Singlet oxygen mediated iron-based Fenton-like catalysis under nanoconfinement

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For several decades, the iron-based Fenton-like catalysis has been believed to be mediated by hydroxyl radicals or high-valent iron-oxo species, while only sporadic evidence supported the generation of singlet oxygen ($\cdot O_2^\ast$) in the Haber-Weiss cycle. Herein, we report an unprecedented singlet oxygen mediated Fenton-like process catalyzed by $\sim$2-nm Fe$_3$O$_4$ nanoparticles distributed inside multiwalled carbon nanotubes with inner diameter of $\sim$7 nm. Unlike the traditional Fenton-like processes, this delicately designed system was shown to selectively oxidize the organic dyes that could be adsorbed with oxidation rates linearly proportional to the adsorption affinity. It also exhibited remarkably higher degradation activity (22.5 times faster) toward a model pollutant methylene blue than its nonconfined analog. Strikingly, the unforeseen stability at pH value up to 9.0 greatly expands the use of Fenton-like catalysts in alkaline conditions. This work represents a fundamental breakthrough toward the design and understanding of the Fenton-like system under nanoconfinement, might cause implications in other fields, especially in biological systems.

Fenton-like catalysis | confinement | singlet oxygen | nanoparticles | water treatment

The seminal study by Fenton in 1894 (1) opened the door to create strong oxidants using Fe(II) and H$_2$O$_2$. This ubiquitous industrialized oxidation and its derivatives, i.e., Fenton-like reagents such as Fe(III)/H$_2$O$_2$, photo-/electro- Fenton, have been utilized in a versatile way in various fields including the cognition of biological stress response (2) and sensing (3), chemical analysis (4), molecular synthesis (5), material preparation (6), and environmental remediation (7) in the past century. Notwithstanding the obscure mechanism of Fenton’s reaction (8–10), the main oxidative intermediate species involved in the bulk phase or at aqueous interfaces are proved to be the hydroxyl radicals (HO$^\ast$) generated through the Haber–Weiss cycle (8, 9) or high-valent iron-oxo species [Fe(IV)=O/Fe(V)=O] produced via the Bray–Gorin mechanism (10, 11).

Recently, thriving researches on nanotechnology and nanomaterial have created tremendous opportunities for reinvestigation of various chemical reactions at the nanoscale, generating new insights on fundamental understanding and tools for various applications (12). For examples, under nanoconfinement provided by carbon nanotube (CNT), molecular-dynamics simulations showed pulse-like water transmission with concerted and rapid motion along the tube axis, as well as tunable channel occupancy and conductivity (13, 14). Similarly, a stable polymorphous crystal formed from ionic liquid [bmm][PF$_6$] inside multiwalled carbon nanotubes (MWCNTs) exhibited a melting point of above 473 K, much higher than that of the unconfined analog (279 K) (15). With respect to RhMn nanoparticles inside CNTs, the electron-deficient interior surface of CNTs was shown to increase the tendency of confined Mn to accept electrons from CO, resulting in one order of magnitude improvement of C2 oxygenate yield from syngas (16).

Herein, we report an attempt to understand the behavior of the Fenton reaction under nanoconfinement of CNTs with size of $\sim$7 nm and demonstrate a singlet oxygen ($\cdot O_2^\ast$) mediated pathway. As shown in Fig. 1, two different structures were designed, i.e., distribution of Fe$_3$O$_4$ nanoparticles on the outer surface of CNT (upper route, referred to as Fe$_3$O$_4$/FCNT-L), anchoring of Fe$_3$O$_4$ nanoparticles inside the CNT for nanoconfinement (lower route, referred to as Fe$_3$O$_4$/FCNT-H). The former exhibited traditional Fenton-like reaction pathways with HO$^\ast$ as the main active species; however, an unprecedented reaction pathway with $\cdot O_2^\ast$ as the reactive intermediate was discovered in the latter design. We further used the latter as a catalyst for the oxidation of several organic dyes. Surprisingly, this nanoconfined system selectively oxidized the compounds that could be adsorbed with the reaction rates linearly proportional to the adsorption affinity. For the degradation of a model pollutant methylene blue (MB), the latter catalyst exhibited a remarkably faster kinetics (22.5 times) as well as an exceptionally higher pH stability (pH 5.0–9.0) than its nonconfined analog.

