

Collaborative Catalysis of Single Atoms and Atomic Clusters as Dual Sites for Confined Peroxymonosulfate Activation to Coordinate Radical and Singlet Oxygen Pathways

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Abstract

Single-atom catalysts have attracted tremendous research interest in advanced oxidation water treatment, while their efficiency and recyclability were restricted by speciation. Deliberate manipulation of single-atom (SAs) accumulation and distribution to tune the catalyst efficiency and route constitutes an area of great interest but a challenging pursuit. Here, we developed a series of novel spherical porous carbon materials from biomass waste with a three-dimensional distribution of Fe. Fe SAs and atomic clusters (ACs) are simultaneously formed in catalysts, and their distribution from the outer surface to the inner core varies with pyrrolic N content. The cooperation of SAs and ACs serves as a pair of redox sites linked with graphitic carbon to coordinate the electron circulation with peroxymonosulfate (PMS), generating radical and singlet oxygen for antibiotic degradation. The confined environment and the cooperation of dual sites perpendicular to the carbon plane were first reported, which enhanced the generation of reactive species. These advantages afforded efficient degradation (up to 229% improved in kinetics and 133% improved in degradation) with heightened recyclability (up to 150% improved) compared to surface-doped SAs or ACs-dominated catalyst. Furthermore, this approach achieved efficient utilization of atomic metal sites compared to previously documented metal-based ADCs. This study reveals the synergy of SAs and ACs in a confined environment for cyclic electron transfer and inspires a new version for designing atomically dispersed Fe within the 3D structure for advanced water decontamination.

Keywords: atomic Fe sites; three-dimensional distribution; peroxymonosulfate activation; confined environment

1. Introduction

Persulfate-based advanced oxidation processes (PS-AOPs) have received extensive attention in solving the problem of antibiotics in wastewater, which are toxic and poorly biodegradable (Yang et al., 2022). Removal of antibiotics relies on the generation of reactive species (Li et al., 2023; Yan et al., 2023), including sulfate radicals ($\text{SO}_4^{\cdot-}$), hydroxyl radicals ($\cdot\text{OH}$), and singlet oxygen ($^1\text{O}_2$). Metal catalysts are one of the most common and practical approaches to overcoming the energy gap during reactive species generation. It is imperative to enhance their atom utilization efficiency and minimize consumption to advance sustainable decontamination and green chemistry (Shang et al., 2021). Atomically depositing metals onto substrates has recently been developed in response to achieving efficient PS-AOPs with nearly 100% atom utilization.

Various attempts (*e.g.*, ion exchange (Ma et al., 2020), wet impregnation (Velisoju et al., 2024), and electrochemical deposition methods (Wei et al., 2024)) have been conducted to fabricate atomically dispersed catalysts (ADCs), and carbon-based substrates (Zeng et al., 2023) are used as the base for the atomic catalyst. However, these approaches incur high cost as they require expensive chemicals and substantial energy input, hindering their potential for scalable practical applications. Precursors with high surface reactivity (*e.g.*, carbon nanotubes, graphene, carbon quantum dots, metal-organic frameworks) (Zeng et al., 2023; Xia et al., 2021; Yu et al., 2024) and with sacrificial templates (*e.g.*, Zn, CdS, and MgO) (Zhou et al., 2024; Mehmood et al., 2022; Liu et al., 2025) are often used to overcome the metal aggregation problem but are time-consuming, low-yield, and high-cost for bulk production. Hence, finding

environmentally friendly and economically competitive methods to synthesize metal-loaded carbon-based substrates is crucial. Waste-derived carbon substrates, such as glucose (Lee et al., 2022; Liu et al., 2022) and glucosamine (Cao et al., 2022), that can be readily derived through a biorefinery process (Kumari et al., 2023), are promising renewable feedstocks. Employing a thermochemical process with metal-laden feedstock enables the synthesis of a carbon base with atomically dispersed metal in a single step (Li et al., 2025). However, atom dispersion and chelation during the thermal process using waste-derived carbon precursors often lack precision.

The fabrication of carbon-based ADCs has been achieved mainly by the surface chelation of metal atoms with O/N-functionalities on carbon (Chen et al., 2023), but it faces the problem of poor stability with high leachability (Li et al., 2022). Two-dimensional carbon substrates offer a suitable choice for surface doping due to their large exposure area, facilitating the doping process. However, their synthesis typically requires additional energy and chemicals (Dong et al., 2023; Li et al., 2024), including activators and templates. Using bulk carbon materials as a substrate for traditional surface doping presents challenges for lower doping amounts, as only the limited outer surface can be effectively doped with metals (Wang et al., 2023). Atomically bulk doping, defined as the distribution of SAs throughout the entire carbon matrix, encompassing both subsurface regions and particle interiors, is promising for improving overall material stability due to high doping amounts. However, it is unclear whether bulk doping ADCs leads to different catalytic routes and energy barriers during PS-AOP compared to surface doping ADCs.

Formation of atomic clusters (ACs) is unavoidable for practical ADCs production with decreased atom efficiency. However, recent research has indicated the potential of incorporating ACs in enhancing the selectivity and efficiency of catalytic reactions (Mo et al., 2023; Ding et al., 2023). ACs can regulate the coordination energy of the SAs and reactants/intermediates (*e.g.*, PMS or $\text{SO}_5^\bullet$) (Mo et al., 2023) or enable synergy with SAs to optimize the configuration of the key intermediates (Ding et al., 2023), leading to high reactivity. The suitable size of the ACs (*e.g.*, Pd–Pd coordination numbers of 4.4) may result in full exposure of the active sites (Dong et al., 2022), leading to higher reactivity compared to larger or smaller particles. The uncertainties pertaining to the sizes and distribution of the ACs and SAs are further intensified within the bulk doping system, considering the additional dimensional distribution and the interactions that occur in three-dimensional (3D) space rather than two-dimensional planes. Moreover, confinement within the porous structure may direct different electron transfer routes during catalytic reactions (Meng et al., 2024), whereas less understanding has been obtained in the bulk doping system. Understanding these uncertainties is crucial in revealing collaboration between SAs and ACs and determining the degradation route in PS-AOPs, which is essential for establishing a bulk doping strategy for ADCs that utilizes designated active species coordination to achieve efficient catalytic degradation.

We hypothesize that manipulating the 3D distribution of SAs and ACs in the bulk-doped ADCs can lead to a synergistic performance for efficient wastewater treatment. To test this hypothesis, we fabricated spherical porous carbon materials with bulk doping of Fe atoms (Fe–PC) through a combined hydrothermal and pyrolysis process of biomass-oriented

glucose/glucosamine and iron salts. The efficiency of as-prepared Fe–PC for the PS-AOPs in the degradation of ciprofloxacin (CIP), a third-generation quinolone antibiotic with complex structures and poor biodegradability (He et al., 2022), was tested. We established the 3D distribution of Fe SAs and ACs within the carbon substrate and scrutinized their impact on the coordination of radical and singlet oxygen for antibiotic degradation. The evaluation specifically considered the impact of confinement, synergistic coordination between SAs and ACs, and their distinct electrostatic properties. This study introduces an innovative strategy for utilizing renewable feedstocks in fabricating atomically dispersed Fe catalysts with bulk doping for environmental decontamination, revealing the underlying electron transfer pathway and activation mechanisms of pore-confined SAs and ACs to achieve high performance and stability.

