

**Supporting Information for**  
**Gel-limiting strategy for large-scale fabricating Fe-N-C**  
**single-atom ORR catalysts**

Youpeng Wang, Qiulin Li, Long-Cheng Zhang, Yuanke Wu, Hao Chen, Tianhao Li,  
Maowen Xu\* and Shu-Juan Bao\*

Key Laboratory of Luminescent and Real-Time Analytical Chemistry, Ministry of  
Education, Institute for Clean Energy and Advanced Materials, Faculty of Materials  
and Energy, Southwest University, Chongqing 400715, P. R. China

\*Corresponding authors.

*E-mail* addresses: [xumaowen@swu.edu.cn](mailto:xumaowen@swu.edu.cn) (M. W. Xu), [baoshj@swu.edu.cn](mailto:baoshj@swu.edu.cn) (S. J. B).

## Experimental Procedures

**Materials.** Agarose, soluble starch, dextran, and ferric trichloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) were purchased from Aladdin Co. Ltd, China. Pt/C (20-wt% on Vulcan XC-72R) was purchased from Hesen Co. Ltd, Shanghai, China. Nafion® solution (5 wt %) was purchased from Alfa Aesar Co. Ltd. Deionized water (DI) with a specific resistance of  $18.25 \text{ M}\Omega \text{ cm}^{-1}$  was prepared in a purification instrument (Millipore Elix® Advantage 10, MERCK MILLIPORE). All chemicals were of analytical grade and used as-received without any further purification.

**Preparation of Fe-AC.** For the synthesis of Fe-AC,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (200 mg) and agarose (600 mg) were dissolved in 30 mL deionized water under oil-bathing at  $70 \text{ }^\circ\text{C}$  and continuous magnetic stirring. Then, 600 mg AC was added into the above solution, which was stirred continuously at  $70 \text{ }^\circ\text{C}$  for 2 h, and cooled to room temperature ( $25 \text{ }^\circ\text{C}$ ) to form a gel. The product was centrifuged at 9000 r/min to separate the supernatant. The obtained AC-gel mixture was freeze-dried and then transferred into a ceramic crucible and placed in a tube furnace. The as-prepared precursor was heated to  $500 \text{ }^\circ\text{C}$  at  $5 \text{ }^\circ\text{C min}^{-1}$  in ammonia atmosphere and held for 1 h, followed by continued heated to  $800 \text{ }^\circ\text{C}$  at  $2 \text{ }^\circ\text{C min}^{-1}$  and kept for 2 h. After cooling to room temperature, the samples were collected and marked as Fe-AC. The samples with different Fe contents were prepared under the same conditions, except the Fe-feeding was varied. According to the input amount of Fe, the samples containing theoretical contents of Fe in Fe-AC is 1% 3.2%, 14.7%, 34.1%, and 46.3% were respectively marked as Fe-AC-1, Fe-AC-2, Fe-AC-3, Fe-AC-4, and Fe-AC-5.

**Preparation Fe-AC-ST and Fe-AC-DE.** Following same procedure as described above Fe-AC and replacing agarose with soluble starch or dextran, additional samples were prepared and marked as Fe-AC-ST and Fe-AC-DE, for better comparison, here remark Fe-AC-2 as Fe-AC-AG.

**Electrochemical measurements.** The electron-transfer number ( $n$ ) was calculated from the Koutecky-Levich equation, which is expressed as follows:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (2)$$

Here,  $J$  is the measured current density,  $J_K$  and  $J_L$  are the kinetic- limiting and diffusion-limiting current densities, respectively,  $\omega$  is the electrode rotating speed in  $\text{rad s}^{-1}$ , the K-L plots ( $\omega^{-1/2}$  vs  $J^{-1}$ ) in  $\text{O}_2$ -saturated 0.1 M KOH can be come from LSV curves at various rotation speeds. B can be determined from the slope of Koutecky-Levich plots as given by

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (3)$$

where  $F$  is the Faraday constant ( $F = 96485 \text{ C mol}^{-1}$ ),  $C_0$  is the bulk concentration of  $\text{O}_2$  in 0.1 M KOH ( $1.2 \times 10^{-6} \text{ mol cm}^{-3}$ ),  $D_0$  is the diffusion coefficient of  $\text{O}_2$  in 0.1 M KOH ( $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ), and  $\nu$  is the kinetic viscosity of 0.1 M KOH ( $0.01 \text{ cm}^2 \text{ s}^{-1}$ ).

