Electrocatalysis

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Selective Electrocatalytic Reduction of Oxygen to Hydroxyl Radicals via 3-Electron Pathway with FeCo Alloy Encapsulated Carbon Aerogel for Fast and Complete Removing Pollutants

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Abstract: We reported the selective electrochemical reduction of oxygen (O_2) to hydroxyl radicals (OH) via 3-electron pathway with FeCo alloy encapsulated by carbon aerogel (FeCoC). The graphite shell with exposed -COOH is conducive to the 2-electron reduction pathway for H_2O_2 generation stepped by 1-electron reduction towards to 'OH. The electrocatalytic activity can be regulated by tuning the local electronic environment of carbon shell with the electrons coming from the inner FeCo alloy. The new strategy of 'OH generation from electrocatalytic reduction O_2 overcomes the rate-limiting step over electron transfer initiated by reduction-/oxidation-state cycle in Fenton process. Fast and complete removal of ciprofloxacin was achieved within 5 min in this proposed system, the apparent rate constant (k_{obs}) was up to $1.44 \pm$ 0.04 min^{-1} , which is comparable with the state-of-the-art advanced oxidation processes. The degradation rate almost remains the same after 50 successive runs, suggesting the satisfactory stability for practical applications.

Introduction

With the increased utilization of organic compounds in industry and daily life, the consequent growing discharges of persistent organic pollutants irreversibly affect the environment and potentially threaten human health as well. Advanced oxidation processes (AOPs) have been deeply studied for removing recalcitrant organic contaminants through the generation of reactive oxygen species (ROS).^[1] It is well known that hydroxyl radicals ('OH) possess the highest oxidation potential (2.80 V) among ROS that can efficiently and unselectively oxidize most of organic pollutants. From the economic and environmental points of view, O_2 is an ideal oxidant since it is abundant and cheap. Numerous investigations concerning about oxygen reduction reaction (ORR) have been carried out. In electrochemical system, O_2 would

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 Supporting information and the ORCID identification number(s) for
 the author(s) of this article can be found under: https://doi.org/10.1002/anie.202101804. be selectively reduced to H_2O_2 and H_2O via 2- and 4-electron reduction reactions [Eq. (1) and (2), respectively].^[2]

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
 (1)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 (2)

Very recently, the direct H_2O_2 synthesis through ORR over carbonaceous materials has gained increasing attention in environmental remediation,^[3] avoiding the transport, storage and handling of bulk H_2O_2 to site.^[4] Additionally, homogeneous ferrous irons (Fe²⁺) and heterogeneous solids can efficiently catalyze the electrogenerated H_2O_2 into 'OH. This is a variant of Huron-Dow process named as electro-Fenton (EF) [Eq. (3)],^[5] producing abundant 'OH in ambient condition. However, the one-time depleted H_2O_2 reactant and continuous consumption of metal species make EF process unsustainable with poor recyclability and secondary pollution. Meanwhile, the degradation rate in EF process is severely restricted by the rate-limiting step over the reduction of Fe³⁺ to Fe²⁺ [Eq. (4)]. Unfortunately, these problems are difficult to be solved by conventional approaches.

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow OH + Fe^{3+} + H_2O$$
 (3)

$$\mathrm{Fe}^{3+} + \mathrm{e}^{-} \rightarrow \mathrm{Fe}^{2+}$$
 (4)

Inspired by the concept that electron penetration through carbon layer from active metal core to the carbon layer can stimulate electrocatalytic activity of carbon surface in a variety of catalytic reactions,^[6] we turn our research interest to the 'OH production during electrocatalytic reduction of O₂. The remaining key point is how to simultaneously trigger the selective electrocatalytic reduction of O_2 and H_2O_2 but without the contribution of Fenton reaction. In this case, carbonaceous electrode with graphite shell can be considered as a promising material to promote the electrocatalytic activity and prevent the core sites from reacting with external solution. However, the electrocatalytic mechanism of converting O2 to 'OH yet remains underexplored, which is not only critical in helping realize a multi-electron oxygen reduction process, but provides fundamental insight into the development of novel technologies in environmental remediation.

Herein, we propose a new strategy of designing FeCo alloy-encapsulated carbon aerogel (FeCoC) as working electrode directly, conducting the electrochemical reduction of O_2 to 'OH via overall 3-electron pathway [Eq. (6)]. Carbon-based aerogel is one of particular interest since it



can be shaped into desired dimensions according to the actual requirements. The encapsulated FeCo alloy with optimal metal doping ratio favors the in situ formation of oxygenenriched functional groups, benefiting the 2-electron ORR. Meanwhile, The electrons from encapsulated FeCo alloy endow the carbon shell with the activity of electrocatalytic reducing H_2O_2 to 'OH via 1-electron pathway [Eq. (5)],^[7] whereby all problems originating from the continuing H_2O_2 supply, poor catalyst recyclability, and accumulation of metal-containing sludge in traditional Fenton reaction are solved.^[6b] Moreover, investigating the mechanism of transient ROS formation and resolving the rate-limiting step of classic EF reaction can boost the removal of various pollutants.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
 (1a)

$$H_2O_2 + e^-_{carbon shell} \rightarrow OH + OH^-$$
 (5)

 $O_2 + 2H^+ + 3e^- \rightarrow OH + OH^-$ (6)

