

Selective radical pathways on defect-engineered electrophilic biochar for sustainable water purification

Received: 13 January 2026

Accepted: 22 September 2026

Published online: 05 October 2026

Check for updates

Ying Hu^{1,5}, Wei Ren^{2,5,6}✉, Min Wang^{1,6}✉, Zhenqi Xu¹ & Yongfa Zhu^{3,4,6}✉

Traditional advanced oxidation processes are frequently hindered by limited efficiency in complex wastewater, primarily due to the short lifetime and nonselective nature of hydroxyl radicals ($\bullet\text{OH}$). While peracetic acid activation involves competing nucleophilic and electrophilic pathways, selectively channeling this process toward the acetylperoxyl radical ($\text{CH}_3\text{C}(\text{O})\text{OO}\bullet$)-mediated electrophilic route remains a formidable challenge. Here, we report a universal nitrogen-removal strategy to engineer 5-14-5 vacancy-pentagon defects in nitrogen-containing agro-forestry biomass-derived biochar. These vacancy-based topological defects reconfigure the electronic landscape by downshifting the Fermi level and upshifting the p -band center. This electronic modulation transforms the carbon framework from a traditional electron donor into a potent electrophilic sink with a superior electron accepting capacity ($\text{EAC} = 3.77 \text{ mmol}\cdot\text{e}^{-}\cdot\text{g}^{-1}$). This reconfiguration renders the electrophilic pathway thermodynamically favorable ($\Delta G = -0.09 \text{ eV}$), achieving near-total selectivity ($> 99\%$) for $\text{CH}_3\text{C}(\text{O})\text{OO}\bullet$ over $\bullet\text{OH}$. More importantly, this system delivers a high normalized kinetic constant ($409.82 \text{ min}^{-1} \text{ M}^{-1}$) and sustains high-flux radical production over 260 hours of continuous operation. Furthermore, life-cycle assessment validates its environmental sustainability, highlighting a net-negative carbon footprint. This study provides fundamental insights into defect-mediated radical chemistry and offers a scalable, sustainable paradigm for precision water decontamination.

The rapid accumulation of recalcitrant organic pollutants in water systems has necessitated the development of advanced oxidation processes (AOPs)¹. Traditionally, these systems rely on highly reactive radicals, such as hydroxyl radicals ($\bullet\text{OH}$, $E^0 = 1.9 - 2.7 \text{ V}$ vs. NHE) and sulfate radicals ($\text{SO}_4^{\bullet-}$, $E^0 = 2.6 - 3.1 \text{ V}$ vs. NHE), but their indiscriminate reactivity leads to excessive oxidant consumption and severe vulnerability to complex water matrices^{2,3}. In real-world wastewater, background constituents (e.g., Cl^- , CO_3^{2-} , and natural organic matter) act as aggressive scavengers, drastically quenching these short-lived radicals

and resulting in compromised treatment efficiency and prohibitive energy demand^{4,5}.

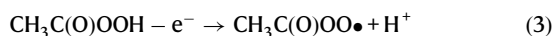
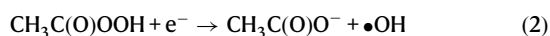
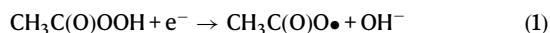
To enhance selectivity, recent studies have shifted toward non-radical pathways, including singlet oxygen ($^1\text{O}_2$, $E^0 = 0.8 - 1.0 \text{ V}$ vs. NHE)^{6,7}, high-valent iron-oxo species ($\text{Fe}^{\text{IV}}=\text{O}$, $E^0 = 1.3 - 2.0 \text{ V}$ vs. NHE)^{8,9}, and direct electron-transfer process (ETP, $E^0 = 0.6 - 1.2 \text{ V}$ vs. NHE)¹⁰⁻¹², which offer molecular-level selectivity owing to their moderate oxidation potentials. However, a critical bottleneck remains that $\text{Fe}^{\text{IV}}=\text{O}$ and ETP are strictly surface-confined, lacking the ability to detach from

¹School of Mechanical Engineering and Automation, Northeastern University, Shenyang, China. ²School of Chemical Engineering, Adelaide University, Adelaide, SA, Australia. ³School of Chemistry and Molecular Sciences, Anhui Normal University, Wuhu, China. ⁴Department of Chemistry, Tsinghua University, Beijing, China. ⁵These authors contributed equally: Ying Hu, Wei Ren. ⁶These authors jointly supervised this work: Wei Ren, Min Wang, Yongfa Zhu.

✉ e-mail: wei.ren@adelaide.edu.au; wangmin@me.neu.edu.cn; zhuyf@ahnu.edu.cn

the catalyst interface. This spatial constraint renders them highly susceptible to the accumulation of adsorbed intermediates, leading to rapid active-site poisoning and poor long-term stability in continuous flow systems. Consequently, there is an urgent need for a catalytic framework to generate migratory, highly selective reactive oxygen species (ROS).

Acetylperoxyl radical ($\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$) emerges as a promising candidate, effectively bridging the gap between radical and nonradical chemistry^{13,14}. Unlike conventional free radicals, such as $\cdot\text{OH}$ ($t_{1/2} \approx 10^{-3} \mu\text{s}$) and superoxide radical ($\text{O}_2^{\cdot-}$, $t_{1/2} \approx 10^{-6} \mu\text{s}$), $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ possesses an extended half-life ($t_{1/2} \approx 28 \mu\text{s}$) and demonstrates moderate reactivity ($E^0 = 1.6 \text{ V}$ vs. NHE) for the selective oxidation of target pollutants^{13–16}. Meanwhile, $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ can freely migrate into the interfacial zone, preventing catalyst deactivation, compared with surface-bound $\text{Fe}^{\text{IV}}=\text{O}$ or ETP. However, peracetic acid (PAA) is an asymmetric oxidant characterized by competing electronic pathways¹⁷. It typically undergoes a nucleophilic (reductive) activation route to yield acetate radical ($\text{CH}_3\text{C}(\text{O})\text{O}\cdot$, Eq. 1) or $\cdot\text{OH}$ (Eq. 2), whereas the desired electrophilic (oxidative) activation route to produce $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ (Eq. 3) is thermodynamically demanding and rarely achieved with traditional catalysts^{17–19}. To selectively generate $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$, most studies primarily highlight the role of Co(III) metal sites in PAA activation^{16,17,20}. To optimize this pathway, catalyst design typically focuses on the introduction of oxygen vacancies and the strategic modulation of Co valence state distributions²¹. Similarly, CuO has been utilized to promote $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ production by inducing Cu(II)/Cu(I) redox cycles²². However, a significant inherent limitation of these metal oxides is the inevitable formation of low-valent metal states, such as Co(II) and Cu(I), during the catalytic process, which subsequently activate PAA to generate substantial $\text{CH}_3\text{C}(\text{O})\text{O}\cdot$ (Eq. 1). This simultaneous formation of both $\text{CH}_3\text{C}(\text{O})\text{O}\cdot$ and $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ radicals creates a technical bottleneck, hindering the high-purity and selective generation of $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$.



Metal-free carbon catalysts, such as carbon nanotubes (CNTs), graphene, biochar, etc., have emerged as promising alternatives to metal-based catalysts for PAA activation^{23–25}. Among these carbonaceous frameworks, biochar offers distinct advantages for large-scale water remediation owing to its low cost, vast feedstock availability, and inherent environmental compatibility, rendering it an attractive and scalable platform^{26,27}. However, carbon catalysts are generally reported to favor the PAA nucleophilic activation pathway (Eqs. 1 and 2), producing $\text{CH}_3\text{C}(\text{O})\text{O}\cdot$ and $\cdot\text{OH}$ rather than $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ ²⁸. This mechanism preference stems from the inherent electronic nature of carbon surfaces, which are typically characterized by abundant sp^2 -hybridized π -electron networks that readily donate electrons to PAA²⁹. Furthermore, common surface nitrogen species (e.g., pyrrole and pyridine nitrogen), further reinforce this electron-rich character, promoting non-selective nucleophilic routes^{30–33}. Strategic defect engineering in carbon catalysts serves as an effective route to selective $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ generation³⁴. By disrupting the delocalized sp^2 π -conjugation network, such structural modifications attenuate the surface electron density, thereby breaking the nucleophilic pathway that typically leads to non-selective radical production. High-temperature annealing presents a robust strategy to achieve this goal by simultaneously stripping electron-donating nitrogen groups and facilitating the formation of intrinsic carbon defects. These structural perturbations reconfigure the electronic landscape, generating localized, electron-deficient active sites that increase the electron-accepting capacity (EAC) and

steer the reaction thermodynamics toward the desired PAA electrophilic activation route into $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ ^{35–38}.

Here, we report a series of defect-engineered biochar catalysts featuring 5-14-5 vacancy-pentagon motifs, synthesized via high-temperature annealing of nitrogen-containing agro-forestry biomass-derived precursors, including corn straw, sorghum straw, reed straw, sugarcane bagasse, and rose petal. This process simultaneously facilitates the removal of electron-donating nitrogen species and the introduction of intrinsic carbon defects, which disrupt π -conjugation to generate localized, electron-deficient active sites. Tailoring defect density and configuration through controlled pyrolysis promotes selective $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ generation, as confirmed by comprehensive material characterization, kinetic experiments, and density functional theory (DFT) calculations. The optimized catalyst demonstrates high $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ selectivity, robust degradation of pollutants in complex matrices, and long-term stability in continuous-flow reactors. Biological toxicity evaluation and life-cycle assessment (LCA) further validate its environmental safety and sustainability. Overall, this work establishes a scalable defect-engineering strategy to steer PAA activation toward solution-phase selective radical chemistry, offering a sustainable route for precision water purification and providing a framework for the rational design of selective oxidation systems.

Results

Structural evolution of biochar enriched with 5-14-5 pentagon-vacancy defects

The structural evolution of nitrogen-containing agro-forestry biomass-derived biochar is primarily driven by the thermal removal of nitrogen atoms and subsequent lattice reconstruction. Taking corn-stalk-derived biochar (CBC) as a representative example (Fig. 1a), annealing at temperatures from 900 to 1150 °C (yielding CBC-I to -IV) triggers in situ nitrogen elimination^{39,40}. The resulting physical morphologies and pore structures are detailed in Supplementary Text 1, Supplementary Figs. 1–5, and Supplementary Table 1. This chemical driving force was directly captured by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy (Fig. 1b). The transition from the N-containing samples (1.30 at.% CBC-I and 0.86 at.% CBC-II, Supplementary Table 2) to the N-depleted framework (0 at.% CBC-III, Supplementary Table 2) is initiated by the sharp attenuation of the shoulder at 286.6 eV (assigned to C=N π^* transitions), signaling the successful elimination of lattice-bound nitrogen^{30,41}. This process fundamentally modifies the electronic landscape, causing the aromatic C=C π^* resonance to shift from 285.1 eV to 285.4 eV, which reflects the localization of π -electrons as the continuous conjugated network is fragmented by nitrogen-removal-induced vacancies⁴¹. Furthermore, the graphitic exciton at 291.6 eV (a signature of long-range structural order) is markedly attenuated in CBC-III⁴¹. Together with the dramatic decline in spectral intensity across the C–C σ^* band at 292.7 eV, these features provide definitive electronic evidence for the fragmentation of the graphitic lattice into localized, defect-rich domains⁴². Quantitative analysis via X-ray photoelectron spectroscopy (XPS, Supplementary Figs. 6–9 and Supplementary Tables 2–4) and inductively coupled plasma mass spectrometry (ICP-MS, Supplementary Table 5) further confirms that lattice-bound nitrogen removal is the primary driver of defect generation, while the influence of metal content is negligible (see Supplementary Text 2).

