rich N atoms to PS molecules via a connected N(-)-C(+)-O(-)-PS bridge to produce reactive species. Pyridinic N behaves as a p-type doping whose lone-pair electron is firmly positioned around the nitrogen atom, making it hard to donor electron in PS activation than the original C atom (Long et al., 2012). But it is still an important active site during catalytic process (Saputra et al., 2013). Pyrrolic N does not introduce electrons or holes into the graphite lamellas of carbocatalyst and it can be stable with the help of hydrogen atoms. The role of pyrrolic N in PS activation seems to be still in an argument. Many studies reported that it induced little enhancement of PS activation. However, a recent study supported that pyrrolic N played an important role in the generation of free radicals in hydroxylated carbon nanotubes (CNT-OH) based PDS system (Pan et al., 2018). That is to say, although different N species might coexist in a N doped CNT, the role of N species varied due to different carbon configurations and experimental conditions. Amine groups (-NH_2) can be regarded as electron donors to elevate overall electron abundance of CNT and enhancing adsorption capacity simultaneously (Chen and Carroll, 2016).

Except for single N doping, B atom (0.82 Å) with similar atomic dimension to C atom (0.77 Å) is also suitable for being incorporated into carbon lattice. B has shown high hardness, commendable strength and good chemical resistance, which could be viewed as an ideal single doping atom. Similar to N atoms, B doped carbon materials can change the electroneutrality of carbon-containing catalyst, lower the Fermi energy level at the impurity states near the valence band and increase the electrical properties of carbocatalyst by creating more active sites (Wang et al., 2018). Meanwhile, similar atomic radius between B and C atoms enables little or no structural damage of CNT when replacing original C atom with B atom (Li et al., 2021). It is expected that their catalytic ability would be improved in water bodies compared with pristine CNT (Wang et al., 2018). Many studies have proposed the preparation of B-doped carbon nanomaterials and used them as oxygen reduction catalysts, or applied them in energy storage. However, the study concerning its catalytic performance towards PS activation is rare, especially for single B doping. Basically, the structure formed at the edge of carbon configuration including BCO_2 and BC_2O is indispensable in the carbon/PS activation system, which is regarded as the main catalytic active sites on carbocatalyst. Generally, dual reaction pathway exists in the catalytic degradation of organic pollutant (Li et al., 2021). One is to promote direct electron transfer pathway and the other is to accelerate radical pathway. For the direct electron transfer process, PMS is first adsorbed on the B doped CNT to form metastable composite B-CNT-PMS* . Then, electron-deficient B is prone to accept the electron from organic pollutant and transport it to CNT-PMS* structure with a higher redox potential. Here the doped B contributes to boosting the adsorption interaction between PDS and B doped CNT and electron transport. However, the role of doped B in activating PMS through radical pathway is quite disparate. •OH and $SO_4^{\cdot-}$ are produced with the electron transfers from defects after B doping, and B dopants are regarded as a bridge to introduce defects or other active sites. Other simple configurations such as B–B, B–O and B–C bond make little contribution to PS activation in N doped CNT materials.

4.1.3. *Co-doping of metal-free atoms*

In addition to aforementioned single dopants, S dopants are another alternative agent for preparation of doped carbocatalyst to tune their catalytic performance (Guo et al., 2018). However, the studies concerning effect of single doped S on CNT have not been reported yet. As an alternative, S is mainly introduced as a secondary adventitious atom to produce new features on CNT. Similar multiple doping appears to be an effective way to strengthen the usage potential of CNT as there is a synergistic effect between different heteroatoms. Double-doping or three-doping of N, B and S is commonly-used strategy and exhibits improved catalytic activity for the degradation of organics compared with single heteroatom doped materials (Liu et al., 2016). As illustrated in Fig. 6, the co-doped CNT shows a higher isoelectric point (IEP) than that of original and single doped CNT, promoting the adsorption of PS (Luo et al., 2021). Different second dopants have different effect on catalysis. For B co-doped agents, adsorption energies of PS onto CNT would provide a moderate adsorption energy, which is in favor of the release of free radicals and active species. Second S dopants could further modulate the active sites generated by N doped CNT and lower the energy barrier for generation of reactive species (Duan et al., 2015c). Up to now, a variety of multiple heteroatom doped CNT composites including B-N co-doped CNT, N-S co-doped CNT-COOH and edge-enriched N,S doping CNT have been prepared and showed great catalytic performance in PS activation. Formed dipole moments including S-C-N or N-C-B in sp^2 covalent carbon network atoms would show stronger spin and charge densities as compared with connected neighboring C atom, which is an advantageous method for the expansion of reaction area. Different from single heteroatom doping, the relative position of heteroatom rather than doping level determines synergy (Nie et al., 2020). If atoms substitute adjacent C atoms in the same benzene ring and form structure such as C-N-B simultaneously, active sites on the surface of CNT might decrease with the occurrence of neutralization reaction. In particular, complementary effects between n- and p-type dopants are not conductive to the interaction between PS and carbon materials (Zhao et al., 2013). On the contrary, a B-C-N heterostructure in sp^2 hexatomic ring can effectively excite the generation of positively charged adjacent C atoms to break the inertia of carbon lattice, which can contribute to the adsorption and dissociation of PMS (Duan et al., 2015b).

Aside from the atoms mentioned above, other nonmetal atoms including F-, I-, and P- have been applied as single or binary (B,P-carbon, P,S-carbon) doping materials (Cao et al., 2013; Huang et al., 2017; Michel et al., 2006). Although relevant research concerning their application in PS activation for organic pollutant removal is still rare, it is expected that their efficiency could be satisfactory.

