



Single-atom iron catalysts on carbon nanosheets with specific defects for efficient phenol degradation by peroxydisulfate activation

Wang Ruixue¹, Qiu Zihan¹, Zhang Runmeng¹, Leng Changyu²,
Wang Xuzhen^{1,*}, Qiu Jieshan³

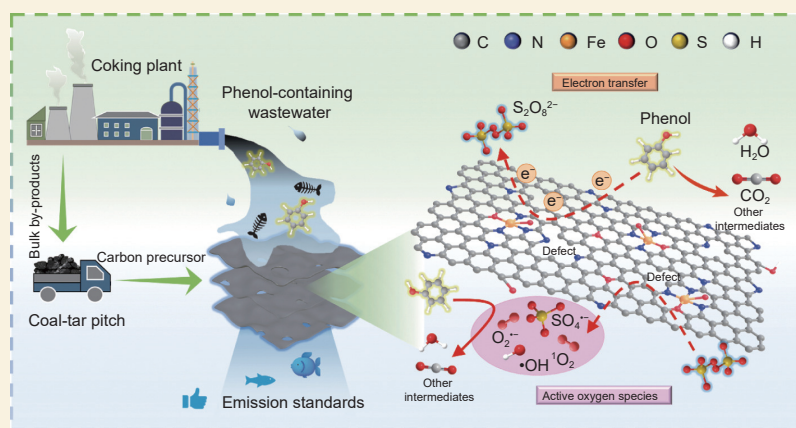
(1. School of Chemistry, Liaoning Key Lab for Energy Materials and Chemical Engineering, Dalian University of Technology, Dalian 116024, China;

2. College of Chemistry, State Key Laboratory of Chemistry and Utilization of Carbon-Based Energy Resources, Xinjiang University, Urumqi 830017, China;

3. College of Chemical Engineering, State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China)

Abstract: Phenolic compounds are typical refractory organic pollutants in coal chemical coking wastewater. The large-scale use of high-performance Fe-C composites in advanced oxidation processes for water treatment is limited by their complex synthesis and high cost. We report a low-cost Fe/N-C catalyst composed of nitrogen-doped carbon nanosheets containing abundant defects ($\text{sp}^3\text{-C}/\text{sp}^2\text{-C} = 0.66$) coordinated with single-atom iron species. The catalyst was prepared using coal-tar pitch, a common by-product of the coal chemical industry, as the carbon precursor, dicyandiamide as the auxiliary nitrogen source, and $\text{Fe-Cl}_3 \cdot 6\text{H}_2\text{O}$ as the iron precursor, using a self-assembly and pyrolysis strategy with graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) as a template. The Fe/N-C catalyst has an outstanding catalytic performance for the activation of peroxydisulfate, achieving over 98% phenol degradation within 30 min and a 60% total organic carbon removal rate. Characterization and mechanism studies have shown that in the Fe/N-C/PDS system, the degradation of phenol proceeds by both radical and non-radical path, with singlet oxygen ($^1\text{O}_2$) acting as the primary reactive oxygen species. Furthermore, compared with N-C, Fe/N-C has a greater ability to mediate interfacial electron transfer. This work provides an economical way to convert coal-tar pitch to carbon-based materials for efficient water treatment.

Key words: Defect carbon materials; Single-atom iron; Advanced oxidation; Electron transfer; Coal-tar pitch



1 Introduction

Phenolic compounds are typical persistent organic pollutants in coal chemical coking wastewater, exhibiting significant biotoxicity and environmental persistence, posing serious threats to ecosystems and human health^[1]. Conventional water treatment processes exhibit limited removal efficiency for these refractory compounds, promoting the development of efficient and economical advanced treatment technologies^[2]. Persulfate-based advanced oxidation processes (PS-AOPs) demonstrate significant potential for removing recalcitrant organic pollutants. Their efficacy in-

volves multiple pathways: the generation of reactive oxygen species (ROS) (e.g., sulfate radical ($\text{SO}_4^{\cdot-}$) and singlet oxygen ($^1\text{O}_2$)), the formation of high-valent metal-oxo species (HVMOs), and non-radical processes mediated by interfacial electron transfer on catalysts^[3].

Among various catalysts for activating per-

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sulfates (including peroxymonosulfate (PMS) and peroxydisulfate (PDS)), iron-carbon composites have garnered significant attention due to their relatively low cost, environmental friendliness and excellent catalytic activity^[4]. The catalytic mechanism is typically attributed to the synergistic effect between the iron active sites and the carbon support^[5]. For instance, Shi et al.^[6] demonstrated that iron-carbon composites prepared by pyrolyzing MIL-101(Fe) exhibited outstanding performance in activating PDS for the degradation of 2,4-dichlorophenol. Liu et al.^[7] employed iron phthalate loaded on carbon nanotubes (FePc-CNTs/300) as a catalyst to achieve stable degradation of sulfamethoxazole for over 60 h in a continuous-flow reaction (decoloration rate >95%). Mechanistic analysis and density functional theory calculations have jointly demonstrated that carbon nanotubes not only disperse the active components and modulate the electronic structure of the iron active sites, but also induce the adsorbed PMS to enter an electron-deficient state. However, the aforementioned studies typically rely on metal-organic framework (MOF) compounds and advanced carbon materials (e.g., carbon nanotubes and graphene), which are relatively expensive, thereby limiting the practical application of such catalysts^[8].

In recent years, increasing attention has been devoted to the preparation of carbon supports from low-cost precursors such as waste plastics and biomass. For instance, Wang et al.^[9] employed a salt-templating approach, in which layered FeCl₃ served simultaneously as a graphitization catalyst and structural template, to convert high-density polyethylene into N/Cl co-doped Fe single-atom catalysts (Fe-N/Cl-C). The resulting Fe-N/Cl-C demonstrated outstanding performance in the degradation of acyclovir (ACV) by activated PMS, achieving complete removal of 10 mg L⁻¹ ACV within 30 min. Huang et al.^[10] utilized chitosan derived from fish waste as a template to prepare zero-valent iron-loaded biochar (Fe-CS@BC). Although Fe-CS@BC exhibited high initial activity in PDS-activated phenolic degradation, continuous leaching of initially agglomerated iron particles dur-

ing the reaction led to active site loss. Cycling tests revealed over 70% activity decline after three consecutive uses, highlighting the inherent limitations of conventional granular iron-carbon composites in terms of stability and reusability.

To address these challenges, research focus has shifted toward iron single-atom catalysts (Fe SACs) featuring highly dispersed and stable active sites. Their exceptionally high atomic utilization, tunable local coordination structures, and outstanding intrinsic activity endow these materials with significant potential in PS-AOPs^[11]. However, existing Fe SACs synthesis primarily relies on expensive carriers such as MOFs, graphene, and carbon nanotubes, and typically requires complex preparation processes to achieve effective iron single-atom anchoring^[7,12]. This significantly limits their large-scale production and practical applications. Therefore, developing carbon-based Fe SACs prepared from low-cost precursors and simple processes, and systematically elucidating their structure-activity relationships and reaction mechanisms during persulfate activation, holds critical significance for advancing the practical application of PS-AOPs^[13].

