Single-Atom Fe Catalyst Outperforms Its Homogeneous Counterpart for Activating Peroxymonosulfate to Achieve Effective Degradation of Organic Contaminants

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ABSTRACT: Recently, reactive iron species (RFeS) have shown great potential for the selective degradation of emerging organic contaminants (EOCs). However, the rapid generation of RFeS for the selective and efficient degradation of EOCs over a wide pH range is still challenging. Herein, we constructed FeN4 structures on a carbon nanotube (CNT) to obtain single-atom catalysts (FeSA-N-CNT) to generate RFeS in the presence of peroxymonosulfate (PMS). The obtained FeN4-N-CNT/PMS system exhibited outstanding and selective reactivity for oxidizing EOCs over a wide pH range (3.0–9.0). Several lines of evidences suggested that RFeS existing as an FeN4 intermediate was the predominant oxidant, while SO4•− and HO• were the secondary oxidants. Density functional theory calculation results revealed that a CNT played a key role in optimizing the distribution of bonding and antibonding functional theory calculation results revealed that a CNT played a key role in optimizing the distribution of bonding and antibonding states in the Fe 3d orbital, resulting in the outstanding ability of FeSA-N-CNT for PMS chemical adsorption and activation. Moreover, CNT could significantly enhance the reactivity of the FeN4=N intermediate by increasing the overlap of electrons of the Fe 3d orbital, O 2p orbital, and bisphenol A near the Fermi level. The results of this study can advance the understanding of RFeS generation in a heterogeneous system over a wide pH range and the application of RFeS in real practice.

INTRODUCTION

Selective degradation of emerging organic contaminants (EOCs) from water is important because these pollutants, although low in concentration, pose a significant threat to the ecological environment and humanity.1−3 Radical-based advanced oxidation processes (AOPs) are the most widely employed approaches to degrade EOCs in an aqueous phase.4−6 However, the radicals, such as HO•, SO4•−, and Cl−, suffer from the disadvantages of a low steady-state concentration (10−12−10−15 M), ultrashort lifetime (10−8−10−9 s), and consumption by the background matrix.7−9 Thus, the AOPs with these radicals as major reactive oxidants perform generally not very well in the selective degradation of EOCs in water. Compared with these radical species, reactive iron species (RFeS), such as Fe(VI)=O and Fe(III)=O, are less reactive but more selective oxidants.8,10−12 Moreover, their steady-state concentration (>9.76 × 10−9 M) and lifetime (>10−1 s at pH 3.0) are larger than those of radicals.13,14 Consequently, the oxidation process with RFeS as a major oxidant is expected to be a good choice for the selective degradation of EOCs. RFeS can be generated both by reducing ferrate (Fe(VI)=O) with some reductants (e.g., Na2SO3, Na2S2O3, CaSO3, and biochar) and by the oxidation of low-valent iron with some oxidants.8,15−17 However, the absence of commercially available ferrate makes the first method remain in the laboratory. It is well documented that Fe(VI)=O can be generated during the reaction of Fe2+ with ozone, peroxides (hydrogen peroxide (H2O2)), peroxymonosulfate (PMS), peroxysulfate (PDS), and peracetic acid (PAA)), or hypohaloclorous acid.13,18−22 However, these homogeneous Fe(VI)-involved oxidation systems are only effective at acidic pH and can inevitably result in the undesirable generation of iron oxide sludge.23 Therefore, exploring methods to enhance the formation of RFeS in a wide pH range is still imperative and challenging.

Single-atom catalysts (SACs) are attracting increasing attention in the fields of gas thermal catalysis, electrochemical catalysis, and photocatalysis, owing to the utmost metal utilization, special electronic structure, excellent catalytic activity, and structural stability.24−27 Several SACs had been fabricated to activate peroxides (H2O2, PMS, PDS, and O3/H2O2) for EOC abatement.28−32 For instance, Fe-SiO2 SACs were employed to activate H2O2 to degrade p-hydroxybenzoic acid and phenol.29 Li and co-workers prepared CoN4 SACs by anchoring Co atoms on porous N-doped graphene for the efficient catalytic oxidation of recalcitrant organics via the activation of PMS.30 However, these SACs were reported to be only more efficient than their particulate counterparts to activate peroxides and only effective at acidic pH (3.0−6.0).