## Results and Discussion

The inner diameters of the CNTs are estimated to be $\sim$7 nm (SI Appendix, Fig. S1). Representative high-angle dark-field scanning transmission electron microscopy (HADDF-STEM) images with energy-dispersive X-ray spectroscopy (EDX) elemental mapping (Fig. 2 A and B and SI Appendix, Fig. S2) clearly show that in Fe$_3$O$_4$/FCNT-L, nanoparticles are randomly distributed along the direction of CNT; however, in Fe$_3$O$_4$/FCNT-H, the distribution of the nanoparticles is dictated by the center of the CNT (pointed at by the red arrows). The insets of high-resolution transmission electron microscopy (HRTEM) images in both figures show the (311) crystalline lattice of Fe$_3$O$_4$ nanoparticles. The size-distribution histograms of Fe$_3$O$_4$ nanoparticles in both samples in Fig. 2C show the average size to be 2.4 nm (Fe$_3$O$_4$/FCNT-L) and $\sim$7 nm (Fe$_3$O$_4$/FCNT-H).

## Significance

In the bulk phase, hydroxyl radical from the one-electron transfer and high-valent iron-oxo species from the O-atom transfer compete to be the reactive intermediates in the Fenton and related reactions. In the confined space at a nanoscale, however, the behavior of the Fenton reaction is elusive. Herein, we report an unprecedented singlet oxygen mediated Fenton’s reaction occurred inside carbon nanotube with inner diameter of $\sim$7 nm, showing exotic catalytic activities, unforeseen adsorption-dependent selectivity, and pH stability for the oxidation of organic compounds. Our results suggest the use of Fenton’s reaction in more scenarios than ever explored.

## Author contributions

B.P. conceived the research; Z.Y., B.P., and J.Q. designed experiments; Z.Y., B.P., and J.Q. analyzed data; and Z.Y., B.P., and J.Q. wrote the paper.

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1.9 nm (Fe$_2$O$_3$@FCNT-H). The mass fractions of Fe$_2$O$_3$ nanoparticles in both samples were determined to be similar, i.e., 2.09\% for Fe$_2$O$_3$/FCNT-L and 1.93\% for Fe$_2$O$_3$@FCNT-H. The XRD patterns in Fig. 2D show that both Fe$_2$O$_3$/FCNT-L and Fe$_2$O$_3$@FCNT-H exhibit four characteristic diffraction peaks of the (002), (100), (004), and (110) crystal planes of CNTs with typical hexagonal graphite structure. Meanwhile, two weak peaks at 35.9\° and 62.3\° appear in both samples (Fig. 2D), highly suspected to be the diffractions of (311) and (440) crystal planes of Fe$_2$O$_3$ (Joint Committee on Powder Diffraction Standards 04-0755), which was further confirmed by the sole presence of Fe$^{3+}$ species by $^{57}$Fe Mössbauer spectra of both samples (SI Appendix, Fig. S3) (17, 18).