The  $\text{H}_2\text{O}_2$  yield ( $\% \text{H}_2\text{O}_2$ ) and the number of electron transfer ( $n$ ) were calculated by the following equations:

$$\%(H_2O_2) = \frac{200 \times I_R/N}{I_D + I_R/N} \quad (3)$$

$$n = \frac{4 \times I_D}{I_D + I_D/N} \quad (4)$$

where  $I_D$  is the disk current,  $I_R$  is the ring current, and  $N$  ( $= 0.27$ ) is the collection efficiency of RRDE.

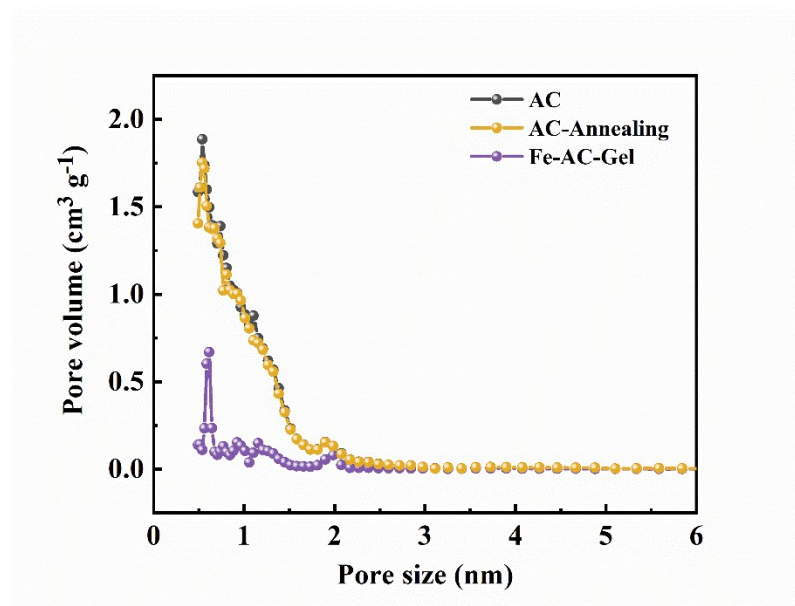
### Zn-Air Batteries testing

For Zn-air battery, an air cathode was prepared by mixing Fe-AC-1 or 20% Pt/C mixed with 5 wt% Nafion solution and loading on carbon fiber paper ( $\Phi = 2.4 \text{ cm}$ ). The catalyst mass loading was  $1 \text{ mg cm}^{-2}$  and then dried at  $60 \text{ }^\circ\text{C}$  for 4 h in an oven. The air cathode paired with a polished zinc plate ( $\Phi = 2.4 \text{ cm}$ ) and assembled in a home-made electrochemical cell shown in Figure 6a, 6 M KOH and 0.2 M  $\text{ZnCl}_2$  were used for