In this work, low-cost nitrogen-doped carbon nanosheets featuring atomically dispersed iron sites and abundant defect structures (Fe/N-C) were successfully synthesized using coal-tar pitch (CTP) as the carbon precursor, dicyandiamide as an auxiliary nitrogen source, and FeCl₃·6H₂O as the iron source, by a self-assembled pyrolysis strategy employing g-C₃N₄ as a sacrificial template. The as-prepared Fe/N-C catalysts exhibited efficient activation of PDS for phenol degradation and demonstrated strong practical applicability, as confirmed complex water body interference resistance experiments, cyclic stability testing, and degradation intermediate analysis. Quenching experiments and electron paramagnetic resonance (EPR) studies confirmed that ¹O₂ is the dominant ROS involved in phenol degradation. A series of electrochemical analyses further indicated that the introduction of iron single-atom sites significantly enhances the electron transfer pathways, thereby improving

catalytic degradation efficiency. This study not only provides a facile approach for designing high-performance PDS-activated catalysts from inexpensive industrial byproducts, but also deepens the understanding of metal-support synergistic effects in carbon-based single-atom catalysts.

2 Experiment

2.1 Materials

The coal-tar pitch (CTP) was obtained from Angang Steel Group Co., Ltd. (Anshan, China), an industrial byproduct derived from the distillation of coal tar. For the specific batch of CTP used in this work, the key parameters are as follows: softening point 79 °C, coking value of 50.89%, quinoline-insoluble (QI) content of 2.54%, and toluene-insoluble (TI) content of 17.98%. Elemental analysis of this batch gives C 88.59%, H 4.49%, N 0.90%, S 0.78% and O 5.24% (by difference), corresponding to an H/C atomic ratio of approximately 0.60. Urea, dicyandiamide (DCD), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), and N,N-dimethylformamide (DMF, analytical grade) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd.

2.2 Synthesis of Fe/N—C(*T*) catalysts

Synthesis of $\text{g-C}_3\text{N}_4$ template: 10 g of urea (white powder) was placed in a crucible and heated in a muffle furnace at a rate of 2 °C min^{-1} to 550 °C. This temperature was maintained for 2 h. After cooling to room temperature, the resulting $\text{g-C}_3\text{N}_4$ (light yellow powder) was ground for later use.

Synthesis of Fe/N—C(*T*) catalysts: In a typical synthesis procedure, 0.3 g of CTP, 0.3 g of dicyandiamide (DCD), and 0.3 g of $\text{g-C}_3\text{N}_4$ were added to 30 mL of N,N-dimethylformamide (DMF). Meanwhile, 0.1 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL of DMF. After ultrasonication for 10 min, both solutions were combined and stirred at room temperature for 12 h. The solvent was then evaporated in an oil bath at 120 °C. The resulting solid residue was ground, placed in an alumina boat, and heated at a rate of 5 °C min^{-1} to 800 °C under a nitrogen atmosphere, where it was held for 2 h. The Fe/N—C(800) catalyst

was obtained after cooling to room temperature. By varying the pyrolysis temperature, Fe/N—C(*T*) samples were also obtained at 700 and 900 °C, respectively. As a representative catalyst, Fe/N—C(800) is hereafter referred to as Fe/N—C in the discussion section.

Preparation of contrast samples: Using different raw materials—specifically, without adding DCD, $\text{g-C}_3\text{N}_4$, and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; or without adding $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; or without adding DCD and $\text{g-C}_3\text{N}_4$ —the remaining steps were identical to the above-mentioned preparation process for the Fe/N—C material, yielding three kinds of samples labelled as pristine C, N—C, and Fe-C, respectively.

2.3 Material characterization

The microstructure of the catalyst was observed using a field emission scanning electron microscope (SEM500) and a transmission electron microscope (JEM-1400Flash). The phase composition was characterized by X-ray diffraction (D8 Advance) to determine the crystal structure of the samples. Raman spectroscopy measurements were performed on a Raman Spectra (inVia Qontor, Renishaw) instrument at an excitation wavelength of 532 nm. Specific surface area and pore structure parameters were obtained by collecting N_2 adsorption-desorption isotherms using a Kubo X1000 physical adsorption analyzer. Surface elemental composition and chemical state analysis were conducted on an X-ray photoelectron spectrometer (ESCALAB 250Xi).

3 Results and discussion

3.1 Structure and composition of materials

The self-assembly pyrolysis strategy for the preparation of Fe/N—C(*T*) is shown in Fig. 1a. CTP serves as the carbon precursor, providing an aromatic carbon framework, while $\text{g-C}_3\text{N}_4$ functions simultaneously as a nitrogen source and self-assembly template. Its layered structure guides the ordered arrangement of CTP by π – π stacking interactions^[14]. DCD serves as an auxiliary source, facilitating the formation of a nitrogen-rich carbon matrix and providing abundant anchoring sites for iron incorporation. Addi-

tionally, the intrinsic O atoms contained in CTP (Text S1) can act as anchoring sites to stabilize Fe atoms and regulate the electronic structure of the catalyst. During the self-assembly phase, all components form a homogeneous composite precursor through π - π stacking, coordination interactions, and electrostatic attraction. During pyrolysis, the decomposition of g-C₃N₄ and DCD releases gaseous species that induce carbon layer delamination, thereby forming porous structures and vacancy defects^[15]. Meanwhile, the iron species are transformed from precursors states into atomically dispersed active sites, ultimately yielding Fe/N-C catalysts enriched with structural defects and Fe-N₃O₂ active configurations.

Compared to the bulk-structure samples pristine C (Fig. 1b) and Fe-C (Fig. S1a) without g-C₃N₄ template or nitrogen doping, the samples N-C (Fig. S1b) and Fe/N-C (Fig. 1c, d) synthesized using g-C₃N₄ and DCD exhibit more developed porous structures. Transmission electron microscopy (TEM) images (Fig. 1e) reveal the thin-layer lamellar morphology of Fe/N-C, with no observable agglomerated iron spe-

cies particles. Energy-dispersive X-ray spectroscopy (EDS) analysis (Fig. 1f) further confirms the uniform distribution of C, N, O and Fe elements within the catalyst. These results confirm that the g-C₃N₄ template plays a crucial role in regulating the morphology of the carbon carrier, thus promoting the uniform dispersion of metal elements.