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Moreover, the ROS generated in these SAC-based AOPs include HO•, SO4•−, and O2•−, suffering from the similar disadvantages of radical-based homogeneous systems. Therefore, researchers have tried to overcome these defects by designing SAC-based AOPs, where RFeS is proved to be the main active species. It is well known that FeN4 sites in heme can generate RFeS with either molecular oxygen or hydrogen peroxide in the human body (pH = ∼7.4).33

Very recently, SACs with an FeN4 structure were employed to activate PMS or PDS to generate RFeS in situ in a wide pH range.32,34 However, the performance of the as-reported SACs in activating PMS or PDS for EOC degradation remains unsatisfactorily considering the ratio of the amount of organic contaminants removed in unit time to the catalyst dosage (the detailed data are present in Figure S8c and Table S5). To date, few of the documented SACs were reported to be greatly reactive and even better than their homogeneous counterparts. There are still insufficient reference cases and design ideas on how to obtain highly reactive SACs for PMS activation and EOC degradation.

Analogous to the function of organic ligands in heterogeneous catalysis, a support may greatly affect the reactivity of SACs.35 Generally, the roles of a support in SACs are as follows. (i) Via strong metal−support interactions (SMSI),36 the support can isolate and stabilize the atomically dispersed metals. Moreover, it can tune the electronic structures of a single-atom metal center and thus promotes the catalytic process.38,39 (ii) The special morphological support, e.g., the high surface area, facilitates the loading of metals and thus promotes the catalytic process.40 Recent studies have shown that different supports have variable effects on the same catalytic center,41−43 i.e., only the CoO4 support allows the high activity of Pt−O sites in Pt SACs toward the hydrolytic dehydrogenation of ammonia borane.37 Thus, the rational regulation of a support may be an effective means to make the SACs more reactive in activating PMS for EOC degradation than that of the as-reported SACs without a suitable support. However, there are still lack of comprehensive examples from this view of point in SAC-based AOPs.

A proper electron transfer conductor can improve the performance of PMS activation by SAC for EOC degradation. A carbon nanotube (CNT) with electron potential distribution in a wide range.32,34 However, the performance of the as-reported SACs in activating PMS or PDS for EOC degradation remains unsatisfactory considering the ratio of the amount of organic contaminants removed in unit time to the catalyst dosage (the detailed data are present in Figure S8c and Table S5). To date, few of the documented SACs were reported to be greatly reactive and even better than their homogeneous counterparts. There are still insufficient reference cases and design ideas on how to obtain highly reactive SACs for PMS activation and EOC degradation.

Synthesis of Fe-C3N4. In brief, the mixture of 0.4 mmol of Fe(acac)3 and 60 mmol of C6H4N4 was milled in a planetary ball mill (Boyuntong Instrument Technology, Nanjing, China) with stainless steel jars (100 mL) and stainless steel balls (15 balls with 10 mm in diameter and 80 balls with 6 mm in diameter in one jar). The milling was performed at 900 rpm and at room temperature (the change of temperature was not detected during milling). After ball milling for 2.0 h, the obtained powder was placed into a tube furnace and heated to 500 °C at 5 °C/min under a N2 flow. After 3.0 h of pyrolysis, the as-obtained yellow sample was ground and named as Fe-C3N4.

Synthesis of FeSA-N-CNT. In brief, a certain amount of Fe-C3N4 (1.0, 1.5, 2.0, 2.5, and 3.0 g) and 2.0 g of CNT were mixed and ball-milled following the identical procedure mentioned in the last paragraph. Then, the as-prepared powders were heated to 700 °C at 5 °C/min under a N2 flow and kept for 2.0 h. The as-obtained samples were ground and named as FeSA-N-CNT-1, FeSA-N-CNT-2, FeSA-N-CNT-3, FeSA-N-CNT-4, and FeSA-N-CNT-5, respectively. To study the influence of calcining temperature on the activity of FeSA-N-CNT-4, different calcination temperatures were chosen.