This nitrogen-stripping process acts as a structural trigger, leading to significant macroscopic lattice expansion and reorganization. High-resolution transmission electron microscopy (HRTEM, Figs. 1c–f and Supplementary Figs. 1–6 in Supplementary Data 1) analysis confirmed the development of curved edges and disordered regions in response to these vacancy formations, with the interlayer spacing expanding from 0.37 nm in CBC-I to a maximum of 0.46 nm in CBC-III. This lattice distortion was further corroborated by X-ray diffraction (XRD, Fig. 1g), where the (002) reflection shifted significantly from

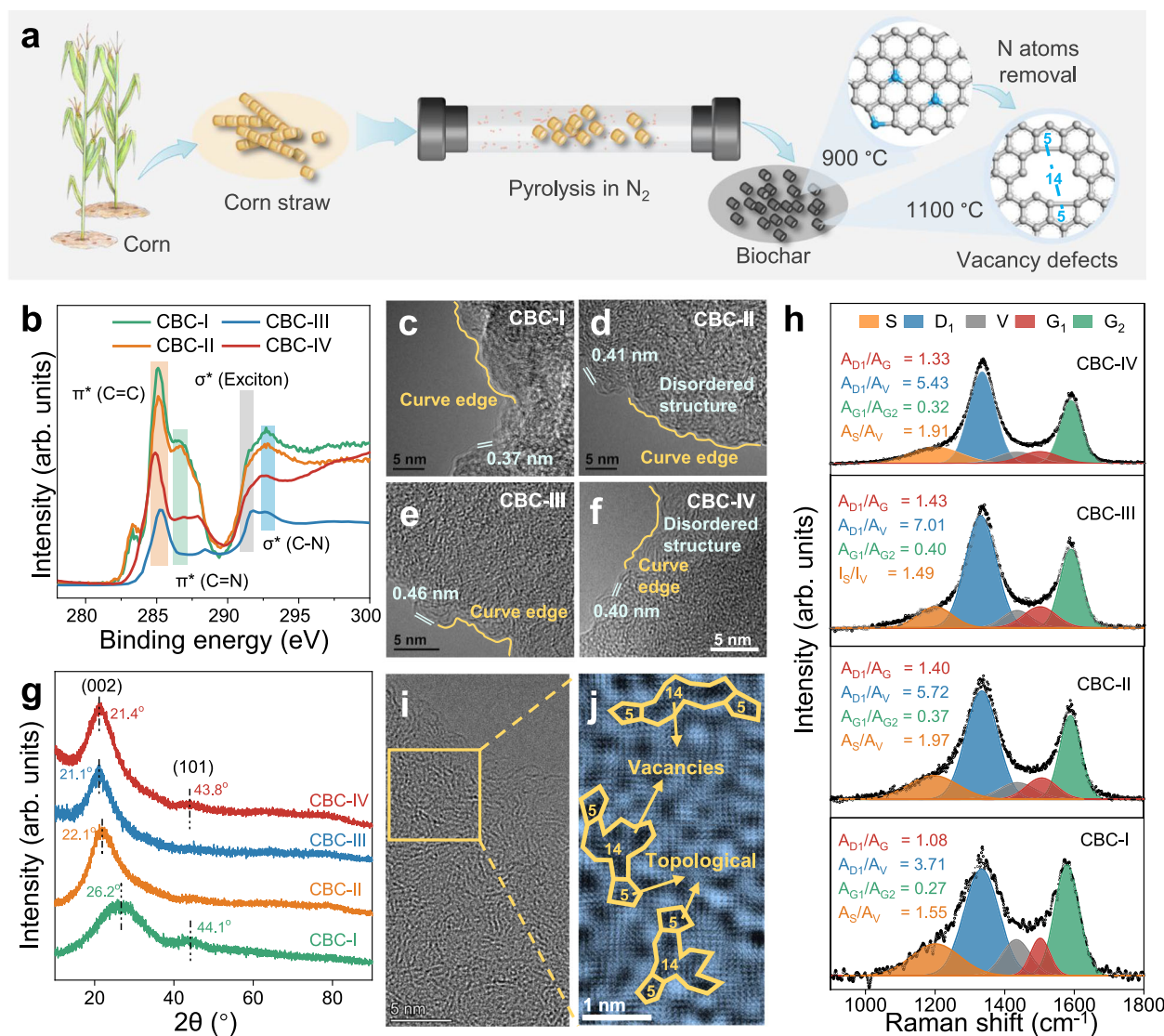


Fig. 1 | Synthesis and structural characterization of corn-stalk-derived biochar (CBC-X) catalysts. **a** Schematic illustration of the synthetic procedure for CBC-X, outlining the sequential stages of raw corn straw pretreatment, inert N_2 pyrolysis, and microstructural evolution from N-doped graphene-like domains (900 °C) to vacancy defect structures (1100 °C) via the removal of N atoms. **b** C K-edge near-edge X-ray absorption fine structure (NEXAFS) spectra of CBC-X. **c–f** High-resolution transmission electron microscopy (HRTEM) images of CBC-X. **g** X-ray

diffraction (XRD) patterns of CBC-X. **h** Raman spectra of CBC-X. **i** Aberration corrected scanning transmission electron microscopy (AC-STEM) image of CBC-III, and **j** the corresponding Fourier transform fitting result of CBC-III. TEM images presented in Fig. 1c–f, i and j were measured three times, and each experiment was independently repeated with consistent results. The unedited versions of the images for Fig. 1c–f, i and j are supplied in Supplementary Data 1. Source data are provided as a Source Data file.

26.2° to 21.1°, reflecting π -conjugation disruption and weakened interlayer van der Waals interactions⁴³. Notably, CBC-III exhibits the largest d -spacing (0.46 nm) and the lowest (002) diffraction angle (21.1°), confirming that the degree of lattice distortion and turbostratic character reached their peak in this sample.

To precisely define the nature of these distortions, Raman spectroscopy and aberration-corrected scanning transmission electron microscopy (AC-STEM) were utilized to provide a microscopic fingerprint of the defects. Deconvolution of the Raman spectra (Fig. 1h) identified five distinct bands (S, D₁, V, G₁, and D₂ bands), allowing for the evaluation of defect characteristics via four diagnostic ratios (A_{D1}/A_G , A_{D1}/A_V , A_{G1}/A_{G2} , and A_S/A_V), and their physicochemical assignments are detailed in Supplementary Text 3. From CBC-I to CBC-III, the A_{D1}/A_G and A_{D1}/A_V ratios increased from 1.08 and 3.71 (CBC-I) to 1.43 and 7.01 (CBC-III) (Supplementary Table 6), respectively, marking a shift from edge to vacancy-type defects. The simultaneous rise of the A_{G1}/A_{G2} ratio to 0.40 suggested the accumulation of pentagonal carbon rings

at vacancy sites⁴⁴. In CBC-IV (1150 °C), however, these ratios decreased, reflecting defect coalescence and partial graphitic restoration⁴⁵. Overall, the maximized ratios in CBC-III ($A_{D1}/A_V = 7.01$; $A_{G1}/A_{G2} = 0.40$) confirm a structure dominated by pentagon-enriched vacancy defects. This was corroborated by AC-STEM imaging, which clearly resolved 5-14-5 defect motifs (vacancy sites bonded with two adjacent pentagons) in CBC-III (Fig. 1i, j). These results collectively confirm that CBC-III possesses a turbostratic structure dominated by pentagon-enriched vacancy defects, engineered by the precise removal of nitrogen atoms.

Electronic landscapes and redox capacities of defect-rich biochars

The tailored structural reconstruction into 5-14-5 motifs profoundly alters the electronic landscape of the CBC framework. Initially, electrochemical impedance spectroscopy (EIS) was employed to evaluate the macroscopic charge-transfer kinetics. As shown in Fig. 2a, the charge-transfer resistance (R_{ct}) decreased from 156 Ω (CBC-I) to a

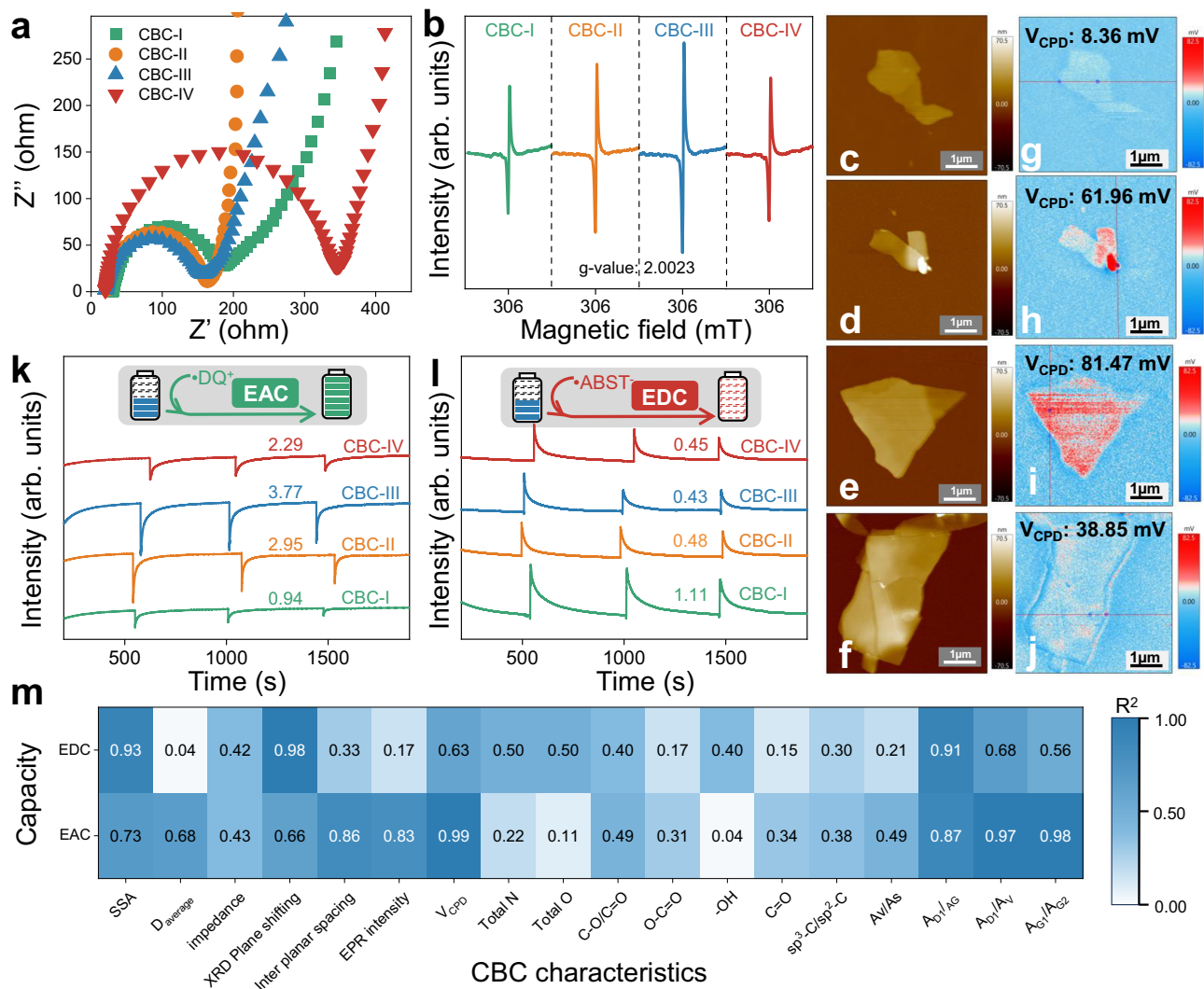


Fig. 2 | Electronic properties and electron transfer capacities of corn-stalk-derived biochar (CBC-X). **a** Electrochemical impedance spectroscopy (EIS) Nyquist plots of CBC-X. **b** Electron paramagnetic resonance (EPR) spectra of CBC-X. **c–f** Morphological characterization by atomic force microscope (AFM) of CBC-X, and **g–j** the corresponding surface potential difference (V_{CPD}) determined by Kelvin probe force microscopy (KPFM). **k** Chronoamperometric curves for the electron accepting capacity (EAC) of CBC-X (inset: schematic electron transfer pathway mediated by diquat dibromide monohydrate, DQ^+), and **l** chronoamperometric

curves for the electron donating capacity (EDC) of CBC-X (inset: schematic electron transfer pathway mediated by 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt, $ABTS^+$). **m** Heatmap illustrating the Pearson correlations between electron transfer capacities and various physicochemical characteristics of CBC-X. AFM images presented in Fig. 2c–j were measured three times, and each experiment was independently repeated with consistent results. Source data are provided as a Source Data file.

minimum of 138 Ω (CBC-III), indicating that the formation of vacancy-rich domains within the turbostratic lattice facilitates efficient electron transport. To probe the micro-electronic consequences of these defect sites, electron paramagnetic resonance (EPR) was measured. The intense resonance signal at $g = 2.0023$ (Fig. 2b) is attributed to carbon-centered π -type radicals originating from unpaired electrons localized at vacancy sites⁴¹. Crucially, the EPR signal intensity reaches its maximum in CBC-III, confirming the highest accumulation of unpaired spin density and localized electronic polarization within its defect-rich framework^{39,46}. These results substantiate that the 5-14-5 defect motifs act as electronic sinks, effectively localizing spin density and creating a highly polarized carbon framework to facilitate interfacial electron transfer.

Driven by the localized spin polarization inherently tied to the 5-14-5 motifs, the surface charge distribution is significantly modulated to enhance the electrophilic character of the catalysts. To visualize this structural influence on the electronic landscape, Kelvin probe force

microscopy (KPFM) was used to map the surface potential of the CBC samples (Fig. 2c–f). The measured Volta contact potential difference (V_{CPD}) followed the order: CBC-III (81.47 mV) > CBC-II (61.96 mV) > CBC-IV (38.85 mV) > CBC-I (8.36 mV) (Fig. 2g–j and Supplementary Fig. 10). The maximum V_{CPD} in CBC-III indicates that the enrichment of 5-14-5 topological defects creates a highly electron-deficient and positively polarized surface⁴⁷. This structure-driven polarization fundamentally governs the interfacial redox behavior of the catalysts, which was quantitatively assessed through the EAC (Fig. 2k) and electron donating capacity (EDC) (Fig. 2l) using diquat dibromide monohydrate (DQ^+) and 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt ($ABTS^+$) as redox probes, respectively^{48,49}. As the defect types of 5-14-5 motifs were optimized via annealing, the EAC increased initially from 0.94 mmol·e⁻·g⁻¹ (CBC-I) to a maximum of 3.77 mmol·e⁻·g⁻¹ (CBC-III), and then declined to 2.29 mmol·e⁻·g⁻¹ for CBC-IV (Fig. 2k), whereas the EDC followed an opposite trend (Fig. 2l). Notably, CBC-I was the only sample with

EAC < EDC (Supplementary Fig. 11), indicating a predominantly nucleophilic surface, whereas the other samples exhibited markedly stronger electrophilicity. In particular, CBC-III exhibited an EAC that was 8.7-fold greater than its EDC, signifying that the 5-14-5 defects trigger a profound transition of the carbon framework from a nucleophilic state to a highly electrophilic state.