The Raman spectra (SI Appendix, Fig. S4) show that in comparison with CNT, the two samples exhibit an adsorption band at around 280 cm$^{-1}$ after the Fe$_2$O$_3$ loading, which could be assigned to the Fe$_6$O-Vibration mode (19). The blue shift of this band from 281.2 cm$^{-1}$ of Fe$_2$O$_3$/FCNT-L to 285.2 cm$^{-1}$ of Fe$_2$O$_3$@FCNT-H indicates the interaction of Fe$_2$O$_3$ with the inner surface of the CNT in Fe$_2$O$_3$@FCNT-H (19). The Fe 2p XPS spectra in Fig. 2E show surprising difference of the Fe 2p peak intensities between both samples, i.e., much weaker Fe 2p peaks of Fe$_2$O$_3$/FCNT-H than Fe$_2$O$_3$/FCNT-L despite their similar Fe contents. This is probably due to the limited probe depth of the photoelectrons (3-5 nm) for the detection of Fe$_2$O$_3$ inside the CNT. The N$_2$ adsorption-desorption isotherms are shown in Fig. 2F, from which the Brunner–Emmet–Teller (BET)-specific surface areas are calculated to be 197 m$^2$g$^{-1}$ (Fe$_2$O$_3$/FCNT-L) and 206 m$^2$g$^{-1}$ (Fe$_2$O$_3$@FCNT-H), and the BJH pore volumes are 0.59 and 0.43 cm$^3$g$^{-1}$, respectively.

We first identified the generated active species in various systems. The electron spin resonance (ESR) spectra (Fig. 3A) show that, by using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the trapping agent, one could observe the quadruple peak signals of DMPO-HO• (1:2:2:1, $\alpha_H = 14.9$ G, g = 2.0055) in Fe$_2$O$_3$/FCNT-L/H$_2$O and Fe$_2$O$_3$@FCNT-H$_2$O$_2$ systems, which are expected in traditional Fenton-like systems. On the contrary, the DMPO-HO• signal was not detected in Fe$_2$O$_3$/FCNT-H/H$_2$O$_2$ system at all. Instead, when 2,2,6,6-tetramethyl-4-piperidinol (TEMP) was used as the trapping agent, a triplet peak signal (1:1:1, $\alpha_H = 16.9$ G, g = 2.0054) of 2,2,6,6-tetramethyl-4-piperidinol- N-oxyl radical (TMPN) emerged, indicating the presence of O$_2^•$ (20, 21). Not surprisingly, it was not detected in both Fe$_2$O$_3$/FCNT-L/H$_2$O$_2$ and Fe$_2$O$_3$@FCNT-H$_2$O$_2$ systems. More credible evidence was discovered based on the determination of indicative products from the specific reactions between classical chemical probe 9,10-diphenylanthracene (DPA) and O$_2$ (22). As presented in Fig. 3B, the chromatographic peak of anthracene endoperoxide (DPAO$_2$) appeared in Fe$_2$O$_3$/FCNT-H/H$_2$O$_2$ system and its concentration also increased when the dosage of Fe$_2$O$_3$/FCNT-H increased from 1.5 $\times$ 10$^{-2}$ gL$^{-1}$ to 2.5 $\times$ 10$^{-2}$ gL$^{-1}$, clearly showing the generation of O$_2^•$.

We further evaluated the role of O$_2$ in Fe$_2$O$_3$/FCNT-H/H$_2$O$_2$ system by calculating the material balance of furfuryl alcohol (FFA) oxidation (see SI Appendix, Texts S1 and S2 for details). Consistent with the results from previous studies (23, 24), three typical products, C$_6$H$_{12}$O$_3$ (m/z 129.0181 in negative ionization mode), C$_6$H$_{12}$O$_3$ (m/z 99.0072 in negative ionization mode), and C$_6$H$_{12}$O$_3$ (m/z 129.0181 in positive ionization mode), were detected when 2,2,6,6-tetramethyl-4-piperidinol (TEMP) was used as the trapping agent. Not surprisingly, it was not detected in both Fe$_2$O$_3$/FCNT-L/H$_2$O$_2$ and Fe$_2$O$_3$@FCNT-H$_2$O$_2$ systems.
mode), and C$_2$H$_5$O$_3$ (m/z 113.0228 in negative ionization mode) were detected at the retention time of 5.38, 5.86, and 7.56 min, respectively (see Fig. 4A and SI Appendix, Fig. S5 for details). Moreover, a >98% conversion to three classical products from the oxidation of FFA indicated the exclusive role of O$_2$ as the reactive intermediate in Fe$_3$O$_4$/FCNT-H/H$_2$O$_2$ system (Fig. 4B). It is accepted that O$_2$ could be generated via oxidation, disproportionation, and/or decomposition of peroxymetal species in the H$_2$O$_2$-based systems catalyzed by halide ions, metal salts, and minerals (e.g., hypochlorite, molybdate, and lanthanum oxide) (25, 26). Nevertheless, the generation of O$_2$ in the iron-based Fenton-like reaction was challenged in the bulk phase from both kinetic and thermodynamic points of view (25, 26). Our solid proof of the exclusive role of O$_2$ in Fe$_3$O$_4$/FCNT-H system might suggest that the nanoconfinement changes the Fenton-like reaction pathway both kinetically and thermodynamically.