Results and Discussion

Properties of FeCo Alloy-Encapsulated Carbon Aerogel (FeCoC) Electrode

As schematically illustrated in Figure 1a, FeCoC was prepared through a copolymerization method by controlling the introduction of ferric-/cobalt- acetylacetonate during the synthesis of phenolic polymer aerogel from resorcinol and formaldehyde. The obtained FeCoC (exemplified with Fe0.5Co0.5C here, see Table 1 for the synthesized series of electrodes) was directly used as working electrode with adjustable size. The high-resolution transmission electron microscopy (HRTEM) image (Figure 1b) revealed that the lattice fringe of well-defined shell was 0.34 nm, matching with the C (002) plane of graphitic carbon, whereas the interplanar spacing of encapsulated nanoparticles was 0.20 nm, corresponding to the (110) plane of FeCo alloy (Figure 1c). Moreover, the energy dispersive X-ray spectroscopy elemental mapping in Figures 1 d-f explicated that Fe (yellow) and Co (magenta) atoms were perfectly correlated with each other, further authenticating the existence of FeCo alloy structure. The element map of O (red) uniformly distributed with C (green). Furthermore, only graphitic carbon shell (JCPDS. No. 01-1578) and FeCo alloy (JCPDS No. 65-4131) were detected on Fe0.5Co0.5C electrode by X-ray diffraction (XRD) measurement (Figure 1 g).^[8] Notably, according to the results of X-ray photoelectron spectroscopy (XPS) measure-

Table 1: Textural properties and element contents of as-prepared electrodes.

| Electrode | ICP [wt.%] | | Atom ratio of Fe/Co | Mass conc. of O [wt%] | $S_{BET}[m^2g^{-1}]$ |
|---------------------------------------|-----------------|---------------|------------------------|--------------------------|----------------------|
| | Fe | Co | - | | |
| FeC | 1.23 ± 0.04 | _ | _ | 4.71 | 395 |
| $Fe_{0.7}Co_{0.5}C$ | 0.71 ± 0.03 | 0.48 ± 0.02 | 1.5 | 4.98 | 295 |
| Fe _{0.5} Co _{0.5} C | 0.55 ± 0.03 | 0.47 ± 0.02 | 1.2 | 27.3 | 287 |
| Fe _{0.5} Co _{0.7} C | 0.48 ± 0.02 | 0.78 ± 0.03 | 0.6 | 4.75 | 293 |
| CoC | - | 1.25 ± 0.05 | _ | 4.31 | 313 |



Figure 1. a) Synthetic route and chemical reaction pathway of FeCoC. b) HRTEM images of $Fe_{0.5}Co_{0.5}C$. Inset: a photography of the FeCoC electrode. c) TEM images of $Fe_{0.5}Co_{0.5}C$. d–f) Energy dispersive X-ray spectroscopy elemental mappings of $Fe_{0.5}Co_{0.5}C$. g) XRD patterns and h) XPS spectra of pure carbon aerogel and $Fe_{0.5}Co_{0.5}C$. i) ⁵⁷Fe Mössbauer spectrum of $Fe_{0.5}Co_{0.5}C$. Scale bar: b) 5 nm, c) 40 nm, and d–f) 30 nm.

ment (Figure 1h and Table 1), the estimated oxygen content for Fe_{0.5}Co_{0.5}C (27.3%) was higher than that of pure carbon aerogel (4.1%), indicating the encapsulated FeCo alloy was conducive to the stabilization of oxygen-rich groups on graphite carbon shell. 57Fe Mössbauer spectroscopy is a powerful atom-selective technique to reveal the local structure of Fe atoms (Figure 1i, and the related Mössbauer parameters were listed in Table S4). Fe_{0.5}Co_{0.5}C exhibited a dominant resonantlines sextet to be attributed to the formation of FeCo alloy (Center shift: 0.03 mm s^{-1} ; H: 35.2 T), and the spectral area of FeCo was up to 78.0%. An additional magnetically split sextet (13.1%) attributed to Fe_xO (CS: 0.40 mm s⁻¹; H: 48.3 T) was due to the surface oxidation of partial Fe when exposed in the air. Besides, a singlet and a quadrupole split doublet were observed at the center of the spectrum. The singlet was assigned to γ -Fe (CS: -0.09 mm s^{-1}), accounting for 3.3%, while the doublet was ascribed to FeC_x (CS:

 0.50 mm s^{-1}) owing to the reaction of iron and carbon substrate during the calcination process at a high temperature (950 °C). The spectral area of FeC_x was ca. 5.0%. Based on the results, majority of Fe atoms in Fe_{0.5}Co_{0.5}C electrode are coordinated with Co, existing in the form of FeCo alloy. The graphite shells prevent the direct contact between inner FeCo alloy and external solution during wastewater treatment, as evidenced by spin-trapping electron paramagnetic resonance (EPR) analysis in the following section.