To elucidate the structural origins of the EAC in CBCs, comprehensive correlation analyses were performed (Fig. 2m). The EAC exhibits robust positive correlations with Raman-derived ratios that are sensitive to topological reconstructions, specifically A_{D1}/A_V ($R^2 = 0.97$), A_{G1}/A_{G2} ($R^2 = 0.98$). These high structure-property correlations, alongside the clear linear trend observed with A_{D1}/A_G ($R^2 = 0.87$) (Supplementary Fig. 12a), suggest that electrophilicity is intimately associated with these specific vacancy defects (e.g., 5-14-5 defects). These findings are further corroborated by correlations with interlayer spacing ($R^2 = 0.86$, Supplementary Fig. 12b), EPR signal intensity ($R^2 = 0.83$, Supplementary Fig. 12c), and surface potential ($R^2 = 0.99$, Supplementary Fig. 12d), indicating a clear alignment between lattice distortion, defect-driven charge polarization, and the resulting electron-accepting capability⁴⁷. Notably, EAC showed no meaningful relationship with impedance, chemical functional groups, sp^3 fraction, or amorphous carbon fractions (Supplementary Figs. 13–S15). Furthermore, selective deactivation of surface oxygen groups produced negligible changes in EAC (Supplementary Text 4 and Supplementary Fig. 16), ruling out surface functionalities as the governing factor. Instead, the moderate correlations with surface area ($R^2 = 0.73$, Supplementary Fig. 17a) and pore size ($R^2 = 0.68$, Supplementary Fig. 17b) suggest that increased porosity enhances EAC by exposing a higher density of active defect sites. In contrast, EDC correlates strongly with the XRD (002) shift ($R^2 = 0.98$, Supplementary Fig. 18a), specific surface area ($R^2 = 0.93$, Supplementary Fig. 18b), and overall defect density ($R^2 = 0.91$, Supplementary Fig. 19a), but no clear trends with other parameters (Supplementary Figs. 19b–22). These results indicate that EDC originates from surface-accessible π -electron reservoirs and heteroatom modulation, while the EAC is primarily dictated by the 5-14-5 topological vacancy motifs.

The EAC of CBC-III exhibits superior performance, establishing a benchmark that surpasses reported values for similar materials (Supplementary Fig. 23 and Supplementary Table 7). In general, conventional biochars act predominantly as electron donors because their surface is typically rich in electron-donating oxygen-containing functional groups (e.g., hydroxyls) and relatively intact π -electron clouds that serve as electron reservoirs. Thus, most biomass-derived chars (e.g., wheat, cotton, and sawdust) show minimal electron-accepting capacity, whereas CBC-III exhibits an 8- to 40-fold increase in performance. Furthermore, CBC-III maintains a decisive lead over advanced engineered carbons, nearly doubling their capacities. These results suggest that the 5-14-5 pentagon-vacancy motifs are the fundamental drivers of this electronic transformation, successfully engineering high electrophilicity into a traditionally inert carbon lattice.

Selective generation of acetylperoxyl radical on defect-rich biochars

Since PAA activation can follow either a nucleophilic pathway toward $\bullet OH$ (Eq. 2) or an electrophilic pathway toward $CH_3C(O)OO\bullet$ (Eq. 3), the specific ROS generated provides direct evidence of the direction of interfacial electron transfer. Given the record-high EAC of CBC-III, identifying the dominant ROS is essential to verify whether the 5-14-5 electron sink can force a mechanism shift by accepting electrons from PAA. To test this hypothesis, EPR measurements were performed using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin trap in ethanol under nitrogen-purged conditions. All four CBC/PAA systems exhibited the characteristic quartet signals of the $DMPO - CH_3C(O)OO\bullet$ ($a_N = 13.9$ G, $a_{H\beta} = 8.8$ G, $a_{H\gamma} = 1.7$ G, Fig. 3a and Supplementary Fig. 24)²², with CBC-III showing the highest intensity. Notably,

additional $DMPO - \bullet OH$ signals appeared exclusively in the CBC-I/PAA system, whereas no $O_2^{\cdot -}$ or 1O_2 features were detected in any sample (Supplementary Fig. 25). To further verify the ROS in aqueous media, diisopropoxyphosphoryl-5,5-dimethyl-1-pyrroline-N-oxide (DIPPMPO) was employed. The CBC-III/PAA system displayed a distinct $DIPPMPO - CH_3C(O)OO\bullet$ spectrum ($a_N = 14.3$ G, $a_P = 53.0$ G, $a_{H\beta} = 12.2$ G, Fig. 3b). In contrast, the CBC-I/PAA system showed an additional $DIPPMPO - \bullet CH_3$ signal ($a_N = 15.2$ G, $a_P = 46.8$ G, $a_{H\beta} = 22.0$ G, Fig. 3b), consistent with $\bullet OH$ -induced secondary decarboxylation of PAA or acetic acid. Complementary liquid chromatography-mass spectrometry (LC-MS) analysis using 2,2,6,6-tetramethylpiperidiny-1-oxide (TEMPO) as a radical trapping agent further supported these findings^{5,19}. As shown in Fig. 3c–e, $CH_3C(O)OO\bullet - TEMPO$ adduct ($m/z = 232.12$) adducts were clearly detected in the CBC-III/PAA system, while no obvious $CH_3C(O)O\bullet - TEMPO$ adducts were observed (Supplementary Fig. 26).

To unambiguously identify the ROS and elucidate the role of the 5-14-5 motifs in PAA activation, comprehensive scavenging experiments and steady-state quantifications were performed. To decouple physical adsorption from chemical oxidation in the apparent removal, a solid-phase extraction procedure was performed prior to analysis, thereby confirming that bisphenol A (BPA) removal was strictly attributable to chemical oxidation. The sensitivity of the systems to various scavengers revealed fundamentally different activation modes (Supplementary Figs. 27–31). The CBC-I/PAA system was significantly affected by a wide range of quenchers, a behavior characteristic of the non-selective oxidation typically mediated by $\bullet OH$ (Fig. 3f). In contrast, only $CH_3C(O)OO\bullet$ -related scavenger Mn^{2+} exhibited a pronounced inhibitory effect on the CBC-III/PAA system (Fig. 3f). This specificity confirms the dominant role of $CH_3C(O)OO\bullet$ in the presence of highly electrophilic defects^{18,22}. While tert-butyl alcohol (TBA) suppressed BPA degradation in all systems, further investigation showed that TBA also impeded PAA consumption (Supplementary Fig. 31)¹⁹. This suggests that its inhibitory action reflects a non-selective disruption of the oxidant stability rather than the specific trapping of $\bullet OH$. In addition, detailed ROS quenching investigations are provided in Supplementary Text 5 and Supplementary Figs. 27–44, while the influence of catalyst dosage on the radical pathway is discussed in Supplementary Text 6, Supplementary Figs. 45 and 46.

To determine if the reaction occurs on the catalyst surface or in the bulk solution, four critical tests were performed. First, pre-mixing the catalyst with PAA prior to BPA addition substantially diminished oxidation efficiency (Supplementary Text 7 and Supplementary Fig. 47). This suggests that the reactive species generated during PAA activation are transient; in the absence of a target pollutant during the premixing stage, these species undergo self-quenching or dissipation rather than forming stable, surface-bound reactive complexes. Second, PAA consumption was found to be independent of the initial BPA concentration (Supplementary Fig. 48), indicating that PAA activation is a substrate-independent process rather than a substrate-induced ETP. Third, galvanic oxidation using catalyst-modified electrodes failed to remove BPA (Supplementary Fig. 49), further ruling out the catalyst-mediated ETP (Fig. 3g). Fourth, the presence of NaF (a surface-probing agent) failed to suppress BPA degradation or PAA consumption (Supplementary Fig. 50), suggesting that the reaction is not strictly confined to the catalyst interface⁵⁰. These results confirm that CBC-I activates PAA through mixed nucleophilic and electrophilic activation pathways, yielding both $\bullet OH$ and $CH_3C(O)OO\bullet$, whereas the 5-14-5 defect-rich CBC-III selectively drives the electrophilic activation pathway, producing $CH_3C(O)OO\bullet$ as the primary reactive species.

The steady-state concentrations of $CH_3C(O)OO\bullet$ ($[CH_3C(O)OO\bullet]_{ss}$) and $\bullet OH$ ($[OH]_{ss}$) were quantified using naproxen (NAP) (Supplementary Figs. 51 and 52) and NB as chemical probes (Supplementary Figs. 33 and 34)³⁴. In the electrophilic CBC-II/PAA, CBC-III/PAA, and CBC-IV/PAA systems, the $[CH_3C(O)OO\bullet]_{ss}$ values reached 1.74×10^{-11} M, 2.26×10^{-11}

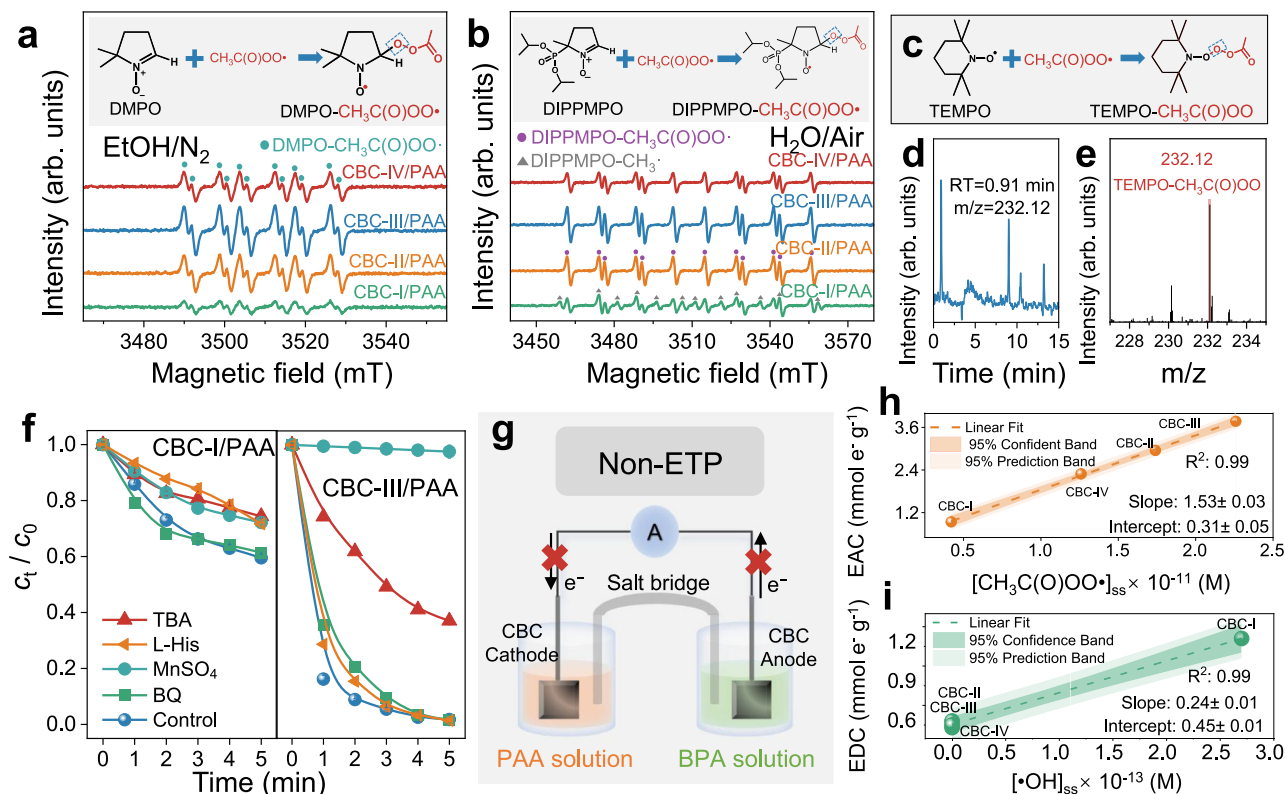


Fig. 3 | Identification of reactive species and investigation of reaction mechanisms. **a** Electron paramagnetic resonance (EPR) spectra of radical adducts trapped by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) in ethanol under N_2 -saturated conditions (inset: trapping mechanism of $CH_3C(O)OO\cdot$ by DMPO to form DMPO- $CH_3C(O)OO\cdot$). **b** EPR spectra of radical adducts trapped by diisopropoxyphosphoryl-5,5-dimethyl-1-pyrroline-N-oxide (DIPPMPPO) in aqueous solution (inset: trapping mechanism of $CH_3C(O)OO\cdot$ by $CH_3C(O)OO\cdot$ to form DIPPMPPO- $CH_3C(O)OO\cdot$). **c** Trapping reaction of $CH_3C(O)OO\cdot$ by 2,2,6,6-tetramethylpiperidinyl-1-oxide (TEMPO) to form TEMPO- $CH_3C(O)OO\cdot$ adduct. **d** Liquid chromatography-mass spectrometry spectra (LC-MS) at a retention time (RT) of 0.91 min ($m/z = 232.12$), and **e** corresponding LC-MS/MS of TEMPO- $CH_3C(O)OO\cdot$ adducts ($m/z = 232.12$) in

the CBC-III/peracetic acid (PAA) system. **f** Effects of various chemical quenchers on bisphenol A (BPA) degradation in CBC-I/PAA and CBC-III/PAA systems. Reaction conditions: [Catalyst] = 0.1 g L^{-1} , [PAA] = 0.22 mM , [BPA] = $44\text{ }\mu\text{M}$, initial pH = 6.0, Temp. = $23.0 \pm 2.0\text{ }^\circ\text{C}$, quencher concentrations: [TBA] = 132 mM , [p-BQ] = 0.22 mM , [L-His] = 4.4 mM , [MnSO₄] = 11 mM . **g** Schematic diagram of BPA removal in the two-chamber galvanic oxidation system with CBC-III-modified carbon electrodes. Linear correlations between steady-state concentrations of reactive species ($[CH_3C(O)OO\cdot]_{ss}$ **h** and $[•OH]_{ss}$ **i** and the electron transfer capacities (the electron accepting capacity (EAC), and electron donating capacity (EDC)). Error bars are the standard error values of three tests ($n = 3$). Source data are provided as a Source Data file.