2. Materials and Methods

2.1 Materials

Most of the chemicals used in this study were of analytical grade, mainly including Glucose monohydrate (Macklin), Glucosamine hydrochloride (Macklin), urea (Bidepharm), potassium monopersulfate ($\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$, Aladdin), iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Fisher), CIP (Acros), L-histidine (Aladdin), furfuryl alcohol (FFA, Aladdin), methanol (MeOH, Duksan), Tert-butanol (TBA, J&K), chloroform (CHCl_3 , Aladdin), and potassium iodide (KI, J&K). Details of chemicals and materials were shown in Text S1.

2.2. Synthesis of Bulk-doping ADC with Biomass Feedstock

The hydrothermal process was conducted first to prepare ADCs. The reactor (100 mL stainless steel reactor) was filled with a 60 mL mixed solution of glucose (240 mM), urea (96 mM), and a certain amount of iron (III) nitrate, where different $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ -to-glucose molar ratios were 0.01, 0.02, and 0.1, respectively. The reactor was heated to 180 °C in an oil bath and maintained for 12 h. The obtained solid was washed with deionized (DI) water several times, dried at 80 °C for 24 h, and then pyrolyzed at 850 °C for 2 h under an N_2 atmosphere. After cooling naturally to room temperature, the solid product was immersed by 3 mol/L HCl at room temperature for 20 h. The acid-washed solid was washed with DI water several times and freeze-dried to obtain Fe-loaded porous carbon. Depending on the different amounts of iron loading, the synthesized catalysts were donated as Fe-PC-1 (0.31 wt% Fe), Fe-PC-2 (0.78 wt% Fe), and Fe-PC-3 (0.92 wt% Fe). When the Fe addition ratio increased fivefold, the yield only increased by about 15%, indicating that the loading capacity had reached its maximum and no further pursuit of a higher Fe-to-glucose ratio was made. Compared with Fe-PC, Fe/N-PC-1 (0.57 wt% Fe) and Fe/N-PC-2 (0.86 wt% Fe) were obtained from identical synthesis process, except that glucosamine was used instead of glucose for adjusting the N doping on the carbon, with the Fe-to-glucosamine molar ratios of 0.01 and 0.02. Raman spectra, X-ray diffraction (XRD) characterization, and Brunauer-Emmett-Teller (BET) test were conducted to identify the properties of the Fe-PC and Fe/N-PC. Details of these characterizations were shown in Text S3.

To compare the effect of surface Fe loading, surface Fe SAs doping was achieved through a simple impregnation process, and the synthesized catalyst was named Fe–PC–Impregnation (see Text S2 for details).

2.3. Catalytic Reactivity

To investigate the active species during the PMS activation process, MeOH, TBA, FFA, and CHCl_3 were employed as scavengers for $\bullet\text{OH}/\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, $^1\text{O}_2$, and $\text{O}_2^{\bullet-}$, respectively. KI was used to scavenge all the surface-bound radicals. In a typical experiment, 10 mg catalyst was added to a 100 mL DI solution containing 10 mg/L CIP and 1 mM PMS in a conical flask. The reaction was initiated by shaker stirring at 200 rpm at $25^\circ\text{C} \pm 1^\circ\text{C}$. At predetermined time intervals, a 2 mL solution sample was acquired and quenched by 2 mL MeOH. Then, the liquid and solid phases were separated by a 0.22- μm mixed cellulose ester membrane before further analysis. High-performance liquid chromatography (HPLC, Hitachi Chromaster) system equipped with Grace C18 chromatography column (Thermal Fisher Scientific) and an ultraviolet and visible spectrophotometry (UV–VIS) detector was utilized to quantify the concentration of CIP. The mobile phase consisted of 0.02 M tetrabutylammonium bromide solution and acetonitrile with a volume ratio of 89:11, and phosphoric acid was used to adjust the solution pH to 3.0 ± 0.2 . Its flow rate was 0.8 mL/min, with a column temperature fixed at 35°C and the UV wavelength set at 275 nm. The concentration of total organic carbon (TOC) was measured using a TOC analyzer (SSM-5000A, Shimadzu). All experiments were performed in triplicate, and data were presented as mean values $\pm$ standard errors.

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148 **2.4. Mechanisms Evaluation**

149 Electron paramagnetic resonance (EPR) spectrometer (EMXplus-6/1, Bruker) was used to
150 determine the reactive species generated in the systems. Electrochemical measurements were
151 performed on a CHI760E electrochemical workstation through current-time (I-t) curve and
152 electrochemical impedance spectroscopy (EIS). We employed the periodic density functional
153 theory (DFT) calculations to support the electron transfer and catalytic route during the
154 degradation process, and the details can be found in Text S8. Briefly, $\text{SO}_5^{\bullet-}$ was considered an
155 important intermediate (Mo et al., 2023) during the electron-accepting process, and the
156 pathway is $\text{HSO}_5^- \rightarrow \text{SO}_5^{\bullet-} \rightarrow {}^1\text{O}_2$. The electron-donating pathway used in the DFT calculation
157 is $\text{HSO}_5^- \rightarrow \text{SO}_4^{\bullet-} + \text{OH}^-$ based on the EPR and quenching results. Considering the pore
158 structures in porous carbon, we set two distances (5 Å and 10 Å) between the up and down
159 layers, representing the pore size (8.8–16.5 Å), to evaluate the cooperation of the Fe SAs and
160 ACs within the confined environment. The Fe atom number was set based on the high-angle
161 annular dark-field scanning transmission electron microscopy (HAADF–STEM) observation
162 of FeSAs and ACs in the Fe-PC. A detailed description of the model setting was provided
163 during the discussion.

164

165 **3. Results and Discussion**

166 **3.1. Characterization of Three-dimensional Fe Distribution on Spherical Porous Carbon**

A series of Fe-doped spherical carbon catalysts were synthesized in a combined hydrothermal and pyrolysis process, illustrated in Figure S1. The Fe-PC and Fe/N-PC existed as spherical carbon particles (5–10 μm , Fig. 1a) with surface cracks and holes (Figure S2). BET adsorption-desorption isotherms analysis confirmed the porous nature of the formed Fe-PC and Fe/N-PC with micropores (diameter range of 0.7–1.5 nm, Figure S3). The catalytic pyrolysis generated tunnels within the carbon substrate as the Fe particles irregularly moved during the thermal process, accompanied by graphitization of the carbon (Patera et al., 2018). The rich porous structure facilitated the subsequent transport of antibiotic molecules to doped Fe atoms during catalytic degradation. Additionally, it created a confined environment for catalytic reactions.

