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Supporting Information

Defect-stabilized and oxygen-coordinated iron single-atom sites facilitate hydrogen peroxide electrosynthesis

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1. Experimental Section

1.1 Preparation of the CNT-D-O, CNT-O-Fe, and CNT-D-O-Fe

Fe(NO₃)₃ (80.8 mg) was added into 30 mL of ethanol solution, which was fully stirred until completely dissolved. Next, multi-walled carbon nanotubes (CNT, 200 mg) were added to the above solution under ultrasonic processing. Then, ammonium hydroxide (2 mL, 25 wt.%) was dripped into the above mixture under stirring, which is further dried in a water bath with a temperature of 60 °C to obtain CNT-Fe-OH. CNT-Fe-OH was placed in an air atmosphere and treated at 490 °C for 60 min at a rate of 10 °C min⁻¹. After which CNT-D-O-Fe-Fe₂O₃ was produced. Then, concentrated hydrochloric acid solution (10 mL, 36-38 wt.%) was mixed with CNT-D-O-Fe-Fe₂O₃, which was transferred into a Teflon-lined stainless-steel autoclave at 120 °C for 2 h in an oven. After the above hydro-thermal treatment, the residues were washed with ethyl alcohol and deionized water, alternatively, which was followed by a drying process to obtain CNT-D-O-Fe. CNT went through a similar preparation condition above except that Fe(NO₃)₃ was not introduced, resulting in the control sample of CNT-D-O. Besides, CNT-Fe-OH underwent a thermal treatment in an argon environment instead of an air atmosphere to prepare CNT-O-Fe as another control sample.

1.2 Characterizations

The surface topography of the catalytic materials was characterized via the field emission scanning electron microscope (Japan, S4800, Hitachi). A probe-corrected transmission electron microscope with aberration correction (Japan, JEM-ARM300F, JEOL) was used to obtain the High-angle annular dark-field scanning transmission electron microscopy image (HAADF-STEM). X-ray diffraction (XRD) patterns were characterized via an X-ray powder diffractometer (China, CX-2700, Danton). The SPring-814b2 beamline of the Synchrotron Radiation Facility of Japan was used to conduct the X-ray absorption fine structure spectroscopy (XAFS) analysis, including the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES). X-ray photoelectron spectra were performed on a photoelectron spectroscope (U.S.A., K-Alpha, Thermo Scientific). An inductively coupled plasma-optical emission spectroscopy (U.S.A., 5110, Agilent) was used to analyze the metal content in the catalytic materials. Nitrogen adsorption-desorption was conducted via an automated surface area and pore size analyzer ((U.S.A., Quadrasorb Nava 4000, Quantachrome), and Brunauer-Emmett-Teller (BET) formulations were used to obtain specific surface area. The thermal gravity (TG) and differential thermal gravity (DTG) curves were obtained via a simultaneous thermal analyzer (Germany, STA4495F5, Netzsch).

1.3 Electrochemical measurements

The catalysts (4 mg) were dispersed into the solution consisting of distilled water (375 μ L), isopropanol (125 μ L) and Nafion ionomer (20 μ L, 5 wt.%,) under ultrasonic processing for 30 min. Then dispersion liquid (8 μ L) was dripped to the surface of the rotating ring disk electrode (RRDE, with a diameter of 5 mm). After drying, the working electrode was obtained and the mass loading of catalyst is 0.31 mg cm⁻². All electrochemical tests were performed at room temperature via an electrochemical workstation (China, 7003, Donghua). The traditional three-electrode system was constructed using Ag/AgCl (saturated KCl aqueous solution) electrode, a carbon plate, and RRDE as the reference electrode, counter electrode, and working electrode, respectively. Linear sweeping voltammograms (LSV) were obtained by using oxygen-saturated 0.1 M KOH solution as the electrolyte at the scanning rate of 10 mV s⁻¹ with different speeds (400, 900, 1600, and 2500 rpm, respectively).

The potentials in this work were all transformed to the reversible hydrogen electrode (RHE) according to the calibration equation: $E_{(vs. RHE)} = E_{(Ag/AgCl)} + 0.059 \times pH + 0.198$.

The Faraday efficiency, selectivity for H₂O₂ (H₂O₂%), and electron transfer number (n) were calculated as follows:

Faraday efficiency
$$(H_2O_2) = 100*(I_R/N)/I_D$$
 %;
 H_2O_2 % = 200* $(I_R/N)/((I_R/N)+I_D)$ %;
 $n = 4*I_D/((I_R/N)+I_D)$;

Where I_D and I_R are the disk and ring current, respectively. N is the current collection efficiency of the Pt ring, which is 0.32 in our test system.