We are intrigued to investigate the catalytic performance of the nanoconfined Fenton’s catalyst. As presented in Fig. 5A, using MB as a model pollutant, one can see that in the absence of H$_2$O$_2$, both samples exhibited noticeable MB removal, presumably due to the adsorption of MB. However, in the presence of H$_2$O$_2$, Fe$_3$O$_4$/FCNT-H exhibited a remarkably higher MB degradation rate with the value of pseudo-first-order constant ($k_{app}$) = 5.25 × 10$^{-2}$ min$^{-1}$, which is 22.5 times higher than that of Fe$_3$O$_4$/FCNT-L (2.33 × 10$^{-3}$ min$^{-1}$) (SI Appendix, Fig. S6). Meanwhile, Fe$_3$O$_4$/FCNT-H/H$_2$O$_2$ is more effective than Fe$_3$O$_4$/FCNT-L/H$_2$O$_2$ in reducing the total organic carbon (25 vs. 15%) in 60 min (SI Appendix, Fig. S7). As shown in Fig. 5B, H$_2$O$_2$ alone has negligible effect on the MB removal even with the presence of Fe$_3$O$_4$; CNT/H$_2$O$_2$ has identical effect as CNT alone due to the adsorption effect (27). Samples of Fe$_3$O$_4$ nanoparticles loaded on various commercial substrates including carboxylated CNFs (CNT-COOH), SBA-15, and graphene oxide (GO) also exhibit significantly lower MB removal activities than Fe$_3$O$_4$/FCNT-H (SI Appendix, Fig. S8). All these results emphasize the key role of the interaction of the Fe$_3$O$_4$ nanoparticles inside the CNT for the surprisingly high MB removal activity of Fe$_3$O$_4$/FCNT-H.

The versatility of Fe$_3$O$_4$/FCNT-H under different conditions is of great general importance. The MB removal by the Fe$_3$O$_4$/FCNT-H/H$_2$O$_2$ system under different conditions is shown in SI Appendix, Fig. S9 with the accompanying discussion. The key information one could acquire is that the generation of O$_2$, represented by the apparent MB degradation kinetics, can be effectively elevated by increasing catalyst dosage, H$_2$O$_2$ concentration, and reaction temperature.

We then investigated the reusability and pH stability of Fe$_3$O$_4$/FCNT-H. Fig. 5C shows a slight deactivation of Fe$_3$O$_4$/FCNT-H for five consecutive MB additions, presumably due to either the gradual occupation of active sites or the competitive reaction with O$_2$ by the cumulative degradation products (28). However, the catalytic activity was fully recovered after washing with ethanol for later use without detectable ion leaching, suggesting excellent reusability of Fe$_3$O$_4$/FCNT-H. One can see from Fig. 5D that the value of $k_{app}$ increases with the increase of pH.
value from 2.0 to 5.0, and unprecedently, remains stable as the pH value further increases to 9.0 (SI Appendix, Fig. S10). On the contrary, $k_{\text{app}}$ of Fe$_2$O$_3$/FCNT-L/H$_2$O$_2$ system decreased as the pH value increased from 3.0 to 9.0 (SI Appendix, Fig. S11), which is a common phenomenon observed in traditional Fenton-like systems (29, 30). We discuss the effect of pH on MB removal of our Fe$_2$O$_3$/FCNT-H/H$_2$O$_2$ system in detail (SI Appendix, Part S1). Based on the results of SI Appendix, Figs. S12–S15, we reckon that pH plays a crucial role in the MB removal through affecting the $O_2$ generation as well as the MB adsorption. The precise understanding for this unusual phenomenon still needs more elaborate future exploration; nevertheless, it presents a much more improved suitability in a broad pH range than the classical Fenton-like systems.