The low temperature N₂ adsorption-desorption test results (Fig. 2a) demonstrate that the specific surface areas (S_{BET}) of N-C and Fe/N-C were significantly enhanced, indicating the important contribution of g-C₃N₄ template and DCD nitrogen source. The control carbon sample (noted as C) obtained by direct carbonization of CTP exhibited the S_{BET} value of only 5.42 m² g⁻¹. Even with the addition of ferric chloride, the S_{BET} value of Fe-C sample remains only 31.60 m² g⁻¹. In contrast, the nitrogen-doped N-C sample demonstrated a type IV adsorption curve with the S_{BET} of 438.58 m² g⁻¹. Further incorporation of iron species into N-C resulted in a slightly reduced S_{BET} of 340.86 m² g⁻¹ for Fe/N-C. Pore size distribution analysis (inset in Fig. 2a, Table S1) revealed a

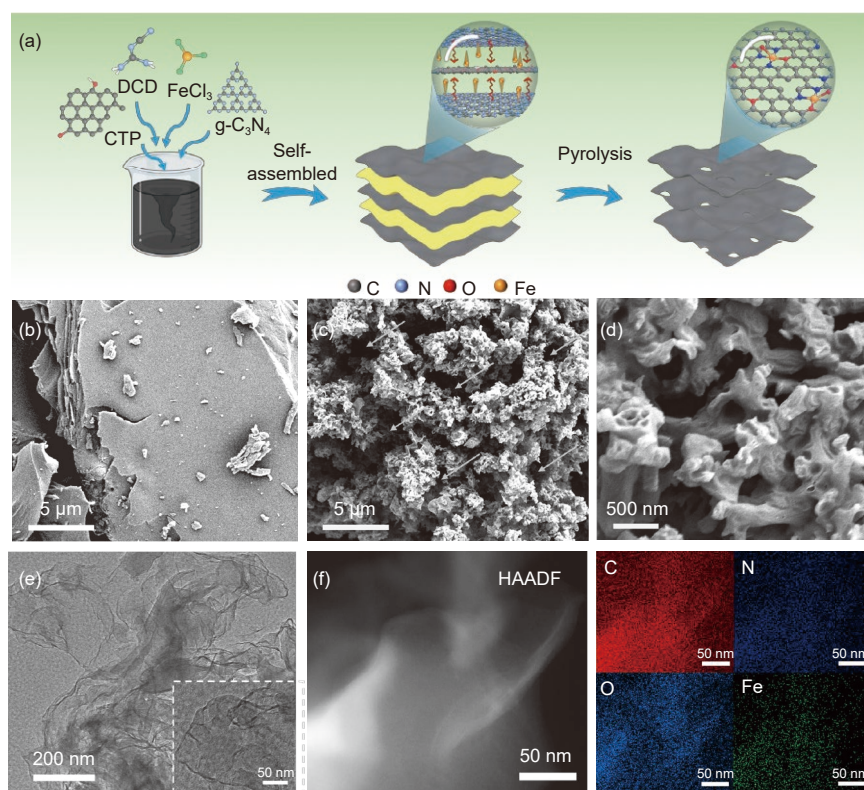


Fig. 1 (a) Schematic for the preparation of Fe/N-C material. SEM images of (b) C sample and (c, d) Fe/N-C. (e) TEM image (inset: localized enlarged view), (f) HAADF-STEM image and corresponding EDS elemental mappings (element C, N, O, Fe) of Fe/N-C

hierarchical porous structure in Fe/N—C, containing both micropores and mesopores. This multi-level pore structure helps to improve the accessibility of active sites on the catalyst surface and the mass transfer efficiency during the phenol degradation process, thereby enhancing the utilization of active sites and catalytic performance^[16].

In Raman spectroscopy, the intensity ratio of the *D* peak to the *G* peak (I_D/I_G) is an important parameter for evaluating the defect density and structural disorder of carbon materials^[17]. These defects serve as key sites for subsequent PDS activation. As shown in Fig. 2b, among the samples carbonized at 800 °C, N—C exhibited an I_D/I_G value of 0.990, which is higher than that of pristine C (0.912), derived solely from coal-tar pitch. This result indicates that the introduction of g-C₃N₄ and DCD effectively increases the defect density within the carbon matrix. The addition of iron source resulted in a slight reduction in the defect

level, as indicated by I_D/I_G ratios of 0.886 for Fe-C and 0.963 for Fe/N—C. Furthermore, pyrolysis temperature plays a key role in tuning the carbon structure. The I_D/I_G value of Fe/N—C(*T*) materials gradually decreased with increasing temperature from 700 to 900 °C (Fig. S2), reflecting an enhanced structural order, a reduced defect density, and progressive transformation toward a graphitized structure^[18].

The crystal structure of the as-prepared materials was analyzed using X-ray diffraction (XRD). As shown in Fig. 2c, after introducing the g-C₃N₄ template and DCD, the diffraction peaks corresponding to graphitic carbon at $2\theta \approx 25^\circ$ and 43° exhibited significant broadening for both N—C and Fe/N—C, compared with their counterparts C and Fe—C, indicating reduced graphitization and increased structural disorder^[19]. In addition, no distinct diffraction signals other than graphite peaks were observed in the XRD pattern of Fe/N—C sample, implying iron species ex-