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AOPs Performance of Selective Electrochemical O₂ Activation

Antibiotics are extensively used for the treatment and prevention of infectious diseases. Ciprofloxacin (CIP), a synthetic third-generation fluoroquinolone antibiotic, is selected as a model contaminant to evaluate the electrocatalytic performance of synthesized electrodes in converting O₂ to 'OH. As depicted in Figure 2a, only 5.0 ± 1.2 % (the values in this work are expressed as mean \pm standard deviation. See equation S1 for the detailed information) CIP was degraded with pure carbon aerogel, which was possibly due to the electrochemical adsorption effect. 100.0 % CIP removal was astonishingly achieved in 5 min by using Fe_{0.5}Co_{0.5}C. Pseudofirst-order plot for the CIP removal was obtained with the apparent rate constant (k_{obs}) of $1.44 \pm 0.04 \text{ min}^{-1}$ with correlation coefficient $(R^2) = 0.990$. While the contribution of physical adsorption and electrochemical adsorption to the CIP removal were inappreciable 2.7 ± 0.1 % and 8.1 ± 0.2 % in 5 min, respectively (Figure S1), indicating that the satisfactory CIP degradation was mainly induced by heterogeneous catalytic reaction with Fe_{0.5}Co_{0.5}C cathode in the presence of O₂.

To Figure out the active sites for catalytic degradation efficiency, EPR analysis was conducted to identify the



Figure 2. a) The CIP degradation of C/E(O₂) and Fe_{0.5}CO_{0.5}C/E(O₂). Insets: the corresponding degradation rate constant of Fe_{0.5}CO_{0.5}C cathode and structural models of pure carbon aerogel (up) and Fe_{0.5}CO_{0.5}C (down). b) The cycle stability experiments within Fe_{0.5}CO_{0.5}C for the CIP degradation. c) Spin-trapping EPR spectra for detection of 'OH using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as trapping agent in different systems. d) Comparison of the reaction rate under different quenching conditions. e) Comparison of k_{obs} and J among various electrodes (Fe_{0.5}CO_{0.5}C, C/Fe²⁺, CeO₂/RGO,^[11] Ce_{0.75}Zr_{0.25}O₂/RGO,^[12] MnCo₂O₄-CF,^[13] Fr-ErGO,^[14] Ni-CF^[15]) for the CIP removal in electrocatalytic degradation processes.

generation of ROS by using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 5-tert-butoxycarbonyl-5-methyl-1-pyrroline-Noxide (BMPO) as the trapping agents to observe the characteristic peak signals of DMPO- \cdot OH and BMPO- \cdot O₂⁻. In the electrocatalytic process using $Fe_{0.5}Co_{0.5}C$ as cathode in the presence of O_2 (denoted as $Fe_{0.5}Co_{0.5}C/E(O_2)$), a high intensity of the particular quartet line with an intensity ratio of 1:2:2:1 corresponding to the DMPO-'OH adduct was observed (Figure 2c).^[9] No DMPO-OH signal appeared in $Fe_{0.5}Co_{0.5}C/E(N_2)$ when replacing O_2 with N_2 , indicating that 'OH are originated from the electrochemical reduction of O_2 . Previous studies have suggested that H₂O₂ can be electrogenerated via 2-electron ORR pathway over carbon-based materials.^[5a,10] The concentration of accumulated H₂O₂ with pure carbon aerogel (C) was $1350 \pm 38.9 \,\mu\text{M}$ in 2 h, while almost no H₂O₂ was detected with Fe_{0.5}Co_{0.5}C (Figure S2). In order to clarify whether FeCoC is involved in the catalytic decomposition of H₂O₂, a clear comparison of generating OH was carried out by using Fe_{0.5}Co_{0.5}C cathode with externallysupplied H₂O₂. Very weak DMPO-OH signal was observed in Fe_{0.5}Co_{0.5}C/H₂O₂, suggesting that inner FeCo alloy was perfectly protected by outer graphite shell to impede the Fenton reaction. However, strong DMPO-OH signal appeared in presence of externally-supplied H₂O₂ with applied electric current in N₂ atmosphere ($Fe_{0.5}Co_{0.5}C/H_2O_2/E(N_2)$), suggesting the 'OH generation came from electrocatalytic reduction of H₂O₂. Iron-site-shielding test was further conducted by employing the chelation agent 1,10-phenanthroline in $Fe_{0.5}Co_{0.5}C/E(O_2)$ system to investigate whether inner FeCo alloy was involved in Fenton reaction. There was no inhibition for 'OH generation after adding 10 mmol L^{-1} 1,10-phenanthroline. However, in FeCo alloy and externally-supplied H₂O₂ system, OH production from Fenton-like reaction was completely depressed (Figure S3). Moreover, inner FeCo alloy was tightly encapsulated by graphite shell ever after the treatment with 0.1 mol L^{-1} H₂SO₄ at 80 °C for 8 h (Figure S4), and the DMPO-OH signals were comparable to that with Fe_{0.5}Co_{0.5}C (Figure S5). Besides, no 'OH was produced with pure C in a series of control experiments including $C/E(O_2)$, C/H_2O_2 , and $C/H_2O_2/E(N_2)$. Thus, it is reasonable to indicate that, in $Fe_{0.5}Co_{0.5}C/E(O_2)$, O₂ was efficiently reduced to 'OH through electrocatalytic reduction way on the graphite carbon shell enriched by electrons coming from inner FeCo alloy. This is completely different from traditional Fenton reaction with poor electron transfer initiated by reduction-/oxidationstate cycle.