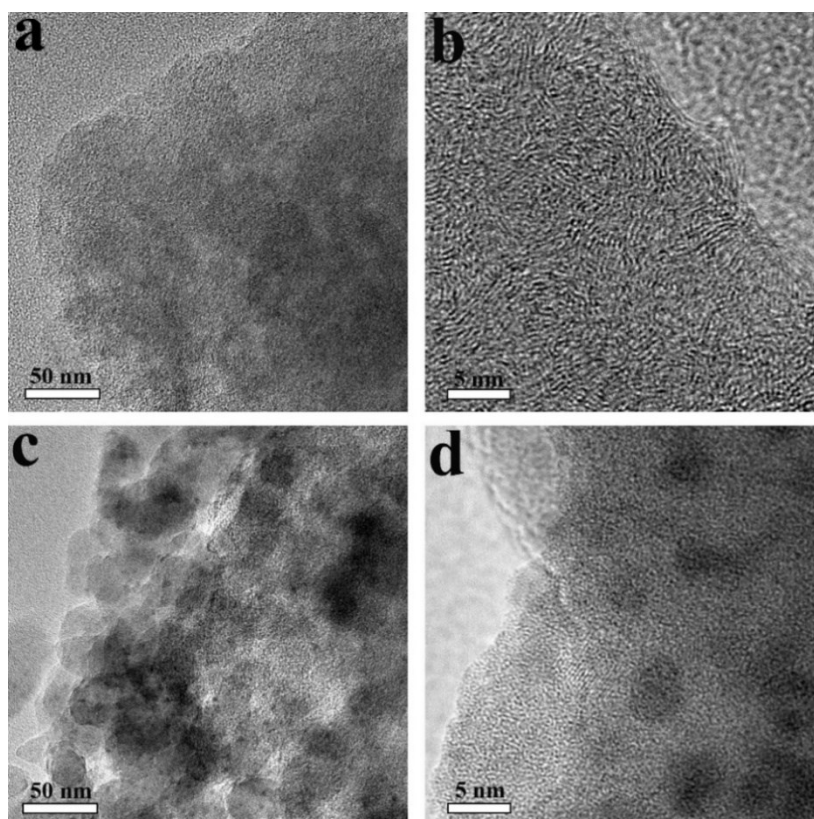
electrolyte. Before testing, the electrolyte was bubbled with oxygen for 30 min. The electrochemical measurements were carried out using an electrochemical workstation.

**Materials Characterization.** The surface morphologies of catalysts were characterized by using field-emission scanning electron microscopy (FE-SEM, JSM-7800F, Japan), transmission electron microscopy (TEM, Jeol-2100, Japan) and F30 S-TWIN electron microscope (TecnaiG2, FEI Company). The N<sub>2</sub> adsorption-desorption isotherms and corresponding pore size distribution were measured using automatic specific surface area and pore analyzer (Quadrachrome evo 2QDS-MP-30, Quantachrome Instruments, USA). The crystalline structure of the catalyst was recorded by XRD-7000 (XRD, Shimadzu XRD-7000). The Raman spectroscopy reflected the disorder and defect of catalyst was performed on Raman Spectrometer (LabRAM HR, JYEvolution, 532 nm). X-ray photoelectron spectroscopy (XPS, Escalab 250xi, USA) was used to analyze the surface compositions and element chemical state of various catalysts. The thermal properties of the samples were studied by a Thermo Gravimetric Analyzer (TGA, Q50, USA).