Synthesis of Control Samples. (1) FeNP-CN was synthesized in parallel with the same method as that for FeSA-N-CNT, except for adding CNT; (2) N-CNT was synthesized in parallel with the same method as that for FeSA-N-CNT, except for using 60 mmol of C6H4N4 instead of Fe-C3N4; (3) FeNP-CNT was synthesized in parallel with the same method as that for FeSA-N-CNT, except for using 0.24 mmol of Fe(acac)3 instead of Fe-C3N4; (4) FeNP-N-CNT was synthesized by ball milling 0.24 mmol of Fe(acac)3, 60 mmol of C2H8N2, and 2.0 g of CNT following the same procedure. The obtained powder was heated to 700 °C at 5 °C/min under a N2 flow and kept for 2.0 h.

Characterization. The crystal structure and morphology of the catalysts were examined with powder X-ray diffraction (XRD), PANalytical X’Pert-Pro X-ray diffractometer) equipped with Cu Kα radiation (λ = 0.15406 nm), scanning electron microscopy (SEM, JSM 7800F), high-resolution transmission electron microscopy (HRTEM, JEM-2100), and energy-dispersive X-ray spectroscopy (EDX, JEM-2100). Aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) was performed using a JEOL ARM200F equipped with double aberration correctors and a cold field emission gun operated at 80 kV. STEM images were recorded using a HAADF detector with a convergence angle of 30 mrad and a collection angle between 90 and 370 mrad. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCALAB 250Xi X-ray photoelectron spectroscopy. The elemental compositions were analyzed with atomic absorption spectroscopy (AAS). Raman spectra were collected using a Renishaw confocal micro-Raman spectroscopy system with a 532 nm excitation laser. Fe K-edge X-ray absorption fine structure (XAFS) spectra of the catalysts were recorded at the BL14W1 and BL11B beamlines of the Shanghai Synchrotron Radiation Facility (SSRF). The details for collecting Fe K-edge XAFS spectra are present in the Supporting Information Text S1.
Evaluation of the Catalytic Performance. In a typical experiment, 2.0 mg of the catalyst was added into 100 mL of 50 \( \mu \)M BPA solution and stirred for 10 min to establish the adsorption–desorption equilibrium (the preliminary experiments revealed that 10 min was enough to achieve the adsorption equilibrium). The oxidation reaction was then initiated by adding 0.40 mL of PMS stock solution (0.10 M). The initial pH values were adjusted with sodium hydroxide and/or perchloric acid. If it was not otherwise specified, the experiments were performed at initial pH 3.0, where no buffer was employed, and the final pH was >2.8. The pH of the experiments conducted at pH 3.5 and 4.0 was adjusted by manually adding NaOH. When the experiments were performed at pH 5.0 or above, the decomposition of PMS can result in a strong decrease in pH. To keep pH constant during the reaction, the mixture of acetic acid and sodium acetate solution and that of boric acid and sodium borate solution were employed as the buffer for the reaction conducted at pHs 5.0 and 7.0–9.0, respectively. At predetermined time intervals, 5.0 mL of the reaction solution was withdrawn and immediately quenched with 0.050 mL of sodium hyposulphite solution (0.40 M). For the cycling test, the catalyst was recycled after each run of the experiment by filtration and washed thoroughly with copious amounts of deionized water. The concentration of BPA was analyzed with ultra-performance liquid chromatography (UPLC, Waters Co.) at a detection wavelength of 280 nm with a methanol/water mixture (70:30, v/v) as the mobile phase. The details of analytical methods of the tested EOCs are summarized in Table S1. The concentration of leached iron was quantified with AAS. The batch experiments were conducted in duplicates at least, and the average values with standard deviations were presented.

Computational Details. All the calculations were performed with Dmol3 module. The generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) was utilized as the exchange-correlation function and DFT Semi-core pseudopots were adopted to treat the core electrons. A Grimme dispersion-corrected density function and DFT Semi-core pseudopots was adopted to treat the core electrons. A Grimme dispersion-corrected density function (DFT-D2) was employed to consider van der Waals (vdW) force, and the conductor-like screening model (COSMO) was used to simulate a solvent environment for the calculation. FeN4 was simulated using a (7 × 7 × 1) supercell with a vacuum layer of 20 Å. The k-point was set to \( 5 \times 5 \times 1 \), and the global orbital cutoff was set to 4.6 Å.