Considering $O_2$ is not such a general oxidant as HO·, we list a number of both organic and inorganic species that have been studied previously in $O_2$-mediated oxidation systems (SI Appendix, Table S1). In this work, the catalytic degradation of several different compounds [i.e., cationic ones including methyl violet, crystal violet, chrysoidine, and malachite green oxalate; anionic ones including methyl orange (MO) and chromotrope 2R (C2R) and neutral aniline] in Fe$_2$O$_3$/FCNT-H/H$_2$O$_2$ system was carried out to further demonstrate the versatility of Fe$_2$O$_3$/FCNT-H (SI Appendix, Fig. S16). We show that anionic compounds including MO and C2R and neutral aniline could not be effectively adsorbed by Fe$_2$O$_3$/FCNT-H; consequently, only a small fraction was degraded. Those cationic compounds which could be efficiently adsorbed were rapidly degraded. Fig. 6A shows the values of $k_{\text{app}}$ versus $q_{\text{cal}}$ of Fe$_2$O$_3$/FCNT-H toward various cationic compounds. One can see that the value of $k_{\text{app}}$ is linearly proportional to the value of $q_{\text{cal}}$ calculated from the pseudo-second-order adsorption kinetics ($r > 0.97$) (SI Appendix, Fig. S17). This result clearly shows an exotic adsorption-dependent removal feature of Fe$_2$O$_3$/FCNT-H, while the degradation kinetics is normally proportionally to the concentration of HO· irrelevant to adsorption in traditional Fenton’s reactions (31). As a consequence, our nanoconfined Fenton’s reagent could be used to selectively degrade the compounds which are prone to be adsorbed (SI Appendix, Fig. S18). One might also be interested in the precise location where the pollutant is oxidized by the $O_2$ i.e., on the outer surface of CNT or inside the CNT. Although we have our preference guess of the latter based on the adsorption-dependent process (32–39), we do not have solid proof at this point. We would like to leave this question for further exploration.

Based on the previous results and discussion, a possible catalytic pathway of Fe$_2$O$_3$/FCNT-H/H$_2$O$_2$ system for pollutant degradation is presented in Fig. 7A. One might also be interested in the precise location where the pollutant is oxidized by the $O_2$ i.e., on the outer surface of CNT or inside the CNT. Although we have our preference guess of the latter based on the adsorption-dependent process (32–39), we do not have solid proof at this point. We would like to leave this question for further exploration.

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**Fig. 5.** Catalytic properties of Fe$_2$O$_3$/FCNT-H and Fe$_2$O$_3$/FCNT-L. (A) Plots of MB concentrations versus time of Fe$_2$O$_3$/FCNT-H and Fe$_2$O$_3$/FCNT-L with/without H$_2$O$_2$. (B) Plots of MB concentrations versus time of different systems. (C) Five consecutive MB removal experiments with two more regeneration studies of Fe$_2$O$_3$/FCNT-H. (D) The plot of $k_{\text{app}}$ versus solution pH. Reaction conditions: $T = 293.2$ K, $[\text{MB}] = 10$ μM, $[\text{H}_2\text{O}_2] = 50$ mM, $pH = 5.0$ for A–C and 3.0–9.0 for D, [catalysts] (except Fe$_2$O$_3$) = 1.5 × 10$^{-2}$ g–L$^{-1}$ for A, B, and D and 4.0 × 10$^{-2}$ g–L$^{-1}$ for C, [Fe$_2$O$_3$] = 1.0 × 10$^{-1}$ g–L$^{-1}$ in B.