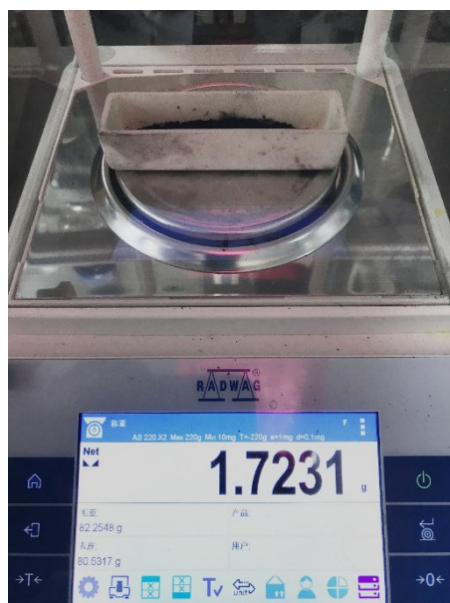
## Results and Discussion



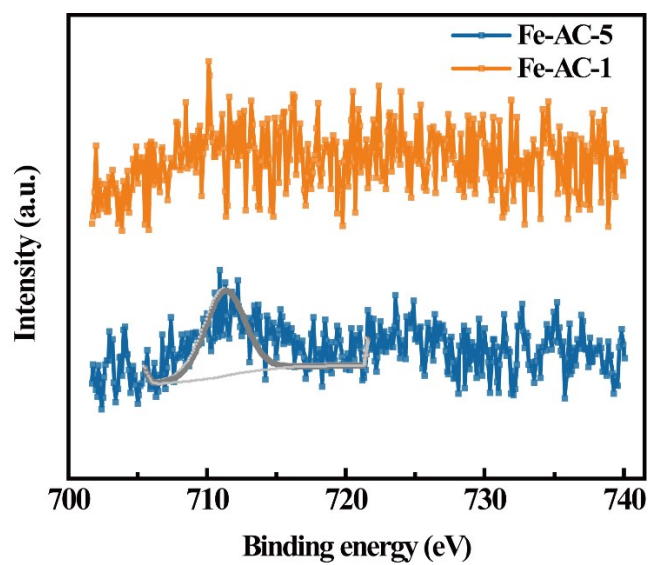
**Figure S1.** Pore size distribution of initial activated carbon, high temperature calcined activated carbon and gel-filled activated carbon.



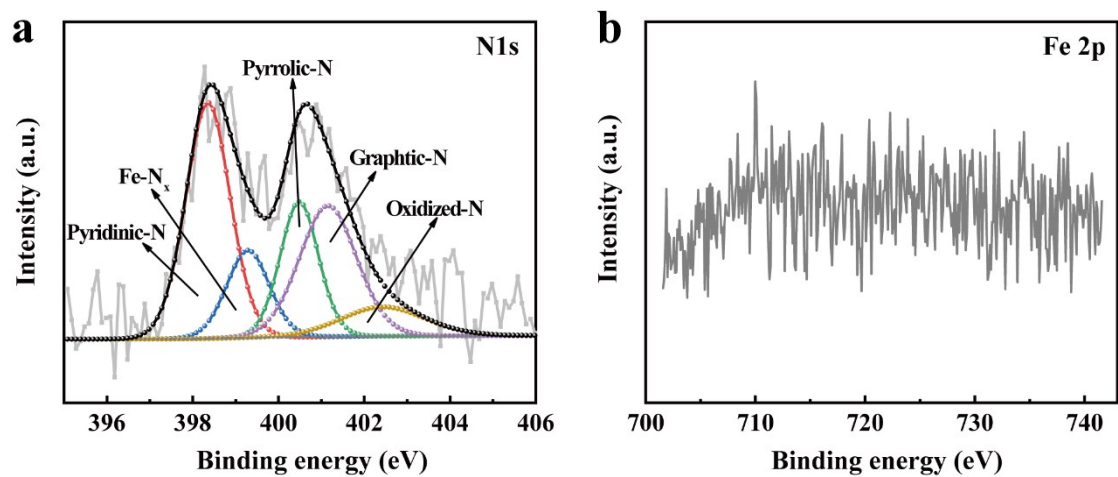
**Figure S2.** (a) and (b) TEM of Fe-AC-1, (c) and (d) TEM of Fe-AC-5.