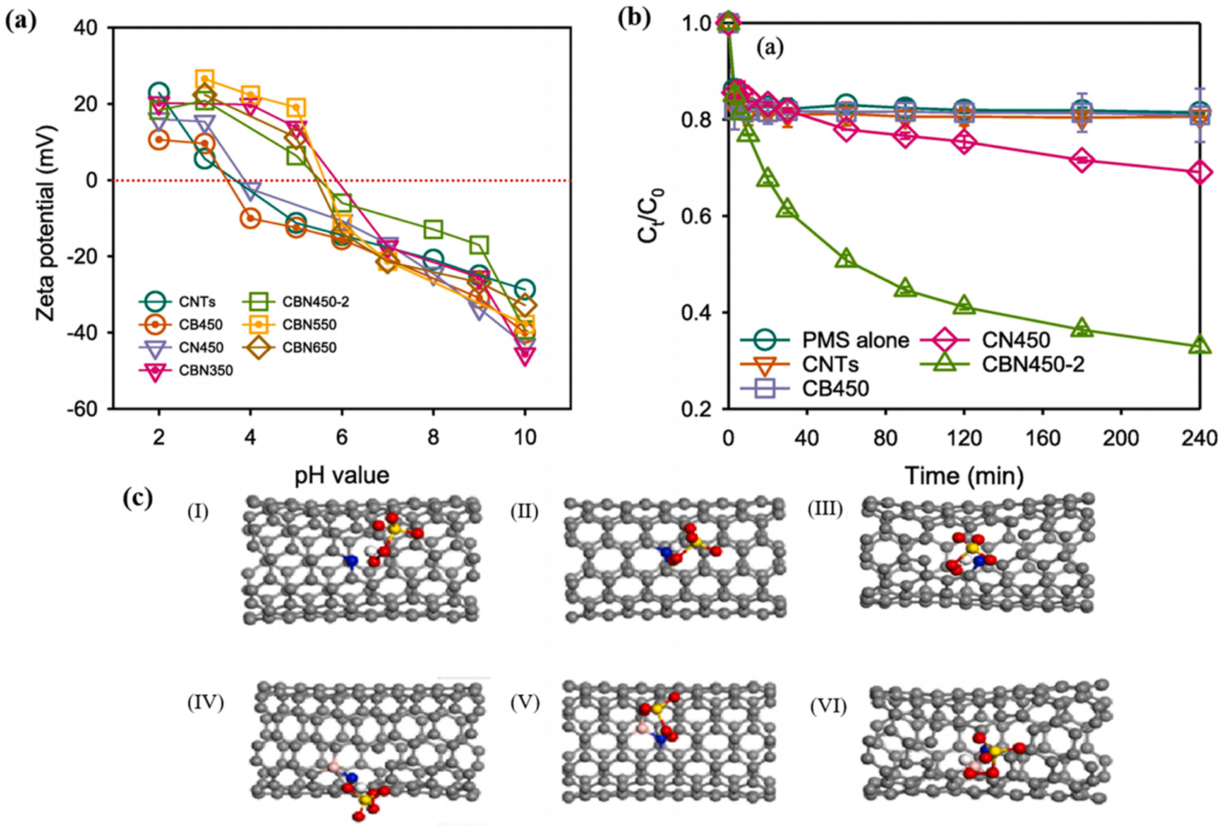


Fig. 6. (a) Zeta potentials of CNT and B, N single and co-doped CNT; (b) The removal of 2, 4-D over different CNT, CB450, CN450 and CBN450–2; (c) Atomic structures of CNT before and after doping: (I) pyridinic N-doped CNT, (II) graphitic N-doped CNT and (III) pyrrolic N-doped CNT in CN450, (IV)pyridinic N and B co-doped CNT, (V) graphitic N and B-co-doped CNT and (VI) pyrrolic N and B co-doped CNT in-CBN450–2. Copyright 2021, Elsevier.
Reproduced with permission from Luo et al. (2021).

4.2. Metal doping in CNT

In addition to heteroatom doped CNT, metal nanoparticles (NPs) embedded beneath or loaded at curved carbon layer of pristine or mesh doped CNT has also been researched widely to active PS. Metal NPs are mono-dispersed on or seriatim-confined in CNT, thus increasing contact areas of metal NPs (Peng et al., 2021; Wang et al., 2017a). Doping of metal atoms on CNT can also reduce the electron escape probability and improve the electron donating ability of carbon (Aijaz et al., 2016; Deng et al., 2013). Nowadays, metal NPs are often buried in heteroatom doped CNT to further increase the property of CNT. Firstly, heteroatom doping might change the interfaciarl reaction process (Cheng et al., 2016). The hybrid molecular orbitals of nonmetal-metal bond (N-M or S-M) show an extended space compared with that of oxygen-metal bonds (O-M), which promotes orbital-interaction and electron transform between the connected metal and adsorbed persulfate reagents. Secondly, the dopants could form trap-states to capture the generated charge to induce a new PS activation process (Guo et al., 2010).

4.2.1. Preparation of metal doped CNT

Metal doping in mesh of CNT means fabricating CNT with encapsulated nanoparticles mainly including single metal or metal oxide, multiple metal oxide, and single atom (Boczkaj and Fernandes, 2017). Transition metals including cobalt (Co) and iron (Fe) have been validated as promising doped CNT because 1) Co or Fe doped CNT shows a higher activity for PS activation compared with other transition metals; 2) their magnetism enables them to be recycled easily; 3) the metals with variable valence states make them easy to offer electron to PS. The preparation of metal doped CNT is diverse and can be classified in two types. Jiang et al. (2020) fabricated nano-Co_3O_4 encapsulated in N doped CNT (Co_3O_4 @NCNT) by one-pot hydrothermal method as shown in Fig. 7(a). At first, Co precursors are mixed with prepared C or C/N precursors. Then resultant powders are calcined under N_2 atmosphere. On another condition, metal doped CNT are prepared according to impregnation-precipitation method as presented in Fig. 7(b). Briefly, CNT is impregnated with prepared metal precursor solution and then undergoes a pyrolysis at about 300–800 ℃. Different advantages have been assigned towards different synthesis methods. Prepared doped CNT by one-pot hydrothermal method usually show a core-shell structure with CNT encompassing dark nanocrystals, which is in favor of the preservation of contained nanometals. Su prepared Fe doped CNT using Fe^{3+} ions as precursor. Under Ar atmosphere, Fe species outside CNT were transferred into Fe_3O_4 due to the slow oxidation by air during pyrolysis period while they were partly reduced to Fe^0 inside CNT due to the protection from formed graphitic layer (Su et al., 2021). On the contrary, CNT synthesized by impregnation-precipitation method usually exhibits a modified structure with nanometals exposed directly. Herein, an increasing reaction area would be attained. In CNT based AOPs system, most of contained metals are regarded as important active sites. Herein, simple one-pot hydrothermal method is recommended to keep the integrity of catalytic center. In addition, the wrapped metals are more prone to accept electrons under the nano-confined environment provided by CNTs, which is valid for activation of oxidants in AOPs (Pan et al., 2007; Su et al., 2021).