The absence of Fe crystal signals in the XRD pattern (Figure S4a) indicated the good dispersion of Fe without crystal structure formation. To evidence the atomic dispersion of Fe within the whole carbon particles, a focused ion beam (FIB) system was used to cut the selected carbon spherical particle into a thin slice (Fig. 1b and Figure S4), and the Fe distribution was visualized by HAADF-STEM (Fig. 1c,f and Figure S5). Accordingly, both Fe SAs and ACs were found in the Fe-PC and Fe/N-PC, while their distribution differed. A higher number of Fe SAs (marked by white circles) and relatively lower amount of ACs with 2-4 Fe atoms (marked by blue circles) were anchored on the surface layer of Fe-PC-2 (Fig. 1d), while aggregated Fe ACs with a lattice spacing of 1.30 Å (marked by yellow circles, Fig. 1e) were observed inside of Fe-PC-2. With a higher Fe content in Fe-PC-3, small amounts of Fe ACs can be detected on the outside layer and surrounded by single Fe atoms. By contrast, for the

Fe/N-PC, Fe ACs with a higher Fe aggregation were mainly formed in the surface layer with a lower average diameter of 0.72 nm (Fig. 1g and Figure S5). A limited amount of Fe SAs was detected in the surface layer, while a much higher proportion of Fe SAs was detected in the interlayer (Fig. 1h). Contrasting Fe ACs and SAs distribution is attributed to the different chelation paths and elemental speciation, which were scrutinized in the following section.

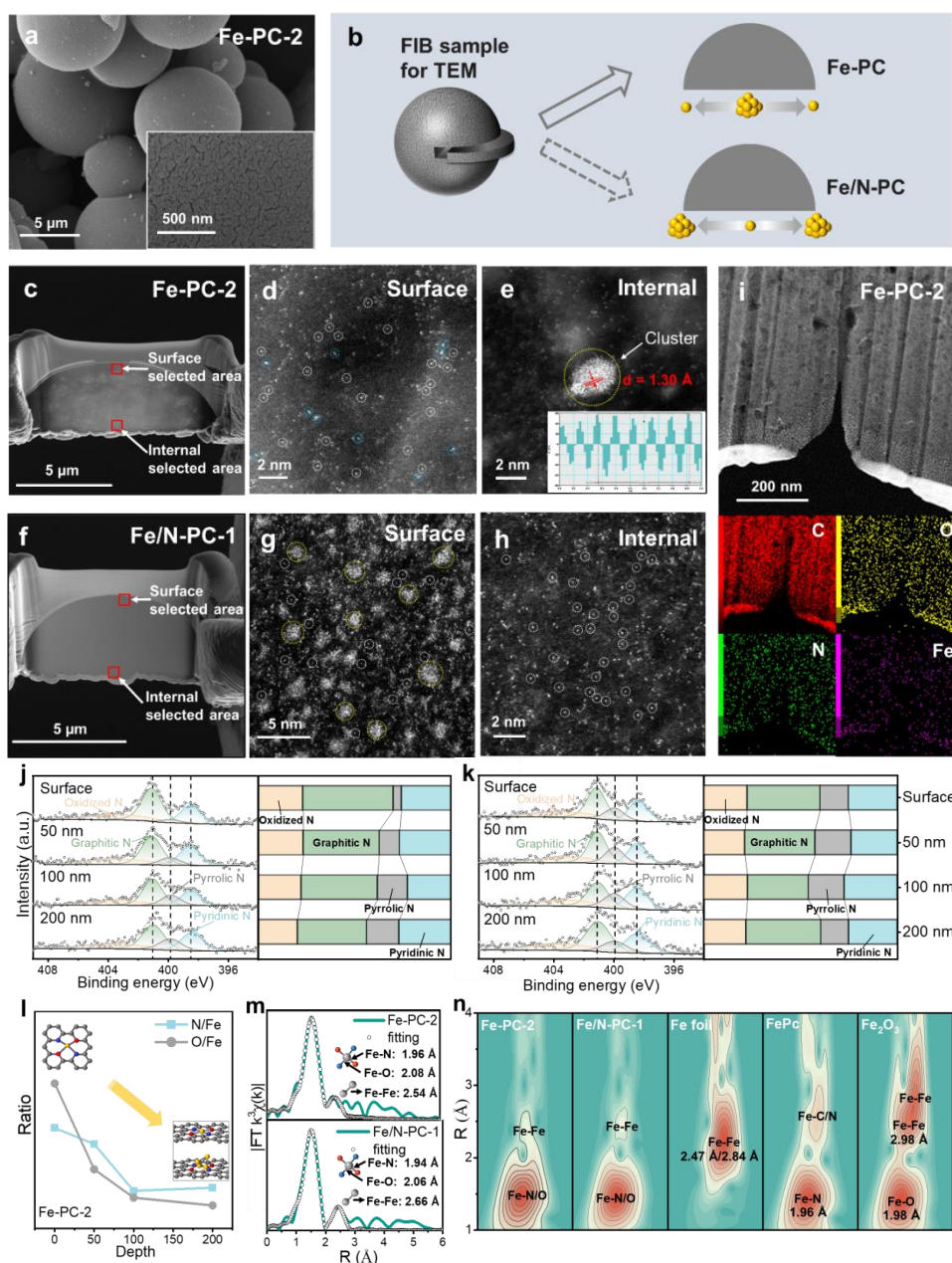


Fig 1. (a) SEM images of the Fe-PC-2. (b) Schematic of making FIB samples for TEM test and corresponding Fe atomic dispersion in Fe-PC and Fe/N-PC. STEM images of the (c)

Fe-PC-2 and (f) Fe/N-PC-1. (d, e) HADDF-STEM images of the selected area of Fe-PC-2. (g, h) HADDF-STEM images of the selected area of Fe/N-PC-1. (i) HAADF-STEM images of Fe-PC-2. XPS spectra of N 1s in (j) Fe-PC-2 and (k) Fe/N-PC-1 at different depths. (l) Atomic ratio of N/Fe and O/N at different depths and the corresponding atomic dispersion in Fe-PC-2. (m) EXAFS fitting results of Fe-PC-2 and Fe/N-PC-1 in R space. (n) WT analysis of Fe-PC-2, Fe-PC-3, Fe/N-PC-1, Fe foil, FePc, and Fe₂O₃, respectively.

3.2. N/O Regulation for Fe Distribution and Aggregation.

Energy dispersive X-ray spectroscopy (EDX) mappings on the cut slices revealed the homogeneous distribution of C, Fe, O, and N (Fig. 1i and Figure S6), indicating that O or N functionality should be responsible for the Fe anchoring. X-ray photoelectron spectroscopy (XPS) analysis with depth profiling evaluated the elemental ratio at different depths of the Fe-PC or Fe/N-PC. Higher N/Fe ($10.44 > 8.10$) and O/Fe ($12.18 > 7.41$) atomic ratios were found on the surface layer for Fe-PC compared to those inside, supporting the better dispersion of Fe atoms in the surface layer and enriched accumulation of Fe in deeper areas (Table S2). In comparison, lower N/Fe ($7.40 < 9.77$) and O/Fe ($9.27 < 12.72$) ratios on the surface of Fe/N-PC enhanced the formation of ACs (Fig. 1l and Table S2).