■ RESULTS AND DISCUSSION

Synthesis and Structural Analysis of FeSA-N-CNT. The preparation procedure of FeSA-N-CNT is demonstrated in Figure 1a. First, the mixture of Fe(acac)3 and C2H4N4 was calcined to obtain Fe-C3N4 with homogeneously distributed Fe-doping sites, where the Fe-doping sites, which can be observed in both FeSA-N-CNT and FeNP-N-CNT, while Fe0 is only observed in FeSA-N-CNT. The loading of FeSA-N-CNT determined with XPS analysis was up to 6.08 wt %, larger than that determined with the AAS (5.81 wt %), suggesting that most of the single atoms are exposed on the surface of the catalyst (Table S3). In addition to the localized microstructural information, element-selective XAFS spectra were further used to unveil the chemical state and the coordination environment of Fe sites in the FeSA-N-CNT sample. As shown in Figure S3, the absorption edge position of FeSA-N-CNT is located between those of Fe2O3 and Fe3O4, suggesting that the valence state of Fe in FeSA-N-CNT is between +2 and +3. The XANES spectrum of FeSA-N-CNT is very similar to that of the reference FePc that has well-defined FeN4 coordinated sites (Figure 2b). As shown in Figure 2c, the Fourier transform (FT) \( k^2 \)-weighted Fe K-edge EXAFS curve...
of FeSA-N-CNT presents only a major peak at ∼1.6 Å. In reference to FePc, this peak can be assigned to the Fe–N first shell. The higher fraction of FeN in the N 1s XPS spectrum of FeSA-N-CNT compared to FeNP-N-CNT agrees well with the XAFS results (Figure S4). The best fitting results for the first shell of FeSA-N-CNT show that each Fe atom is coordinated by ∼4 N atoms in average, and the average Fe–N bond length is about 2.01 Å (Figure 2d, Figures S5 and S6, and Table S4). Based on the above analysis, the atomic structure model of FeSA-N-CNT is constructed and illustrated in Figure 2d (inset).

**Performance of FeSA-N-CNT for Activating PMS to Degrade EOCs.** BPA was selected as the probe EOC to evaluate the performance of FeSA-N-CNT for activating PMS to degrade EOCs (Figure S7). As shown in Figure 3a, BPA can be completely decomposed within 1 min in the FeSA-N-CNT/PMS system, although PMS alone shows negligible reactivity toward BPA degradation. However, less than 50% of BPA is degraded by PMS within 60 s when FeNP-N-CNT and other materials are employed as catalysts. It should also be noted that the FeSA-N-CNT/PMS system shows a much better performance for BPA degradation than its homogeneous counterpart (Fe(III)/PMS) and various Fe complexes/PMS systems when the same amount of iron is employed as the activator (Figure 3b). The rate constant of BPA decomposition with FeSA-N-CNT as the activator exceeds that with FeNP-N-CNT as the activator by a factor of 11.5 (Figure S8a). Furthermore, a modified kinetic model (k-value), through dividing the reaction rate of organic contaminant degradation by the catalyst concentration followed by multiplying organic contaminant concentration, is employed to determine the degradation rates of organic contaminants in various heterogeneous Fenton-like processes (Table S5). It is found that the k-value of the FeSA-N-CNT/PMS system is as high as 256 μmol s−1 g−1, 7.1 to 2844.4 times higher than those of various reported heterogeneous Fenton-like systems (Figure S8b) including state-of-the-art SACs (Figure S8c). Moreover, the FeSA-N-CNT/PMS system shows an excellent BPA decomposition performance not only under acidic conditions but also under neutral and alkaline conditions (Figure 3c). Figure 3d shows the degradation kinetics of various EOCs whose chemical structures are summarized and shown in Table S6, in the FeSA-N-CNT/PMS system. It can be found that complete BPA and BPF can be decomposed within 1 and 2 min in the FeSA-N-CNT/PMS system, respectively. However, only 15% of BA, 53% of CBZ, and 71% of SMX were degraded within 4 min. Obviously, the FeSA-N-CNT/PMS system prefers to degrade phenolic contaminants than other aromatics, indicating that there are other oxidizing species besides radicals in the FeSA-N-CNT/PMS system.