The type of metal precursor also affects the formation of doped CNT. Frequently used Co precursors can be divided into inorganic Co complexes and organic Co components. Inorganic Co complexes including $CoCl_2$, $CoSO_4$, $Co(NO_3)_2$ and $Co(CH_3COO)_2$ have been extensively used in the preparation process of Co modified carbocatalyst for PS activation (Espinosa et al., 2019; Tian et al., 2020). For organic Co precursors, it

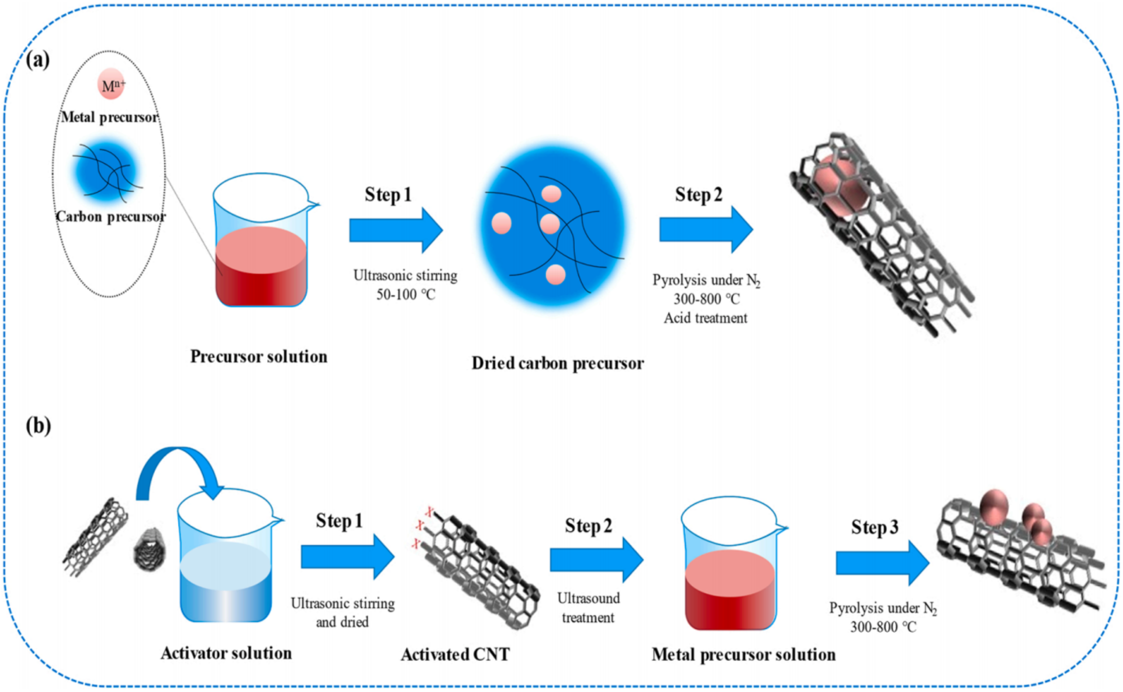


Fig. 7. Synthesis process of capsule doped CNT by (a) one-pot hydrothermal method and (2) impregnation-precipitation.

has been reported that cobalt phthalocyanine (CoPc), vitamin B_{12}, binuclear cobalt phthalocyanine (Co_2CPc), and polyphenolic-Co^{2+} complex can be employed to activate PMS by post-loading or direct carbonization of these Co-containing materials (Zhao et al., 2020). Compared with inorganic Co ions applied alone, organic precursors prevent the loss of Co species as a direct covalent linkage is formed between the supporter and Co-containing materials (Guo et al., 2017). In addition, carbonization of organic Co materials enables the good dispersion of Co, which avoids agglomeration of Co particles during pyrolysis (Zhang et al., 2019). Nevertheless, studies on organic Co encapsulated in CNT are rare. For Fe doped CNT, Fe precursors usually contain basic chemical reagents such as $FeCl_3.6\ H_2O$, $FeSO_4.7\ H_2O$ or their mixture. More recently, many scientists try to find the usage potential of Fe-containing wastes based on the idea of "waste controlled by waste". Red mud or other solid waste containing Fe has been used as Fe precursor of Fe doped CNT and shows good removal efficiency in Fenton-like process (Yang et al., 2021). However, how to minimize possible secondary pollution and improve the production of catalyst are two keys to be considered. In addition, the balance of the increasing active sites and the agglomeration caused by metal particles also requires further study.

4.2.2. *Single metal modification*

Single Co modified CNT is used as bifunctional electro-catalysts in oxygen electrode of fuel cells and metal–air batteries at first. Then the strategy of assembling Co oxides using CNT as carriers is gradually applied to PS activation. Cobalt oxide nanocrystals, especially Co_3O_4, are used as doping materials because: 1) Co_3O_4 has shown excellent activity for degradation of organic pollutants due to its strong redox ability (Shang et al., 2017). Active sites of cobalt and CNT appear to have synergistic effects in promoting the electron transfer. 2) cobalt oxide nanoparticles can be easily incorporated into carbon matrix without causing damage to structure of CNT during catalyst preparation and 3) new reactive sites including Co-C-C, Co-N-C, Co-O-C on CNT materials can be introduced.

As an electron donor, Co species (inside- or outside-CNT surface) independently participate in the production of reactive species as shown in Eqs. (9)-(12) (Nguyen et al., 2021). As a counsequence, the activation efficiency could be improved efficiently. Liu et al. (2020a) prepared tube-filled Co_3O_4 @CNT and degraded 97.5% norfloxacin (NX) within 60 min in the PMS based AOP system. It has been proved that the properties of CNT would be changed after Co_3O_4 filling. Firstly, relevant DFT calculation shows that doped Co species contribute to weaken the localization of electrons caused by ionic bonds, and form extended valence band structure. Herein electron transfer ability can be strengthened. In addition, a high adsorption energy (ΔE_{ads}) of PMS molecules adsorbed on Co oxide unit region (−2.03 eV) shows a bifunction including improved adsorption and activation for PMS molecule. For Co species buried in heteroatom doped CNT, Co species are stabilized much better after the formation of heteroatom-containing structure such as pyridinic N and quaternary N (Nguyen et al., 2021). The strong synergistic effect between heteroatom and contained NPs has been emphasized in many studies (Jiang et al., 2020). Specifically, Co-N coupling center at hetero-interface between N doped CNT and Co NPs is conductive to PS adsorption and promotes electron transfer. Similarly, coupling Co species within other multiple heteroatoms doped CNT provides a theoretical possibility to activate PS, due to the synergistic effects of confined Co species and heteroatoms. However, no relevant research has been reported yet.