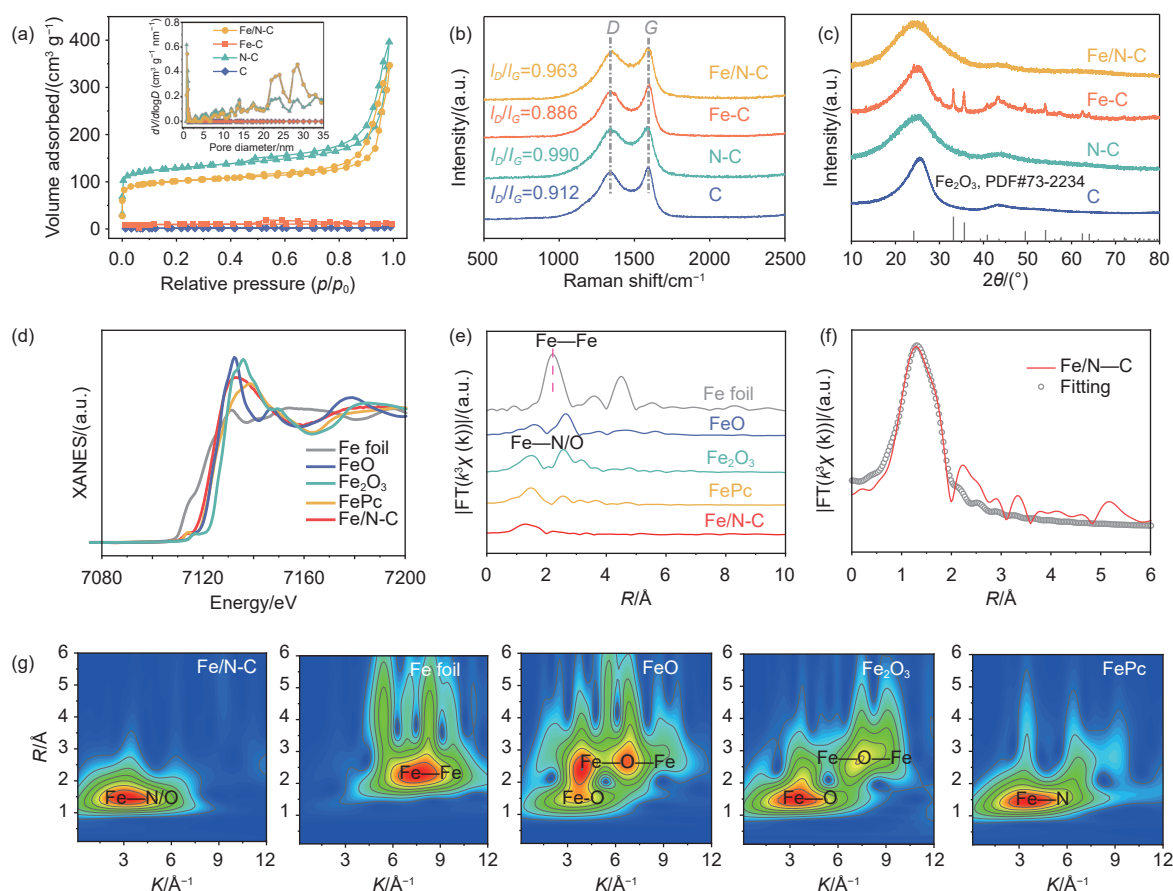


Fig. 2 (a) N₂ adsorption-desorption isotherms, Inset: corresponding pore size distributions. (b) Raman spectra and (c) XRD patterns of Fe/N—C and C, Fe—C, N—C samples. (d) Normalized Fe *K*-edge XANES spectra. (e) FT-EXAFS spectra of the Fe foil, FeO, Fe₂O₃, FePc and Fe/N—C in *R* space. (f) FT-EXAFS fitting results for Fe/N—C in *R* space. (g) Wavelet transform plots of Fe/N—C and the reference materials

ist in a highly dispersed amorphous form within the carbon matrix. Further comparison of annealing temperatures (Fig. S3) revealed that when the pyrolysis temperature rose to 900 °C, crystalline diffraction peaks of Fe₂O₃ appeared in Fe/N—C sample, indicating a high temperature causes the iron species to agglomerate and crystallize, thus difficult to be uniformly dispersed^[20]. The iron loading in Fe/N—C(800) catalyst was 2.83% (from ICP-OES test), being close to the theoretical value (2.88%, mass fraction) calculated based on the initial iron feed amount and single-batch yield. This fact confirms that iron is almost entirely retained without loss throughout the synthesis process from precursor to final material. The full X-ray photoelectron spectroscopy (XPS) spectrum of Fe/N—C(800) reveals that its primary four elements are carbon, nitrogen, oxygen and iron (Fig. S4).

Through X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy analyses, the local coordination environment and atomic-level dispersion characteristics of iron species in Fe/N—C and standard materials were systematically elucidated. As displayed in Fig. 2d, the Fe K-edge XANES absorption edge position of Fe/N—C lies between that of Fe foil (Fe⁰) and phthalocyanine iron (FePc, Fe²⁺), indicating an average oxidation state of the iron center between 0 and +2^[21]. The *k*³-weighted Fourier-transform EXAFS (FT-EXAFS) spectra (Fig. 2e) exhibit a dominant peak at approximately 1.5 Å, reflecting that the first coordination shell around the Fe center consists of N or O atoms^[22]. In the O 1s XPS spectrum (Fig. S5, ESI[†]), a distinct Fe—O characteristic peak is observed at approximately 530.4 eV, further confirming the rationality of oxygen coordination around the iron center^[23].

Quantitative fitting analysis of the Fe K-edge EXAFS data (Fig. 2f, Table S2) further reveals that the best-fit model for the first coordination shell consists of both Fe—N and Fe—O scattering paths, with corresponding coordination numbers of approximately 3 and 2, respectively. As shown in Fig. 2g, the

wavelet transform (WT) spectrum of Fe/N—C exhibits significant differences from those of Fe foil, FeO, and Fe₂O₃ reference standards, ruling out the presence of Fe—Fe or Fe—O—Fe coordination pathways and confirming the atomic-level dispersion of Fe^[24]. Furthermore, compared to the FePc reference sample featuring an Fe—N₄ structure, the shift of the maximum WT intensity of Fe/N—C toward the low-*k* region aligns with its distinct coordination environment from pure Fe—N structures (such as the fitted Fe—N₃O₂ configuration). This further corroborates the coordination of N/O light atoms within the first coordination shell of the Fe center^[25–26].

3.2 Catalytic performance evaluation

Using phenol as the target pollutant, the catalytic performance of PDS activated by different materials was systematically evaluated. Prior to introducing PDS, the adsorption behavior of various materials toward phenol was investigated. As shown in Fig. S6 (ESI[†]), the phenol adsorption removal efficiencies of pristine C, N—C, Fe—C and Fe/N—C were 4.9%, 33.8%, 10.5% and 23.4%, respectively. Further analyses revealed a strong positive linear correlation between adsorption capacity and specific surface area (Fig. S7). In the presence of PDS, the Fe/N—C system exhibited outstanding catalytic oxidation performance, achieving over 98% phenol degradation within 30 min (Fig. 3a), along with a PDS consumption rate of 42.5% (Fig. S8). The degradation process followed a pseudo-first-order kinetic model (Text S1), with an apparent rate constant (*k*_{obs}) of 0.127 min^{−1} for Fe/N—C. This value is 63.5, 1.84 and 25.4 times higher than those of pristine C, N—C and Fe—C, respectively (Fig. 3b). This result highlights the synergistic effect between the N-doped carbon framework and atomically dispersed iron active sites, which is a key factor in enhancing the activation performance of PDS^[27]. The superior oxidative degradation performance of phenol by the Fe/N—C/PDS system has been demonstrated, when compared with those of catalyst/PDS or catalyst/PMS systems previously reported in the literature (Table S3).

The effect of pyrolysis temperature on the cata-

lytic performance of Fe/N-C(T) is illustrated in Fig. 3c. within the same 30-min reaction period, the optimal removal rate of phenol was achieved over Fe/N-C(800). The performance variation is closely linked to 2 key structural parameters of Fe/N-C(T) catalyst: on the one hand, the physical adsorption capacity for phenol (green column) continuously increases with the synthesis temperature rising; on the other hand, the intrinsic catalytic activity (orange column) towards activating PDS exhibits a peak for Fe/N-C(800). This is due to the relatively high defect density in the carbon substrate and the atomically dispersed iron species within the carrier (Fig. S2-S3). Thus, 800 °C is determined as the optimal pyrolysis temperature for Fe/N-C catalyst preparation, so that the synergetic effect between these 2 factors can be guaranteed. Using Fe/N-C(800) as the representative sample, the detailed investigation was conducted, and it was simply noted as Fe/N-C in the following text.