The N speciation was scrutinized by deconvoluting into four characteristic peaks: pyridinic N at 398.6 eV, pyrrolic N at 399.9 eV, graphitic N at 401.1 eV, and oxidized N at 403.6 eV (Xiong et al., 2022). A low proportion of pyrrolic N was found on the surface of Fe-PC, while it increased from 3.8–4.2% to 15.0–16.7% (Fig. 1j,k and Figure S7) with the decrease of graphitic N from 45.3–46.8% to 35.5–35.9%. A higher proportion of the pyrrolic N (14.7–18.6%) and pyridinic N (25.1–27.3%) was observed on the Fe/N-PC than the Fe-PC, and the

content of different N remained unchanged across the whole depth (Fig. 1k). As both pyridinic N and pyrrolic N show the potential to anchor Fe atoms with the formation of Fe–N bonding (Mo et al., 2023; Liu et al., 2022), the high pyridinic N and pyrrolic N contents on the surface of Fe/N–PC would be conducive to high Fe accumulation with ACs formation. The increasing pyrrolic N with depth in the Fe–PC might account for the accumulation of Fe atoms at the deeper depth, indicating that pyrrolic N might be the main chelation species for Fe in the Fe–PC system.

The speciation of C and O was potentially significant for the anchoring of Fe. Raman spectrum showed the graphitic nature of the Fe–PC and Fe/N–PC with rich carbon defects (Figure S8), which were generated by the catalytic pyrolysis process. The defective nature of carbon might also originate from the construction of pyrrolic N, as the five-membered ring will increase the defect sites within the conjugated sp^2 carbon network. XPS deconvolution (Figure S9) confirmed that the main C speciation within the 100 nm depth of carbon particles should be $-sp^2C$ ($C=C$, 284.8 eV) (Wang et al., 2024). For the O speciation, a higher O content in the main speciation of conjugated $O=C$ (44.4–57.1%) was detected on the surface of Fe–PC and Fe/N–PC. The O content decreased at the deeper depth (Table S2), while the $O-C$ proportion increased. These conjugated O structures could support the Fe chelation through Fe–O–C.

3.3. Coordination Environment of Fe within the Spherical Particles

The average oxidation state of the Fe was assessed between +2 and +3 based on the X-ray absorption near-edge structure (XANES) spectra (Figure S10). The Fourier-transform

Extended X-ray absorption fine structure (FT-EXAFS) spectrum showed a solitary peak at approximately 1.6 Å ($R+\alpha$) in the first shell, attributed to the Fe–N(O) paths, and a small peak indexed to the Fe–Fe path of 2.3–2.4 Å in the second shell. The wavelet transform (WT) plot confirmed the similarities of the Fe–N(O) and Fe–Fe paths on the Fe-doped carbon spherical particles compared to the iron phthalocyanine (FePc) and Fe foil, respectively. All these findings again indicated the coexistence of Fe ACs and SAs with N/O chelation (Fig. 1n).

With the shell-by-shell fitting of the EXAFS spectra of Fe–PC–2, Fe–PC–3, and Fe/N–PC–1 (Fig. 1m and Figure S11), the coordination numbers and radius of Fe–N (2.0–2.4 and 1.93–1.96 Å) and Fe–O (2.1–2.4 and 2.06–2.08 Å) were similar in all samples, constructing the tetra coordination for Fe (Fe–N₂O₂). A lower coordination number of Fe–Fe was found in the Fe/N–PC (1.1) compared to the Fe–PC samples (1.2–1.5), which is a mutual corroboration for the higher accumulation of Fe atoms in the Fe–PC samples than Fe/N–PC together with HAADF–STEM results. Notably, the distance of Fe–Fe in the Fe–PC (2.54–2.59 Å) was smaller than that in the Fe/N–PC (2.66 Å), which was closer to that of the Fe–Fe path in the Fe foil (2.49 Å), again indicating the Fe accumulation with large-size Fe ACs construction in the Fe–PC.

3.4. Catalytic Reactivity Related to the Fe Distribution.

We used CIP as a target pollutant to evaluate the catalytic performance of different Fe–PC with PMS (Fig. 2a). The sorption of CIP could reach equilibrium within 30 min with less than 20% of CIP removal, and the carbon particles without Fe doping have low catalytic activities

for CIP degradation (< 30%). With the bulk doping of Fe, Fe-PC exhibited an effective degradation of CIP, where the removal efficiency reached 69.5–85.7%, while a less effective degradation was found with Fe/N-PC (57.5–61.5%). Notably, the removal rate of CIP was relatively stable in the Fe-PC-1/PMS and Fe-PC-2/PMS systems, while a faster degradation was found in the initial 2 min with other catalysts. The first-order rate constants were calculated to compare the catalytic efficiency (Fig. 2b). A faster catalytic kinetics was found with Fe-PC (0.012–0.018 min⁻¹) compared to the Fe/N-PC (0.005–0.006 min⁻¹), and the fastest degradation was observed with Fe-PC-2 (0.018 min⁻¹). These results confirmed the distinctive catalytic reactivity controlled by the Fe atom aggregation and distribution within the carbon spherical particles.

We compared the catalytic reactivity of the Fe-PC with various Fe-based catalysts (Fig. 2c), including ferrous/ferric ions, zero-valence iron (ZVI), Fe₂O₃, and Fe₃O₄. A significantly lower degradation efficiency was found for the iron ions (36.6% for Fe²⁺ and 17.6% for Fe³⁺), iron oxides (29.0% for Fe₂O₃ and 28.5% for Fe₃O₄), and ZVI (42.3%). The catalytic activity of Fe-PC was compared with that of other counterpart ADCs, further spotlighting its remarkable attributes. As summarized in Table S3, despite the relatively modest k_{obs} of Fe-PC when compared to previously documented ADCs with carbon-based substrates, its $k_{\text{normalized}}$ values excelled (1321.03 > 168.16–1275.27 L min⁻¹ mol⁻¹). This underscores that even with minimal loading of Fe atoms, the catalytic potency of carbon substance can be significantly enhanced. Additionally, the catalytic reactivity of surface-doped Fe on PC under similar conditions was tested. The efficiency for surface-doped Fe was substantially lower (33.7% removal; $k = 0.003$

min⁻¹), compared to bulk-doped Fe (78.8% removal; $k = 0.018 \text{ min}^{-1}$). Surface doping restricted the total metal loading amount ($0.11 < 0.78 \text{ wt\%}$) due to limited anchoring sites, leading to the lower reactivity for PMS activation. The durability of catalysts is an important aspect of field applications, and the stable catalytic efficiency of Fe-PC-2 and Fe-PC-3 could be maintained for 5 cycles (Fig. 2d). In contrast, Fe/N-PC and Fe-PC with surface doping lost their catalytic effect in the second and fourth cycles, respectively. The minimal Fe leaching (less than 0.001 mg/L), strong coordination structure, and protection from the bulk doping in the carbon particles are conducive to high durability.