$$Co^0\ @CoCNT \rightarrow Co^{2+}@CoCNT + 2e^- \tag{9}$$

$$e^- + HSO_5^- \rightarrow SO_4^{\cdot-} + OH^- \tag{10}$$

$$Co^{2+}@CoCNT + HSO_5^- \rightarrow Co^{3+}@CoCNT + SO_4^{\cdot-} + OH^- \tag{11}$$

$$Co^{3+}@CoCNT + HSO_5^- \rightarrow Co^{2+}@CoCNT + SO_5^{\cdot-} + H^+ \tag{12}$$

Recently, many studies demonstrate that Fe modified CNT shows their advantages in treatment of environmental pollutants with Fe species dispersed in the sp^2 carbon lattice evenly (Cheng et al., 2016; Wu et al., 2019; Yao et al., 2016). Usually, Fe encapsulated in CNT is more favorable for PS adsorption and removal of pollutant with a confined space than Fe loaded CNT. The confinement space of CNT for Fe increases the possibility for embedded Fe species to react with adsorbed PS molecule in CNT cavity. On the other hand, the formed confined space is isolated from other environments thus gathering reactive species to accelerate possible reactions at a wide pH range (Su et al., 2021). Fe NPs including zero valent iron (Fe^0), magnetic composites have been widely encapsulated in CNT for PS activation and have been regarded as main active sites. Active centers such as Fe^{2+} (generated via reaction between Fe^0 and PS) and Fe^0 species on the CNT are able to prolong or break O-O bond of PS directly and generate $^1O_2$ and free radicals, respectively (Eqs. 13–16) (Pham et al., 2021). Notably, the active center for PS activation is still in debate. Wang et al. (2017a) demonstrated that both the quaternary N and external iron on the CNT surface acted as active sites to induce PMS activation at ferric carbide nanocrystals encapsulated in N doped CNT. Similar synergistic effect is also confirmed by other study (Yao et al., 2016). However, a recent study by Wu et al. (2022) showed that it was the original active sites in CNT (abundant C=O) rather than special structure induced PDS activation by coupling iron species on S doped CNT (S-nZVI@CNT). Formed S-nZVI structure just contributes to accelerating electron transfer. Hence, the mechanism of activation of PS by Fe modified CNT remains unclear. More studies should be carried put to identify the relationship between Fe NPs and heteroatom in CNT.

$$2HSO_5^- + Fe^0 \rightarrow Fe^{2+} + 2SO_4^{\cdot -} + 2OH^- \quad (13)$$

$$HSO_5^- + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\cdot -} + OH^- \quad (14)$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\cdot -} + SO_4^{2-} \quad (15)$$

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \quad (16)$$

Other metal species with variable valence states including Mn (Mn^{2+}, Mn^{3+} and Mn^{4+} species) and Ni (Ni^0, Ni^{2+}, and Ni^{3+} species) also showed prospect in carbocatalyst based PS activation process, in which Me@ (N/O)-C (Me means metal) engagement as a facile electron transfer bridge has been emphasized (Liu et al., 2021a; Yao et al., 2017a, 2018). However, metal leakage is a severe problem faced by metal modified CNT. The combination of metal and other dopants such as N offers a superior stability than original Fe modified CNT. Similarly, the metal species embedded in CNT presents more organic removal and less metal leakage compared with metal species loaded on surface of CNT (Su et al., 2021; Zhang et al., 2018).

4.2.3. *Multiple metal modification*

Through introducing a foreign metal, metal modified CNT exhibits higher redox potential and less leaching. The significance lies in that this modification combines main metal and foreign metal in one catalyst to simultaneously benefit from a higher pore structure, electrical conductivity and active site accessibility of CNT, thereby achieving a higher elimination rate of organics and regeneration of active metal species (Zhang et al., 2021). Based on the single activation mechanism of other carbocatalyst, the activation of persulfate through multiple metal modified CNT might involve two mechanistic pathways (Mady et al., 2019): 1) activation reaction. The active sites, mainly the contained metals, induce an interior activation on the nanohybrid and generate active radicals; 2) regeneration of active metal species. Part of reduced foreign metals can induce a recovery reaction to make the main metal change back to original states on the hybrid. As a result, a unique activation cycle can form. Fe, Zn, Co, Ni, Cu are widely used for the preparation of multiple metal modified CNT. Many studies prepared multiple metal modified CNTs by combining different metals on CNT, which exhibited an increased contact area and improved PS utilization efficiency (Kang et al., 2019; Tang et al., 2012). For example, $CuFe_2O_4$/MWCNT has been prepared and achieved 100% removal of diethyl phthalate with little leakage (Zhang et al., 2016). Compared with primary N doped CNTs, the magnetic Ni-Co alloy encapsulated N doped CNT catalyst exhibited higher PS absorption. Hence, along with faster electron transfer rate and unique redox cycle ability of Ni-Co in hybrids, the removal capability of this system towards ibuprofen was 23.4 and 5.8 times higher than pristine CNT and single metal (Ni or Co) doped CNT, respectively (Kang et al., 2019).

In conclusion, CNT catalysts containing multiple metals can be applied to control redox cycle through their unique interaction, thus strengthening removal capability of CNT towards refractory pollutants. In addition, the metal modified CNT used by multiple times also exhibit a good magnetic separation and recovery ability, making it more advantageous in realistic elimination of organics. To this end, the reports regarding a synergistic multiple metal redox cycling process in CNT are still rare. There is an urgent need to investigate effects of different coupling of transition metals on CNT towards PS activation and organic removal.