Radical quenching experiments were conducted to identify the active species generated during electrochemical activation of O₂, using *Tert*-butanol (TBA) and superoxide dismutase (SOD) to scavenge 'OH and 'O₂⁻, respectively. As exhibited in Figures 2d and S7, the addition of TBA led to a significant decrease of k_{obs} from 1.44 ± 0.04 min⁻¹ to $0.05 \pm$ 0.02 min⁻¹, demonstrating that CIP was eliminated through the surface catalytic oxidation by 'OH. Additionally, the CIP degradation efficiency decreased significantly with k_{obs} of 0.07 ± 0.02 min⁻¹ in the presence of SOD, even no BMPO-'O₂⁻ signal was detected during EPR analysis. These results manifested that O₂ was firstly reduced to 'O₂⁻ intermediate via 1-electron pathway, which followed by subsequent reduction to H_2O_2 and then to OH. In order to verify the stability and durability of Fe_{0.5}Co_{0.5}C electrode, we conducted 50 cycles of degradation experiments. As expected, the electrocatalytic performance almost remained as high as 95.5 % after 50 successive runs, causing only 3.5% electrocatalytic activity loss than the first run (99.8%) (Figure 2b). Furthermore, the generated intermediates and possible degradation pathway of CIP during the cyclic experiments were also investigated in Table S5 and Figure S11. The morphology, crystalline phases and surface oxygen groups of Fe_{0.5}Co_{0.5}C were well preserved (Figures \$12-15), and the negligible metal leaching of Fe and Co ions were 0.037 ± 0.002 and $0.050 \pm 0.001 \text{ mg L}^{-1}$, respectively with Fe0.5Co0.5C after the degradation process, indicating its excellent catalytic stability and reusability. There is no contribution of homogeneous Fenton-like reaction with released metal ions for 'OH generation and CIP removal (Figure S16).

To further evaluate the electrocatalytic performance, the CIP removal within Fe0.5Co0.5C cathode was assessed by comparing k_{obs} and applied current density $(J, mA cm^{-2})$ with previously reported catalysts. As shown in Figure 2e and Table S6, k_{obs} were 0.02, 0.01, 0.03, 0.22 and 0.04 min⁻¹ in traditional electrochemical advanced oxidation processes (EAOPs) with CeO_2/RGO ,^[11] $Ce_{0.75}Zr_{0.25}O_2/RGO$,^[12] MnCo₂O₄-CF,^[13] Fc-ErGO^[14] and Ni-CF^[15] as cathodes, respectively. Moreover, k_{obs} in homogeneous EF system (C/ Fe^{2+}) with carbon aerogel as cathode and Fe^{2+} as Fenton catalyst were $0.11 \pm 0.01 \text{ min}^{-1}$ under the same conditions. Remarkably, $Fe_{0.5}Co_{0.5}C$ cathode had the k_{obs} of $1.44 \pm$ 0.04 min^{-1} to be 7–144 times higher than other catalysts. Additionally, the lowest current density $(J = 2.5 \text{ mA cm}^{-2})$ was applied with Fe_{0.5}Co_{0.5}C to achieve high degradation efficiency. The specific energy consumption of 0.16 kWhg⁻¹ TOC was required for complete removal of CIP with $Fe_{0.5}Co_{0.5}C$, which only accounted for 1.5–8.9% of the energy consumption in traditional EAOPs (Figure S17). The removal of dissolved organic carbon (DOC) and defluorination efficiency were explored as shown in Table S7, Figures S19 and S20. Meanwhile, compared to the traditional electrodes, the electrochemical stability is much higher with $Fe_{0.5}Co_{0.5}C$ during the wastewater purification. These advantages endow Fe_{0.5}Co_{0.5}C electrode with great prospect in practical applications.

The textural properties and element contents in different cathodes are illustrated in Table 1. The total concentration of doped metal in series of cathodes was regulated to 0.97-1.31 wt.%. The Fe/Co ratio varied from 0.6-1.5 with the increasing amount of doped Fe from 0.48 ± 0.02 to $0.71 \pm$ 0.03 wt.%. The as-prepared electrodes were nominated as FeC, Fe_{0.7}Co_{0.5}C, Fe_{0.5}Co_{0.5}C, Fe_{0.5}Co_{0.7}C and CoC, respectively, according to the ratio of mass concentration of doped Fe and Co. Fe_{0.5}Co_{0.5}C had the smaller specific surface area of 287 $m^2 g^{-1}$ than FeC, $Fe_{0.7} Co_{0.5} C, \ Fe_{0.5} Co_{0.7} C$ and CoC with 395, 295, 293 and 313 m^2g^{-1} , respectively, indicating that the astonishing CIP degradation efficiency within Fe_{0.5}Co_{0.5}C was not ascribed to the CIP adsorption, in great accordance with the results in Figure S1. Noticeably, the content of surface oxygen in Fe_{0.5}Co_{0.5}C was highest. According to the observation in literatures,^[7a,16] when the Fe/Co ratio was 1.0, Fe_{0.5}Co_{0.5}C possessed a properly high Fermi level ($E_{\rm F}$) of encapsulated metal, leading to lower metal work function ($W_{\rm m}$). In general, the normalized electron transfer ($\Delta Q_{\rm ET}$) from encapsulated metal to outer carbon layer could be promoted with lower $W_{\rm m}$, and thereby increased the oxygen binding energy of outer carbon layer for obtaining abundant oxygen-contained functional groups.

