

Supplementary Information

Fe/Co/N-C/graphene derived from Fe/ZIF-67/graphene oxide three dimensional frameworks as a remarkable efficient and stable catalyst for oxygen reduction reaction

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Part 1: Physical Characterization

The morphology and structure of the ZIF-67, ZIF-67/GO, Fe/ZIF-67, Fe/ZIF-67/GO, Co/N-C, Co/N-C/graphene, Fe/Co/N-C and Fe/Co/N-C/graphene were analyzed by scanning electron microscopy (SEM) (Tescan Mira 3xh) and transmission electron microscopy (TEM) (Jeol JEM2100). The surface characteristics and composition of the ZIF-67, ZIF-67/GO, Fe/ZIF-67, Fe/ZIF-67/GO, Co/N-C, Co/N-

C/graphene, Fe/Co/N-C and Fe/Co/N-C/graphene were determined by X-ray diffraction (XRD) (Smart Lab). The elemental composition of the Co/N-C and Fe/Co/N-C/graphene were investigated by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific Escalab 250XI). The defect degree and graphitization degree of the ZIF-67, ZIF-67/GO, Fe/ZIF-67, Fe/ZIF-67/GO, Co/N-C, Co/N-C/graphene, Fe/Co/N-C and Fe/Co/N-C/graphene were analyzed by Raman spectroscopy (Thermo DXR 2XI). Quadrasorb EVO was used to measure the specific surface area and pore size distribution of the Co/N-C and Fe/Co/N-C/graphene at a temperature of 77.3K, based on the N₂ adsorption-desorption isotherm. The specific surface area and pore size distribution were calculated by Brunauer Emmet-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model.

Part 2: Electrocatalytic testing

The electrocatalytic performance of the catalysts was evaluated using a standard three-electrode system at the Chenhua Electrochemical Workstation in Shanghai. Glass carbon electrode, silver/silver chloride and platinum wire are used as working electrode, reference electrode and counter electrode, respectively. Commercial 20%Pt-C catalyst purchased from Johnson Matthey (UK).

Preparation of catalyst slurry: The collected catalyst samples were ground for about 30 min. Then, 1 mg of the ground catalyst sample was taken and added with 10 μ L Nafion 117 solution and 200 μ L water and alcohol dispersant (water: ethanol =4:1). The catalyst slurry was obtained after ultrasonic treatment for about 40 min. Then, the catalyst slurry was dripped onto the working electrode, 4 μ L each time, dried naturally,

and repeated three times to make the catalyst adhere to the working electrode. The electrochemical experiments were conducted in a 0.1 M KOH aqueous electrolyte. Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV) tests were performed at 10 mV s⁻¹ scanning rate. The voltage range of CV test was -1 to 0.25 V and the rotating speeds was controlled from 400 rpm to 2000 rpm.

The applied potential vs. Ag/AgCl (3M KCl) was converted to reversible hydrogen electrode (RHE) potential using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E^{\circ}_{\text{Ag/AgCl}}$$

where $E_{\text{Ag/AgCl}}$ is the experimentally measured potential using Ag/AgCl as the reference electrode and $E^{\circ}_{\text{Ag/AgCl}}$ is 0.210 V.

The electron transfer number can be calculated by Koutecky- Levich (K-L) equations:

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

$$B = 0.62nFD_0^{2/3}C_0\nu^{-1/6}$$

$$J_K = nFkC_0$$

where J is the measured current density, J_K and J_L are the kinetic- and diffusion limiting current densities, ω is the angular velocity of the rotating electrode, F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$), C_0 is the concentration of O₂ in 0.1 M KOH ($1.2 \times 10^{-3} \text{ M}$), D_0 is the diffusion coefficient of O₂ in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$), and k is the electron transfer rate constant.

Tafel slopes were calculated according to the Tafel equation:

$$\eta = b \log(j) + a$$

where η , j and b are the over potential, measured current density, and Tafel slope, respectively. Moreover, rotating ring-disk electrode (RRDE) of the catalyst was performed at 1600 rpm in 0.1 M KOH medium, the values of n and H_2O_2 yields could be determined according to the following equations:

$$H_2O_2\% = 100 \times \frac{2 I_r/n}{I_d + I_r/N}$$

$$n = \frac{4I_d}{I_d + I_r/N}$$

where I_d and I_r are disk current and ring current, respectively, N is the H_2O_2 collection efficiency at the ring.