5. Future development of CNT based PS-AOP system

5.1. *Improvement of derived materials*

As mentioned above, many C and/or N precursors have been used to prepare CNT material. However, conventional methods have irregular morphology and non-uniform dimension as well as a single active site. MOFs (metal-organic frameworks) have attracted widespread attention through constructing a suitable nanostructure to maintain the catalytic activity (Hu et al., 2022). As one kind of crystalline material with a continuous metal-organic hybrid framework, advantages of MOFs are their adjustable external structure and numerous internal metal sites. MOFs-derived CNT composites show outstanding catalytic efficiency towards organic pollutant through generated activated hydrogen adsorbed on the surface of catalysts (Liu et al., 2021d). Nowadays, MOFs have been used as precursors for the synthesis of CNT based metal nanoparticles with core-shell nanostructures (Pan et al., 2018b). There are two major MOF-derived CNT materials used for PS activation. The former one is direct pyrolysis of sacrificial precursors to form CNT (as shown in Fig. 8(a)). Adenine frameworks (AD) and zeolitic imidazolate frameworks (ZIF) are regarded as good self-sacrificing templates for the formation of novel N doped CNT. Through a simple pyrolysis-oxidation strategy, organic ligands in the core-shell MOFs are converted into carbocatalyst (Peera et al., 2018). The intertwined CNT with mesoporous structure is formed after calcination, which is in favor of the electron transfer. Mass transport and diffusion of substances involved in reaction are also strengthened (Yao et al., 2017b). Zn is often used as the assisted dopant for the stabilization of single metal atoms. The spatial interval between adjacent metal atoms could be finely controlled, and part of Zn sites generated defective sites during pyrolysis. As a result, both mass transportation and PS activation can be promoted. Liu et al. (2020b) prepared magnetic heterogeneous catalyst to activate PS through the pyrolysis of Zn/Co MOFs under a constant nitrogen flow, which exhibited a high degradation rate for oxytetracycline through radical pathways The special 3D-structure of the synthesized material can preserve integrity of metal catalytic agent without hindrance in the mass transfer, because the formed porous structure ensures the accessibility of reactant to exposed Co sites (Xiao et al., 2018). Recently, Mi's group exploited MOFs-derived Co and N co-doped CNTs to activate PMS. Compared with traditional CoN_4 site (a CoN_4 moiety anchored in a complete graphitic layer), a CoN_{2+2} site (CoN_4 moiety linking with two adjacent graphitic edges) dominated the activation of PMS and achieved 98.89% PMS conversion to $^1O_2$ (Mi et al., 2021). The above results indicate that the degradation pathway of the MOF-derived CNT based catalytic system is complicated. The activation pathway is dependent on their structures, metal types, and other factors including metal states, crystalline structure and their coordination environment. For the latter MOFs-derived CNT architecture, CNT is in situ and evenly buried in the porous MOFs microcages, as shown in Fig. 9(b). Lan et al. (2021) prepared $ZnFe_2O_4$/CNT with hybridization of CNT into porous $ZnFe_2O_4$ architecture under Ar atmosphere and presented excellent ability for BPA elimination under wide pH ranges (3.0–9.0). CNT inserted into porous frameworks promote the directional electron transfer. In addition, the strong interactions between $ZnFe_2O_4$ and defective CNT also

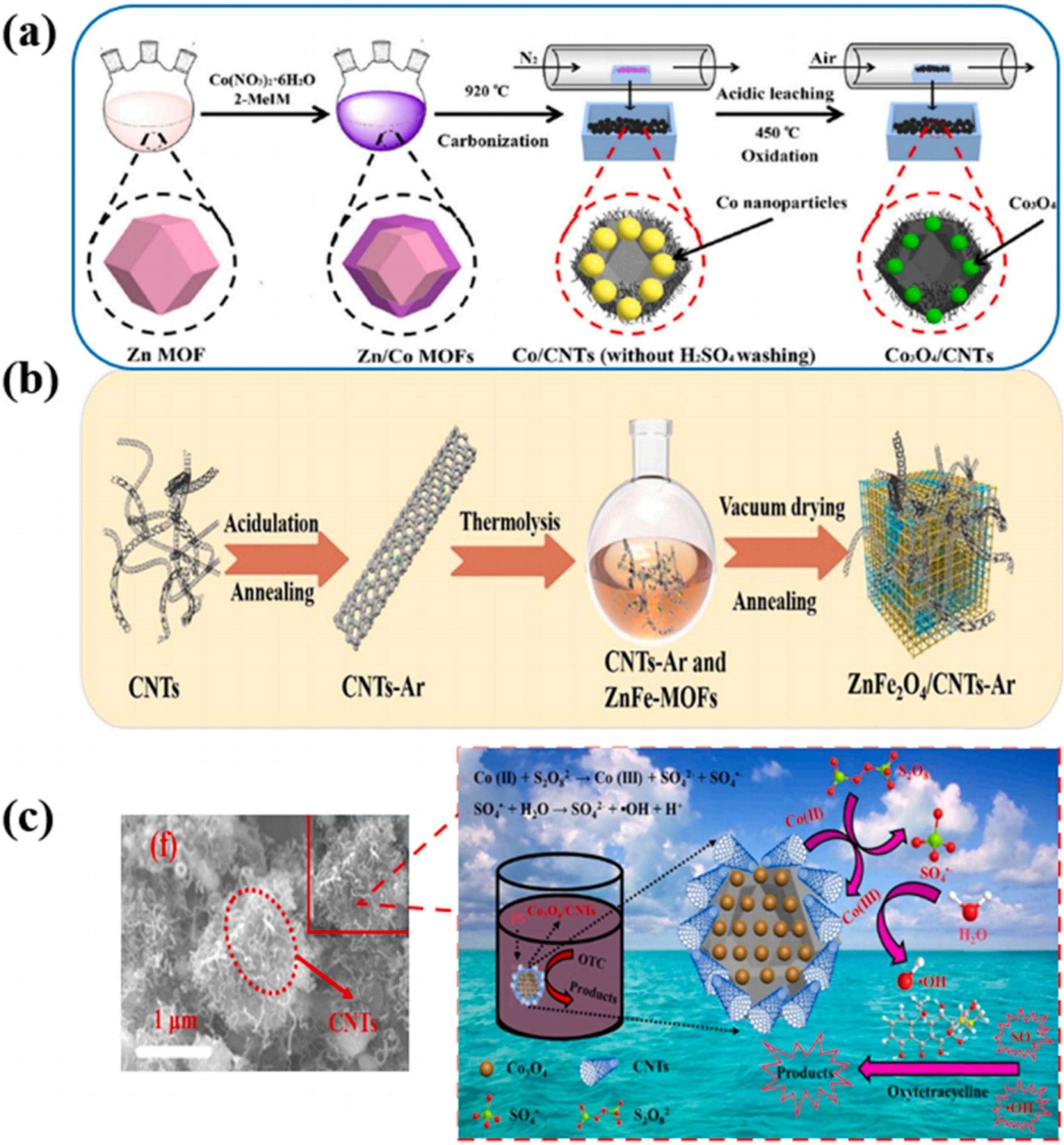


Fig. 8. (a): Preparation of core-shell MOF-derived hybrid composite Co@NCNT-1–800 catalyst; (b): Illustration for the fabrication process of CNT embedded in MOF-derived microcages and (c) Mechanism for PS activation by MOF-derived CNT to eliminate organics. Copyright 2020, Elsevier.
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tunes the ratio of Fe^{2+}/Fe^{3+}, which provides ample active centers for the high catalytic activity.

