

Supporting information

Direct Transformation of Raw Biomass into Fe-Nx-C Single-Atom Catalyst for Efficient Oxygen Reduction Reaction

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Chemicals

Fresh pork liver is bought at a supermarket in dalian. Sodium chloride (NaCl) and potassium chloride (KCl) were purchased from TianDa Chemical Reagent Co. Ltd. (China). Iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were supplied commercially by Aladdin Chemical Reagent Co. (Shanghai, China). All chemicals were used as received without further purification.

Catalyst synthesis

Synthesis of Fe-N/C-SAC

The pristine pig liver is washed thoroughly, then cut into small pieces. The clean small pieces of pig liver are dried in a vacuum oven at 80 °C for 24 h. The sample is then ball-milled at a speed of 450 rpm for 6 h to obtain pig liver power. In a typical procedure, NaCl (5.0 g) and KCl (5.0 g) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (80 mg) were mixed with 1.0 g treated pig liver power by ball mill. Next, the mixture was transferred to a quartz boat, followed by the pyrolysis process under N_2 atmosphere with a heating rate of 5 °C min^{-1} to 800 °C and keeping for 2 h in a tubular furnace. After the natural cooling, the obtained power was collected and rinsed completely with sufficient deionized water several times to remove soluble salts. Finally, the Fe-N/C-SAC sample was fabricated for use by vacuum drying overnight at 80°.

Synthesis of Fe-N/C, N/C

Fe-N/C sample was prepared by the same procedures as Fe-N/C-SAC without introduction of molten salts system. For comparison, N/C sample was obtained by the same procedures as Fe-N/C-SAC but in the absence of metal source.

Characterization

X-ray diffraction (XRD) was carried out by a Bruker-D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ source ($\lambda = 1.5406 \text{ \AA}$). To study the morphology of samples, the scanning electron microscopy (SEM, Hitachi SU8020) was performed. Transmission electron microscopy (TEM) images were conducted on a JEOL JEM-1200EX instrument equipped with an energy dispersive X-ray (EDX) spectroscopy operating at 200 kV. STEM characterization was performed on a JEOL ARM-200F (S)TEM with CEOS CESCOR aberration corrector at 80 kV. The convergence semi-angle and acquisition semi-angle were 28-33 and 68-280 rad for the ADF imaging. Raman data were recorded on a Renishaw inVia spectrometer with laser radiation at a wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) data were collected on a Thermo ESCALAB 250XI with Al $\text{K}\alpha$ irradiation X-ray source (150 W, 500 μm). The specific surface areas and pore size distribution were obtained by nitrogen adsorption-desorption measure 3H-2000PS1 analyzer at 77 K. The X-ray absorption fine structure (XAFS) spectra were tested at BL1W1B station in Beijing Synchrotron Radiation Facility (BSRF), China. The measurements were operated in fluorescence excitation mode with a Lytle detector.

XAFS Analysis and Results

The collected EXAFS data was standardized employing the ATHENA module of the Demeter software packages. The EXAFS spectrum is acquired through subtracting the post-edge background from the total absorption, and then normalizing the edge-jump. Next, We Fourier transformed the collected $\chi(k)$ data to R space using a hanning windows ($dk=1.0 \text{ \AA}^{-1}$) to identify the EXAFS paths from coordination shells. In order to obtain the quantitative chemical configuration of iron atom, the Artemis module in Demeter software packages was used to fit the parameters of the least-squares curve. All the fitting is carried out in R space with k -weight 2. The internal atomic distances R , Debye-Waller factor σ^2 , and the edge-energy shift ΔE_0 were allowed to operate freely. The $\chi(k)$ data were applied for wavelet transform.

Electrochemical measurements

All the electrochemical measurements were carried out on the CHI 700E electrochemical workstation with a three-electrode system including KCl-saturated Ag/AgCl reference electrode and Pt wire counter electrode. A rotating ring-disk electrode was utilized as the working electrode. All the potentials were converted in relation to the reversible hydrogen electrode (RHE) criterion basing on the following correspondence.

$$E_{(RHE)} = E_{(Ag/AgCl)} + E_{(Ag/AgCl)}^{\theta} + 0.059PH$$

For the preparation of catalyst slurry, 4.0 mg sample was dispersed in 960 μL of ethanol, and 40 μL of Nafion (5 wt.%) was added to form the homogeneous mixture via ultrasonication for 30 minutes. The catalyst ink was then dripped on the surface of the GC substrate. The loadings of all samples on working electrode were controlled at 0.1 $\text{mg} \cdot \text{cm}^{-2}$. All electrochemical data were recorded in O_2 -saturated 0.1 M KOH electrolyte under room temperature.

The corresponding Koutecky–Levich (*K-L*) equation derived from RDE plots to calculate the transferred electron number (*n*) during ORR process was given as follows:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.62nFC_{\text{O}_2}D_{\text{O}_2}^{2/3}\gamma^{-1/6}$$

Where *j* and *j_k* are the recorded current density and kinetic limiting current density, ω is the rotating rate ($\text{rad} \cdot \text{s}^{-1}$) of the disk, *F* is the Faradaic constant ($96485 \text{ C} \cdot \text{mol}^{-1}$), C_{O_2} is the concentration of O_2 in 0.1 M KOH ($1.2 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$), D_{O_2} is the diffusion coefficient of O_2 in 0.1 M KOH ($1.90 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$), γ is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \cdot \text{s}^{-1}$).