M, and $1.26 \times 10^{-11}\text{ M}$, respectively (Supplementary Text 8 and Supplementary Fig. 52). In contrast, CBC-I generated markedly lower $[CH_3C(O)OO\cdot]_{ss}$ ($4.17 \times 10^{-12}\text{ M}$) together with detectable $[•OH]_{ss}$ ($2.70 \times 10^{-13}\text{ M}$) (Supplementary Fig. 52). This divergence arises from fundamentally different electronic structures. CBC-I possesses a nearly balanced electron-donating and electron-accepting character, enabling bidirectional electron flow with PAA and thus concurrent generation of $CH_3C(O)OO\cdot$ (electrophilic activation pathway) and $•OH$ (nucleophilic activation pathway). In sharp contrast, CBC-II, CBC-III and CBC-IV are strongly electrophilic ($EAC > 2.0\text{ mmol e}^- \text{ g}^{-1}$, $EAC/EDC = 5.09\text{--}8.77$), allowing them to preferentially withdraw electrons from PAA and promote the electrophilic activation route. A nearly perfect correlation between EAC and $[CH_3C(O)OO\cdot]_{ss}$ ($R^2 = 0.99$, Fig. 3h), as well as between EDC and $[•OH]_{ss}$ ($R^2 = 0.99$, Fig. 3i), provides quantitative evidence that the electron-transfer direction at the catalyst-PAA interface governs the dominance of electrophilic ($CH_3C(O)OO\cdot$) or nucleophilic ($•OH$) activation pathways.

Selective catalytic mechanism of peracetic acid into acetylperoxyl radical

The electrophilicity of the carbon matrix is physically defined herein as its localized electron-deficiency and the thermodynamic propensity of its electronic structure to accept external electrons. While the EAC provides a macroscopic measure of this property, its

electronic origin lies in the lowered Fermi level (E_F) and the increased density of unoccupied states near E_F . To establish the physical link between the 5-14-5 pentagon-vacancy motifs and the record-breaking EAC, density functional theory (DFT) calculations were conducted (the models as shown in Supplementary Fig. 53). Charge density mapping reveals that, compared with intact graphite (Fig. 4a), the presence of the 5-14-5 defect (Fig. 4b) markedly disrupts the electron density distribution, inducing significant localized charge polarization. Additionally, the density of states (DOS) further elucidates the electronic origin of the enhanced performance. The introduction of 5-14-5 defects effectively modulates the electronic structure of the carbon matrix, resulting in a significantly higher state density near the E_F . This enrichment of electronic states facilitates near-zero-energy transitions, thereby boosting both the electron-transfer efficiency and the intrinsic reactivity of the defective carbon. In addition, the *p*-band center of the defective carbon exhibits a pronounced upshift from -1.8 eV (intact graphite, Fig. 4c) to -1.3 eV (Fig. 4d). This migration toward E_F suggests an enhanced potential for orbital hybridization between the carbon framework and reactant molecules⁵¹. Furthermore, the work function (Φ) was calculated to evaluate the absolute energy position of the Fermi level relative to the vacuum level. The defective carbon exhibits a more negative E_F (-2.6 eV) and a higher Φ (1.78 eV , Fig. 4e) than pristine graphite ($E_F = -2.1\text{ eV}$, $\Phi = 1.45\text{ eV}$, Fig. 4f). This downward shift in E_F

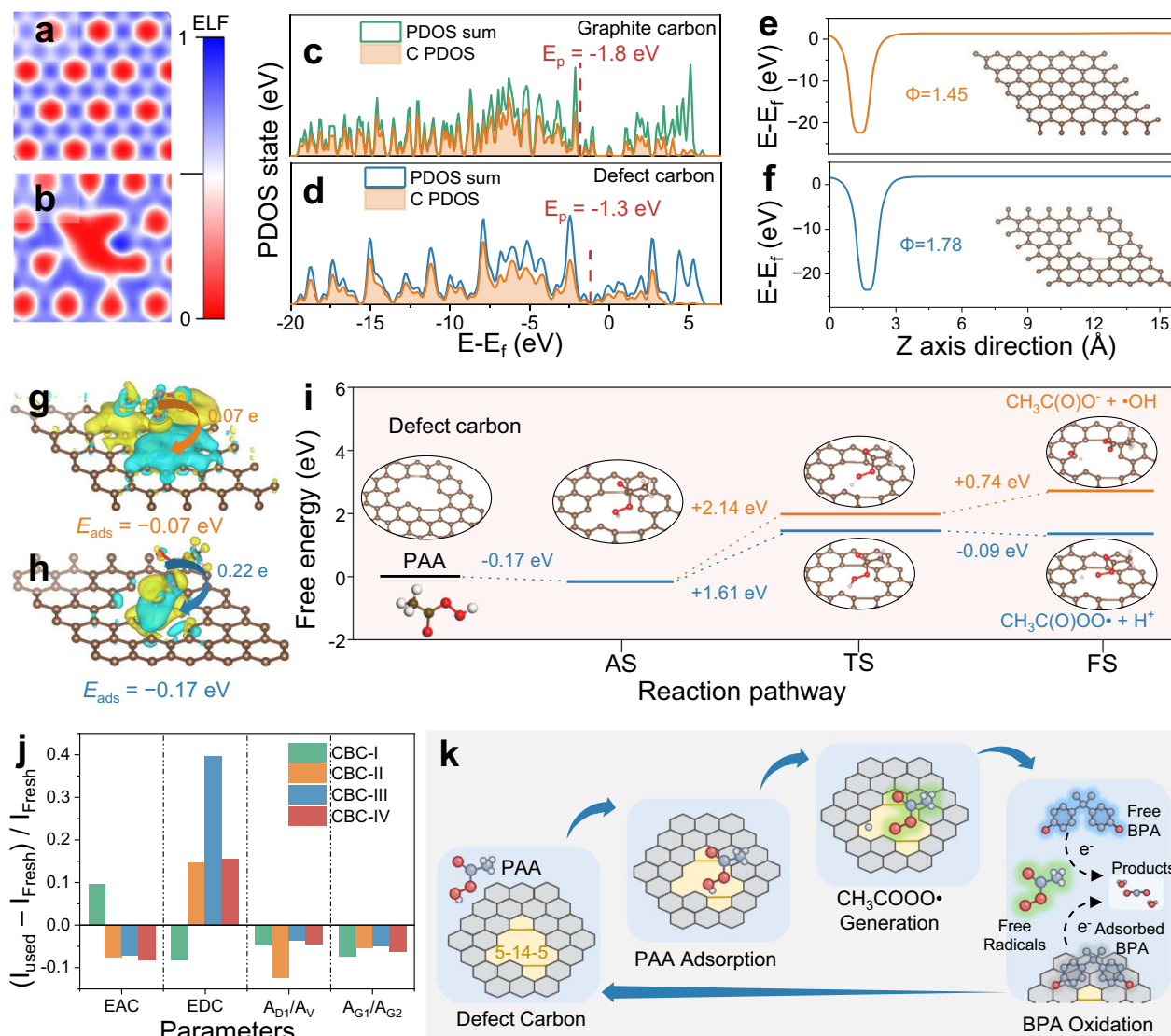


Fig. 4 | Theoretical insight into PAA activation and reaction mechanism. Electron localization function (ELF) maps of pristine graphite carbon **a** and defect carbon with a 5-14-5 topological defect **b**. Projected density of states (PDOS) and the calculated p -band center of graphite carbon **c** and defect carbon **d** relative to the Fermi level ($E-E_f$; Energy referenced to the Fermi level). The work function (Φ) graphite carbon **e** and defect carbon **f**. Differential charge density distributions of graphite carbon **g** and defect carbon **h** upon PAA adsorption. **i** Gibbs free energy profiles for PAA activation on defect carbon via two pathways: generation of

$\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ (blue) and $\cdot\text{OH}$ (orange). AS, TS, MS, and FS denote adsorption state, transition state, and final state, respectively. Brown, red, and white balls represent C, O, and H atoms, respectively. **j** Relative variations in electrochemical capacities (EAC, EDC) and Raman spectral ratios (A_{D1}/A_V , A_{G1}/A_{G2}) of CBC catalysts after reaction indicate structural stability. **k** Schematic illustration of the proposed mechanism for BPA oxidation in the CBC-III/PAA system. Gray, red, and white balls represent C, O, and H atoms. Gray hexagons represent graphite carbon. Source data are provided as a Source Data file.

signifies a deeper energy level that thermodynamically favors the acceptance of electrons from electron-rich species, reinforcing the role of the 5-14-5 defect as a potent electron sink.

To further decode the interfacial activation mechanism, the direction of charge transfer and adsorption energetics were analyzed. The adsorption affinity of PAA is significantly enhanced, as reflected by the shift in adsorption energy (E_{ads}) from -0.07 eV (Fig. 4g) on intact graphite to -0.17 eV (Fig. 4h) on the defective carbon surface, indicating that PAA molecules are much more firmly anchored at the vacancy sites. Furthermore, charge population analysis reveals that the number of electrons transferred from the PAA molecule to the carbon framework is substantially increased upon adsorption at the defect sites ($0.22 e$) compared to the intact lattice ($0.07 e$). This quantitative leap in both adsorption affinity and charge transfer confirms that

vacancy-induced electrophilicity effectively withdraws more electronic density from PAA.

To gain deeper thermodynamic insight into the catalytic process, the Gibbs free energies associated with the generation of reactive species during PAA activation were calculated. The introduction of vacancy defects fundamentally reconfigures the catalytic reaction coordinate, providing a thermodynamically spontaneous and kinetically favorable pathway that is absent in intact graphite. Specifically, the formation energies of $\cdot\text{OH}$ and $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ were compared on both intact graphite and defective carbon models. On the intact graphite (Supplementary Fig. 54), the formation of both $\cdot\text{OH}$ ($+0.67$ eV) and $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ ($+0.20$ eV) is thermodynamically prohibited due to their endothermic nature. In contrast, the presence of 5-14-5 defects dramatically alters the energetic landscape. Notably, the Gibbs free energy (ΔG) for $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ formation drops to a spontaneous value

of -0.09 eV (Fig. 4i), whereas the formation of $\bullet\text{OH}$ remains highly unfavorable ($+0.74$ eV). This stark energy contrast indicates that PAA activation is channeled exclusively toward the electrophilic pathway (Eq. 3) rather than the conventional nucleophilic route (Eqs. 1 and 2). Crucially, the adsorption energy of $\text{CH}_3\text{C}(\text{O})\text{OO}\bullet$ on the 5-14-5 defective motifs is marginal (-0.04 eV, Supplementary Fig. 55). This near-zero value is comparable to the ambient thermal fluctuation energy ($k_{\text{B}}T = 0.0257$ eV at room temperature)⁵². This implies that the weak binding interaction can be readily overcome by ambient thermal motion, ensuring that the catalytic reactions are not restricted to the catalyst interface. To further address the role of BPA adsorption in the catalytic process, interfacial charge transfer was examined through Bader charge analysis for both individual BPA adsorption and the BPA/PAA co-adsorption system (Supplementary Fig. 56). While single BPA molecules gain a minor charge of $0.05e$ from the defective carbon surface, this value remains approximate (0.07 e) when PAA is co-adsorbed. Meanwhile, PAA donates 0.18 e to the carbon lattice, confirming the role of the 5-14-5 motifs as a potent electron sink. The absence of direct electronic crosstalk or synergistic charge flow between BPA and PAA further substantiates that the reaction is driven by radical-mediated oxidation rather than a surface-dependent, non-radical ETP, even when the pollutant is pre-adsorbed on the catalyst surface.