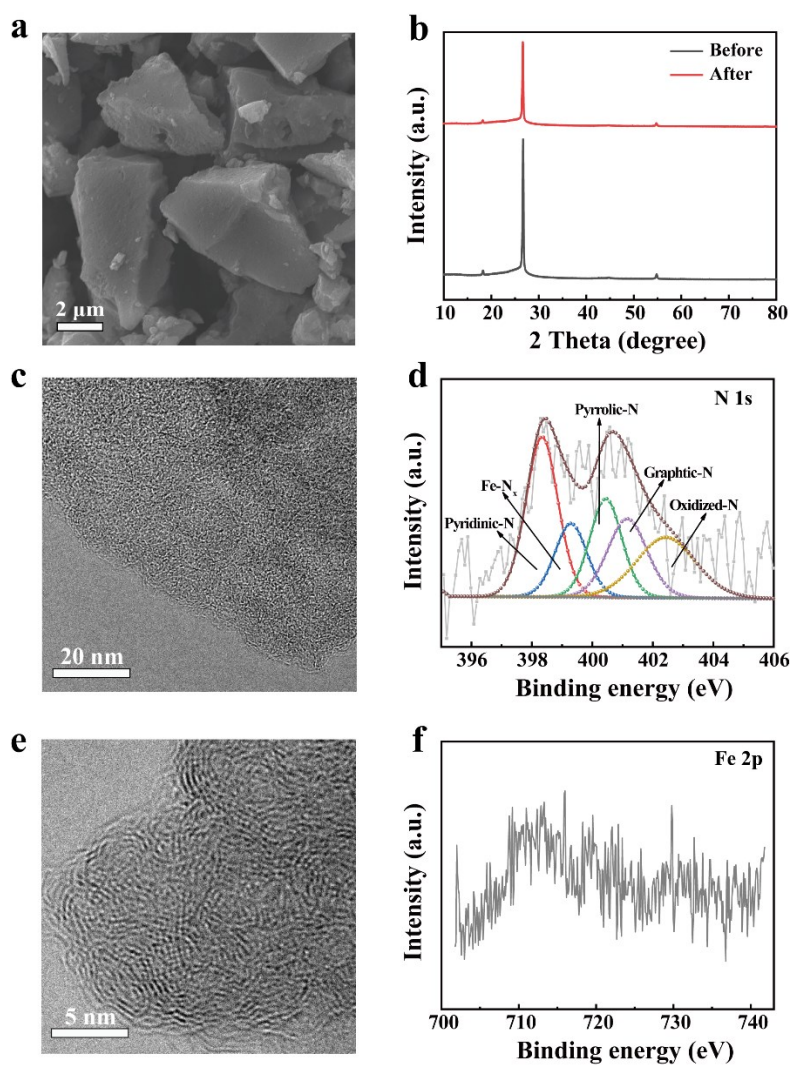
**Figure S3.** Picture of sample weighing of that calcined in the same batch.



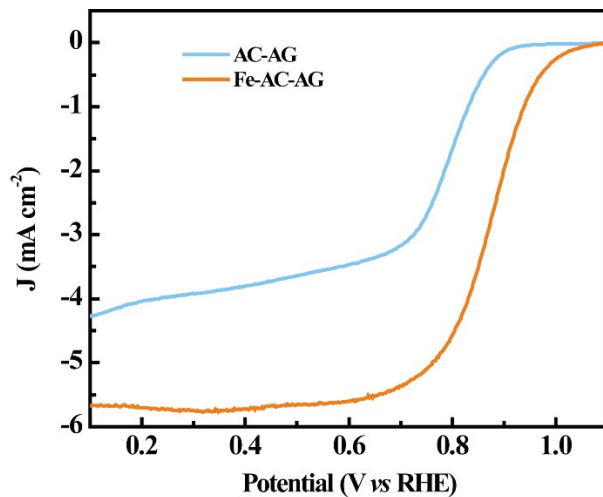
**Figure S4.** (a) Deconvoluted Fe 2p XPS spectra of Fe-AC-1 and Fe-AC-5.