**Fig. 6.** The role of adsorption and possible mechanism scheme. (A) Plots of $k_{\text{app}}$ versus $q_{\text{cal}}$ manipulated through the addition of Al$^{3+}$ for Fe$_2$O$_3$/FCNT-H toward various cationic compounds. Reaction conditions: $pH = 5.0$, $T = 293.2$ K, [Fe$_2$O$_3$/FCNT-H] = 1.5 × 10$^{-2}$ g–L$^{-1}$, [target compounds] = 10 μM, $[\text{H}_2\text{O}_2] = 50$ mM, [Al$^{3+}$] = 0.1–1 mM. (B) Illustration of possible mechanism of pollutants degradation in Fe$_2$O$_3$/FCNT-H/H$_2$O$_2$ system.
degradation is illustrated as a scheme in Fig. 6B. Since both light and oxygen do not contribute to the process (SI Appendix, Fig. S19), we assert that H₂O₂ is the only source for ¹O₂ generation in Fe₃O₄@FCNT-H/H₂O₂ system, via the gain of two electrons by H₂O₂ to generate ¹O₂. There are three possible oxidation pathways of H₂O₂, a one-step two-electron transfer and two-step one-electron transfer with or without the contribution of high-valent iron-oxo species. The one-step two-electron transfer involving the reduction of Fe(III) to Fe(I) only exists in Fe-catalyzed cross-coupling reactions theoretically (40). The two-step one-electron transfer involving the oxidation of H₂O₂ by high-valent iron-oxo species depicted by Collins and coworkers could also be excluded because the pivotal intermediate could not be detected (see DMSO quenching experiment for the detection of high-valent iron-oxo species in SI Appendix, Fig. S13) (41). In contrast, the two-step one-electron transfer following the Haber–Weiss cycle is the most likely pathway for ¹O₂ generation. In the first step, the Fe(III) species on the surface of the Fe₃O₄ nanoparticles inside CNT is reduced by H₂O₂ to produce HO₂/·O²⁻, which can be further supported by the obvious shift to the lower region by 0.7 eV with the addition of H₂O₂ in situ X-ray absorption near edge structure (XANES) analysis as depicted in SI Appendix, Fig. S20. The nanoconfinement by CNT poses strong electronic interaction with Fe₃O₄ nanoparticles due to the electron-deficient concave surface, facilitating this process compared with the Fe₃O₄ nanoparticles outside (42–44). The second step deals with several possibilities contributing to the oxidation of HO₂/·O²⁻ to form ¹O₂ since we have demonstrated HO₂/·O²⁻ to be the key intermediate for ¹O₂ generation (SI Appendix, Part S1 and Figs. S12–S14). (i) One is the oxidation by Fe(III) in the favored spin state, regulated by the confined space and the unique electronic structure of CNTs (25). (ii) The second is the radical–radical reactions including HO₂/·O²⁻ recombination and the reaction between HO₂/·O²⁻ and HO⁻ (45–48). The Gibbs free energy for HO₂/·O²⁻ recombination is −6.4 kcal/mol at pH 7, indicating its thermodynamic spontaneity (45). However, we could not obtain even tiny evidence for the presence of HO⁻ in Fe₃O₄@FCNT-H/H₂O₂ system by chemical quenching or trapping experiment (Fig. S4 and SI Appendix, Fig. S13), which is probably due to either the slow diffusion of quenching molecules or the accelerated radical recombination (49). Consequently, we do not exclude the possible contribution of HO⁻ in the ¹O₂ generation but we reckon its contribution is small (49). (iii) The reaction between HO₂/·O²⁻ and HO⁻ (50). The reaction constant is 10−10 magnitude smaller than those in (i) and (ii) (SI Appendix, Table S2); however, its contribution to the ¹O₂ generation might be compensated by significantly higher H₂O₂ concentration than radicals. These three possible reactions could be well accelerated via the enrichment as well as the limited migration of the as-formed radicals in the confined space (37, 48, 49). Another key role of the nanoconfinement in Fe₃O₄@FCNT-H/H₂O₂ system is suspected to largely improve the selectivity of these reactions to produce ¹O₂ rather than O₂ in the traditional bulk systems (51).