The practical application potential of the Fe-PC/PMS system was assessed by investigating the effects of inorganic ions and natural organic matters (NOMs) on pollutant degradation performance (Figure S12). The results demonstrated that CIP could be efficiently removed in the presence of HA (10 mg L^{-1}) and inorganic anions (10 mM), including chloride (Cl^-), sulfate (SO_4^{2-}), and nitrate ions (NO_3^-), respectively. Notably, a slight suppression was observed in the presence of dihydrogen phosphate ions (H_2PO_4^-), attributable to the pH-buffering capacity of the phosphate species (Wang et al., 2021). Furthermore, the system maintained consistently high efficacy in representative water matrices, including tap water and artificial groundwater (**Fig. 2e**). Tap water represents a common low-interference scenario (*e.g.*, residual chlorine, hardness), while artificial groundwater simulates a complex ionic environment (Xiao et al., 2024), which can mimic wastewater with different properties. These results collectively underscore the promising application potential of the Fe-PC/PMS system under real water matrices.

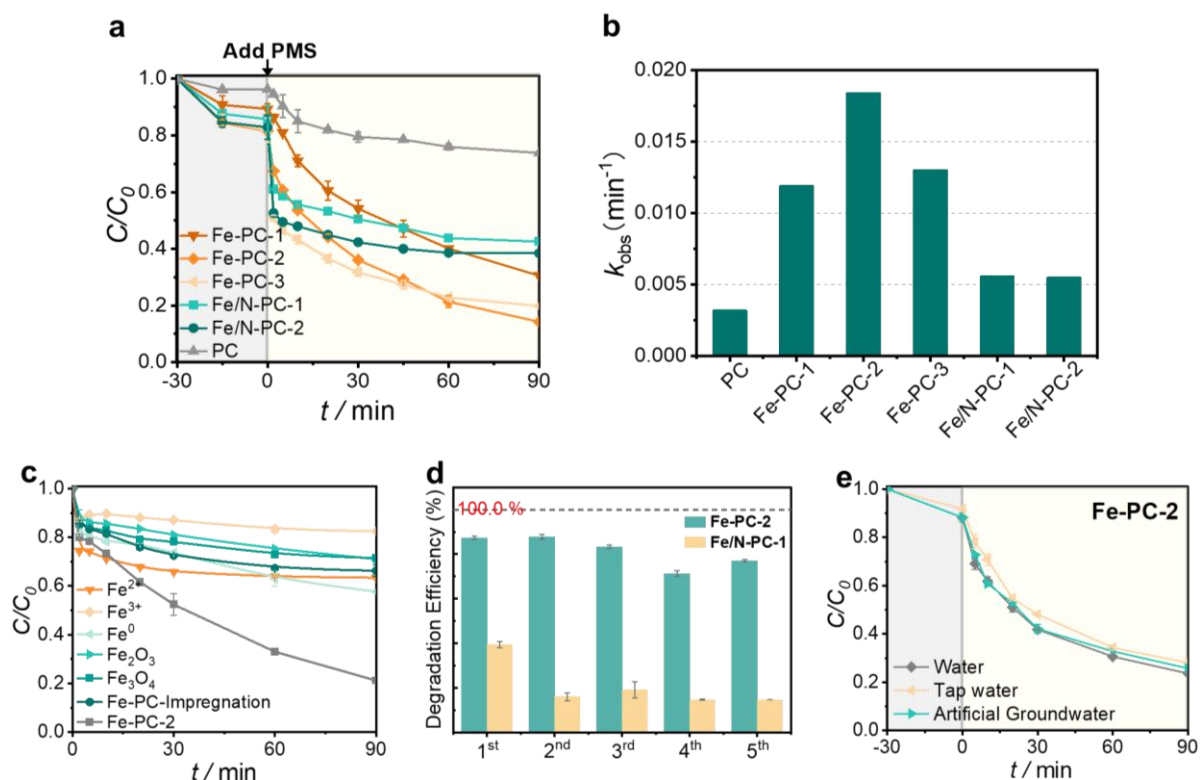


Fig. 2. Catalytic performance for Fenton-like reactions. (a) CIP removal performance and (b) first-order kinetic rate constant k of PC, Fe-PC-1, Fe-PC-2, Fe-PC-3, Fe/N-PC-1, Fe/N-PC-2. (c) Comparison of CIP removal performance of Fe²⁺, Fe³⁺, Fe⁰, Fe₂O₃, Fe₃O₄, Fe-PC-Impregnation, and Fe-PC-2. (d) Recycle tests of Fe-PC-2 and Fe/N-PC-1. (e) Application of Fe-PC/PMS system under tap water and artificial groundwater. Artificial groundwater (per liter): 0.006g NaCl, 0.012g CaSO₄, 0.012g NaHCO₃, 0.002g KNO₃, 0.035g MgSO₄·7H₂O. Experimental condition: [CIP]₀ = 10 mg L⁻¹, [PMS]₀ = 1mM, [catalyst]₀ = 0.1 g L⁻¹, initial pH = 7±0.2, T = 25 °C.

3.5. Reactive Species Regulated by Fe distribution and Aggregation

Only weak signals of ¹O₂, •OH, and SO₄^{•-} were observed in the Fe/N-PC/PMS system based on the EPR analysis, the intensity of which was significantly lower than that in the Fe-PC/PMS system (Fig. 3a, b). The intensity of ¹O₂ was much stronger than other reactive species, which might be the key oxidizing species instead of free radicals generated with other

Fe-based materials (*e.g.*, Fe/MOFs (El Asmar et al., 2021) and Fe/g-C₃N₄ composite (Zuo et al., 2021)). The distribution and aggregation of the Fe atoms in the bulk carbon can primarily manipulate the overall degradation routes with different reactive species.

Quenching experiments were performed with typical scavengers, specifically TBA, MeOH, FFA, and KI, to evaluate the contribution of different reactive species further (Table S4) (Zhang et al., 2021; Wang et al., 2023). For Fe-PC-2/PMS and Fe-PC-3/PMS systems (Fig. 3d-f and Figure S13), the presence of excess TBA and MeOH exhibited a negligible effect on the degradation of CIP, suggesting the limited contribution of solution $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ species. The better quenching by TBA than MeOH indicated the contribution of surface-bound free radicals, which can be blocked by the TBA with a low dielectric constant ($12.5 < 33.0$ at 20 °C) (Wang et al., 2021; Huang et al., 2020). The higher electrophobicity of TBA might affect the sorption and pore diffusion of organics (Gould et al., 2020). Adding 5 mM KI, which can block the surface-bound radicals ($\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$) (Zhang et al., 2022; He et al., 2022), significantly inhibited the degradation, confirming the importance of surface-bound radicals for Fe-PC. The typical $^1\text{O}_2$ scavenger FFA ($k = 1.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) (Wang et al., 2023) significantly inhibited the degradation of CIP, suggesting the critical role of $^1\text{O}_2$ as the reactive species during the catalytic reaction, which is consistent with the EPR results. To explore this further, we conducted a solvent exchange experiment, switching part of H₂O to D₂O, as the lifetime of $^1\text{O}_2$ in D₂O (20–32 μs) is longer than in pure water (<2 μs) (Jiang et al., 2023). As shown in Figure S14, the degradation effect of Fe-PC/PMS systems on CIP was significantly improved after replacing H₂O with D₂O, thus confirming the key contribution of $^1\text{O}_2$. Hence,

both surface-bound radicals ($\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$) and $^1\text{O}_2$ were probably the dominant reactive species in the Fe-PC/PMS systems.