The turnover frequency (TOF) was calculated using the following equation:

$$TOF = \frac{I}{4NF}$$

where I is the value of limiting current density at 1600 rpm min^{-1} , N is the number of catalytic active sites, and F is Faraday constant.

Part 3: Figures

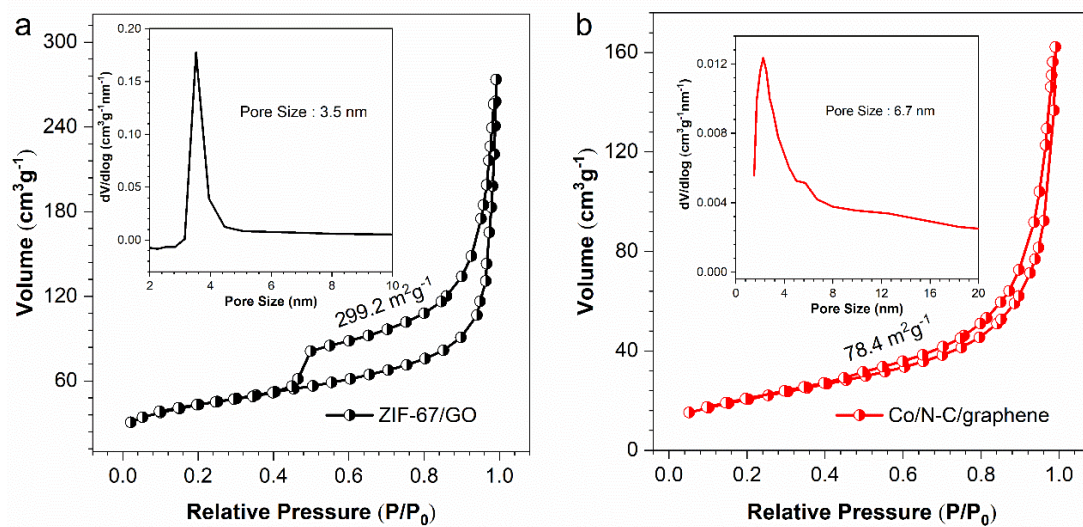


Fig. S1 N_2 adsorption/desorption isotherms (insert: pore size distribution) of ZIF-67/GO and Co/N-C/graphene composites.

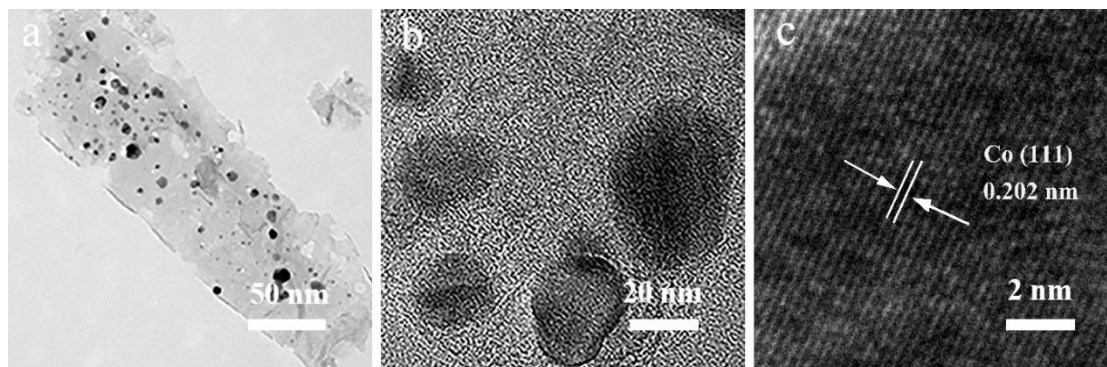


Fig. S2 (a) TEM and (b, c) HRTEM image of Co/N-C composites.