These two MOF-derived CNT composites have excellent surface properties, and their ability to degrade organics via free radical chain reaction mechanism is much better than that of ordinary metal NPs. However, to the best of our knowledge, currently, most of MOF-derived CNT materials are employed as electrocatalysts for gas reduction and peroxide activation. Their PS activation efficiency towards degradation of organic pollutant is a field deserves further research.

5.2. Assisted technology

What is noteworthy is that, due to the limitations of CNT-PS based AOP system, the urges of developing coupling technologies emerge. Some studies put forward that the activation of persulfate by carbon materials can be enhanced by adsorbing outer light, ultrasound and electricity (Duan et al., 2020; Kakavandi et al., 2019; Kemmou et al., 2018; Liu et al., 2019). Apart from the solo activation ability, these technologies also play important parts in boosting the activation capability of carbon materials. Ultrasound has been reported to result in the formation of sono-induced carriers and generate electron-hole pairs while light irradiation tends to generate photo-induced electron-hole pairs in carbon materials. Then the electrons could be received by adsorbed persulfates thus forming $SO_4^{\cdot-}$ and·OH. Numerous reports have demonstrated the improved degradation rate and degradation efficiency by extra introduction of light and ultrasound (Kakavandi et al., 2019; Kemmou et al., 2018). External electric field could improve the efficacy of carbon materials towards activation of persulfate. The wet carbon can be oxidized into OFGs, which might enhance activation of PS (Chaplin et al., 2013). On the other hand, when CNT is combined with dopant molecules via chemical p-doping, hole carriers will form due to electron transfer from the carbon π states to electron acceptors. What's more, hole carriers could maintain for at least 5 min according to the in situ Raman measurements (Rao et al., 1997). This offers CNT a theoretical basis in different electronic/electrochemical applications.

Although extra energy input assisted PS activation processes are still

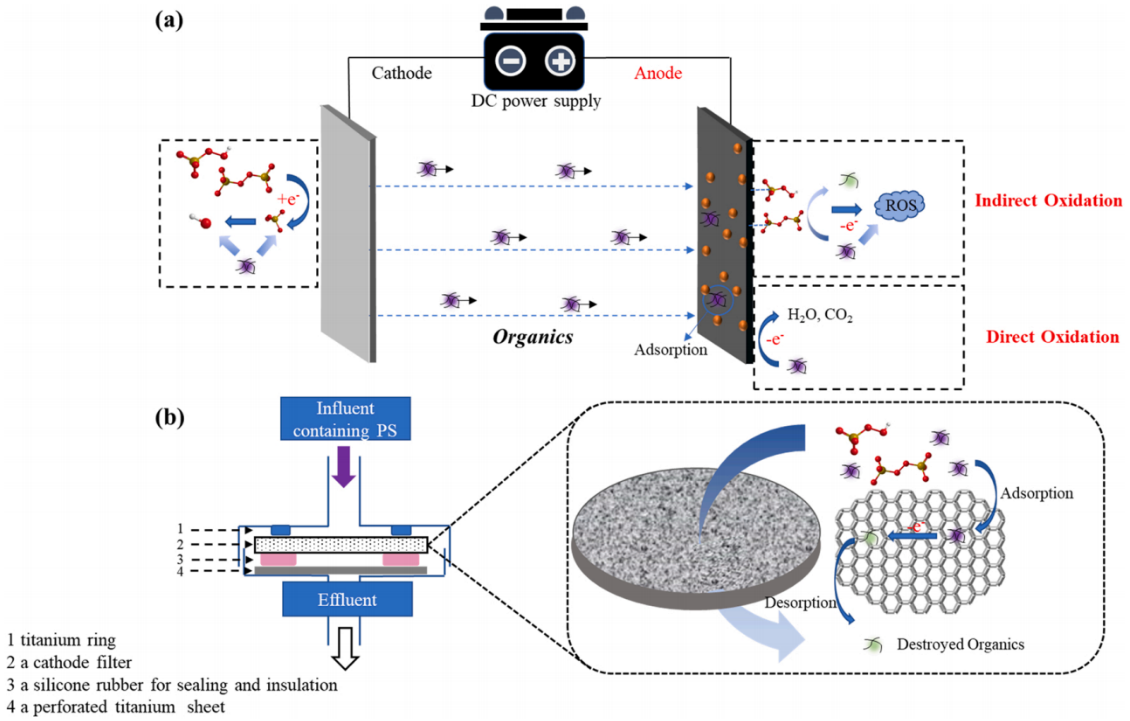

Fig. 9. CNT based (a): batch electrode reactor and (b) plug-flow membrane reactor in EAOPs.

in its infancy, they are undoubtedly a green and promising way for organics elimination. We hope that this section will provide a crucial reference point for future development of CNT-based AOPs. Commonly used assisted activation technologies in CNT (etc., photocatalysis or electrocatalysis) are summarized in Table 3.

Semiconductor catalyst makes full use of external light source and can be regarded as a promising AOP to eliminate various organic compounds. The photocatalytic performance of original CNT is not satisfactory due to fast recombination of the photo-induced electron-hole pairs. The generated electrons will be captured when coupled with AOPs technology with PS agents adsorbed on defect part, avoiding undesirable electron-hole recombination. As a result, the removal rate of organic pollutants could be significantly improved (Hao et al., 2019). However, when CNT is used as a dopant to form a TiO_2-CNT hybrid catalyst system, electron generated in CNT can be overlooked. CNT and PS play the role as electron transport bridges and electron sink to prevent charge recombination in TiO_2, respectively (Zhang and Chu, 2022).