Intrinsic Mechanism of OH Generation in Oxygen Electrochemical Reduction System

In order to investigate the intrinsic roles for converting O₂ to OH in electrocatalytic process, a series of $Fe_x Co_y C$ (x:y = 0.7:0.5, 0.5:0.5, 0.5:0.7) as well as pure FeC and CoC were fabricated. As expected, all FeCoC electrodes exhibited higher degradation efficiency than FeC and CoC (Figure S21). Remarkably, the highest CIP removal (100.0%) was achieved for Fe_{0.5}Co_{0.5}C electrode with an optimal Fe/Co ratio of 1.0, while the CIP removal in 5 min were 85.1 ± 1.6 %, $72.9 \pm 1.2\%$, $63.2 \pm 1.4\%$ and $42.4 \pm 0.8\%$ for $Fe_{0.7}Co_{0.5}C$, Fe_{0.5}Co_{0.7}C, FeC and CoC electrodes, respectively. The X-ray absorption near edge structure (XANES) measurement was conducted to further explore the chemical state and coordination environment of doped metal species at the atomic level. Taking Fe_{0.5}Co_{0.5}C as an example, the Fe K-edge profile of Fe_{0.5}Co_{0.5}C in XANES was close to that of Fe foil, but far from that of iron oxides, manifesting that the valence state of Fe in Fe_{0.5}Co_{0.5}C was very close to 0. Simultaneously, the absorption edge positions of Fe_{0.7}Co_{0.5}C and Fe_{0.5}Co_{0.7}C at the Fe K-edge almost overlapped with that of Fe_{0.5}Co_{0.5}C, revealing that the existence form of Fe species did not change with the altered ratio of Fe/Co (Figure 3a). Furthermore, the Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) spectra of $Fe_x Co_y C$ at Fe K-edge are illustrated in Figure S22. All $Fe_x Co_y C$ showed a prominent peak at 2.15 Å that interpreted as a Fe-Co contribution, demonstrating that atomically dispersed Fe atom existed in the form of Fe-Co coordination. In addition, further structural configuration of Fe_rCo_vC was obtained from Raman spectra (Figure 3 b). The intensity ratio (I_D/I_G) of the D band (1360 cm⁻¹) and G band (1600 cm⁻¹) is considered as a significant parameter that reflects the defect-site and graphitic structure of carbon-based electrodes.^[17] The values of I_D/I_G were 0.58 and 0.70 for FeC and CoC, respectively, indicating a high degree of graphitization. By comparison, much higher values of I_D/I_G for Fe_xCo_vC (0.94, 0.92, 0.93 for $Fe_{0.7}Co_{0.5}C$, Fe_{0.5}Co_{0.5}C, Fe_{0.5}Co_{0.7}C, respectively) solidly confirmed the formation of encapsulated FeCo alloy resulted in a relatively lower graphitization degree. Additionally, the ideal electrical conductivity of synthesized $Fe_x Co_y C$ with different I_D/I_G was conducted as shown in Figures 3c and S24. The conductivity values for FeC, Fe_{0.7}Co_{0.5}C, Fe_{0.5}Co_{0.5}C, Fe_{0.5}Co_{0.7}C and CoC were 2.52 ± 0.05 , 2.80 ± 0.08 , 4.19 ± 0.12 , 3.24 ± 0.14 and 3.12 ± 0.16 S mm⁻¹, respectively. The carbon layers not only protect the inner FeCo alloy, but also act as conductor for electron transfer from inner alloy to out carbon shell. In general, the electrocatalytic activity depends on how much the carbon shell is activated by inner FeCo alloy and how



Figure 3. a) Fe K-edge XANES of Fe_xCo_yC , standard Fe foil, Fe_2O_3 , and Fe_3O_4 samples. b) Raman spectra of Fe_xCo_yC . c) The electrical conductivity of Fe_xCo_yC . d) C-K edge NEXAFS of FeC, $Fe_{0.5}Co_{0.5}C$ and CoC. e) Comparison of selectivity of H_2O_2 and the content of -COOH groups from XPS analysis for Fe_xCo_yC electrodes. f) EPR spectra for detection of 'OH in $Fe_xCo_yC/E(O_2)$ systems.

much the surface is enriched with electrons coming from inner FeCo alloy.^[7a,18] The ideal conductivity of $Fe_{0.5}Co_{0.5}C$ can accelerate the electron transfer process and thus enrich the electron density on graphite shell.

Recent studies demonstrated that the oxygen functional groups can enhance the electrochemical reactivity during ORR process. To investigate the "depth profile" information about the electronic structure of the designed electrodes, the near-edge X-ray absorption fine structure (NEXAFS) was applied. As shown in Figure 3d, a much more intense peak centered at 288.5 eV observed in Fe0.5Co0.5C electrode was assigned to oxygen-containing function group (-COOH),[17b] owing to the promoted $1s \rightarrow \pi^*$ resonances after the doping of Fe and Co into the carbon matrix at the same time. Correspondingly, a sharp and intense peak at 531.3 eV ascribed to the π^* of -C=O also demonstrated that the coexistence of Fe and Co caused more intense $1s \rightarrow \pi^*$ resonance and thus increased -COOH (Figure S25). This feature was found to be strengthened with co-doping of Fe and Co and lower degree of graphitization, which was consistent with the Raman spectral results. The identification of oxygen-based sites was further revealed by X-ray photoelectron spectroscopy (XPS). The O1s spectra of $Fe_x Co_y C$ in Figure S26 were decomposed to different oxygen groups including C-O-C (\approx 533.8 eV), C-O-M (\approx 532.4 eV), -COOH $(\approx 531.6 \text{ eV})$ and O-M $(\approx 530.8 \text{ eV})$ in carbon matrix. The surface -COOH content of 3.09 wt% for Fe_{0.5}Co_{0.5}C was the highest among FeC (0.09 wt%), $Fe_{0.7}Co_{0.5}C$ (0.29 wt%), $Fe_{0.5}Co_{0.7}C$ (0.25 wt%) and CoC (0.04 wt%) (Figure 3e).