Quantitative correlation analyses were further conducted to establish the structural determinants of radical generation. The $[\text{CH}_3\text{C}(\text{O})\text{OO}\bullet]_{\text{ss}}$ exhibits strong positive correlations with the Raman-derived ratios $A_{\text{D1}}/A_{\text{V}}$ ($R^2 = 0.96$ and Supplementary Fig. 57a), $A_{\text{G1}}/A_{\text{G2}}$ ($R^2 = 0.99$, Supplementary Fig. 57a), $A_{\text{D1}}/A_{\text{G}}$ ($R^2 = 0.87$). These are further supported by strong relationships with the (002) interplanar spacing ($R^2 = 0.86$, Supplementary Fig. 57b), EPR intensity ($R^2 = 0.84$, Supplementary Fig. 57c) and surface potential ($R^2 = 0.99$, Supplementary Fig. 57d). These correlations reinforce a strong structure-property-activity relationship, indicating that vacancy-induced electrophilicity and electronic localization highly trend with $\text{CH}_3\text{C}(\text{O})\text{OO}\bullet$ production. In contrast, the $[\bullet\text{OH}]_{\text{ss}}$ correlates strongly with parameters governing the EDC, such as the shifting of XRD (002) reflections and specific surface area (Supplementary Fig. 58).

The redox evolution of the CBC catalysts before and after PAA activation was examined to further elucidate the interfacial redox behavior on the CBC-X catalysts. As shown in Supplementary Fig. 59, CBC-I exhibited an increase in EAC and a concomitant decrease in EDC post-reaction. In contrast, a reverse trend was observed for CBC-II, CBC-III, and CBC-IV, where the EAC declined while the EDC increased (Fig. 4j). These divergent shifts underscore fundamentally different catalytic regimes: CBC-I likely participates in a balanced redox cycle involving both PAA reduction and oxidation, whereas the other three catalysts principally function as interfacial electron sinks that facilitate the electrophilic activation of PAA. Notably, CBC-III displayed the most significant variation, with its EAC decreasing by 0.27 $\text{mmol}\cdot\text{e}^{-}\cdot\text{g}^{-1}$ and its EDC increasing by 0.17 $\text{mmol}\cdot\text{e}^{-}\cdot\text{g}^{-1}$. This redox titration effect confirms that during the reaction, the vacant electronic states in CBC-III were progressively occupied by electrons withdrawn from PAA, leading to the high-flux generation of $\text{CH}_3\text{C}(\text{O})\text{OO}\bullet$. Furthermore, the post-reaction decreases in $A_{\text{D1}}/A_{\text{V}}$ and $A_{\text{G1}}/A_{\text{G2}}$ (Fig. 4j and S60) demonstrate that the 5-14-5 defect motifs were the primary active sites consumed or electronically modified during PAA activation.

In summary, the catalytic mechanism of PAA activation and BPA degradation in this system is illustrated in Fig. 4k. The introduction of specific vacancy-pentagon (5-14-5) motifs transforms the carbon lattice into a powerful electron sink. Within this catalytic cycle, PAA is first captured and anchored at these localized defect sites. The tailored electronic environment surrounding the vacancies induces a spontaneous interfacial electron transfer from the PAA molecule to the carbon framework. This electron-withdrawal effect triggers a selective electrophilic activation pathway, primarily generating $\text{CH}_3\text{C}(\text{O})\text{OO}\bullet$.

Consequently, the oxidative process extends beyond a strictly surface-confined regime, enabling radicals to target both surface-bound BPA molecules and those in the near-surface fluid zone, ensuring comprehensive oxidation across the solid-liquid interface.

Practical water purification and environmental implications. The CBC-X materials were evaluated for their Fenton-like catalytic performance in pollutant degradation. As shown in Fig. 5a, BPA was completely degraded within 5.0 min in the CBC-III/PAA system, whereas negligible oxidation occurred within 30 min when PAA, CH_3COOH , H_2O_2 or CBC-III was used individually (Supplementary Fig. 61a). Moreover, BPA degradation was negligible ($<0.52\%$) when CH_3COOH as oxidant was employed as the oxidant. Similarly, only marginal degradation (6.47%) was observed in the CBC-III/ H_2O_2 system under identical pH conditions (Supplementary Fig. 61b), a trend that remained consistent across a wide pH range (2–10) in buffer solutions (Supplementary Fig. 62). These results collectively confirm that PAA activation is indispensable for the efficient degradation of BPA. The inferior performance of H_2O_2 compared to PAA is primarily attributed to its high molecular symmetry and significantly higher O-O bond energy (213 $\text{kJ}\cdot\text{mol}^{-1}$ vs. 159 $\text{kJ}\cdot\text{mol}^{-1}$ for PAA)²⁴, which imposes a higher thermodynamic barrier for catalytic activation and subsequent ROS generation.

Among the four catalysts, CBC-III exhibited the highest PAA activation capability toward BPA degradation, featuring markedly accelerated reaction kinetics (Fig. 5a). The process followed pseudo-first-order kinetics, with CBC-III achieving the highest apparent rate constant ($k_{\text{obs}} = 0.92$ min^{-1}), which was 7.7, 1.4, and 2.9 times higher than that of CBC-I, CBC-II, and CBC-IV, respectively (Supplementary Fig. 63). After normalizing the kinetic data by catalyst dosage and oxidant concentration, the CBC-III/PAA system exhibited a high intrinsic activity, with a normalized kinetic constant ($K = 409.82$ $\text{min}^{-1}\cdot\text{M}^{-1}$, Supplementary Table 8). This value surpasses nearly all previously reported heterogeneous catalytic systems (Fig. 5b), highlighting the high efficiency of defect-engineered carbon in activating PAA. Furthermore, under identical conditions, the CBC-III/PAA system far outperformed eleven commercial biochar samples (Supplementary Figs. 64–66), confirming its superior catalytic reactivity and robustness.

To evaluate the universality of the defect-engineering strategy, corn stalk waste was harvested from diverse agricultural hubs across China. According to the 2024 corn stalk yield distribution (Fig. 5c), samples were selected from top-tier producing regions, including Heilongjiang (1st) and Jilin (2nd), alongside Liaoning and Jiangsu. Irrespective of their geographic origin, all regional biochars exhibited homogenous PAA activation efficiencies, achieving $>98.12\%$ BPA removal with k_{obs} tightly clustered at 1.00 ± 0.10 min^{-1} (Supplementary Fig. 67). Quenching analyses confirmed a unified mechanism pathway, where $\text{CH}_3\text{C}(\text{O})\text{OO}\bullet$ was exclusively identified as the primary ROS (Supplementary Figs. 68–74). Furthermore, the applicability of this strategy was extended to diverse nitrogen-containing biomass precursors (Fig. 5d and Supplementary Figs. 75–77), including sorghum straw (SS), reed straw (RS), sugarcane bagasse (SU), and rose petal (RP). Across all biomass types, biochars prepared under identical conditions to CBC-III consistently developed similar defect architectures, characterized by pentagon-enriched vacancy motifs ($A_{\text{D1}}/A_{\text{V}}$: 4.16–8.82, $A_{\text{G1}}/A_{\text{G2}}$: 0.28–0.42, Supplementary Fig. 78). These derivatives also displayed pronounced electrophilicity, with their EAC (1.01 – 5.49 $\text{mmol}\cdot\text{e}^{-}\cdot\text{g}^{-1}$, Supplementary Fig. 79) significantly surpassing their EDC (0.33 – 0.58 $\text{mmol}\cdot\text{e}^{-}\cdot\text{g}^{-1}$, Supplementary Fig. 79). Linear correlation analysis further revealed that the EAC is strongly positively correlated with the Raman descriptors of defect density, namely $A_{\text{D1}}/A_{\text{V}}$ ($R^2 = 0.99$, Supplementary Fig. 80a) and $A_{\text{G1}}/A_{\text{G2}}$ ($R^2 = 0.94$, Supplementary Fig. 80b), highlighting that the relative concentration of 5-14-5 motifs tightly scales with the EAC of catalysts. This robust

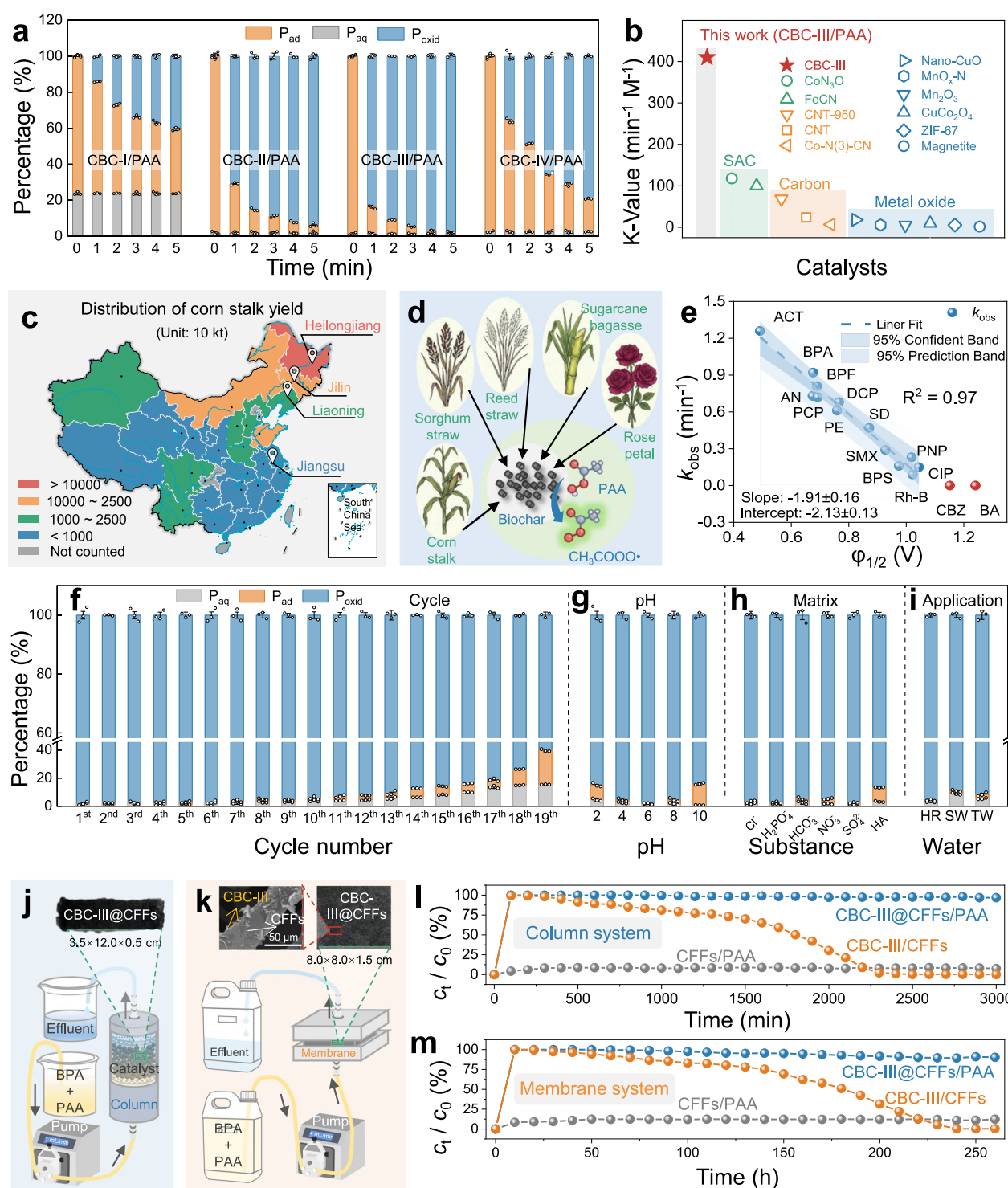


Fig. 5 | Practical application potential and universality of CBC-III/PAA system.

a Mass balance of BPA removal in four CBC systems, partitioning the contributions of oxidation (P_{oxid}), adsorption (P_{ad}), and the remaining aqueous phase (P_{aq}).

b Comparison of normalized kinetic constant (K -value) with other reported PAA-based Fenton-like catalysts (Detailed information is available in Supplementary Table 8 in Supplementary information).

c Geographic distribution of corn stalk yields in China (data from the National Bureau of Statistics, 2024; the base map of China was quoted from the Ministry of Natural Resources of the People's Republic of China (<http://bzdt.ch.mnr.gov.cn/>), under the official Map Approval Number: GS(2016)2923).

d Illustration of the universal application of the N-removal strategy for defect-enriched biochar preparation.

e Linear correlation between the half-wave potentials ($\phi_{1/2}$) of organic pollutants and their observed degradation rate constants (k_{obs}).