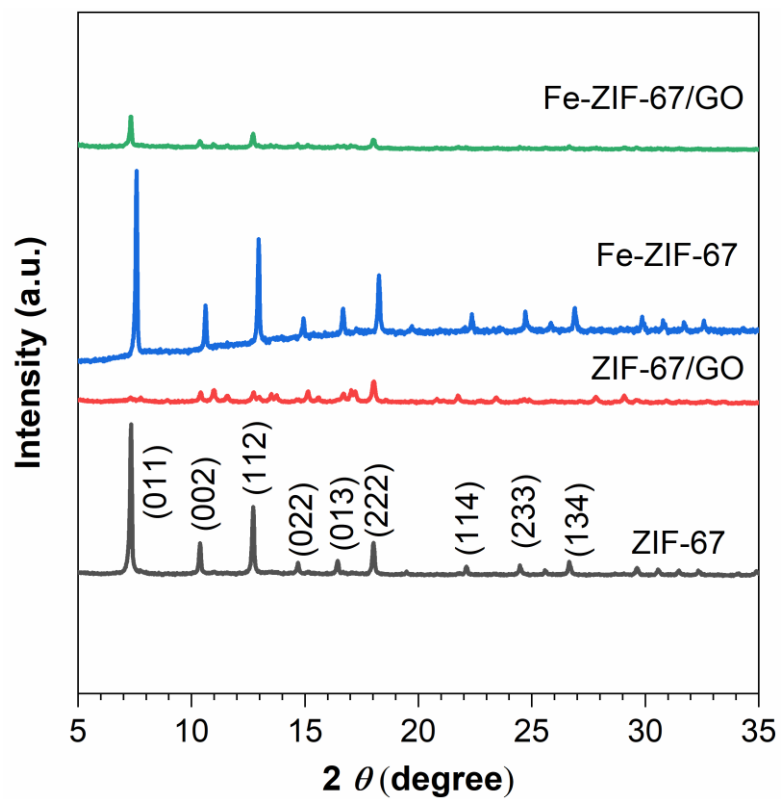


Fig. S3 XRD patterns of ZIF-67, ZIF-67/GO, Fe-ZIF-67 and Fe-ZIF67/GO composites.