Electrochemical advanced oxidation processes (EAOPs) are a group of fast-developing technologies which enjoy the advantages of low cost, high efficiency and strong anti-interference ability (Särkkä et al., 2015). Exerting an electric field is beneficial to mass transport of target pollutants toward CNT surface. At present, CNT has been employed in devices of EAOPs including batch electrode reactor and plug-flow membrane reactor. A typical batch reactor apparatus is shown in Fig. 9 (a). Basically, CNT-polytetrafluoroethylene (CNT-PTFE) is used as an electrode material for both cathode and anode because of its outstanding stability and electrical conductivity. Part of the charged organic species is absorbed onto the surface of oppositely charged electrodes through a non-Faradaic process. This process usually occurs at a lower potential (than that of oxygen evolution reaction). An indirect oxidation is found when the operating potential is higher than expected. ROS formed on the surface of electrode and electro-adsorption both contribute to the removal of organic pollutants near the anode (Nie et al., 2018). Both cathodic and anodic activation have been reported to activate PS, which are also called radical activation and nonradical activation, respectively (Eqs. (17)-(20)) (Song et al., 2018; Zheng et al., 2021). Some studies have claimed that anodic activation exhibited a better capability on degradation of organics (Song et al., 2017).

$$\text{Cathode}: S_2O_8^{2-} + e^- \rightarrow SO_4^{\cdot -} + SO_4^{2-} \tag{17}$$

$$\text{or} HSO_5^- + e^- \rightarrow SO_4^{\cdot -} + OH^- \tag{18}$$

$$\text{Anode}: CNT(PS*) \rightarrow SO_4^{\cdot -} \tag{19}$$

$$CNT(PS*) + H_2O \rightarrow \cdot OH + SO_4^{2-} + H^+ \tag{20}$$

$$HSO_5^- + SO_5^{2-} \rightarrow HSO_4^- + SO_4^{2-} + {}^1O_2 \tag{21}$$

Direct metal modification on CNT anode has been proposed for practical application as shown in Table 3. Anode with target metal doping is synthesized for electrolysis and PS activation. Due to the synergistic reaction between electrolysis and persulfate oxidation, higher degradation efficiency of organic pollutant via electrochemical activation of PS is achieved. Many studies supported the claim that both radical and nonradical oxidation are the main pathways to remove organics in this process. PS trapped in the pores of electrode shows a stretched O-O bond and generates different ROS including $SO_4^{\cdot -}$,·OH and $^1O_2$ as shown in Eqs. (19)–(21) (Nie et al., 2019; Zheng et al., 2021).

As for plug-flow membrane reactor, the prepared CNT membrane formed porous network with pore size ranging from 10 to 100 nm, similar to the pore size of micro/ultrafiltration membranes (Liu et al., 2020c). As a result, it can be incorporated into commercial membrane devices easily. In addition, the conductive membrane also possesses a high anti-fouling performance. Firstly, the strong electrostatic repulsion force can hinder the deposition of charged pollutants (Wang et al., 2021b). Secondly, the formed hydration layer is beneficial to slow the accumulation of organics. Finally, the small bubbles generated on CNT surface are expected to restrain the interaction between CNT and organics (Xu et al., 2022). As shown in Fig. 9(b), the reaction process can be simply summarized as 1) mass transport toward CNT surface, 2) adsorption process, 3) catalytic degradation process with electron transfer and 4) desorption of oxidative species. Here the surface charge of organics plays a significant role in electron transport due to electrostatic attraction or repulsion. Evaluation on the transport situation of

Table 3
CNT involved in light or electricity coupling processes.

Systems	Reaction conditions	Degradation pathways	Ref.
Light assisted system			
UV light assisted CNT-TiO_2/PMS + phenol	20% CNT-TiO_2 and 20 min UV irradiation; Phenol concentration = 10 mg/L; t = 60 min	$SO_4^{\cdot -}$,·OH and $^1O_2$	(Hao et al., 2019)
Defective CNT/PS + bisphenol A	PDS/PMS dosage at 1.5 mM; CNT dosage at 100 mg/L BPA concentration = 20 mg/L; t = 15 min	Direct electron transfer	(Yu et al., 2021)
MWCNT + Co doped TiO_2 + antipyrine	PMS = 2 mM; [Antipyrine] = 0.05 mM; MWCNT dosage at 100 mg/L, Co-TiO_2 content at 100 mg/L; t = 12 min	$^1O_2$	(Zhang and Chu, 2022)
Electricity assisted system			
PDS system with MWCNT cathode + aniline	PDS dosage at 5.55 mM; Voltage = −0.6 V; [Aniline] = 0.45 mM; t = 150 min	Nonradical oxidation process induced by surface-bounded PDS	(Nie et al., 2018)
PDS system with MWCNT cathode + acyclovir	PDS dosage at 11.1 mM; Voltage = 1.2 V; [acyclovir] = 0.45 mM t = 120 min	Nonradical oxidation process induced by surface-bounded PDS	(Nie et al., 2019)
Persulfate system with Ti/CNT/SnO_2-Sb-Er anode and Ni@NCNT cathode + cefotaxime	PS/Fe^{2+} dosage ratio at 1:1; Current density at 40 mA/cm^2 Cefotaxime concentration = 50 mg/L; t = 60 min	$SO_4^{\cdot -}$ and·OH	(Lei et al., 2020)
PDS system with SnO_2/Ni@NCNT anode and Ni@NCNT cathode + cephalexin	PDS dosage at 1.5 mM; Current density at 25 mA/cm^2 Cephalexin concentration = 50 mg/L; t = 30 min	$SO_4^{\cdot -}$ and·OH	(Duan et al., 2021)
PMS system with filtration system with a nZVC–CNT cathode and a perforated Ti plate anode + congo red	PMS dosage at 1.5 mM; nZVC dosage at 0.2 mM; [Congo red] = 0.015 mM; t = 5 min	·OH and $^1O_2$	(Zheng et al., 2021)
PDS system with SnO_2-Al_2O_3/CNT anode and CNT cathode + ceftazidime	PDS dosage at 2 mM; Fe^{2+} dosage at 2 mM; Ceftazidime concentration= 20 mg/L; t = 20 min	$SO_4^{\cdot -}$ and·OH	(Duan et al., 2020)

reactive species and determination of the limiting step are important to guide the practical system design and optimization. Similar to batch reactor, many oxidative pathways such as $SO_4^{\cdot -}$,·OH and $^1O_2$ and direct electron transfer are confirmed to be engaged in catalytic reaction process (Xu et al., 2022; Zheng et al., 2021).