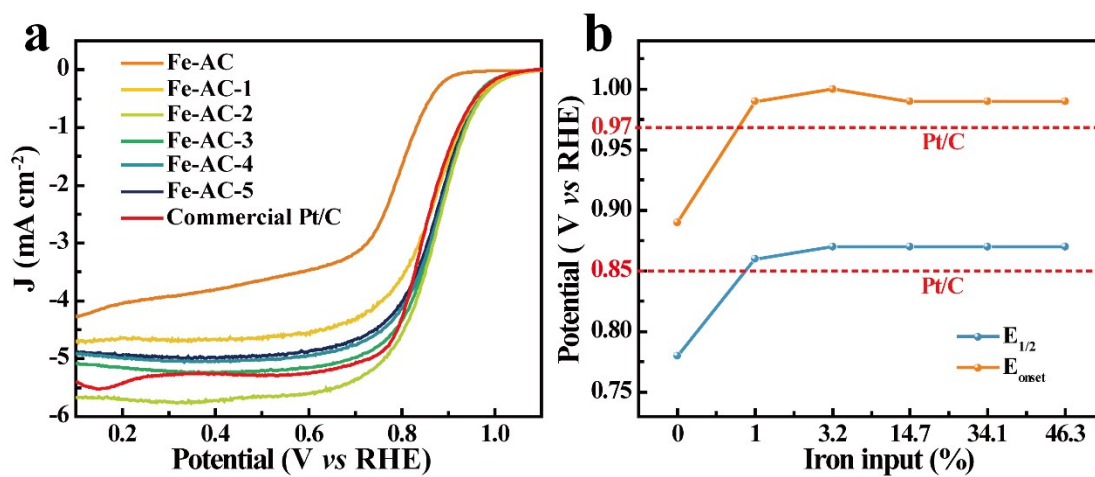
**Figure S5.** Deconvoluted N1s and Fe 2p XPS spectra of Fe-AC-2.



**Figure S6.** The FESEM (a), XRD (b), TEM (c, e) and deconvoluted XPS spectra (d, f) of the sample after 12 h of electrocatalysis.

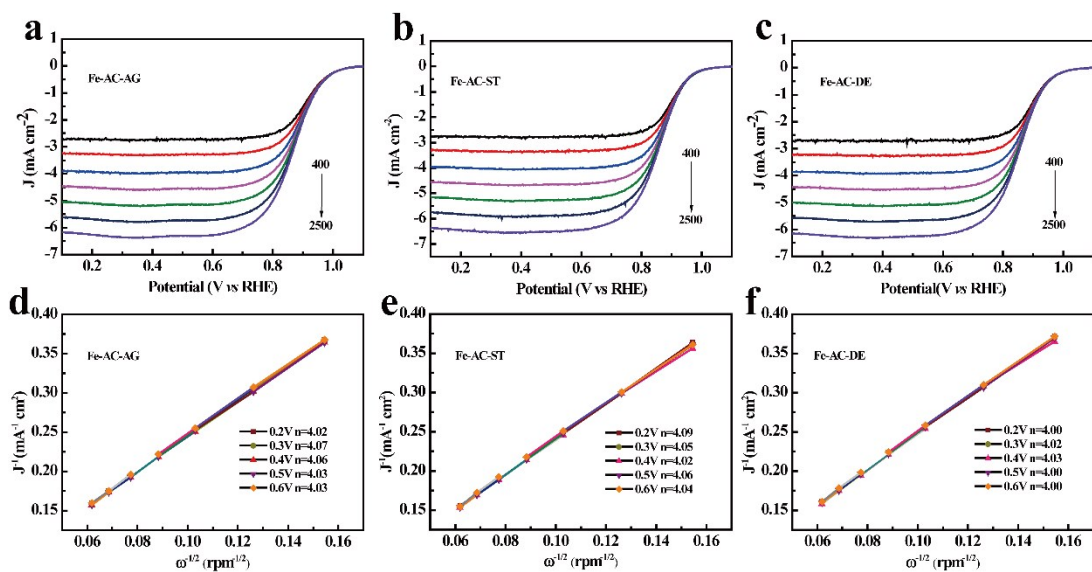


**Figure S7.** LSV curves (1600 rpm,  $5 \text{ mV s}^{-1}$ ) of Fe-AC-AG and AC-AG in 0.1 M KOH.



**Figure S8.** (a) LSV curves(a) and  $E_{\text{onset}}$  and  $E_{1/2}$  (b) of Fe-AC with different sample and commercial Pt/C ORR in  $\text{O}_2$ -saturated electrolyte.





**Figure S9.** LSV curves with different sweep rates: (a) Fe-AC-AG, (b) Fe-AC-ST, (c) Fe-AC-DE; K-L curves: (d) Fe-AC-AG, (e) Fe-AC-ST, (f) Fe-AC-DE.