BPA removed in the FeSA-N-CNT/PMS system can be partially mineralized, and ∼40% of total organic carbon (TOC) was removed within 4.0 min (Figure S10) although 100% of BPA was degraded in the FeSA-N-CNT/PMS system within 1.0 min (Figure 3a). Furthermore, the main transformation products (TPs) of BPA in the FeSA-N-CNT/PMS system were determined with an ultra-performance liquid chromatography-quadrupole-time-of-flight premier mass spectrometry (UPLC-QTOF-MS/MS) technique (Figures S11 and S12, and details can be found in the Supporting Information Text S2). According to the experimental results and previous studies, the possible degradation pathways of BPA in the FeSA-N-CNT/PMS system are proposed and summarized in Figure S13. Various ring-opening products were detected (TP 100, TP 112, TP 116, TP 130, TP 200, and TP 340), and they were expected to be finally mineralized into CO2 and H2O according to the TOC removal test.

In addition, the ecological structure activity relationship (ECOSAR) program was used to predict the acute (short term) and chronic (long term or delayed) toxicity of BPA and its TPs (details can be found in the Supporting Information Text S3). The results of the toxicity assessment (both acute and chronic toxicity) of BPA and its TPs are summarized in Table S8. Based on the Globally Harmonized System of
Classification and Labelling of Chemicals (Table S9), BPA and its TPs are classified into four toxicity levels (Figure S14). The toxicities of the hydroxylation and C=C scission reaction products (TP 95, TP 110, TP 108, TP137, TP166, and TP 228) are similar to or greater than that of BPA. On the contrary, the ring-opening reaction products (TP 100, TP 112, TP 116, TP 130, TP 200, and TP 340) exhibit a much lower toxicity level than BPA. As the oxidation reaction proceeds, the hydroxylation and C=C scission reaction products are gradually transformed to the ring-opening products and eventually mineralized. Thus, the toxicity of BPA was greatly reduced after treatment in the FeSA-N-CNT/PMS system.

Identification of Active Oxidants. The excellent activation performance of FeSA-N-CNT should be first ascribed to the rapid adsorption of BPA by FeSA-N-CNT, which can adsorb 23% of dosed BPA within 60 s (Figure S9). In addition, the degradation of BPA in the FeSA-N-CNT/PMS system is enhanced by increasing the iron content of FeSA-N-CNT (Figure S7b). However, the presence of oxalate, a chelator of Fe, depresses the BPA degradation in the FeSA-N-CNT/PMS system, verifying that the single Fe atom is the major active site for PMS activation and BPA degradation (Figure S15). To further analyze the catalytic activity and surface chemical evolution of FeN₄ sites during activating PMS, the in situ Raman spectra were collected. As shown in Figure 4a, the peak at 1060 cm⁻¹ represents HSO₃⁻ of PMS, while the peak at 982 cm⁻¹ is associated with the symmetric stretching vibration mode of S=O bonds in SO₄²⁻. Therefore, the change in the ratio of the intensity of the peak at 1060 cm⁻¹ to that at 982 cm⁻¹ (I₁₀₆₀/I₉₈₂) can be employed to evaluate the PMS decomposition rate, and the lower I₁₀₆₀/I₉₈₂ manifests the larger fraction of decomposed PMS. It was observed that, with the presence of FeSA-N-CNT, the ratio of I₁₀₆₀/I₉₈₂ decreases from 0.96 to 0.36 within 8 min of the reaction, implying the fast PMS consumption by FeSA-N-CNT. The decrease in the ratio of I₁₀₆₀/I₉₈₂ in the FeSA-N-CNT/PMS system is much more rapid than that in FeNP-N-CNT/PMS (Figure S16a), which agrees well with the results of PMS decomposition kinetics (Figure S16b) and the degradation kinetics of BPA (Figure 3a). Moreover, a new peak at 843 cm⁻¹ was observed due to the reaction between PMS and FeSA-N-CNT. However, the location of this peak is different from that of metal-PMS⁺ (peroxo species bonding to the surface metal sites) at about 834 cm⁻¹ reported in other PMS/catalyst systems, such as PMS/MoS₂, PMS/CuFe₂O₄, and PMS/N-CNT, where radicals or electron transfer are proved to be the major oxidation mechanism. The observed special peak at 843 cm⁻¹ in the FeSA-N-CNT/PMS system may be ascribed to the generation of RFeS (named as FeN₄O), which will be verified in the following part with DFT calculation.