It should be noted that, similar to CNT catalyst, many factors including loss of doping metals, structure change or destruction, attachment of other impurities or by-products and the coverage of active sites will cause deactivation of the CNT anode material to some degree (Olmez-Hanci et al., 2018). Also, energy consumption is also an important parameter in practical use. Herein, EAOPs system with more stable state and less energy consumption are two key issues to be considered in the following optimization process. In a word, the combination of different organic removal strategies introduces a more efficient way with minimum change in catalyst property, which might be the potential direction in the future studies.

6. Environmental applications in real environment

Although numerous works have been conducted regarding degradation of organic matters via CNT materials in PS-AOP system, most of the experiments are performed in the lab. Field tests utilizing pilot-scale or large-scale facilities have not been adequately addressed. The removal of organic pollutants in real environment has been overlooked. To test the practical application potential, CNT based PS-AOP system has begun to be applied in various actual environmental conditions including water purification in river or lake and removal of industrial gaseous volatile organic compounds (VOCs) (Peng et al., 2021; Wang et al., 2021a; Zheng et al., 2021). As for soil, some carbocatalyst based PS-AOPs have shown their degradation potential in soil such as active carbon and biochar. But relevant researches about CNT based PS-AOPs are still restricted to explore the sensitivity of different type of soil and plant to CNT. Whether CNT based PS-AOP system is appropriate for organic pollutants removal in soil and their relevant mechanism is still a topic deserves further research.

The ideal practical degradation process should be environmentally-adapted. Target pollutants would decompose into smaller molecules, or even into CO_2 and H_2O with little cost under different environment conditions. Compared with traditional physical activation processes such as heat- and UV-activated PS-AOPs, CNT based PS-AOPs system avoids multiple energy transformation hence avoiding energy losses and high operating cost. However, these physical activation process mainly induces symmetrical cleavage of the PDS and improves the yield of $SO_4^{\cdot -}$, which decreases the consumption of PDS (Lee et al., 2020). Activated carbon-activated PS-AOPs are another widely used system. Lower cost and mature preparing methods enables them to apply in different environment conditions, even in soil (Tian et al., 2021). On the contrary, CNT based PS-AOPs system is more stable and harder to be broken by impurities than AC even in strict environment. With the research development, some novel activation technologies such as light-heat conversion and piezoelectric activation have been proposed and used to active PDS (Liu et al., 2021b; Yin et al., 2021a). Light-heat conversion refers to loading MoS_2 on carbon cloths as photothermal membrane to convert sunlight to heat to activate PDS. This is an environmentally friendly way because heating with electricity or fuels has been replaced by a cleaner solar energy. However, compared with CNT, their catalytic performance is not good enough to realize the complete activation of PDS due to restricted energy conversion efficiency and rate. Piezoelectric activation means that PS are activated through electron–hole pairs in spontaneous polarization of piezoelectric materials (MoS_2) owing to extrinsic mechanical vibrations. The generated reactive species are more stable than that in CNT based materials. However, continuous mechanical vibrations are difficult to achieve in real environment condition. Herein, their application fields are limited compared with CNT based materials. The use of CNT has proven to be a promising and sustainable solution for the removal of organics under different environment condition. Considering little research has been reported regarding the actual application of CNT in soil, more efforts should be made in expanding the application field of CNT based materials even in a composite environment.

7. Conclusions and perspectives

This review has summarized the recent advances of CNT-driven PS based AOPs for degradation of organic pollutants. Relevant optimizations and mechanisms have been also discussed in detail. Despite the great progress that has been made, more attentions should be paid to the following aspects:

1) How to select the most suitable material

   Type of reactive matters: the PS categories affect the actual removal efficiency. It has been reported that PDS/CNT system mainly generates nonradical species which preferably remove phenolic compounds. On the contrary, PMS/CNT incline to remove more refractory substances containing electron-rich moieties (Guan et al., 2018). Therefore, the choice of reactive matters should be made depending on the type of target pollutant.

   Cost: Actual expense is also one of the key parts to be considered when applying the novel materials into practical use. Chemicals, operation and time are three main factors in normal treatment system, among which chemical cost is considered the most important one. There are two major strategies to save the chemical cost. One is to choose the cheaper chemicals. The price of PDS ($ 0.74 per kilogram) is cheaper than that of PMS ($ 2.2 per kilogram), hence PDS is recommended when applied in large scale. In addition, the low-cost synthesis of CNT composites also provides a good solution such as employing cheap precursors during synthesis period (Phan et al., 2018; Yuan et al., 2021). The other is to improve the recycling efficiency of catalyst powders. Generally, the transformation of CNT powders into membranes or electrode is an advisable research direction to minimize their loss.

   Toxicity: As a kind of nanoparticle material, CNT also causes potential risks to the environment. When discharged into the aquatic environment, CNT might damage the normal growth and breed of aquatic animals with their long-term exposure and accumulation in organs. This risk might be intensified if some toxic pollutants are contained on CNT because of their strong adsorption capability. Hence, relevant strategies to decrease the usage of CNT or improve their stability is an issue deserving deeper consideration.

2) Expected research direction in mechanism of CNT based PS-AOP system

   Up to now, the mechanism of CNT based materials for PS activation includes radical pathways, nonradical pathways and their synergistic effects. It is important to further precisely quantify the contribution of each pathway under different conditions. To estimate the dominated type of active sites and to find the optimal contents of each active sites in CNT based materials are also of great importance to their actual application.

3) Modification of CNT

   Modification is a common strategy to improve the catalytic performance of CNT. However, how to minimize the loss of dopants and maintain their effective properties is also an important problem to be solved. Compared with nonmetal doped CNT, metal loaded CNT could lead to the formation of metal-containing sludge and dissolution of catalytic composites inevitably. In order to meet the actual needs, stabilizing technologies need to be developed to preserve the active metal composites.

4) Practical application of CNT under real conditions

   Nowadays, most of CNT applications are carried out under simplified environmental conditions while their applications to actual or harsh environment like landfill leachate and urine have been seldom studied. Additionally, both PDS and PMS might induce the acidification of aqueous solution as a consequence of H^+ production with the dissociation of persulfate. Herein, further research has to be concentrated on the preservation of their properties without causing secondary pollution when applied in practical use.

Declaration of Competing Interest

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

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