In conclusion, by loading ~2 nm Fe₃O₄ nanoparticles inside the confined space of CNT with inner diameter of ~7 nm, we are able to create a Fenton-like catalyst Fe₃O₄@FCNT-H showing completely different catalytic pathway from traditional Fenton-like catalyst Fe₃O₄@FCNT-L, in which Fe₃O₄ nanoparticles are loaded on the outer surface of CNT. The ¹O₂ radical was observed as the main reactive intermediate generated in Fe₃O₄@FCNT-H/H₂O₂ system, other than HO⁻ that was generated in Fe₃O₄@FCNT-L/H₂O₂ system and has been accepted as the main active species in the Fenton-like systems for many years. Meanwhile, a 22.5x faster MB degradation kinetics in Fe₃O₄@FCNT-H/H₂O₂ than Fe₃O₄@FCNT-L/H₂O₂ was obtained. Moreover, Fe₂O₃@FCNT-H exhibited surprisingly high stability over a broad pH range from 5.0 to 9.0, while it is almost impossible to utilize traditional Fenton-like catalyst under alkaline conditions. We also demonstrated that the oxidation rates of different pollutants in the Fe₂O₃@FCNT-H/H₂O₂ system are highly dependent on the adsorption affinity between the pollutants and the catalyst. Our work has presented a delicate design of Fenton’s catalyst using nanoconfinement for pollutant removal with exceptional activity and pH suitability, and also, has laid a milestone toward the mechanistic understanding of the Fenton-like reactions under nanoconfinement. We hope our work could stimulate the researchers to use nanoconfined Fenton’s reaction in various applications especially biological systems to realize selective and efficient oxidation.

### Methods

The chemicals and materials used in the experiments are described in SI Appendix, Text S3.

#### Preparation of Catalysts

The catalysts used in this work were synthesized according to a slightly modified method (42, 43). Pristine MWCNTs (pCNT) were first refluxed in concentrated HNO₃ solution (65 wt %) at 403 ± 5 K for 5 h. After being filtered and washed with ultrapure water until the pH value of the filtrate reached ~6.1, the solids were ultrasonically dispersed in the ultrapure water and lyophilized (Freezone 2.5; Labconco) for better dispersion of the particles (denoted as FCNT-H). Sample FCNT-L was prepared by refluxing pCNT in HNO₃ solution (30 wt %) at 383 ± 5 K for 5 h. Sample of CNT-COOH was prepared by refluxing commercial sample in HCl solution (38 wt %) at 343 K for 12 h to remove residual metal impurities. The Fe₃O₄ nanoparticles were prepared by chemical precipitation as a green precursor. Afterward, each of 0.2 g of catalyst (i.e., FCNT-H, FCNT-L, CNT-COOH, SBA-15, and GO) was dispersed in 20 mL FeeIl(iii)/acetone solution, respectively. The mixed solution was stirred for 1 h and then treated by ultrasonication for 4 h, while temperature was kept constant at 293.2 ± 0.3 K using a thermostat (THD-5015; Tianheng). As the slow evaporation of acetone, Fe(iii) was deposited on the inner or outer surface of the hollow silica. The as-prepared solid was gradually heated to 413 K in air and kept for 10 h. After being washed with ultrapure water, we obtained samples of Fe₂O₃@FCNT-H, Fe₂O₃@FCNT-L, Fe₂O₃@CNT-COOH, Fe₂O₃@SBA-15, and Fe₂O₃@GO, respectively. The Fe loading of the catalysts was 2 wt % unless else stated. The unsupported iron oxides and FCNT-H for comparison were prepared using a similar method without adding FCNT-H or iron precursor, respectively. Catalysts were stored as the form of aqueous suspensions via direct ultrasonication for 20 min. To maintain homogeneity, the stock suspension was periodically treated by ultrasonication for 10 min before use.