Real-world water bodies contain various background constituents, such as inorganic anions and natural organic matter. These substances can scavenge

reactive radicals and suppress degradation efficiency. To evaluate the practical implication, the effect of three common inorganic anions (HCO_3^- , NO_3^- , Cl^-), humic acid (HA), and different water matrices on the catalytic performance of Fe/N-C was systematically investigated. Results in Fig. 3d indicate that under conditions containing 10 mmol L⁻¹ inorganic anions or 20 mg L⁻¹ HA, the Fe/N-C/PDS system still effectively degrades phenol and demonstrates good adaptability in tap water and lake water, proving its robust interference resistance. Compared to inorganic anions, HA exhibits stronger inhibitory effects. This is primarily attributed to the abundant aromatic rings and oxygen-containing functional groups in the HA molecular structure^[28]. These enable HA to competitively occupy active iron sites on the catalyst surface through strong π - π interactions and coordination effects. Simultaneously, HA itself, as a reducing agent, quenches reactive oxygen species within the system, significantly reducing PDS activation efficiency and pollutant degradation rates^[29]. In catalyst cycling stability tests (Fig. 3e), the phenol degradation rate exhibited a gradual decline after 3 consecutive cycles,

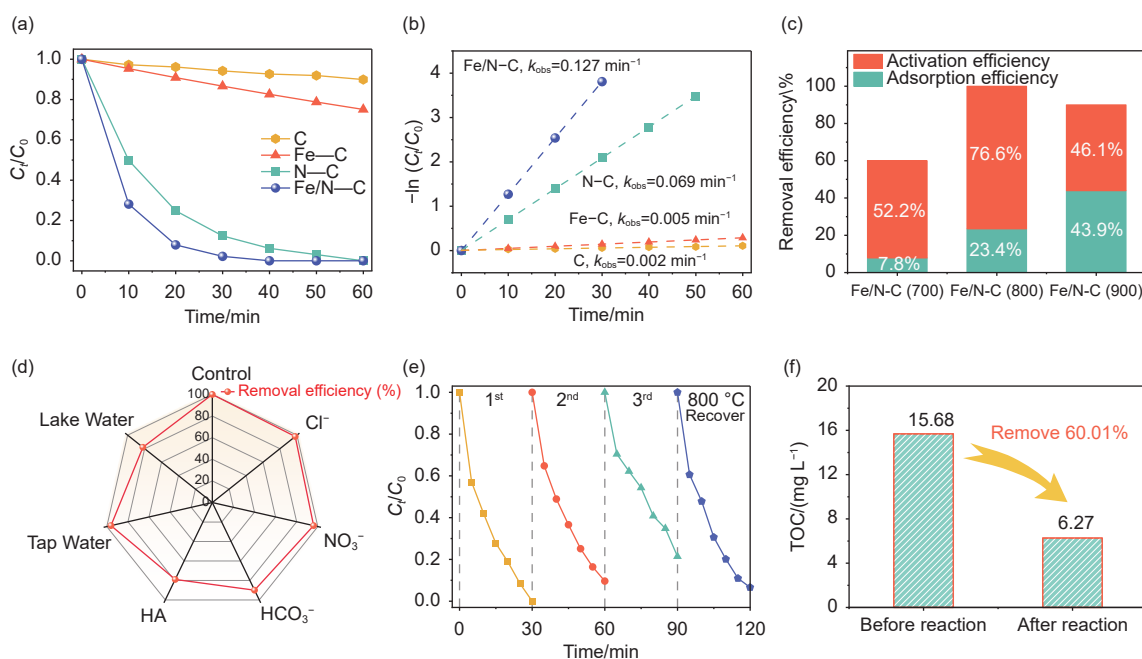


Fig. 3 (a) Kinetic curves of phenol degradation by activated PDS and (b) apparent reaction rate constant (k_{obs}) of Fe/N-C and C, Fe-C, N-C samples. (c) Phenol removal performance of Fe/N-C(T) obtained at different pyrolysis temperatures. (d) The influence of inorganic ions, HA, and actual water matrix on phenol degradation. (e) Cyclic stability test and (f) TOC changes in solution during reaction of Fe/N-C/PDS/phenol system. (Reaction conditions: $\rho_{\text{catalyst}} = 0.2 \text{ g L}^{-1}$, $C_{\text{PDS}} = 1 \text{ mmol L}^{-1}$, $\rho_{\text{phenol}} = 20 \text{ mg L}^{-1}$, $C_{\text{Cl}^-} = C_{\text{NO}_3^-} = C_{\text{HNO}_3^-} = 10 \text{ mmol L}^{-1}$, $\rho_{\text{HA}} = 20 \text{ mg L}^{-1}$, room temperature)

likely due to partial coverage of active sites by reaction intermediates^[30]. After regeneration by heat treatment at 800 °C under an inert atmosphere, adsorbed organic species were effectively removed, re-exposing active sites. The PDS activation performance of Fe/N—C can be recovered to over 92% of its initial level. These results fully demonstrate that the Fe/N—C catalyst holds broad application prospects in practical wastewater treatment.

To evaluate the potential contribution of leached iron from the Fe/N—C/PDS system to PDS activation, solid-liquid separation was performed on the spent Fe/N—C catalyst after reaction completion. Phenol degradation experiments were then conducted using the resulting filtrate. As shown in Fig. S9, the post-reaction filtrate failed to effectively activate PDS for phenol degradation, indicating that the contribution of leached iron during the catalytic process is negligible. Further ICP-MS analysis of the post-reaction solution revealed an iron leaching concentration of 0.23 mg L⁻¹, below the World Health Organization's drinking water iron limit^[31]. Comparison of XRD and Raman spectra of Fe/N—C before and after the reaction (Fig. S10) shows that the main structure of the catalyst remains consistent, further confirming its excellent stability. Total organic carbon (TOC) in the system was determined to be removed by 60.01% (Fig. 3f), indicating the Fe/N—C/PDS oxidation system not only effectively degrades phenol but also achieves significant mineralization of pollutants.

To assess the practical applicability of the Fe/N—C/PDS system, actual secondary coking wastewater was treated, and three-dimensional (3D) excitation-emission matrix (3D EEM) fluorescence spectroscopy was employed to monitor changes in aromatic organic pollutants (Fig. S11). The raw wastewater exhibited a distinct fluorescence peak in the range of E_x 310–360 nm / E_m 380–440 nm, with a peak center at approximately E_x 340 nm / E_m 400 nm (Fig. S11a). According to the 3D EEM region classification reported in the literature, this position corresponds to the typical humic-like fluorescence region, primarily contributed by organic pollutants contain-

ing conjugated aromatic ring structures^[32]. After 15 and 30 min of treatment with the Fe/N—C/PDS system, the fluorescence intensity in this region decreased progressively (Figs. S11b-c), and no new fluorescence peaks appeared throughout the process. These results indicate that the system effectively reduces the concentration of aromatic organic pollutants in actual coking wastewater, demonstrating its good potential for treating complex real-world wastewater matrices.