f Reusability over 19 cycles and **g** the impacts of initial pH, **h** co-

existing water matrices, and **i** real-world water samples (HR: Hunhe River; SW: Sewage Water; TW: Tap Water). Reaction conditions: [Catalyst] = 0.1 g L^{-1} , [PAA] = 0.22 mM , [BPA] = $44 \text{ }\mu\text{M}$, initial pH = 6.0, Temp. = $23.0 \pm 2.0 \text{ }^{\circ}\text{C}$. Schematic diagrams of the continuous-flow column system **j** and membrane system **k**; the inset in **k** shows SEM images of the CBC-III-coated cotton fiber films (CFFs). **l** Long-term BPA degradation performance in the continuous-flow column system. Reaction conditions: flow rate = 1 mL min^{-1} , catalyst loading = 0.02 g (if needed), [PAA] = 0.22 mM , [BPA] = $44 \text{ }\mu\text{M}$, Hydraulic retention time = 5.0 min , Temp. = $23.0 \pm 2.0 \text{ }^{\circ}\text{C}$. **m** Long-term BPA degradation performance in the continuous-flow membrane system. Reaction conditions: flow rate = 4 mL min^{-1} , catalyst loading = 0.08 g (if needed), [PAA] = 0.22 mM , [BPA] = $44 \text{ }\mu\text{M}$, Hydraulic retention time = 12.5 min , Temp. = $23.0 \pm 2.0 \text{ }^{\circ}\text{C}$. The error bars represent the standard deviation of three replicate tests. Source data are provided as a Source Data file.

structure-property relationship ensured the selective generation of $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ during PAA activation, as strongly validated by Mn^{2+} -induced quenching experiments (Supplementary Fig. 81) and DIMMPO-trapped EPR measurements (Supplementary Fig. 82). Such performance consistency indicates that the formation of 5-14-5 pentagon-vacancy motifs is an intrinsic structural reconfiguration driven by thermal nitrogen removal, rather than a precursor-specific phenomenon. The abundant, diverse nitrogen-containing agroforestry biomass waste, combined with this robust catalytic reproducibility, underscores the immense potential of this technology for large-scale, decentralized water purification.

Driven by the intrinsically selective oxidation behavior of $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$, the CBC-III/PAA system exhibited high reactivity toward electron-donating pollutants, whereas molecules bearing electron-withdrawing groups remained largely inert. The selectivity was quantitatively captured by the strong linear relationship between k_{obs} and the half-wave potential ($\phi_{1/2}$) of the pollutants (Supplementary Figs. 83–86). As shown in Fig. 5e, when $\phi_{1/2} < 0.9$ V, $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ readily abstracts electrons to initiate oxidation, although the kinetics still depend on the electron-donating strength of the substrates. In contrast, no oxidation occurred for $\phi_{1/2} > 1.15$ V, as the moderate oxidizing power of $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ is insufficient to withdraw electrons from highly electron-deficient compounds. This selectivity resembles other nonradical oxidants, yet the underlying kinetic mechanism is fundamentally distinct. To mechanistically differentiate $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ oxidation from the interfacial ETP, their kinetic signatures were compared. In ETP systems, the reaction rate is governed by the interfacial electron-transfer step; thus, k_{obs} typically grows exponentially with $\phi_{1/2}$, yielding a linear $\ln k_{\text{obs}}-\phi_{1/2}$ correlation, which is a hallmark of a surface-confined and mass-transfer-limited process^{53–55}. In sharp contrast, $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ exhibits a linear $k_{\text{obs}}-\phi_{1/2}$ dependence, indicating that its oxidation is not strictly confined to the catalyst interface, but is instead free from interfacial charge-transfer limitations and controlled primarily by intrinsic chemical reactivity. The markedly steeper $k_{\text{obs}}-\phi_{1/2}$ slope further highlights the intrinsically faster effective reaction rate of $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ relative to ETP. This mechanism divergence is quantitatively reflected in the normalized kinetic constants $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ -based oxidation exhibits constant values far exceeding those of heterogeneous ETP processes (Supplementary Table 9 and Supplementary Fig. 87), underscoring the superior reactivity and efficiency of selective $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ oxidation.

The defect-engineered CBC-III catalyst exhibited high operational robustness under conditions representative of real-world water treatment. The catalyst maintained a highly efficient performance over 19 consecutive cycles (Fig. 5f). While a gradual decline in intrinsic oxidation emerged after the 12th cycle due to progressive passivation of active sites, a substantial total pollutant removal of approximately 85% was preserved at the 19th run, with catalytic oxidation still contributing over 60%. Furthermore, the CBC-III/PAA process demonstrated excellent stability across a broad pH range (2.0–10.0) in the non-buffered system (Fig. 5g). Owing to the inherent buffering effect of byproduct acetic acid, the solution pH (initially ranging from 4.0 to 10.0) consistently shifts toward and stabilizes at approximately 4.76, which aligns with its pK_a value (Supplementary Fig. 88). To explicitly exclude this potential interference, additional experiments were performed using 10 mM phosphate buffers to maintain a constant pH throughout the process (Supplementary Fig. 89). The BPA adsorption capacity of CBC-III remained consistently stable in both buffered and unbuffered systems, with no significant fluctuations observed within the pH range relevant to the PAA activation process (Supplementary Figs. 90 and 91). As shown in Supplementary Fig. 92, under buffered conditions, a noticeable residual of adsorbed BPA was observed on CBC-III in strongly acidic environments ($\text{pH} \leq 3.75$). This kinetic retardation is primarily attributed to the high concentration of protons,

which shifts the equilibrium of PAA electrophilic activation (Eq. 3). The suppressed $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ production at low pH leads to a decreased oxidation rate, resulting in the observed BPA residuals on the CBC-III surface. Thus, the buffered system significantly favors BPA oxidation under near-neutral and alkaline conditions ($\text{pH} \geq 5.98$). Similarly, high performance (>90% BPA oxidation efficiency) was sustained in the presence of diverse background matrices, including inorganic anions and natural organic matter (Fig. 5h), as well as within various real-world water matrices such as tap, river, and sewage waters (Fig. 5i).

To assess device-level operability, CBC-III was immobilized on cotton fiber films (CFFs) and integrated into two continuous-flow reactors, column (Fig. 5j and Supplementary Fig. 93) and membrane (Fig. 5k and Supplementary Fig. 94) configurations. Both systems delivered stable, high-efficiency purification, achieving 96.8% removal over 50 h in the column system (Fig. 5l) and >90% removal for 260 h in the membrane system (Fig. 5m) under uninterrupted operation. In contrast, in the absence of PAA, the CBC-III/CFFs alone systems reached adsorption breakthrough at only 500 min (column) and 149 h (membrane), respectively, and the effluent BPA concentrations failed to meet treatment standards (1.0 $\mu\text{g/L}$, GB/T 28113-2011, China) as the adsorption sites approached saturation. Mass balance analysis confirmed that in these control groups, the removed BPA was almost (>95%) enriched on the CBC-III/CFFs surface (Supplementary Fig. 95 and Supplementary Text 9). However, for the CBC-III/CFFs/PAA catalytic system, post-reaction analysis revealed that less than 2.0% of the initial BPA could be extracted from the exhausted catalysts, confirming that catalytic degradation, rather than physical adsorption, dominates the pollutant removal process (Supplementary Fig. 95). A noticeable decrease in Raman-based defect density descriptors was observed (Supplementary Fig. 96), with $A_{\text{D1}}/A_{\text{V}}$ and $A_{\text{G1}}/A_{\text{G2}}$ dropping from 7.01 and 0.40 (Fresh CBC-III) to 4.38 and 0.34 (after reaction), respectively. These values are comparable to those of the adsorption-only sample ($A_{\text{D1}}/A_{\text{V}} = 4.29$, $A_{\text{G1}}/A_{\text{G2}} = 0.36$, Supplementary Fig. 96). Concurrently, the EAC decreased from 3.77 to 3.46. Notably, when the operation was extended toward 300 h, the removal efficiency declined further even in the absence of significant BPA accumulation (Supplementary Fig. 97), implying that the persistent coverage by recalcitrant intermediates is the primary cause of site deactivation. To address this, thermal annealing was employed as a regeneration strategy. Experimental results demonstrated that high-temperature treatment successfully removed the surface-bound species, restoring the EAC, defect density, and catalytic activity to levels nearly identical to the fresh CBC-III (Supplementary Fig. 98). Concurrently, batch recycling tests optimized the thermal regeneration temperature, demonstrating that the 800 °C treatment successfully exceeded 70 cumulative cycles across three regeneration rounds, significantly outperforming the 600 °C and 1100 °C counterparts (Supplementary Fig. 99). This temperature-dependent remediation behavior originates from the distinct fates of surface intermediates: lower temperatures (600 °C) are insufficient for intermediate decomposition, whereas excessively high temperatures (1100 °C) likely prompt destructive embedding of residual intermediates into vacancies, clogging the active sites⁵⁶. These results underscore that effective remediation relies on a finely balanced thermal environment to preserve the joint cyclability of surface defects and electronic features. This optimal threshold successfully maintains this structural-electronic integrity, enabling the 5-14-5 motifs to remain intact and guaranteeing sustained, long-term performance for practical, large-scale water purification.

Beyond high efficiency and scalability, the CBC-III/PAA system achieves a profound reduction in BPA-associated toxicity by fundamentally reconfiguring the degradation trajectory of organic pollutants. Unlike the non-selective aromatic hydroxylation and complex multi-hydroxylated derivatives typically associated with $\cdot\text{OH}$ pathways, $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ demonstrates a highly selective electrophilic attack mechanism. Specifically, $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ initiates a targeted attack on the

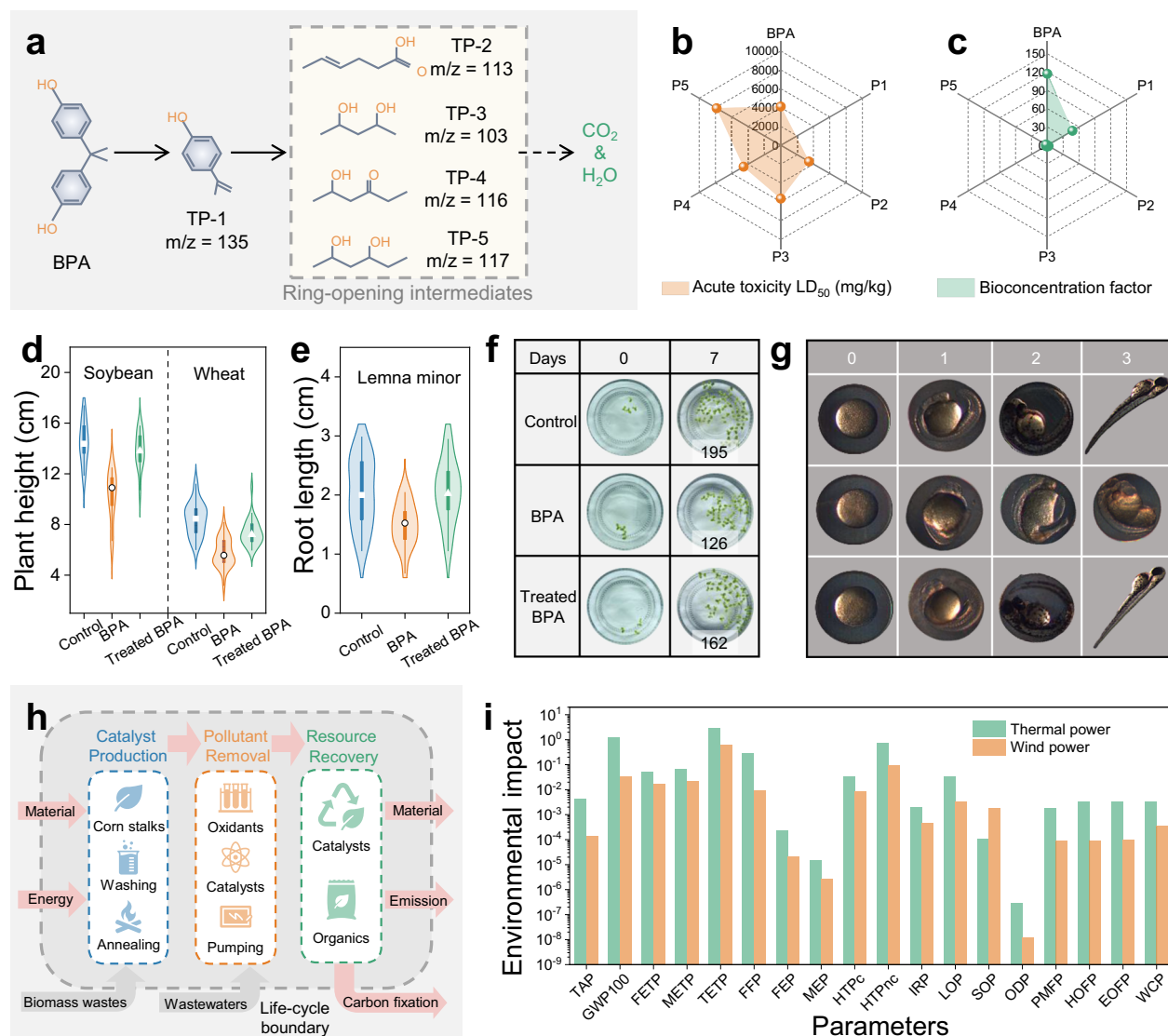


Fig. 6 | Degradation pathways and environmental impact assessment of the CBC-III/PAA system. **a** Proposed degradation pathways of BPA in the CBC-III/PAA system. Evaluation of environmental risks through calculated acute toxicity (LD₅₀) **b** and bioconcentration factors **c** of BPA and its transformation products. Bio-toxicity assessment: plant height of soybean and wheat **d**, root length of *Lemna minor* **e** (the center line indicates the median, the box bounds indicate the 25th and 75th percentiles, and the whiskers indicate the minimum to maximum range), and representative photographs of *Lemna minor* **f** and zebrafish embryos **g** cultured in

pure water (Control), raw BPA solution (BPA), and treated BPA solution (Treated BPA). **h** Defined system boundary for treating 60 L of BPA-contaminated wastewater in the life-cycle assessment (LCA) study. **i** Comprehensive environmental impact categories for BPA treatment powered by thermal versus wind energy. Detailed definitions of all parameters are provided in Supplementary Text 10 in Supplementary Information. The error bars represent the standard deviation of three replicate tests. Source data are provided as a Source Data file.