#### Characterization of Catalysts

The loaded Fe content was determined by an atomic absorption spectrophotometer (AA-7000; Shimadzu) after acidic digestion overnight using the concentrated HCl solution assisted by ultrasonic treatment in a sealed polytetrafluoroethylene (PTFE) bottle. The crystalline structures of the catalysts were determined by XRD patterns recorded by Rigaku (Rigaku) using Mo Kα radiation (λ = 0.7093 Å). For better analysis and comparison with the data from XRD in Cu Kα radiation, the obtained XRD spectra were transferred according to the Bragg equation (SI Appendix, Text S4).

The analysis of surface properties was conducted using N₂ adsorption–desorption test at 77 K (NOVA3000; Quantachrome). XPS (K-Alpha; Thermo) was used to determine the element chemical states near the surface region. The Mössbauer spectra were recorded by proportional counter on Topologic 500 spectrometer (MFD-5000AT) with ⁵⁷Co (Rh) as a γ-ray source at room temperature. The morphologies were examined by TEM (TECNAI G² F20; FEI) at an accelerating voltage of 200 kV. STEM was performed to characterize the dispersion and configuration of the catalysts. Individual heavy atoms can be discerned in the HAADF images. Moreover, STEM-EDX was conducted to map the abundance of C, O, and Fe in the catalysts. Raman spectra were recorded with a Lambda Aranis Raman spectrometer (Horiba Scientific) with an Ar⁺ laser at 532 nm. In situ XANES analysis was carried out at room temperature in Beijing Synchrotron Radiation Facility with Fe foil and Fe₂O₃ as reference, Κ-edge energies of which were located at 7,112.1 and 7,126.6 eV, respectively.

#### Examination of Catalysts

The degradation experiments were conducted in a 50-mL conical flask under magnetic stirring at 293.2 ± 0.3 K. Reactions were initiated by simultaneous addition of the catalyst suspension and H₂O₂ into the solution containing target dyes. Adsorption experiments were also conducted in a 50-mL conical flask on a rotary shaker at 150 rpm at 293.2 ± 0.3 K. The experiment was initiated after adding the catalyst suspension to
the solutions of various target compounds with/without Al3+ ions (0.1–1 mM) at pH 3.0 unless specified. The pH values of solutions were adjusted by diluted HNO3 or NaOH. Reaction aliquots were periodically taken and filtered through a membrane (0.22 μm) to remove the solid catalysts for analysis. The detailed experimental conditions are presented in the legend of each figure. To test the stability and reusability of FeO42−@FCNT-H, a 1.75 L reactor was used to avoid the loss of catalyst during recycle (see SI Appendix, Text S5 for details). The used catalysts were collected by suction filtration and simply washed with ethanol and ultrapure water.

The concentrations of organic dyes were analyzed at the maximum absorption wavelength by a UV-vis spectrophotometer (T6; Beijing Persee) (SI Appendix, Table S3). An ultrahigh-performance liquid chromatography (UHPLC, Ultimate 3000; Thermo) with a symmetry C18 column was used to analyze FFA, aniline, and 4-CP (SI Appendix, Table S4). TOC was measured by subtracting the concentration of inorganic carbon from the total carbon on a Shimadzu TOC-VCPH analyzer (Japan) and the quantification was based on a standard calibration in the range of 0.3–mg L−1.

The concentration of leached iron species was determined through 1,10-phenanthroline method after reduction by hydroxylamine hydrochloride with the limit of detection of 0.36 μM. ESR spectra of DMPO•O2−, DMPO•OOH, and TMPN were obtained with an ESR A30 spectrometer (Bruker). The detailed operation methods are presented in SI Appendix, Text S6. A Thermo U3000 ultrahigh performance liquid chromatography coupled with Thermo Q-Exactive Focus MS with an electron spray ionization source was employed to identify the intermediate products from DPA oxidation and FFA oxidation (see SI Appendix, Text S1 for details). The concentration of products from FFA oxidation was calculated as described in SI Appendix, Text S2.

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