As for the Fe/N-PC/PMS system, KI could significantly quench CIP degradation, implying the existence of surface-bound radicals (Fig. 3f). In contrast to the Fe-PC system, the degradation of CIP was completely inhibited by 500 mM MeOH, indicating that the dominance of $\text{SO}_4^{\bullet-}$ bound to the surface drove the non-radical catalytic degradation in the Fe/N-PC system. Although FFA showed complete inhibition of CIP oxidation, this could be attributed to its scavenging impact on the $\text{SO}_4^{\bullet-}$ ($k = 1.3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) (Wang et al., 2023). The limited generation of $^1\text{O}_2$ was also indicated by the EPR test. Notably, the $\text{O}_2^{\bullet-}$ played an insignificant role in the degradation process of both Fe-PC and Fe/N-PC systems, as CHCl_3 , a scavenger for $\text{O}_2^{\bullet-}$, had a limited impact on the degradation process (Figure S13). Based on the k_{obs} of CIP degradation in the presence of scavengers, we quantitatively analyzed the contributions of diverse ROS to CIP oxidation in Fe-PC and Fe/N-PC systems (Fig. 3c and Text S7). Notably, the Fe/N-PC/PMS was a radical-dominated process, while $^1\text{O}_2$ made a major contribution to CIP oxidation by Fe-PC/PMS. These results reinforced the significant impact of the distribution and aggregation of Fe and the coordination environment on the pathway of reactive species generation.

The potential contribution of high-valence metal-oxo species was determined by evaluating the PMSO consumption and PMSO₂ production (Zong et al., 2020; Li et al., 2021). As shown in Figure S15, the consumption of PMSO in both Fe-PC/PMS and Fe/N-PC/PMS systems was similar to the PMS alone system, indicating that the high-valence metal-oxo

oxidation was not generated. Moreover, the chronoamperometry (I-t curve, Figure S16) was conducted to validate the activation of PMS with different Fe-doped PC (Sun et al., 2023). The addition of PMS induced significant current responses for Fe-PC-2 and Fe/N-PC-1, confirming the electron transfer from catalysts to PMS. Notably, Fe/N-PC exhibited an intensity of current peaks that was much higher than that observed with Fe-PC, demonstrating efficient electron transfer between Fe/N-PC and PMS. This result was further confirmed by EIS analyses where Fe/N-PC showed better electronic conductivity than Fe-PC, according to the smaller semicircle diameter observed by EIS. In other words, the direct electron transfer pathway would be less critical for the Fe-PC system compared to the Fe/N-PC system, based on its lower conductivity but better degradation performance in Fe-PC/PMS system.

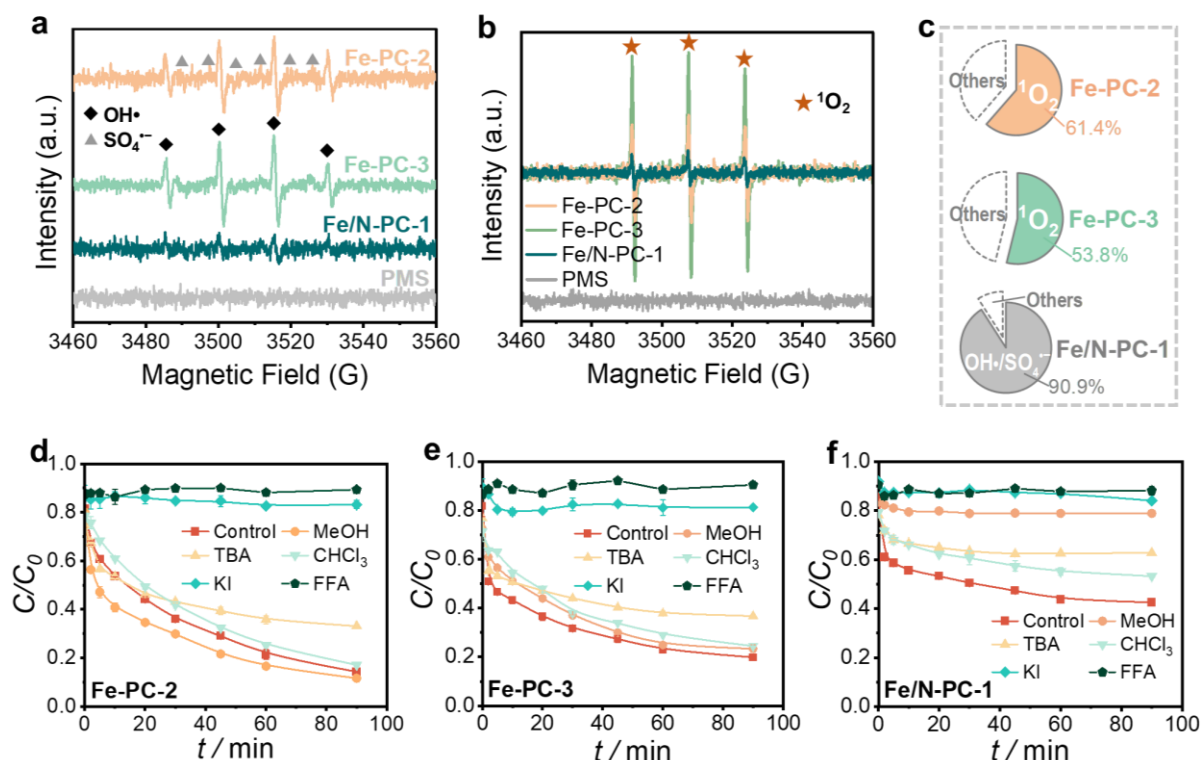


Fig. 3. Spin-trapping EPR spectra of (a) DMPO-•OH/SO₄^{•-} and (b) TEMP-¹O₂. (c) Contribution of various ROS to CIP degradation in different catalyst-activated PMS systems. Quenching experiments of (d) Fe-PC-2, (e) Fe-PC-3, and (f) Fe/N-PC-1. Experimental

condition: $[CIP]_0 = 10 \text{ mg L}^{-1}$, $[PMS]_0 = 1 \text{ mM}$, $[catalyst]_0 = 0.1 \text{ g L}^{-1}$, initial $\text{pH} = 7 \pm 0.2$, $T = 25 \text{ }^\circ\text{C}$, $[\text{MeOH}]_0 = 500 \text{ mM}$, $[\text{TBA}]_0 = 500 \text{ mM}$, $[\text{KI}]_0 = 5 \text{ mM}$, $[\text{CHCl}_3]_0 = 50 \text{ mM}$, $[\text{FFA}]_0 = 20 \text{ mM}$.