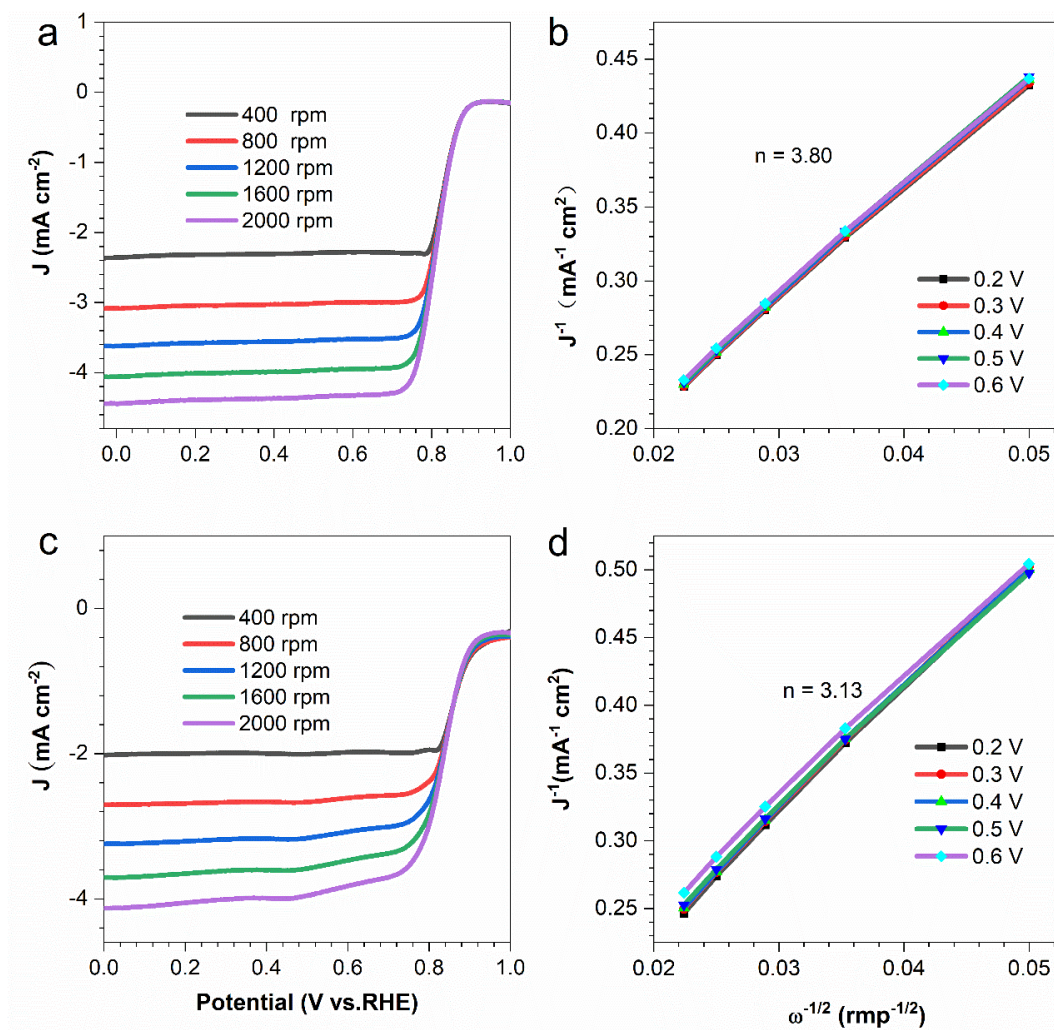


Fig. S4 LSV curves and K-L plots of (a, b) Co/N-C/ and (c, d) Fe/Co/N-C composites.

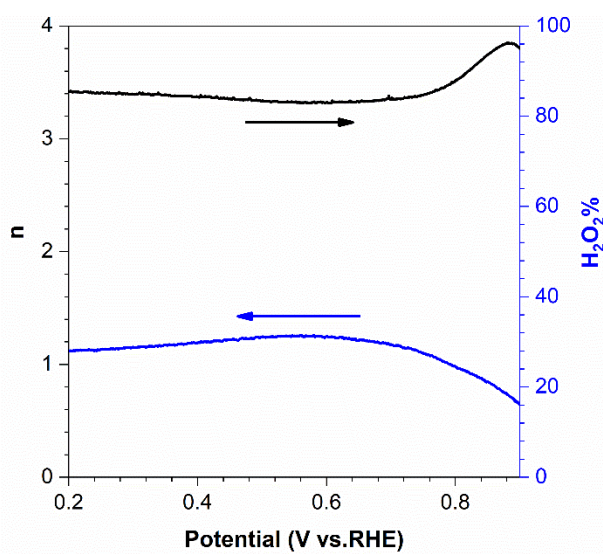


Fig. S5 Electronic transfer number and H₂O₂ yield curves of Co/N-C on a RRDE at 1600 rpm during ORR.

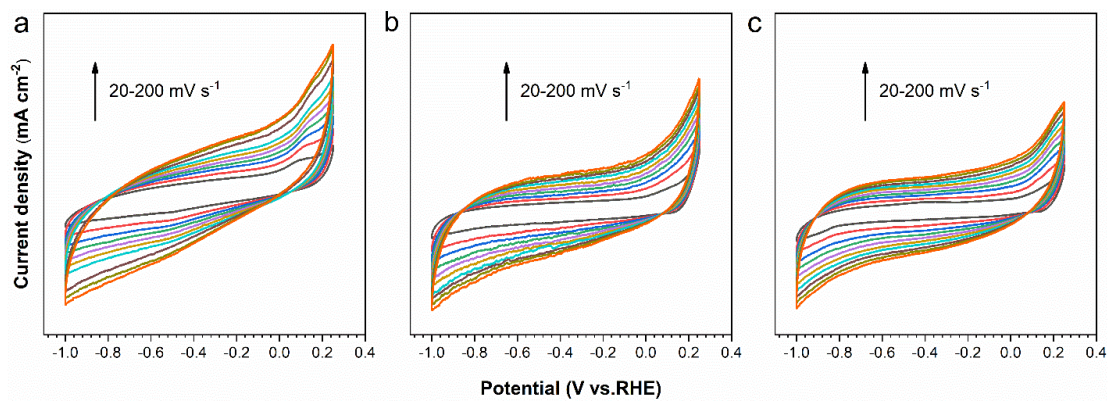


Fig. S6 Non-faradic CVs of (a) Co/N-C, (b) Co/N-C/graphene and (c) Fe/Co/N-C at various scan rates.