3.3 Reactive oxygen species recognition

The mechanism of Fe/N—C activation of PDS for phenol degradation was systematically investigated, the measurement methods are described in detail in Text S2. Radical quenching experiments were conducted to identify the primary ROS involved in phenol degradation. Methanol (MeOH) efficiently quenches both hydroxyl radicals ($\bullet\text{OH}$) and $\text{SO}_4^{\bullet-}$ simultaneously, while tert-butyl alcohol (TBA) exhibits higher reactivity toward $\bullet\text{OH}$ (reaction rate constant $k(\bullet\text{OH}, \text{TBA}) = 3.8\text{--}7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)^[33–34]. As shown in Fig. 4a, even at a TBA concentration of 500 mmol L⁻¹, its inhibitory effect on phenol degradation remains limited. MeOH exhibits slightly higher inhibition than TBA, yet the impact remains insignificant, indicating that $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ participate in the degradation reaction but contribute minimally. Similarly, quenching the $\text{O}_2^{\bullet-}$ radical with CHCl_3 did not result in any significant inhibition (Fig. 4a), indicating that the formation of $^1\text{O}_2$ is independent of the $\text{O}_2^{\bullet-}$ precursor. In contrast, the addition of L-histidine and furfuryl alcohol (FFA), which react efficiently with singlet oxygen ($^1\text{O}_2$)^[12], significantly inhibited phenol degradation. This confirms that $^1\text{O}_2$ is the primary reactive oxygen species driving phenol degradation in the Fe/N—C/PDS system.

Recently, high-valent metal-oxo species (HV-MOs, e.g. Fe(IV) = O) reported in iron-based heterogeneous Fenton-like systems have been demonstrated to exhibit high removal efficiency for organic pollutants^[35]. To verify the role of HVMOs in our case, DMSO was introduced as an effective quencher for Fe(IV) = O and Fe(V) = O ^[36]. As shown in Fig. 4b,

the addition of DMSO had a limited effect on phenol removal efficiency, suggesting that HVMOs are not the primary active intermediates in this system. Furthermore, PDS adsorbed on the catalyst surface can form a metastable, highly reactive surface-bound complex (PDS*), which directly oxidizes pollutants through a non-radical electron transfer pathway^[37]. Compared to transient radical species, the catalyst-PDS* complex exhibits a longer half-life and is relatively stable on the catalyst surface^[38]. This stability difference was confirmed in phenol delayed-addition experiments (Fig. 4c). When phenol was added after a 5-min delay, the degradation rate significantly decreased, which was attributed to the rapid decay of short-lived radical species. However, extending the delay time to 10 min did not lead to a further substantial decline in degradation efficiency, indicating that the non-radical oxidation pathway mediated by surface-bound PDS* continued to play a sustained role in the reaction, thereby jointly contributing to pollutant degradation^[39].

The generation of ROS was further verified using electron paramagnetic resonance (EPR) spectroscopy, employing DMPO and TEMP as radical and $^1\text{O}_2$ scavengers, respectively^[40]. As shown in Fig. 4d-f,

characteristic signals of 4 reactive oxygen species ($\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$) were detected during the degradation of phenol by Fe/N-C-activated PDS^[41]. Their intensities progressively increased with reaction time, indicating the simultaneous generation and accumulation of multiple ROS species within the system.

In situ Raman spectra were applied to identify the conversion of $\text{S}_2\text{O}_8^{2-}$ into SO_4^{2-} (Fig. S12). Upon addition of Fe/N-C to the PDS solution, a SO_4^{2-} peak appeared at approximately 983 cm^{-1} , on the basis of 2 characteristic $\text{S}_2\text{O}_8^{2-}$ peaks (~ 833 and 1076 cm^{-1}) of PDS only, indicating the catalysis effect of Fe/N-C^[42]. After the subsequent addition of phenol, the $\text{S}_2\text{O}_8^{2-}$ peaks weakened, while the SO_4^{2-} peak continued to intensify over time. These results provide direct spectroscopic evidence for the catalytic activation of PDS by Fe/N-C.

3.4 Verification of the electron-transfer pathway

To elucidate the crucial role of atomically dispersed iron sites in the interfacial electron transfer dynamics during the activation of PDS for phenol degradation, we conducted a systematic electrochemical characterization of Fe/N-C and N-C carrier materials. Electrochemical impedance spectroscopy (EIS) results revealed (Fig. 5a) that Fe/N-C exhibited

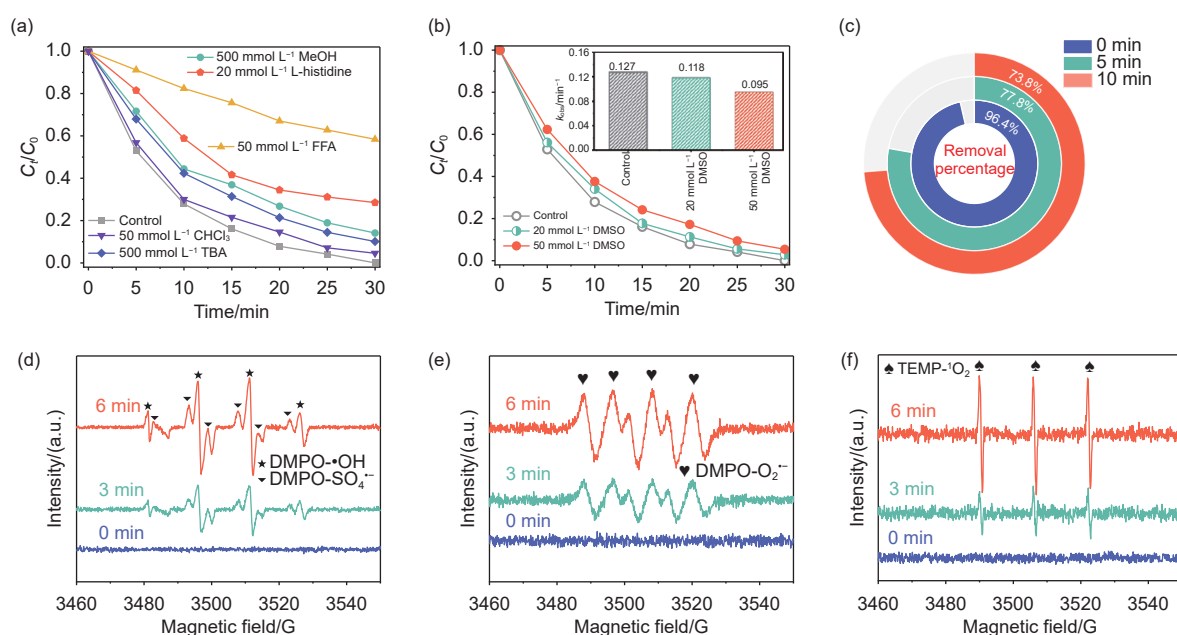


Fig. 4 (a, b) Quenching effects of different scavengers on the Fe/N-C/PDS oxidation system. (c) Effect of Fe/N-C and PDS premixing on phenol removal efficiency. EPR spectra of the Fe/N-C/PDS system for (d) DMPO- $\cdot\text{OH}$, DMPO- $\text{SO}_4^{\cdot-}$, (e) DMPO- $\text{O}_2^{\cdot-}$ and (f) TEMP- $^1\text{O}_2$. (Reaction conditions for (a, b, c):