The peroxide yield (H_2O_2 %) and the transfer number (*n*) are determined by the following equations with only two variables, i.e., the disk current (*I_{Disk}*) and ring current (*I_{Ring}*).

$$n = 4 \times \frac{I_D}{I_D + I_R/N}$$

$$\%(\text{H}_2\text{O}_2) = 200 \times \frac{I_R/N}{I_D + I_R/N}$$

Where *N* is the collection efficiency of the Pt ring of 0.37.

Supplementary Figures and Tables

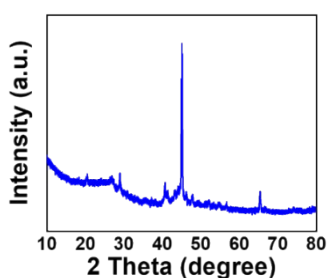


Fig. S1. XRD pattern of Fe-N/C

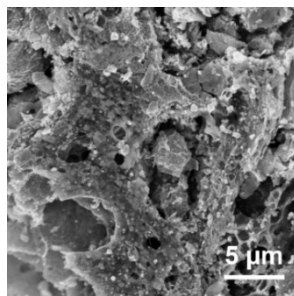


Fig. S2. SEM image of Fe-N/C

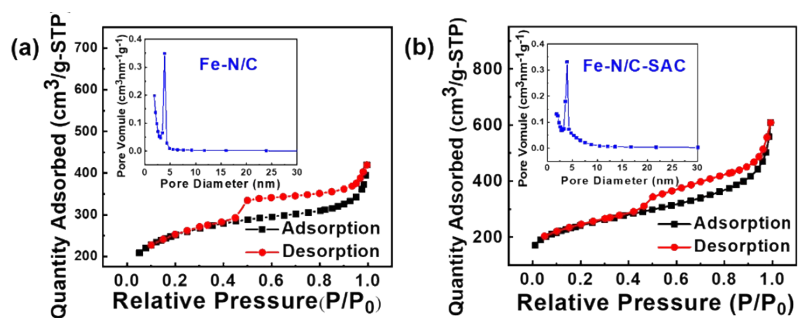


Fig. S3. N₂ adsorption-desorption isotherms of the (a) Fe-N/C and (b) Fe-N/C-SAC (inset: pore size distribution curves)

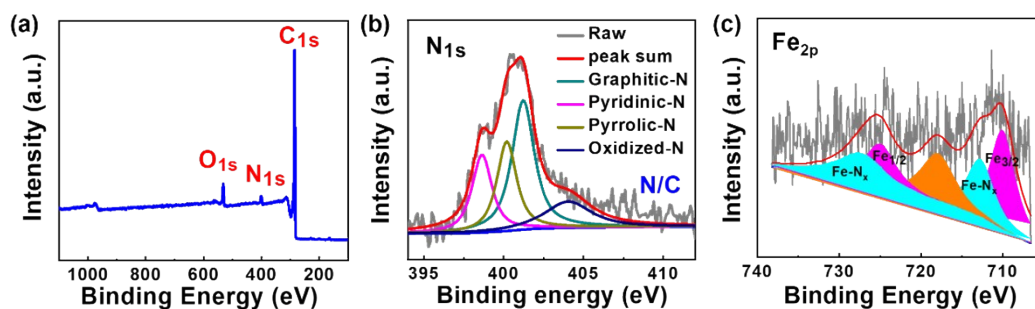


Fig. S4. (a) XPS survey spectrum of Fe-N/C-SAC; (b) high-resolution N 1s spectrum of N/C; (c) high-resolution Fe 2p spectrum of Fe-N/C-SAC

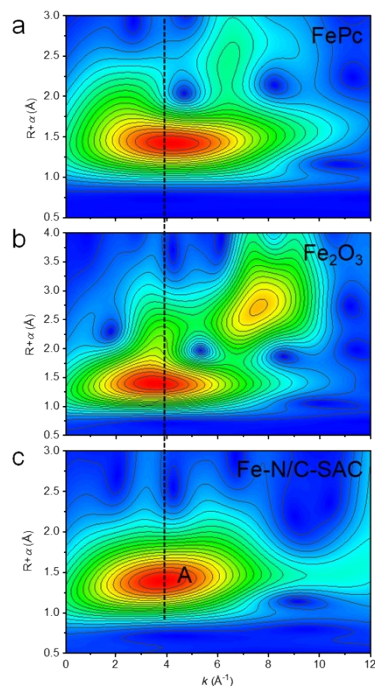


Fig. S5. Wavelet transform (WT) of FePc, Fe₂O₃ and Fe-N/C-SAC

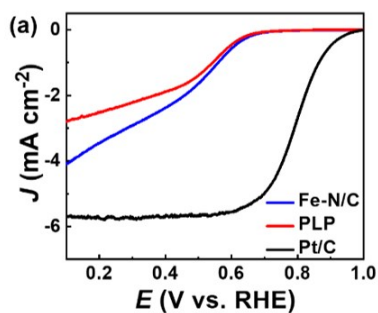


Fig. S6. (a) linear sweep voltammetry (LSV) of Fe-N/C、PLP and Pt/C RDE electrodes at 1600 rpm, PLP represents pork liver power was heated under experimental temperature and atmosphere

Table S1. Structural parameters at Fe K-edge extracted from quantitative EXAFS curve-fitting using the ARTEMIS module of IFEFFIT.

Samples	Path	CN	R (Å)	σ^2 (10^{-3}Å^2)	ΔE_0 (eV)	R -factor
Fe-N/C-SAC	Fe-N/O	5.0	2.00	4.8	-2.7	0.002

N is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); R factor is used to value the goodness of the fitting.