3.6. Electron Transfer Pathways Regulated by Fe Distribution and Aggregation

We set the Fe SAs anchored with pyridinic/pyrrolic N and conjugated O in $\text{N}_2\text{O}_2\text{-Fe}$ form based on the XPS and X-ray absorption spectroscopy (XAS) analysis to evaluate its catalytic impact during PMS-AOPs. Additionally, we assessed the Fe ACs with a size of 4 or 36 Fe atoms to study the size-dependent impact of the atomic clusters according to the results of HADDF-STEM. The Fe ACs exhibit a size distribution ranging from 0.2 to 1.6 nm, with an average diameter of 0.72 nm, and the main particle size is located in the range of 0.4-0.8 nm. Therefore, an Fe cluster with 36 atoms was selected with a size of $7.3 \times 6.0 \times 4.5 \text{ \AA}$. In addition, we also observed the Fe SAs and Fe ACs with 2-4 Fe atoms; and thus, single atom Fe_1 and Fe cluster with four atoms (Fe_4) were also involved. Regarding N-speciation selection, studies have shown that metal active centers are typically bonded to pyrrolic-N or pyridinic-N, with a limited contribution from graphitic-N (Zhang et al., 2020). In addition, XPS analysis of different depths revealed Fe ACs formation consistent with the high pyrrolic N content (Figure S18). Therefore, we selected pyrrolic N for Fe ACs coordination, while coordination with either pyrrolic N or pyridinic N was set for Fe SAs. Notably, although O atoms can coordinate in either cis- or trans- positions relative to N atoms, the formation energy (E_{form}) of the trans- N_2O_2 configuration was more negative than that of the cis configuration for either SAs and ACs (Figure S18), indicating a more thermodynamically stable structure, which is consistent with

previous studies (Zhou et al., 2025). Therefore, the trans-N₂O₂ coordination form was selected for the Fe SAs and ACs coordination in the following modelling.

The analysis of charge density difference for the set of 4 models confirmed the electron-rich nature of Fe₄ and Fe₃₆, while an electrophilic nature with fewer electrons was found on the Fe SAs (Fig. 4a,b). The electrons surrounding the Fe SAs are prone to transfer to the neighboring carbon substrate, leading to a more positively charged Fe SA center. The electron-rich nature of Fe ACs promotes the electron donation pathway ($\text{HSO}_5^- + \text{e}^- \rightarrow \text{SO}_4^{\bullet-} + \text{OH}^-$) during the interactions with PMS. By contrast, Fe SAs is more favorable to coordinate the electron withdrawal pathway to yield singlet oxygen ($2\text{HSO}_5^- \rightarrow 2\text{SO}_5^{\bullet-} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{S}_2\text{O}_8^{2-}(2\text{SO}_4^{\bullet-}) + {}^1\text{O}_2 + 2\text{e}^-$) (Guo et al., 2024; Kang et al., 2025).

We calculated the reaction pathway during the electron-donating or electron-accepting pathways for the reactive species generation. The nucleophilic nature of the Fe ACs can support the electron donation pathway, and a lower energy barrier was found for Fe₄ and Fe₃₆ compared to the Fe SAs (-7.21 – -7.28 eV < -6.40 – -5.57 eV) for generating *SO_4 (* is referred to the intermediate connected to the catalyst surface) (Fig. 4c). The calculation confirmed that a higher energy barrier (4.12 – 5.84 eV) needs to be overcome for the desorption of $\text{SO}_4^{\bullet-}$, especially for Fe ACs (Fig. 4c), in line with the low signal of free $\text{SO}_4^{\bullet-}$ during the EPR analysis. The electron-withdrawal pathway for generating ${}^1\text{O}_2$ was also calculated. The lowest energy barrier was found in the Fe SAs (1.32 – 1.51 eV < 1.71 – 1.79 eV) for the formation of $\text{SO}_5^{\bullet-}$, which can rapidly self-react to form ${}^1\text{O}_2$ due to the high reaction rate ($2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and low activation energy ($7.4 \pm 2.4 \text{ kcal mol}^{-1}$) (Das et al., 2001) (Fig. 4d).

The DFT calculation demonstrated that the aggregation of Fe on the carbon support influences its electrostatic characteristics and consequently dictates a distinct preference in the electron-related catalytic process. Specifically, Fe ACs tend to create *SO_4 through electron donation, while Fe SAs, particularly those chelated with pyrrolic N, exhibit enhanced performance in generating $SO_5^{\bullet-}$ (1O_2) by electron withdrawal. Moreover, the calculation results indicated synergy resulting from the interactions of Fe SAs and Fe ACs during the catalytic process. Such interactions enable them to establish a "pair" comprising an "anode" and "cathode" (Fig. 4e), which can facilitate electron circulation between the two catalytic centers within the carbon materials.

These results can support the higher efficiency of Fe-PC than Fe/N-PC as well as the different reactive species. The Fe ACs on the surface strongly interact with PMS with a higher sorption affinity, which hinders the diffusion of PMS. Thus, a limited amount of PMS can reach the Fe SAs in the bulk for Fe/N-PC to construct the redox pair. Therefore, the electron donation pathway mainly occurs with Fe/N-PC, leading to the substantial generation of surface-bounded $SO_4^{\bullet-}$ with limited 1O_2 . For Fe-PC, as Fe ACs are primarily located in the interior region of the PC, PMS can easily access these active sites without spatial hindrance. The lower sorption potential of Fe SAs for the PMS supports the construction of the redox pair, and bigger sizes of Fe ACs (-3.52 eV for Fe_{36} and -3.18 eV for Fe_4) facilitate the formation of 1O_2 for efficient degradation in Fe-PC.