To examine the role of radicals and RFeS in the FeSA-N-CNT/PMS system, alcohol-scavenging experiments were performed. As shown in Figure 4b and Figure S17, MeOH and TBA, served as radical scavengers for SO₄⁻/HO⁻ and HO⁻, respectively, exhibit slight inhibition on the BPA degradation even when they are dosed at 400 mM, implying that both SO₄⁻ and HO⁻ do contribute to BPA degradation but are not the major oxidants. However, 4 mM PMSO, which can selectively react with RFeS via an oxygen transfer pathway, significantly inhibited BPA decomposition in the FeSA-N-CNT/PMS system. Thus, it is expected that FeN₄O species are the dominant oxidants in the FeSA-N-CNT/PMS system. This is also well consistent with the slight degradation of BA in Figure 3d because SO₄⁻ and HO⁻ react readily with BA, while RFeS is inert to BA. It is well documented that PMSO is oxidized by RFeS to produce the corresponding sulfoxones (e.g., methyl phenyl sulfone and PMSO₂) through an oxygen transfer pathway, which is markedly different from the radical-based oxidation pathway. As shown in Figure 4c and Figure S18a, a large amount of PMSO can be detected during the degradation of PMSO in the FeSA-N-CNT/PMS system with the PMSO₂ yield close to 70%. Moreover, the conversion rate of PMSO is increased from ~70% to ~90% in the presence of methanol (Figure 4c and Figure S18b), verifying the formation of both FeN₄O intermediate and SO₄⁻/HO radicals in the FeSA-N-CNT/PMS system. It should be due to the generation of multiple active oxidants, especially FeN₄O intermediates, in the FeSA-N-CNT/PMS system, that rapid BPA degradation is achieved in the FeSA-N-CNT/PMS system.
XAFS spectrum of the reacted Fe\textsubscript{5A}-N-CNT was collected. As shown in Figure 4d, the FT \(k\textsuperscript{3}\)-weighted EXAFS curve of Fe\textsubscript{5A}-N-CNT after the reaction presents only a strong peak with a position identical to that of the original sample at about 1.6 Å. No obvious metallic Fe–Fe bond can be detected, demonstrating that Fe still exists as a single atom in the reacted Fe\textsubscript{5A}-N-CNT sample. However, compared with the original sample, the intensity of this peak of the reacted Fe\textsubscript{5A}-N-CNT sample increased obviously. It suggests that the formation of other coordination bonds with the FeN\(_4\) site deteriorated the reusability of the Fe\textsubscript{5A}-N-CNT sample. To gain further quantitative coordination configuration of the Fe atom of the reacted catalyst, FT-EXAFS fitting curves in \(R\), \(q\), and \(k\) spaces were performed (Figure S23). The best fitting result for the first shell of the reacted Fe\textsubscript{5A}-N-CNT sample shows that the average coordination number of Fe is increased by 0.7 (the average iron coordination number over an area), which can be attributed to the formation of FeN\(_4\)-OH bonds (Table S4).\(^{40}\) In addition, the peak intensity of the XANES spectrum of the reacted Fe\textsubscript{5A}-N-CNT sample is significantly enhanced (Figure 4d, inset) due to the broadened Fe 1s-to-4p transition, resulting from the interaction of single Fe sites and oxygen species.\(^{59,60}\) The formation of FeN\(_4\)-OH may be accompanied with the increase of the average valence state of iron. The decrease in Fe(II) proportion according to the Fe 2\(p\textsubscript{3/2}\) XPS results (Figure S22) and the slight blueshift of the Fe K absorption edge (Figure 4d, inset) can further confirm this conclusion.\(^{61}\) The formation of FeN\(_4\)-OH in the FeN\(_4\) site may result from the protonation of BPA on the FeN\(_4\) site, forming intermediate (III) with the FeN\(_4\)–O function group. Subsequently, the pollutant BPA is adsorbed (IV), and then the O atom of FeN\(_4\)–O attacks the C atom of BPA and leaves the FeN\(_4\) site, forming intermediate (V). After the desorption of the oxidized BPA with an endothermic process, FeN\(_4\) can be re-activated for next cycle for PMS activation and pollutant oxidation. The total energy released during the reaction on FeN\(_4\) sites are 4.98 and 4.43 eV, respectively, for the cases with and without CNT support, indicating that the oxidation of BPA is thermodynamically favorable, regardless of the presence of a CNT.