$$\rho_{\text{Fe/N-C}} = 0.2\text{ g L}^{-1}, \rho_{\text{PDS}} = 1\text{ mmol L}^{-1}, \rho_{\text{Phenol}} = 20\text{ mg L}^{-1}, \text{room temperature})$$

lower charge transfer resistance (R_c) than N—C material, confirming the introduction of atomically dispersed iron species could enhance the catalyst's ability to mediate electron transfer processes^[43]. The current response of the Fe/N—C electrode was measured via linear sweep voltammetry (LSV) over the voltage range of 0.3 to 1.6 V (vs. Ag/AgCl). As shown in Fig. 5b, the current response of the Fe/N—C electrode increased upon the addition of PDS and phenol, proving the occurrence of an efficient electron transfer process among the 3 species^[44].

Open-circuit potential (OCP) monitoring results (Fig. 5c) further indicate that the addition of PDS causes a sharp increase in the OCP of Fe/N—C electrode, suggesting its rapid binding with PDS to form a PDS* complex with a high redox potential^[45]. Within 400 s, the potential of the Fe/N—C electrode rose by 0.24 V, exceeding the 0.16 V change observed for the N—C electrode. This result directly demonstrates that atomically dispersed iron species serve as key active sites enhancing catalyst binding with PDS and boosting its initial activation capacity. Additionally, the interfacial electron transfer dynamics in the presence of phenol were monitored in real-time by the instantaneous current method (i - t) (Fig. 5d). Upon phenol addi-

tion, the Fe/N—C electrode immediately exhibited a pronounced positive current response, indicating directed electron transfer from phenol molecules to surface PDS* complexes at the interface—a direct electrochemical signal of pollutant oxidation^[46]. In contrast, the N—C electrode exhibited only a weak current change. This contrast clearly confirms that the highly dispersed iron sites serve not only as the activation center for PDS but also as the catalytic active sites driving the subsequent electron transfer steps for pollutant oxidation.

To explicitly verify that the electron transfer process (ETP) in the Fe/N—C/PDS system can degrade organic pollutants, experiments were conducted using a dual-chamber reactor (Fig. 5e and Fig. S13)^[47]. Both electrodes consisted of carbon paper coated with Fe/N—C catalyst. The two chambers contained PDS and phenol solutions, respectively, physically separated by a proton exchange membrane and connected via an ammeter to form a circuit. A sustained positive current signal was detected during phenol degradation ($\sim 50\%$ degradation within 12 h, Fig. 5f), indicating that electrons could be directly transferred from phenol to PDS* by the Fe/N—C electrode, thereby achieving oxidative degradation of phenol^[48]. Compared to the single-chamber system (Fig. 3a), phenol

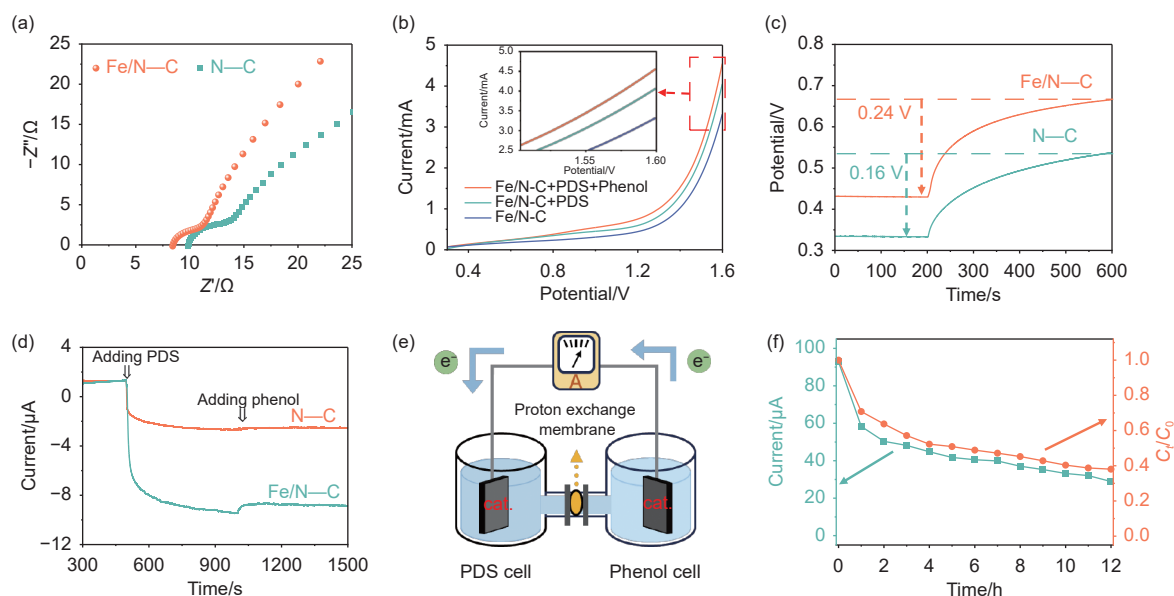


Fig. 5 (a) EIS spectra of Fe/N—C and N—C. (b) Linear sweep voltammetry of Fe/N—C as the working electrode in different condition. (c) Open-circuit voltage and (d) chronoamperometric plots using Fe/N—C and N—C as working electrodes, respectively. (e) Schematic diagram of double-chamber reaction device. (h) Current and phenol removal rate of galvanic oxidation tests with Fe/N—C in the device

removal rates were significantly reduced in the dual-chamber system, revealing that both radical and non-radical pathways contribute to phenol degradation under common single-chamber conditions.

3.5 Identification of reaction center and degradation pathway

The high-resolution N 1s XPS spectra of Fe/N—C materials at different pyrolysis temperatures in Fig. S14 can be fitted into 5 characteristic peaks, with binding energies located at 398.2, 399.0, 400.3, 401.3 and 403.6 eV, corresponding to pyridinic nitrogen, Fe-N, pyrrolic nitrogen, graphitic nitrogen and nitrogen oxide species, respectively^[49–50]. As pyrolysis temperature increases, edge-bound nitrogen (including pyridinic N and pyrrolic N) gradually converts to graphitic N^[51]. Previous studies have demonstrated that both pyridine nitrogen and graphitic nitrogen play crucial roles in the activation of PDS for degrading pollutants^[52].