The kinetic current density (Jk) was calculated based on Koutecký-Levich equation:

$$1/J_{\rm m} = 1/J_{\rm k} + 1/J_{\rm l} = 1/J_{\rm k} + 1/(\mathbf{B}^*(\omega)^{1/2});$$

$$\mathbf{B} = 0.62^* \mathbf{n}^* \mathbf{F}^* \mathbf{C}_{\rm o} \mathbf{D}_{\rm o}^{2/3} \mathbf{v}^{-1/6};$$

where J_m , J_k , and J_l are the disk current density, the kinetic current density, and the diffusion limiting current density; ω is the rotation rate of the electrode. n is the total electron transfer number for O₂ reduction; F is the Faraday constant (F = 96485 C mol⁻¹); C_o is the O₂ volume concentration (1.2 ×10⁻³ mol cm⁻³); D_o is the diffusion coefficient of O₂ in aqueous solution (1.9 × 10⁵ cm² s⁻¹); v is the kinematic viscosity of the electrolyte solution (0.01 cm² s⁻¹).

1.4 Density functional theory (DFT) calculations:

The DMOL[1] code based on Perdew-BurkeErnzerhof (PBE) functional and the plane-wave pseudopotential for the spin-polarized generalized gradient approximation (GGA)[2, 3] was used to conduct the DFT calculations. The empirical DFT-D method based on the Grimme scheme was used to perform the dispersion corrections, including van der Waals

interactions.[4, 5] Oxygen co-doped carbon and metal were modeled based on a hexagonal 7×7 graphene layer containing the oxygen dopants and metal. A vacuum layer (12 Å) perpendicular to the surface was added to the model. The conductor-like screening model (COSMO)[6, 7] was conducted to treat the solvation effects. To confirm the adsorption energy of the intermediate at zero potential, we calculated the reaction energy of the intermediate and corrected them for zero-point energy (ZPE) and entropy (TS) using the equation: $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$; where ΔE_{ZPE} is the difference between the gas phase and the adsorbed molecules in zero point energy; ΔE and ΔS and are the reactions energy and entropy change, respectively.

2. Results and Discussion



Fig. S1. SEM image of CNT-Fe-OH.



Fig. S2. SEM image of CNT-D-O-Fe-Fe₂O₃.



Fig. S3. XRD patterns of CNT, CNT-Fe-OH, and CNT-D-O-Fe-Fe₂O₃.

The diffraction peaks in the CNT-Fe-OH can be assigned to the CNT and ammonium nitrate derived from the combination of ammonium ion and nitrate ion during the preparation process.



Fig. S4. a) TG and b) DTG curves of CNT and CNT-Fe-OH.

The first weight-loss temperature in the TG curve CNT-Fe-OH (ca. 205 °C) is attributable to the sublimation or decomposition of ammonium nitrate.



Fig. S5. SEM images of the CNT-D-O-Fe at the temperature of a) 470 °C and b) 510 °C, respectively.

As shown in **Fig.s 2**b and S5, the number of porous structures greatly increases with the increasing heat treatment from 470 °C to 490 °C. But, when the heating temperature further goes even higher to 510 °C, there are lots of broken carbon materials in CNT-D-O-Fe and the main structure of CNT is obviously destroyed (Fig. S5b). To prepare the CNT-D-O-Fe with abundant porous structures as well as the CNT skeleton, the heating temperature of 490 °C is conducted.

Materials	Fe (wt.%)
CNT-O-Fe	0.03
CNT-D-O-Fe	0.15

Table S1. Fe contents in CNT-O-Fe and CNT-D-O-Fe based on the ICP-AES test.



Fig. S6. SEM image of CNT-O-Fe.



Fig. S7. SEM image of CNT-O-Fe and the O, C, and Fe element mappings.



Fig. S8. SEM image of CNT-D-O.



Fig. S9. a) TEM and b) HRTEM images of CNT-D-O.

As shown in Fig.s S8 and S9a, a few pore structures are observed in CNT-D-O. Besides, Fig. S9b shows the fracture and the increased disorder of lattice fringes near the pore structure, which is similar to CNT-D-O-Fe. However, the number of defective porous structures in CNT-D-O is significantly lower than that of CNT-D-O-Fe. Meanwhile, the iron-based pore-forming reagent is not introduced in the reaction system during the preparation process, so there is no iron single-atom site in CNT-D-O.