Insight into the Catalyst Mechanism and the Importance of CNT. DFT calculations were further performed to probe the insights of PMS activation and BPA oxidation mechanism on the FeN\(_4\) site and function of CNT. The intermediate structures and the corresponding energy profiles are shown in Figure 5a, where the red and blue routes represent the recycling of Fe sites with or without a CNT, respectively. First, FeN\(_4\) absorbs PMS (II) in the solution and releases energy. Then, the adsorbed PMS is activated, forming intermediate (III) with the FeN\(_4\)–O function group. Subsequently, the pollutant BPA is adsorbed (IV), and then the O atom of FeN\(_4\)–O attacks the C atom of BPA and leaves the FeN\(_4\) site, forming intermediate (V). After the desorption of the oxidized BPA with an endothermic process, FeN\(_4\) can be re-activated for next cycle for PMS activation and pollutant oxidation. The total energy released during the reaction on FeN\(_4\) sites are 4.98 and 4.43 eV, respectively, for the cases with and without CNT support, indicating that the oxidation of BPA is thermodynamically favorable, regardless of the presence of a CNT.

Figure 5. (a) Reaction pathways of PMS activation and BPA oxidation at Fe sites with and without a CNT (inset: corresponding intermediate structures); (b) partial density of states (PDOS) of an Fe atom; the PDOS of BPA adsorbed on FeN\(_4\)–O sites without (c) and with (d) CNT.
(−1.41 eV, such as Fe(II)-PC or as-reported SACs\textsuperscript{32,34}), Fe\textsubscript{SA}-N-CNT exhibits larger PMS adsorption energy (−2.72 eV) due to the CNT-optimized Fe 3d orbitals and electrons.

When PMS was adsorbed on the FeN\textsubscript{4} sites of these catalysts, it can be activated, forming intermediates (IV) with the FeN\textsubscript{4}=O function group, which has been proved to be the main active species of BPA oxidation. The PDOSs of these intermediates are shown in Figure 5c,d. It can be seen that electrons of the Fe 3d orbital, O 2p orbital, and BPA have varying degrees of overlap at the red dotted line area near the Fermi level. The higher overlap means the stronger interaction and the easier electron transfer among the Fe atom, O atom, and BPA molecule.\textsuperscript{65} Compared with pure FeN\textsubscript{4}=O, the CNT greatly increases the overlap of electrons of the Fe 3d orbital, O 2p orbital, and BPA near the Fermi energy level by effectively optimizing the electron distribution of Fe 3d orbitals and BPA (Figure 5d). Thus, a large amount of energy (1.62 eV) is released during BPA oxidation in the FeSA-N-CNT/PMS system. In other words, the FeN\textsubscript{4}=O function group is much more reactive on FeSA-N-CNT than that on pure FeN\textsubscript{4}=O, which is consistent with the experimental results (Figure 3b). Based on both experimental and theoretical evidences, we propose that the CNT greatly improves the reactivity of the catalytic sites and the homogeneous-like oxygen transfer mechanism, and thus EOCs can be rapidly degraded via the oxygen transfer mechanism from PMS to BPA through the \textit{in situ} generated active FeN\textsubscript{4}=O sites (Figure S24).