quaternary carbon bridge of the BPA molecule (Fig. 6a). This surgical skeleton cleavage yields the primary intermediate TP-1 (Supplementary Fig. 100 and Supplementary Table 10), which effectively dismantles the estrogenic core (the structural basis for its endocrine-disrupting effects) at the earliest stage of the reaction. This targeted breakdown is followed by rapid ring-opening into benign, low-toxicity aliphatic fragments (TP-2 - TP-5) and ultimate mineralization into CO₂ and H₂O. Furthermore, the neutralization of ecological risk was confirmed through quantitative modeling and bioassays. Predictive toxicity modeling (T.E.S.T., Supplementary Table 11, Fig. 6b, c, and Supplementary Fig. 101) confirmed a significant reduction in overall toxicity⁵⁷. Hydroponic assays showed that treated BPA solutions restored the normal growth of soybean and wheat seedlings (Fig. 6d; Supplementary Figs. 102 and 103), while *Lemna minor* exhibited markedly improved biomass (Supplementary Fig. 104), root development (Fig. 6e), and frond proliferation (Fig. 6f). Zebrafish embryo

assays further demonstrated complete recovery of normal embryonic development, in stark contrast to severe developmental inhibition observed with untreated BPA (Fig. 6g and Supplementary Fig. 105). These results confirm that CBC-III/PAA not only removes BPA but also neutralizes its ecological risk.

A life-cycle assessment (LCA) identified operational electricity use as the dominant environmental burden across the catalyst entire lifecycle (Fig. 6h)⁵⁸. To substantiate this, the assessment was conducted using a “cradle-to-grave” system boundary, covering raw material extraction, synthesis, transportation, and final disposal. The functional unit was set as the treatment of 60 L of BPA-containing wastewater (10 mg/L), utilizing a combination of laboratory-derived foreground data and Ecoinvent 3.9.1 background data (Supplementary Text 10). Nevertheless, all impact categories, including global warming potential, terrestrial ecotoxicity, fossil fuel depletion, and human non-carcinogenic toxicity, were substantially lower than

those of conventional Fenton-like processes (Tables S12–S16; Supplementary Figs. 105 and 106)⁵. While biomass recycling inherently facilitates carbon sequestration, the energy-intensive high-temperature annealing required for catalyst synthesis imposes a substantial carbon footprint. In our baseline scenario, this thermal demand partially nullifies the environmental gains. However, by transitioning from grid electricity to wind-powered energy for the annealing process, the system's global warming potential (GWP) is drastically mitigated. By integrating the long-term carbon storage capacity of the biochar framework and the resource recovery of by-product (acetic acid), the system ultimately achieves a net-negative GWP (Fig. 6i), showcasing its viability as a sustainable, carbon-negative solution for water treatment.

Discussion

In summary, this work provides a universal nitrogen-removal strategy for fabricating 5-14-5 vacancy-enriched biochars, enabling precise control over the PAA activation pathway for $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ generation. The nitrogen-removal-induced structural reconstruction proved highly versatile, enabling the consistent production of high-performance catalysts from geographically diverse nitrogen-containing agro-forestry biomass waste. Theoretical and experimental analyses reveal that these specific topological defects reshape the carbon framework into a powerful electronic sink by downshifting the Fermi level and upshifting the p -band center. This electronic modulation induces spontaneous interfacial electron transfer from PAA to the catalyst, rendering the electrophilic activation pathway for $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ generation thermodynamically favorable while suppressing traditional electron-accepting routes. Unlike nonselective $\cdot\text{OH}$ oxidation, the generated $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ induces a highly selective cleavage of the quaternary carbon bridge in BPA, rapidly dismantling its estrogenic core and ensuring complete detoxification as validated by multi-trophic bioassays. Furthermore, the system maintained > 90% BPA oxidation efficiency over a 260-h continuous operation with high resistance to complex water matrices. Combined with a scenario-dependent net-negative carbon footprint, highly contingent upon wind-powered energy, permanent biochar carbon storage, and by-product recovery credits, this strategy offers a robust and sustainable solution for advanced, decentralized water purification.

Methods

Chemicals and reagents

Detailed information regarding chemicals and reagents is provided in SI Appendix, Supplementary Text 11.

Catalysts preparation

Corn straws were obtained from a local farm (Shenyang city, Liaoning province, China) and cleaned using a dilute HCl solution (2.4 M). The cleaned straws were then pyrolyzed under a nitrogen atmosphere at temperatures ranging from 900 °C to 1150 °C for 2 h with a heating rate of 3 °C min⁻¹. Upon cooling to ambient temperature, the corn straw-derived biochar (CBC-X) catalysts, containing intrinsic carbon defects, were obtained without further treatment. The samples synthesized at 900, 1000, 1100, and 1150 °C were denoted as CBC-I, CBC-II, CBC-III, and CBC-IV, respectively. To assess the generalizability of the defect-engineering strategy, five biochars were also prepared using corn stalks harvested from various Chinese provinces, including Heilongjiang province (BC-1), Jilin province (BC-2), Jiangsu province (BC-3), Liaoyang city, Liaoning province (BC-4) and Chaoyang city, Liaoning province (BC-5) under the same preparation process as CBC-III. Furthermore, to verify the applicability of the defect-engineering strategy, other four biomass precursors including sorghum straw (SS), reed straw (RS), sugarcane bagasse (SU), and rose petal (RP) were obtained

from a local market to prepare biochar under the same preparation process as CBC-III.

Characterization methods

The C K-edge (284 eV) X-ray absorption spectra (XAS), specifically the X-ray absorption near-edge structure (XANES), for the CBC-I, CBC-II, and CBC-IV samples were collected in total electron yield (TEY) mode on the VUV and Soft X-ray beamline at the Singapore Synchrotron Light Source (SSLS). Concurrently, the C K-edge XANES spectra of the CBC-III sample were recorded at beamline TLS07A1 of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were acquired using a high-resolution FEI Titan G2 60-300 microscope. Electron spin resonance (EPR) spectra were recorded on a JEOL JES-FA200 spectrometer. Additional characterization details for the catalysts are provided in the SI Appendix, Supplementary Text 12.

Catalytic performance experiments

The catalytic degradation of BPA (44 μM) was conducted in a 100 mL reaction volume within a 250 mL glass reactor using 0.25 mM PAA and 0.1 g/L CBC-X under continuous magnetic stirring. The initial pH of the distilled water system was approximately 6.0 without further adjustment, and the pH values were precisely regulated using 0.1 M NaOH/H₂SO₄ solution for other pH conditions.

CBC-X catalyst (0.1 g/L) was added to bisphenol A (BPA) solution (100 mL, [BPA]₀ = 44 μM) under continuous magnetic stirring for 30 min to achieve adsorption equilibrium. At designated time intervals, 1.0 mL solution was collected and filtered through a 0.22 μm polytetrafluoroethylene (PTFE) membrane to separate the catalyst powder. The filtered solution was analyzed on UPLC to determine the aqueous concentration of BPA ([BPA]_{aq}) (Eq. 4). The corresponding molar fraction was denoted as P_{aq} .

After the adsorption equilibrium was reached, the BPA oxidation reaction was initiated by adding 0.22 mM peracetic acid (PAA). At the specified time, the reaction was quenched with an excess of sodium thiosulfate. The concentration of degraded BPA solution after the catalysts were separated via filter was measured on UPLC to obtain P_{aq} . At designated time intervals during the adsorption or degradation experiments, the post-reaction catalyst was separated from the solution by vacuum filtration. Subsequently, the separated catalyst was transferred into 100 mL of methanol solution, and continuous magnetic stirring was carried out for 60 min to elute the potentially residual BPA from the catalyst surface into the methanol solution. To ensure the accuracy of the quantification, the measured concentration of BPA in the methanol extract ([BPA]_{ad}) was corrected by dividing it by the predetermined recovery rate (η > 95%) to determine the actual adsorbed amount ([BPA]_{ad}, Eq. 5). This adjusted concentration was then utilized to calculate the molar fraction of BPA adsorbed on the catalyst surface (P_{ad} , Eq. 6). Finally, the oxidation removal efficiency (P_{oxid}) can be obtained via Eq. 7

$$P_{\text{aq}} = [\text{BPA}]_{\text{aq}} / [\text{BPA}]_0 \times 100\% \quad (4)$$

$$[\text{BPA}]_{\text{ad}} = [\text{BPA}]'_{\text{ad}} / \eta \quad (5)$$

$$P_{\text{ad}} = [\text{BPA}]_{\text{ad}} / [\text{BPA}]_0 \times 100\% \quad (6)$$

$$P_{\text{oxid}} = 100\% - P_{\text{ad}} - P_{\text{aq}} \quad (7)$$

The procedures of the other organic adsorption and degradation experiments were the same as those of BPA adsorption and degradation.

For the stability tests, the used catalysts were collected after each cycle and washed with deionized water several times, subsequently dried in a vacuum oven at 60 °C.

Analytical details for pollutant detection, reactive species quantification, and probe experiments are listed in SI Appendix, Supplementary Text 13 and Supplementary Table 17. The reactive species concentrations and probe experiments are listed in SI Appendix, Supplementary Text 14 and Supplementary Text 15. Electrochemical analyses, including EAC and EDC testing, are detailed in SI Appendix, Supplementary Text 16. Toxicity testing experiments and life cycle assessment are listed in SI Appendix, Supplementary Text 17 and Supplementary Text 10.

Toxicity assessment

The toxicity was evaluated using the zebrafish embryo toxicity test, the *Lemna minor* growth inhibition test, and seed germination and root elongation tests (SI Appendix, Supplementary Text 17). All zebrafish experiments were conducted in accordance with the guidelines of the Association for Assessment and Accreditation of Laboratory Animal Care International (AAALAC) and the China Laboratory Animal Administration. This study was approved by the Laboratory Animal Welfare and Ethics Committee of Shenyang SYRICI Testing Co., Ltd., Safe Evaluation Center, under license No. B2025001.

Computational methods

In this work, DFT calculations were performed by using the Vienna ab initio simulation package (VASP) (4.4.4). The simulations are based on density-functional theory (DFT) and the PBE generalized gradient approximation (GGA) function to describe the exchange-correlation energy. First, the perfect graphite and defect graphite structures were established, and a structural configuration was obtained through structural relaxation. The energy cut-off and Monkhorst-Pack k-point grid settings are 450 eV and $3 \times 3 \times 1$, respectively. During the geometry optimization process, the convergence tolerance is set to an energy of 1×10^{-5} eV per atom and a maximum force of $0.03 \text{ eV } \text{\AA}^{-1}$. For the construction of the surface model, a vacuum of $15 \text{ \AA}$ is used to eliminate interactions between the periodic images. The CI-NEB method is used to explore transitional states and improve the accuracy of force calculation by relaxing the structure to 10^{-7} . The optimized atomic coordinates (in VASP CONTCAR format) for the ten computational models and the final ELF files of defect carbon and graphite carbon are provided in Supplementary Data 2.

The adsorption energy (E_{ads}) is calculated as follow:

$$E_{\text{ads}} = E_{\text{tot}} - E_{\text{slab}} - E_{\text{PAA}} \quad (8)$$

E_{tot} and E_{slab} are the energy of the base adsorbed PAA, and the energy of the substrate, respectively, and E_{PAA} is the energy of the PAA molecule.

The Gibbs free energy is calculated as follows:

$$G = H - TS = E_{\text{tot}} + E_{\text{ZPE}} - T\Delta S \quad (9)$$

where E_{tot} is the energy of the optimized structure and ΔZPE and $T\Delta S$ were the change in the zero point energy and entropy at room temperature ($T = 298.15 \text{ K}$).