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The effect of oxygen functional groups on the electrocatalytic performance of oxygen reduction was initially assessed by a standard method via a rotating ring-disk electrode (RRDE). As presented in Figure S27, both FeC and CoC provided a low ring current output, suggesting a less favorable 2-electron pathway with the calculated H_2O_2 selectivity of 19.7% and 18.4%, respectively, while the corresponding electron transfer number were 3.67 and 3.60 (Figure S28). As an alternative, Fe_{0.5}Co_{0.5}C with optimal Fe/ Co ratio and abundant -COOH groups exhibited the highest H_2O_2 selectivity of 70.7 % with the electron transfer number of 2.6. A positive relationship was obtained between -COOH content and H_2O_2 selectivity of $2e^-$ ORR (Figure 3e). Additionally, the exposed -COOH on Fe0.5Co0.5C was removed through chemical reduction with hydrazine hydrate $(N_2H_4 \cdot H_2O)$, denoted as N_2H_4 -Fe_{0.5}Co_{0.5}C. As expected, both the activity and selectivity of 2e- ORR was obviously declined after the elimination of -COOH group (Figure S29).

During the 3-electron pathway, the 2-electron oxygen reductive H₂O₂ stepped by 1-electron electrocatalytic reduction towards to 'OH. It is noteworthy that Fe_{0.5}Co_{0.5}C cathode with the optimal Fe/Co ratio exhibited the highest intensity of the DMPO-OH signals (Figure 3 f). The $Fe_{0.5}Co_{0.5}C$ with the efficient ability of 'OH generation indeed resulted in high degradation efficiency with highest k_{obs} of CIP removal (Figure S21). However, the similar intensities were detected for all $Fe_xCo_yC/H_2O_2/E(N_2)$ with same external H_2O_2 (Figure S30), validating that the electron transfer ability was independent from Fe/Co ratio. Notably, in the absence of applied electric field, the DMPO-OH signals in $Fe_x Co_y C/$ H₂O₂/N₂ were negligibly weak, suggesting the electrocatalytic reduction of H₂O₂ via 1-electron pathway. Figure S31 clearly illustrates why 3-electron oxygen reduction occurs for FeCoC but not for FeCo alloy and pure carbon aerogel. Furthermore, the electrocatalytic performance for producing 'OH remained constant in pH range of 3.0-11.0 in Fe_{0.5}Co_{0.5}C/E(O₂) (Figure S32).

Figure 4a displays the voltammograms for Fe_{0.5}Co_{0.5}C electrode at rotation rates from 400 to 2500 rpm. As expected, well-defined sigmoidal shapes are obtained. The electron transfer number (n) during ORR is calculated to be approximately 2.8 from the Koutecky-Levich (K-L) plots with potential from -0.25 to -0.6 V vs. SCE (Figure 4b). Operando pressure test has been conducted to investigate the fundamental mechanism of electrocatalytic oxygen reduction.^[19] Figure 4c shows the O_2 pressure response on ORR cells in Na₂SO₄ electrolytes at pH 3. Fe_{0.5}Co_{0.5}C follows the 3.1 e/O2 coefficient during electrocatalytic reduction of oxygen, in line with the theoretical value of 3.0 e/O_2 in Equation (6). It is clear that the pressure in the cell can stabilize after repeated galvanostatic ORR periods, which indicates that Fe_{0.5}Co_{0.5}C electrode has good stability. The electrocatalytic reduction of H_2O_2 is also validated by linear sweep voltammetry (LSV) (Figure 4d), and the reduction of H_2O_2 occurs at a more positive potential than oxygen reduction. All of these results support the overall 3-electron oxygen reduction reaction pathway on Fe_{0.5}Co_{0.5}C, referring **Research Articles**



Figure 4. a) Linear-sweep voltammograms of $Fe_{0.5}Co_{0.5}C$ measured on a rotating disk electrode at different rotation speeds at pH 3. b) The Koutecky–Levich curves at various potentials. c) Operando pressure measurement of $Fe_{0.5}Co_{0.5}C$ during the electrocatalytic reduction of oxygen at pH 3. d) Steady-state voltammograms of electrocatalytic oxygen reduction at pH 3 on $Fe_{0.5}Co_{0.5}C$ before (black —) and after the addition of 4×10^{-3} mol L⁻¹ H₂O₂ (red -----).

to the 2-electron oxygen reductive H_2O_2 intermediate simultaneously stepped by 1-electron electrocatalytic reduction toward OH.