Furthermore, the relative density of carbon defects can be semi-quantitatively assessed by the ratio of sp^3 -C to sp^2 -C relative intensities in the C 1s spectrum^[53–54]. The sp^3 -C/ sp^2 -C ratio of Fe/N—C decreased from 0.66 before the reaction to 0.58 afterward (Fig. 6a), suggesting some carbon defects were oxidized or structurally rearranged during the reaction. This further supports the role of carbon defects as active sites in the catalytic degradation of phenol. A decrease in C=O bond abundance was observed alongside a corresponding increase in C—O species (Fig. 6a and Fig. S15). This indicates that residual carbonyl groups act as Lewis base sites, promoting PDS activation by donating electrons to adjacent carbon atoms^[55–56]. XPS results indicate that after the Fe/N—C catalyst participates in the degradation of phenol, the proportion of pyridinic N on its surface significantly decreases, while the proportion of pyrrolic N markedly increases (Fig. 6b). This phenomenon can be attributed to highly reactive oxidative radicals (e.g., $SO_4^{\cdot-}$ and $\cdot OH$) generated during PDS activation preferentially attacking adjacent carbon frameworks anchored by pyridine nitrogen atoms, thereby inducing local structural rearrangement and partial conversion to pyrrole nitrogen structures. In contrast,

the increased Fe—N proportion indicates that the surface Fe—N coordination structure was well preserved after the reaction and may have been relatively enriched due to reconstruction, suggesting it could be a key site in the non-radical oxidation pathway. The stability of graphitic nitrogen demonstrates its strong antioxidant properties and its potential role in assisting electron transfer^[57].

Analyzing the toxicity of intermediates generated during the degradation process is crucial for comprehensively evaluating the environmental risks and treatment efficacy of Fenton-type oxidation systems. In the study of phenol degradation by the Fe/N—C/PDS system, gas chromatography-mass spectrometry (GC-MS) identified its primary degradation intermediates (Table S4). It is worth noting that among the detected intermediates, 1,4-benzoquinone (P-2) and acetone (P-6) are resistant to further oxidation by free radicals due to their electronic and molecular structural characteristics, and thus represent the main contributors to residual TOC^[58–59]. The ecotoxicity of these intermediates was further evaluated using the Ecostructure-Activity Relationship (ECOSAR) model. The results indicate that compared to the initial pollutant phenol, these byproducts exhibit reduced acute and chronic toxicity hazards to aquatic organisms such as fish and green algae (Fig. S16), highlighting the system's potential for practical water treatment applications.

Based on the above analysis, a collaboration mechanism for phenol degradation in the Fe/N—C/PDS system was proposed (Fig. 6c). This process is synergistically driven by both radical and non-radical pathways. Following the reaction, the relative abundances of pyrrolic-N, C=O groups and carbon defects decreased significantly, indicating their consumption as active sites during catalysis. C=O groups are reported primarily to be involved in the non-radical pathway of $^1O_2$, whereas carbon defects participate in both radical and non-radical processes^[60]. Thus, their depletion suggests the synergistic involvement of multiple reaction pathways. In contrast, graphitic-N and Fe—N structures showed

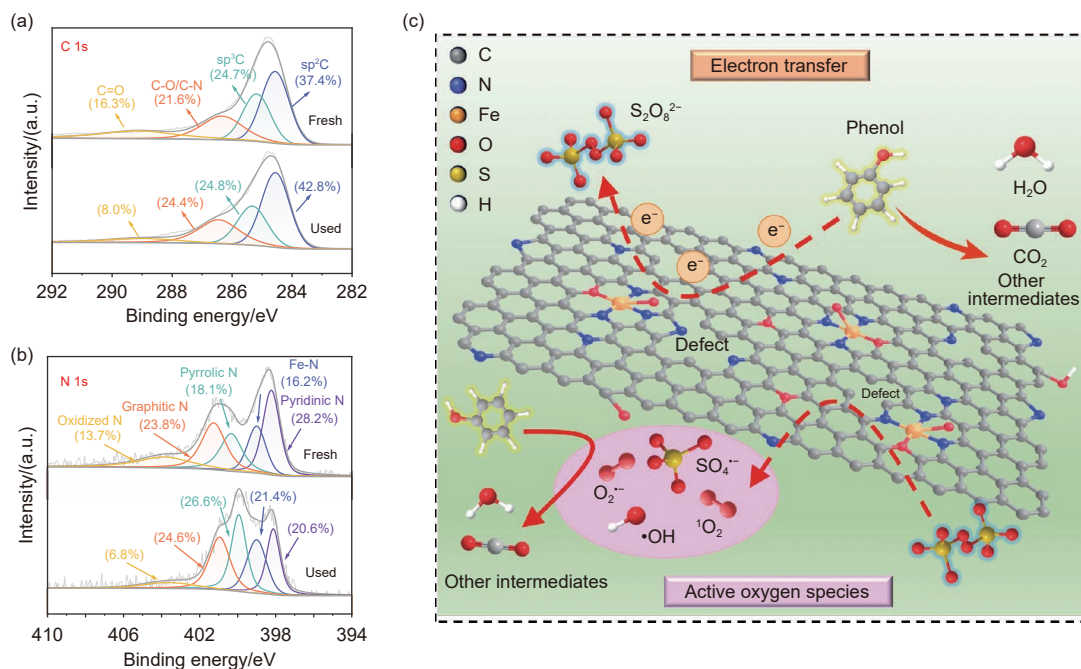


Fig. 6 High resolution (a) C 1s and (b) N 1s XPS spectra of Fe/N—C samples before and after use. (c) Proposed mechanism scheme of phenol removal in Fe/N—C/PDS system

high stability, with their abundances either unchanged or slightly increased after the reaction, confirming them as stable active centers for non-radical electron transfer. Through the synergetic action of these 2 types of active sites, phenol is effectively degraded into less toxic intermediates such as 4-hydroxypentan-2-one. This ultimately achieves approximately 60% of TOC removal rate, reducing overall ecological risks and demonstrating a potential application of the Fe/N—C/PDS for wastewater treatment.

4 Conclusion

This study transforms coal-tar pitch into a nitrogen-doped carbon support with a flaky morphology and abundant defect sites by using g-C₃N₄ as both a template and nitrogen source, while precisely controlling the pyrolysis temperature. This strategy enables the anchoring of highly dispersed iron single-atom catalysts within the resulting Fe/N—C material. The as-prepared Fe/N—C catalyst exhibits high catalytic activity and excellent stability for phenol degradation. Radical quenching and EPR experiments identified ¹O₂ as the primary reactive oxygen species. Post-reaction characterization showed decreased abund-

ances of pyrrolic-N, C=O, and carbon defects, suggesting their consumption as active sites, while graphitic-N and Fe—N structures remained stable. Electrochemical analyses verified that atomically dispersed Fe sites significantly enhanced interfacial electron transfer. This work achieves the high-value conversion of coal-tar pitch into high-performance catalytic materials, providing an effective strategy for advanced phenolic pollutant treatment and embodying the circular economy concept of “waste-to-resource utilization”.

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