\section*{ENVIRONMENTAL IMPLICATIONS}

In this work, a novel and simple strategy was utilized to prepare a single-atom material named Fe\textsubscript{SA}-N-CNT to activate PMS for the efficient degradation of EOCs. The Fe\textsubscript{SA}-N-CNT/PMS system can achieve an effective oxidation of EOCs over a wide pH range (3.0–9.0). Furthermore, the k-value of the Fe\textsubscript{SA}-N-CNT/PMS system is 7.1 to 2844.4 times higher than that of various reported heterogeneous Fenton-like systems. All of the experimental evidences indicated that RFeS (FeN\textsubscript{4}=O) is the major oxidizing species, and SO\textsubscript{4} and HO are the secondary active oxidants in the Fe\textsubscript{SA}-N-CNT/PMS system. The DFT calculation results revealed that the CNT plays a key role in optimizing the Fe 3d orbital and electron to improve PMS adsorption on FeN\textsubscript{4} sites and enhance the reactivity of generated FeN\textsubscript{4}=O.

Although many studies reported that their fabricated catalysts can activate PMS over a wide pH range, they did not employ a buffer, and the decomposition of PMS resulted in a great drop in pH, and the real effective working pH range was narrow. This study well controlled the pH during the reaction by using a proper buffer and revealed that Fe\textsubscript{SA}-N-CNT could efficiently activate PMS at a pH ranging from 3.0 to 9.0. In addition, RFeS is the major oxidizing species in the Fe\textsubscript{SA}-N-CNT/PMS system, which makes the Fe\textsubscript{SA}-N-CNT/PMS system a good candidate for the selective degradation of EOCs. The DFT calculation results greatly enhanced our understanding on the interaction of FeN\textsubscript{4} with the CNT support, which provide a powerful reference for the design of SACs. Research work is still being carried out in our laboratory to improve the stability of Fe\textsubscript{SA}-N-CNT during PMS activation so as to make the Fe\textsubscript{SA}-N-CNT/PMS system an amazing approach for decomposing EOCs.

\section*{ASSOCIATED CONTENT}

\section*{Supporting Information}

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c08805.

Details of characterizing the solid phase (Text S1); identification of transformation products (Text S2); toxicity prediction of BPA and its TPs (Text S3); ultra-performance liquid chromatography (UPLC) conditions (Table S1); synthetic conditions of different samples (Table S2); Fe contents (%) of different catalysts (Table S3); best fitting EXAFS data (Table 4); comparison of the kinetics (Table S5); chemical structures of EOCs (Table S6); retention time (\textit{R}) and empirical formula, as well as their calculated and experimental m/z values (Table S7); toxicity values of BPA and its TPs (Table S8); toxicity classification (Table S9); SEM images of CNT and FeSA-N-CNT samples (Figure S1); X-ray diffraction patterns (Figure S2); XANES spectra (Figure S3); XPS spectra (Figure S4); EXAFS spectra R-space fitting curve (Figure S5); FT-EXAFS and the corresponding fitting curves (Figure S6); influences of calcination temperature, dosage, and degradation kinetics (Figure S7); comparison of rate constants and k-value (Figure S8); kinetics and adsorption efficiency (Figure S9); kinetics of TOC removal (Figure S10); UPLC-QTOF-MS/MS chromatogram (Figure S11); MS spectra (Figure S12); proposed pathways for the BPA degradation (Figure S13); predicted acute and chronic toxicities (Figure S14); kinetics of BPA removal (Figure S15); \textit{in situ} Raman spectra of PMS and PMS decomposition (Figure S16); kinetics of BPA degradation and influence of quenching agents (Figure S17); PMSO consumption and PMSO\textsubscript{2} generation (Figure S18); influence of recycling use of FeSA-N-CNT on BPA removal (Figure S19); SEM images of FeSA-N-CNT (Figure S20); N 1s XPS spectra of the FeSA-N-CNT sample (Figure S21); Fe 2p\textsubscript{1/2} XPS spectra of FeSA-N-CNT samples (Figure S22); FT-EXAFS spectra and the corresponding fitting curves (Figure S23); and proposed overall degradation mechanism of BPA (Figure S24) (PDF)

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Notes

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