Statistics and reproducibility

All performance experiments were performed in triplicate ($n = 3$), and results are expressed as mean $\pm$ standard deviation. Linear regression analyses were carried out to determine the slopes and intercepts (reported as mean $\pm$ standard errors), along with the corresponding 95% confidence intervals and 95% prediction intervals. For the box plots, the center line indicates the median, the

lower and upper bounds of the box indicate the 25th and 75th percentiles, respectively, and the whiskers extend to the minimum and maximum values (with individual data points shown as outliers).

Reporting summary

Further information on research design is available in the Nature Portfolio Reporting Summary linked to this article.

Data availability

The data supporting the findings of the study are included in the main text and Supplementary Information files. Raw data can be obtained from the corresponding authors upon request. Source data are provided with this paper.

References

- He, C. et al. Future global urban water scarcity and potential solutions. *Nat. Commun.* **12**, 4667 (2021).
- Liu, T. et al. Water decontamination via nonradical process by nanoconfined Fenton-like catalysts. *Nat. Commun.* **14**, 2881 (2023).
- Zhang, S., Zheng, H. & Tratnyek, P. G. Advanced redox processes for sustainable water treatment. *Nat. Water* **1**, 666–681 (2023).
- Shang, Y., Xu, X., Gao, B., Wang, S. & Duan, X. Single-atom catalysis in advanced oxidation processes for environmental remediation. *Chem. Soc. Rev.* **50**, 5281–5322 (2021).
- Zhang, Z.-Q. et al. Surface-hydroxylated single-atom catalyst with an isolated Co-O-Zn configuration achieves high selectivity in regulating active species. *Nat. Commun.* **16**, 2376 (2025).
- Gu, C.-H. et al. Tuning electronic structure of metal-free dual-site catalyst enables exclusive singlet oxygen production and in-situ utilization. *Nat. Commun.* **15**, 5771 (2024).
- Xie, L. et al. Pauling-type adsorption of O_2 induced electrocatalytic singlet oxygen production on N-CuO for organic pollutants degradation. *Nat. Commun.* **13**, 5560 (2022).
- Chen, F. et al. Single-atom iron anchored tubular g-C₃N₄ catalysts for ultrafast fenton-like reaction: roles of high-valency iron-Oxo species and organic radicals. *Adv. Mater.* **34**, 2202891 (2022).
- Cheng, C. et al. Generation of FeIV=O and its contribution to fenton-like reactions on a single-atom iron-N-C catalyst. *Angew. Chem. Int. Ed.* **62**, e202218510 (2023).
- Wang, H. et al. Edge-nitrogenated biochar for efficient peroxodisulfate activation: an electron transfer mechanism. *Water Res.* **160**, 405–414 (2019).
- Wu, Z. et al. Long-range interactions driving neighboring Fe-N₄ sites in Fenton-like reactions for sustainable water decontamination. *Nat. Commun.* **15**, 7775 (2024).
- Miao, F. et al. Insights into the mechanism of carbocatalysis for peracetic acid activation: kinetic discernment and active site identification. *Water Res.* **227**, 119346 (2022).
- Wu, J.-H. et al. Tailoring the selective generation of oxidative organic radicals for toxic-by-product-free water decontamination. *Proc. Natl. Acad. Sci. USA.* **121**, e2403544121 (2024).
- Merényi, G., Lind, J. & Engman, L. One- and two-electron reduction potentials of peroxy radicals and related species. *J. Chem. Soc. Perkin Trans. 2*, 2551–2553 (1994).
- Ao, X. -w et al. Peracetic acid-based advanced oxidation processes for decontamination and disinfection of water: a review. *Water Res.* **188**, 116479 (2021).
- Kim, J. et al. Cobalt/peracetic acid: advanced oxidation of aromatic organic compounds by acetylperoxy radicals. *Environ. Sci. Technol.* **54**, 5268–5278 (2020).
- Wang, Z. et al. Application of cobalt/peracetic acid to degrade sulfamethoxazole at neutral condition: efficiency and mechanisms. *Environ. Sci. Technol.* **54**, 464–475 (2020).

18. Zhang, L. et al. Co–Mn spinel oxides trigger peracetic acid activation for ultrafast degradation of sulfonamide antibiotics: Unveiling critical role of Mn species in boosting Co activity. *Water Res.* **229**, 119462 (2023).
19. He, L. et al. Highly efficient degradation of emerging contaminants with sodium bicarbonate-enhanced Mn(II)/peracetic acid process: formation and contribution of Mn(V). *Environ. Sci. Technol.* **58**, 20313–20326 (2024).
20. Zhang, L. et al. Activation of peracetic acid with cobalt anchored on 2D sandwich-like MXenes (Co@MXenes) for organic contaminant degradation: High efficiency and contribution of acetylperoxyl radicals. *Appl. Catal. B Environ.* **297**, 120475 (2021).
21. Li, X. et al. Unusually improved peracetic acid activation for ultrafast organic compound removal through redox-inert Mg incorporation into active Co₃O₄. *Appl. Catal. B Environ. Energy* **361**, 124601 (2025).
22. Zhang, L. et al. Highly efficient activation of peracetic acid by nano-CuO for carbamazepine degradation in wastewater: The significant role of H₂O₂ and evidence of acetylperoxy radical contribution. *Water Res.* **216**, 118322 (2022).
23. Miao, F. et al. Dual nonradical catalytic pathways mediated by nanodiamond-derived sp²/sp³ hybrids for sustainable peracetic acid activation and water decontamination. *Environ. Sci. Technol.* **58**, 8554–8564 (2024).
24. Miao, F. et al. Carbon-based peracetic acid activation towards advanced water purification. *Appl. Catal. B Environ. Energy* **363**, 124807 (2025).
25. Wang, Z. et al. Non-radical activation of peracetic acid by powdered activated carbon for the degradation of sulfamethoxazole. *Environ. Sci. Technol.* **57**, 10478–10488 (2023).
26. Wang, Y. et al. Carbonaceous materials in structural dimensions for advanced oxidation processes. *Chem. Soc. Rev.* **54**, 2436–2482 (2025).
27. He, M. et al. Waste-derived biochar for water pollution control and sustainable development. *Nat. Rev. Earth Environ.* **3**, 444–460 (2022).
28. Dai, C. et al. Mechanisms and product toxicity of activated carbon/peracetic acid for degradation of sulfamethoxazole: implications for groundwater remediation. *Water Res.* **216**, 118347 (2022).
29. Wu, L. et al. Efficient activation of peracetic acid by mixed sludge derived biochar: Critical role of persistent free radicals. *Water Res.* **223**, 119013 (2022).
30. Kong, F. et al. N-Doped carbon electrocatalyst: marked ORR activity in acidic media without the contribution from metal sites? *Angew. Chem. Int. Ed.* **61**, e202116290 (2022).
31. Wang, J. et al. Roles of structure defect, oxygen groups and heteroatom doping on carbon in nonradical oxidation of water contaminants. *Water Res.* **185**, 116244 (2020).
32. Yuan, J., Wen, Y., Dionysiou, D. D., Sharma, V. K. & Ma, X. Biochar as a novel carbon-negative electron source and mediator: electron exchange capacity (EEC) and environmentally persistent free radicals (EPFRs): a review. *Chem. Eng. J.* **429**, 132313 (2022).
33. Zhong, D. et al. pH dependence of arsenic oxidation by rice-husk-derived biochar: roles of redox-active moieties. *Environ. Sci. Technol.* **53**, 9034–9044 (2019).
34. Shen, W. et al. Activation of peracetic acid by thermally modified carbon nanotubes: Organic radicals contribution and active sites identification. *Chem. Eng. J.* **474**, 145521 (2023).
35. Tao, L. et al. Bridging the surface charge and catalytic activity of a defective carbon electrocatalyst. *Angew. Chem. Int. Ed.* **58**, 1019–1024 (2019).
36. Zhu, J. et al. Effects of intrinsic pentagon defects on electrochemical reactivity of carbon nanomaterials. *Angew. Chem. Int. Ed.* **58**, 3859–3864 (2019).
37. Dong, Y. et al. Ammonia thermal treatment toward topological defects in porous carbon for enhanced carbon dioxide electroreduction. *Adv. Mater.* **32**, 2001300 (2020).
38. Liu, D. et al. Defect engineering of MOF-derived carbon for peroxymonosulfate activation to degrade sulfadiazine: roles of carbon vacancies and edge defects. *ACS ES&T Eng.* **3**, 2038–2050 (2023).
39. Yuan, F. et al. Unraveling the effect of intrinsic carbon defects on potassium storage performance. *Adv. Funct. Mater.* **32**, 2208966 (2022).
40. Chen, S. et al. Defective carbon-based materials for the electrochemical synthesis of hydrogen peroxide. *ACS Sustain. Chem. Eng.* **6**, 311–317 (2018).
41. Gong, L. et al. Hydrogen evolution reactivity of pentagonal carbon rings and p-d orbital hybridization effect with Ru. *Angew. Chem. Int. Ed.* **63**, e202411125 (2024).
42. Wang, W. et al. Intrinsic carbon-defect-driven electrocatalytic reduction of carbon dioxide. *Adv. Mater.* **31**, 1808276 (2019).
43. Jiang, Y. et al. Ultrafast potassium storage in F-induced ultra-high edge-defective carbon nanosheets. *ACS Nano* **15**, 10217–10227 (2021).
44. Gao, H. et al. Topological defect and sp³/sp² carbon interface derived from ZIF-8 with linker vacancies for oxygen reduction reaction. *Carbon* **203**, 76–87 (2023).
45. Choi, G. B. et al. Quantifying carbon edge sites on depressing hydrogen evolution reaction activity. *Nano Lett.* **20**, 5885–5892 (2020).
46. Zhang, C. et al. A Pentagonal defect-rich metal-free carbon electrocatalyst for boosting acidic O₂ reduction to H₂O₂ production. *J. Am. Chem. Soc.* **145**, 11589–11598 (2023).
47. Liu, B. et al. Defect-induced electric field effects direct Fenton-like oxidation pathways towards polymerization for sustainable water treatment. *Nat. Commun.* **16**, 10963 (2025).
48. Wan, Z. et al. Revealing intrinsic relations between Cu scales and radical/nonradical oxidations to regulate nucleophilic/electrophilic catalysis. *Adv. Funct. Mater.* **33**, 2212227 (2023).
49. Saquing, J. M., Yu, Y.-H. & Chiu, P. C. Wood-derived black carbon (biochar) as a microbial electron donor and acceptor. *Environ. Sci. Technol. Letters* **3**, 62–66 (2016).
50. Guo, C. et al. Ball-milled layer double hydroxide as persulfate activator for efficient degradation of organic: Alkaline sites-triggered non-radical mechanism. *J. Hazard. Mater.* **461**, 132219 (2024).
51. Jia, Y. et al. Identification of active sites for acidic oxygen reduction on carbon catalysts with and without nitrogen doping. *Nat. Catal.* **2**, 688–695 (2019).
52. Frighetto, F. F., Barbosa, A. S. & Sanchez, S. D. Improved positron-molecule scattering calculations with the Schwinger multichannel method. *Phys. Rev. A* **112**, 042803 (2025).
53. Ren, W. et al. Origins of electron-transfer regime in persulfate-based nonradical oxidation processes. *Environ. Sci. Technol.* **56**, 78–97 (2022).
54. Ren, W. et al. Electro-induced carbon nanotube discrete electrodes for sustainable persulfate activation. *Environ. Sci. Technol.* **56**, 14019–14029 (2022).
55. Ren, W. et al. Insights into the electron-transfer regime of peroxodisulfate activation on carbon nanotubes: the role of oxygen functional groups. *Environ. Sci. Technol.* **54**, 1267–1275 (2020).
56. Figueiredo, J. L. & Pereira, M. F. R. The role of surface chemistry in catalysis with carbons. *Catal. Today* **150**, 2–7 (2010).
57. Zhang, Z.-Q. et al. Nano-island-encapsulated cobalt single-atom catalysts for breaking activity-stability trade-off in Fenton-like reactions. *Nat. Commun.* **16**, 115 (2025).
58. Zu, D. et al. Comparative life cycle assessment of Fenton-like systems: Insights into the environmental benefits of reductant-driven strategies. *Water Res.* **279**, 123489 (2025).

Author contributions

M.W. designed the research. Y. H. completed most of the experiments. Z.Q.X. assisted in performing part of the characterizations. M.W. and W.R. analyzed data. M.W, W.R. and Y.H. wrote the paper; W.R., M.W. and Y.F.Z. modified the paper.

Funding

The financial support of this work from the Department of Science and Technology of Liaoning Province in China (No. 2022JH2/101300112) is acknowledged. W.R. acknowledges the financial support from the Australian Research Council under the Discovery Early Career Researcher Award (DE260100277).

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41467-026-78421-z>.

Correspondence and requests for materials should be addressed to Wei Ren, Min Wang or Yongfa Zhu.

Peer review information *Nature Communications* thanks Bingcheng Luo, Fei Pan, and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. A peer review file is available.

Reprints and permissions information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

© The Author(s) 2026

This Article in Press is shared early to give you faster access to new research. It is citable and carries a permanent DOI. The final edited version will replace it automatically.