Fig. S10. a) N₂ adsorption-desorption isotherms, b) the pore size distribution of CNT, CNT-O-Fe, CNT-D-O, and CNT-D-O-Fe.

Materials	CNT	CNT-D-O	CNT-O-Fe	CNT-D-O-Fe
Specific surface area $(m^2 g^{-1})$	81.7	116.9	82.1	195.2

Table S2. The specific surface area of CNT, CNT-O-Fe, CNT-D-O, and CNT-D-O-Fe.



Fig. S11. a) XPS survey spectrum, b) Fe 2p, and c) O1s XPS spectra of CNT-D-O-Fe.



Fig. S12. a) XPS survey spectrum, and b) O1s XPS spectrum of CNT-D-O.



Fig. S13. The first-order derivative of XANES data for CNT-D-O-Fe and Fe_2O_3 .



Fig. S14. The fitting curves of Fe K-edge EXAFS spectra of the CNT-D-O-Fe in k a) and R space b).

Bonding mode	Fe-O		
CN	3.60±0.92		
R / Å	2.06±0.061		
σ^2 / ×10 ⁻²	1.45±0.29		
$\Delta E^0 / eV$	5.15±3.63		
k-range	3-7.6		
R-range	1-6		
R factor	0.008329		

 Table S3. First-shell fitting parameters of Fe K-edge EXAFS for CNT-D-O-Fe.

CN: coordination number; R: the distance between absorber and backscatter atoms (or the bond length of Fe-O); σ^2 : the Debye-Waller factor value; ΔE^0 : the inner potential correction to account for the difference in the inner potential between the sample and the reference compound.



Fig. S15. LSV curves of CNT, CNT-O-Fe, CNT-D-O, and CNT-D-O-Fe at the rate of 400, 900, 1600, and 2500 rpm, respectively.



Fig. S16. H₂O₂ Faradaic efficiency of CNT, CNT-O-Fe, CNT-D-O, and CNT-D-O-Fe

Catalysts	Electrolyte	Onset potentialª (V vs, RHE)	Current density (mA cm ⁻²) at 0.550 V vs. RHE	H ₂ O ₂ Selectivity (%) at 0.550 V vs. RHE	References	
FeN ₂ O ₂ /HNC	0.1 M KOH	~0.860	~ -3.60	~89.0	[0]	
FeN ₄ /HNC	0.1 M KOH	~0.860	~ -5.50	~52.0	[8]	
Fe-NC	0.1 M HClO ₄	~ 0.700	~ -0.800	~52.0	[9]	
Fe-CNT	0.1 M KOH	0.822	~ -3.10	~93.0	54.03	
Fe-N-CNT	0.1 M KOH	~0.85	~ -4.40	~23.0	[10]	
Co-N ₂ -C/HO	0.1 M KOH	0.801	~ -2.40	>90.0 (0.1-0.5 V vs. RHE)	[11]	
Zn-N ₃ O SAC (Z-PPy-600)	0.1 M KOH	~0.650	~ -0.800	~93.0	[12]	
LP-NC(Fe)_1(iron content of 3.0 wt%, η - Fe ₂ O ₃ and Fe(0))	0.1 M KOH	0.770	~ -1.65	~40.0		
LP-NC(Fe)_1(iron content of 12.1 wt%, Fe ₃ O ₄)	0.1 M KOH	0.800	~ -1.50	~2.00	[12]	
LP-NC(Fe)_2(iron content of 3.3 wt%, α - Fe ₂ O ₃ , FeO, and Fe(0))	0.1 M KOH	0.700	~ -0.850	~80.0	[13]	
LP-NC(Fe)_2(iron content of 14.5 wt%, α-Fe ₂ O ₃)	0.1 M KOH	0.720	~ -0.750	~5.00		
CNT-D-O-Fe	0.1 M KOH	0.823	-2.72	94.4	This work	

Table S4. The comparison of 2e⁻ ORR catalytic activity.

^aThe potential at the current density of -0.1 \sim -0.15 mA cm⁻².



Fig. S17. The optimal theoretical structures of adsorption species (O2 and *OOH) in different models (Gray ball: C atom, blue ball: O atom, red ball: Fe atom, white ball: H atom). a) CNT-O-Fe-O2, b) CNT-O-Fe-OOH, c) CNT-D-O-Fe-O₂, d) CNT-D-O-Fe-OOH.

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