The insight of the efficient electrocatalytic performance of $Fe_{0.5}Co_{0.5}C$ was further investigated. NEXAFS spectra of Fe and Co L-edge provided direct evidence of charge transfer between Fe and Co. As shown in Figure 5a, the Fe L-edge binding energies of $Fe_{0.5}Co_{0.5}C$ at 708.1 and 720.5 eV corresponding to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ of Fe^{2+} exhibited 0.53 and 1.42 eV shifts to lower compared to FeC with 708.6 and 721.9 eV, respectively, indicating less positive charge of Fe^{2+} : $Fe^{(2-\delta)+}$ (δ , close to 0). The binding energies of Co $2p_{3/2}$



Figure 5. a) Fe L-edge NEXAFS of $Fe_{0.5}Co_{0.5}C$ and FeC. b) Co L-edge NEXAFS of $Fe_{0.5}Co_{0.5}C$ and CoC. c) Fe K-edge and Co K-edge XANES of fresh and used $Fe_{0.5}Co_{0.5}C$, standard Fe foil, Fe_2O_3 and Fe_3O_4 samples. d) Linear fitting curve of fresh and used $Fe_{0.5}Co_{0.5}C$, and reference materials derived from the corresponding Fe K-edge XANES spectra.

 $(\approx 778.9~eV)$ and Co $2p_{1/2}~(\approx 794.0~eV)$ in CoC (Figure 5b) corresponding to Co^{2+} exhibited 0.74 eV and 1.39 eV lower shifts than Co 2p in Fe_{0.5}Co_{0.5}C, suggesting that the valence of Co changed to a slightly higher Co^{(2+\delta)+}, and the negative charge was partly transferred from Co to Fe.^{[20]}

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It has been proposed that FeCo alloy in FeCoC electrode was perfectly protected by the outer graphite shell, leading to prominent electrocatalytic durability. In order to verify this perspective, XANES measurement was performed for Fe0.5Co0.5C cathode before and after the CIP degradation, denoted as fresh/used Fe_{0.5}Co_{0.5}C. Interestingly, as shown in Figure 5c (left), the line position (absorption edge) of used Fe_{0.5}Co_{0.5}C, shifting slightly to lower energy than fresh Fe_{0.5}Co_{0.5}C, was located between Fe foil and fresh Fe_{0.5}Co_{0.5}C, suggesting the valence of iron species in used Fe_{0.5}Co_{0.5}C was more negative and closer to 0. Similarly, the XANES spectra of fresh and used Fe0.5Co0.5C at Co K-edge revealed that the valence of Co remained the same after the elimination of contaminants according to the completely overlapped absorption edge line of fresh and used Fe_{0.5}Co_{0.5}C in Figure 5c (right). The valence of Fe was also examined with the Fe Kedge XANES. The linear-fit curves were obtained from standard Fe foil, Fe₂O₃ and Fe₃O₄ with different Fe oxidation states from 0 to +3. Noteworthily, the valence of Fe species in used $Fe_{0.5}Co_{0.5}C$ was calculated as +0.11, which was more negative than that of fresh $Fe_{0.5}Co_{0.5}C (+0.29)$ (Figure 5d). When $Fe_{0.5}Co_{0.5}C$ was employed, 'OH can be efficiently generated from oxygen via 3-electron pathway. During the electrocatalytic reduction process, the graphite carbon shell was activated and enriched by electrons from encapsulated FeCo alloy.^[21] Simultaneously, the electrons from external circuit would be fast provided to inner FeCo alloy through carbon framework.

As revealed in the above experimental results, abundant -COOH functional groups were formed on the surface of $Fe_{0.5}Co_{0.5}C$. To explore the electrocatalytic mechanism of O_2 reduction, density functional theory (DFT) calculations based on a three-dimensional graphite sheet with FeCoC were carried out (Figures 6a-e). The models of FeCo alloy encapsulated graphene sheet structure with -COOH and C-O-C groups are exhibited in Figure S33. The models of different ORR processes on FeCoC electrode are exhibited in Figure S34. The computational details were provided in the Supporting Information. The 2-electron ORR proceeds via 1electron oxygen reduction to 'OOH [Eq. (7)] and then subsequent 1-electron reduction of 'OOH to H_2O_2 [Eq. (8)]. Thus, the adsorption binding energy of 'OOH is the key descriptor for controlling and modulating the electrocatalytic activity in 2-electron ORR process.^[22]

$$O_2 + (H^+ + e^-) \rightarrow OOH$$
(7)

$$OOH + (H^+ + e^-) \rightarrow H_2O_2$$
 (8)

The *OOH adsorption energies were calculated for FeCoC respectively with -COOH and C-O-C model structures. The obtained results were summarized in Figure 6a in the form of free energy diagram at the equilibrium potential $(U^0_{\rm O_2/H_2O_2} = 0.7 \text{ V})$. An ideal catalyst should have a flat free

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Figure 6. a) Free energy diagram for O₂ reduction to H_2O_2 . Typical noble metal catalysts (Au, Pt and Pd) were compared with the asprepared Fe_{0.5}Co_{0.5}C with -COOH and C-O-C groups. Top and side views of 'OOH-adsorbed configurations on FeCoC with b,d) -COOH and c,e) C-O-C groups, respectively. f) The thermodynamic activity of O₂ reduction over FeCoC with -COOH.

energy diagram at this potential.^[23] Both stronger and weaker binding to *OOH would bring additional overpotential, causing a bottleneck for the reduction of *OOH to H_2O_2 .^[24] Notably, for Fe_{0.5}Co_{0.5}C with -COOH it was 0.13 eV downhill to form *OOH at $U_{O_2/H_2O_2}^0$, suggesting that the lowest thermodynamic overpotential of 0.13 V was required to drive the reaction. However, catalysts such as Au,^[25] Pt,^[25] Pd,^[10a] CN^[10e] respectively with higher thermodynamic overpotential of 0.39, 0.40, 0.16, 0.54 V were not sufficiently active to motivate the 2-electron ORR.