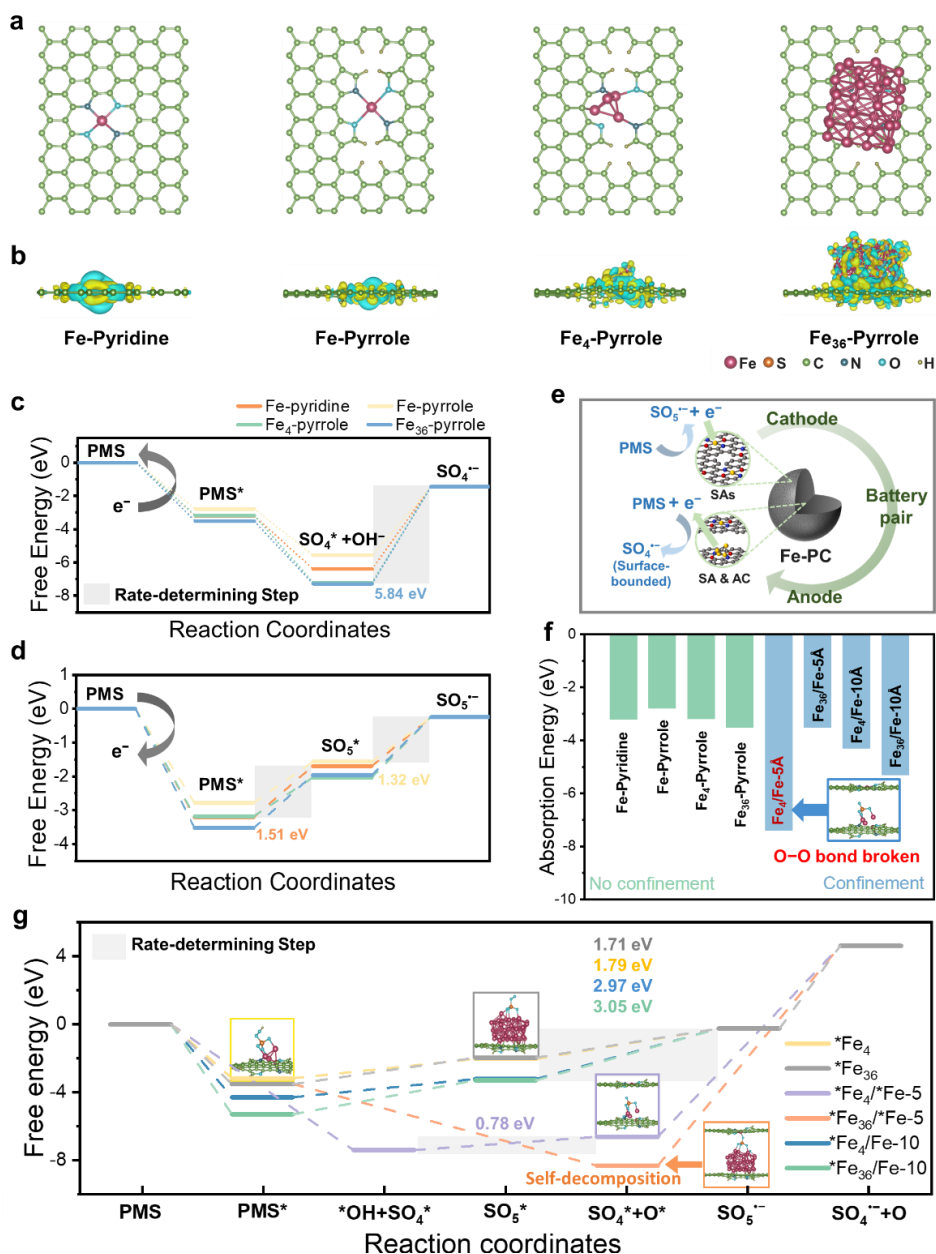


Fig. 4. (a) Optimized model of pyridine-type Fe site, pyrrole-type Fe site, pyrrole-type Fe₄ site, and pyrrole-type Fe₃₆ site and (b) corresponding charge density. Turquoise and yellow regions indicate depletion and accumulation of electrons, respectively. Experimental conditions: the isosurface of 0.002 e Å⁻³. Potential energy profiles of pyridine-type Fe site, pyrrole-type Fe site, pyrrole-type Fe₄ site, and pyrrole-type Fe₃₆ through (c) electron-donating pathway and (d) electron-accepting pathway. (e) Proposed PMS activation pathways catalyzed by Fe-PC. (f) Comparison of adsorption energy of PMS on pyridine-type Fe, pyrrole-type Fe, pyrrole-type Fe₄, and pyrrole-type Fe₃₆ sites in a confinement environment. (g) Free energy diagrams of the formation of SO₅ (¹O₂).

3.7. Cooperation between SAs and ACs in the Confined Environment

Bulk doping of Fe atoms within porous carbon will bring a high chance for the cooperation of SAs and ACs within the confined environment. Considering the pore structures in PC (7.0–15.0 Å) (Figure S3), two distances (5 Å and 10 Å) were set between the up and down layers, representing the pore size of 8.8–16.5 Å (Figure S19). To evaluate the cooperation of the Fe SAs and Fe ACs, we set the up layer as the Fe SAs with pyrrolic N and the bottom layer as the Fe ACs with different Fe atom numbers. The form of collaboration originating from the direction perpendicular to the plane is likely to be prevalent in the bulk doping materials, which would yield a greater impact than the collaboration occurring within the same plane in the surface doping materials (Figure S19).

The existence of the up layer of Fe SAs with a 10 Å distance enhanced the sorption potential of PMS on both Fe₄ and Fe₃₆ in the bottom layer with a decreased sorption energy from -3.18–3.52 to -4.29–5.30 eV. With a smaller distance of 5 Å, the sorption parameter changed from the perpendicular model to the parallel model with a higher sorption energy. The Fe₄ under 5 Å distance induced the fast decomposition of PMS to the SO₄^{•-} and OH⁻ during the sorption process. The energy barrier of the electron donation and withdrawal pathways was calculated concerning the confinement environment. For the generation of ¹O₂, the system with a 10 Å distance showed a negative impact, with a higher energy barrier of 2.97–3.05 eV compared to the system without confinement (1.71–1.79 eV) (Fig. 4g).

For the system with the 5 Å distance, PMS self-decomposed to *SO₄ and *OH during the sorption of PMS on Fe₄/Fe–5 Å, and then the surface-bound *O was formed through O–H bond breakage (Fig. 4f). Similarly, self-decomposition of *SO₅ occurred to form the *SO₄ and *O on Fe₃₆/Fe–5 Å, and the formed *O would quickly transform to the ¹O₂ afterward. No energy barrier was required to be overcome for *O (¹O₂) formation with Fe₃₆/Fe–5 Å, and a small energy barrier of 0.78 eV existed for Fe₄/Fe–5 Å, which was lower than that in the Fe SA. The linkage of Fe SAs with Fe ACs from the direction perpendicular to the plane could support the electron-accepting process for the ¹O₂ generation. For the generation of the *SO₄ through the electron donation process, Fe₄/Fe–10 Å showed the highest possibility with the lowest energy (-7.90 eV), followed by the Fe₃₆/Fe–10 Å (-7.59 eV) and Fe₄/Fe–5 Å (-7.04 eV) (Figure S20). The confinement and the cooperation of Fe SAs and Fe ACs with a larger distance (10 Å) facilitated the production of *SO₄ with a lower energy than sole Fe ACs (-7.21–-7.28 eV) or Fe SAs (-6.40–-5.57 eV). The confinement with the cooperation of Fe SAs and Fe ACs in the bulk-doped material enhanced the generation of surface-bounded SO₄^{•-} and ¹O₂, accomplishing more efficient degradation compared to the surface-doped catalyst.

4. Conclusions

This study evaluated the PMS activation performance by spherical porous carbon materials featuring a three-dimensional distribution of Fe SAs and Fe ACs for water purification. Fe-PC exhibited efficient degradation (up to 229% improvement in kinetics) with enhanced recyclability (up to 150% improvement) compared to surface-doped SA or AC-

dominated catalysts. The distinct electronic properties of Fe SAs (electrophilic) and Fe ACs (electron-rich) mediated the direction of electron transfer with PMS, generating $^1\text{O}_2$ and surface-bounded $\text{SO}_4^{\bullet-}$, respectively. Confinement effects and 3D site cooperation further facilitated ROS generation by greatly reducing the energy gap, resulting in better performance than the surface doping system. Our proposed strategy suggests a promising direction for further improving reaction efficiency and sustainability with bulk-doping catalysts. Future studies related to the (1) precise control of pore size to unveil and maximize the confinement impact; (2) atom-level manipulation and characterization of the metal-N species and distribution in the bulk carbon; and (3) the long-term performance and stability validation in diverse real wastewater.

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