The free energy diagrams of selective electrochemical reduction of O₂ to 'OH via 3-electron pathway over $Fe_{0.5}Co_{0.5}C$ with surface -COOH were exhibited in Figure 6 f. During 3-electron pathway, O₂ is firstly adsorbed on the surface active sites (*) of $Fe_{0.5}Co_{0.5}C$ [Eq. (9)], then *O₂ is reduced and protonated to 'OOH as the intermediate [Eq. (10)], and H₂O₂ is subsequently generated and chemically bound with * to form *H₂O₂ [Eq. (11)]. The corresponding Gibbs free energy differences of these three steps were ΔG_{I} (1.18 eV), ΔG_{II} (0.57 eV) and ΔG_{III} (-0.58 eV), indicating that O₂ adsorption is speculated as the rate-limiting step during the whole electrocatalytic process, and a good O₂ adsorption capability was benefit for 2-electron ORR.

$$* + O_2 \rightarrow *O_2 \tag{9}$$

$$^{*}O_{2} + 2 H^{+} + e^{-} \rightarrow ^{*} + ^{\bullet}OOH + H^{+}$$
 (10)

$$* + OOH + H^+ + e^- \rightarrow *H_2O_2$$
 (11)

Once H_2O_2 is formed via 2-electron pathway, exploring whether the generated H_2O_2 is desorbed from the surface of $Fe_{0.5}Co_{0.5}C$ or further reduced to produce 'OH and OH⁻ via 1electron pathway is necessary.^[26] According to Equations (12) and (13), the kinetic inclination of 'OH reduced from $*H_2O_2$ could be acquired via the actual barriers of forming 'OH and OH⁻ under a certain potential. Therefore, we have determined the eventually generated species by comparing the calculated free energies of producing 'OH and OH- from $*H_2O_2$ according to the thermodynamic formulas [Eqs. (16) and (17), see Supporting Information for more details]. As shown in Figure 6 f, ΔG for 'OH generation process [Eqs. (12) and (13), $\Delta G(\cdot OH) = -3.02 \text{ eV}$ is much lower than ΔG - (H_2O_2) desorption process [Eq. (14), $\Delta G(H_2O_2) = -0.91 \text{ eV}$], indicating that the former pathway is more thermodynamically-favorable. Accordingly, the 3-electron pathway can be expressed as Equation (15). These results of theoretical calculations are consistent with 'OH simultaneously and generously released from the surface active sites in Fe_{0.5}Co_{0.5}C/E(O₂) system [Eq. (14)].

$$^{*}\mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{e}^{-} \rightarrow ^{*}\mathrm{OH} + \mathrm{OH}^{-}$$
(12)

$$^{*}OH + OH^{-} \rightarrow ^{*} + ^{\bullet}OH + OH^{-}$$

$$(13)$$

$${}^{*}H_{2}O_{2} \rightarrow {}^{*} + H_{2}O_{2}$$
 (14)

$$* + O_2 + 2H^+ + 3e^- \rightarrow * + OH + OH^-$$
 (15)

where the asterisk (*) denotes the surface active site.

$$\Delta G_{\mathrm{IV}} = \Delta G(\mathrm{OH}^{-}) = G(\mathbf{OH}) + G(\mathrm{OH}^{-}) - G(\mathrm{H}_{2}\mathrm{O}_{2}) + \mathrm{eU}$$
(16)

$$\Delta G_{\rm V} + \Delta G_{\rm VI} = \Delta G({}^{\bullet}{\rm OH}) = G({\rm OH}^{-}) + 1.9 \,\mathrm{eV} - \mathrm{eU}$$
(17)

where $G(\cdot OH)$, $G(OH^{-})$, and $G(H_2O_2)$ refer to free energies of the generated $\cdot OH$, OH^{-} , and H_2O_2 , respectively. U is the electrode potential vs. SCE.

Conclusion

In summary, a new strategy of selective electrochemical reduction of O_2 to 'OH via 3-electron pathway is demonstrated over integral FeCoC electrode. Surface -COOH groups on graphite shell act as the key role to induce the formation of H₂O₂ via the 2-electron ORR. Simultaneously, H_2O_2 intermediate would be electrocatalytic reduced to 'OH via 1-electron on the graphite shell enriched with electrons coming from inner FeCo alloy. This is completely different from traditional Fenton reaction. The proposed strategy overcomes the restriction of rate-limiting step for reducing oxidized metal ions and requirement of acidic pH condition. 100.0 % removal of CIP is obtained in 5 min with $k_{\rm obs}$ of 1.44 \pm 0.04 min^{-1} . The high degradation efficiency of FeCoC/E(O₂) system maintains even after 50 cycles. This work provides a novel strategy for forming 'OH from electrochemical reducing O₂ without using foreign reagents, which represents a fundamental breakthrough towards the generation of 'OH in advanced oxidation processes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon aerogel · FeCo alloy · hydroxyl radical · oxygen reduction reaction · water purification

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