Supporting Information

An Iron-based Catalyst with Multiple Active Components Synergetically Improved Electrochemical Performance for Oxygen Reduction Reaction

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Calculation of Electron Transfer Number (n) and % HO_2^- for Oxygen Reduction Reaction

On the basis of rotating disk electrode (RDE) measurements, the electron transfer numbers (n) per O_2 involved in ORR were calculated from the slopes of the Koutecky-Levich plots according to the following equations [1]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k} \qquad (1)$$

where j is the measured current density, j_k and j_l are the kinetic and diffusion-limiting current densities, ω is the rotating rate of electrode (rpm). B is determined from the slope of the Koutecky-Levich plots according to the Levich equation.

$$B = 0.2nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6} \qquad (2)$$

where n is electron transfer number per oxygen molecule, F is Faraday constant (96485 C mol^{-1}), C_{O2} is the bulk concentration of O_2 (1.2×10^{-6} mol cm^{-3}), υ is the kinetic viscosity of electrolyte (0.01 cm^2 S^{-1}). D_{O2} is the diffusion coefficient of O_2 in 0.1 M KOH and 0.1 M $HClO_4$ (1.9×10^{-5} cm^2 S^{-1}).

Hydrogen peroxide yields and the electron transfer number (n) were calculated by the following equations:

$$\%(HO_2^-) = 200 \times \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}} \qquad (3)$$

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}} \qquad (4)$$

Where I_d is disk current, I_r is ring current, the collection efficiency (N) was determined to be 0.40 by using 10 mM $K_3[Fe(CN)_6]$.

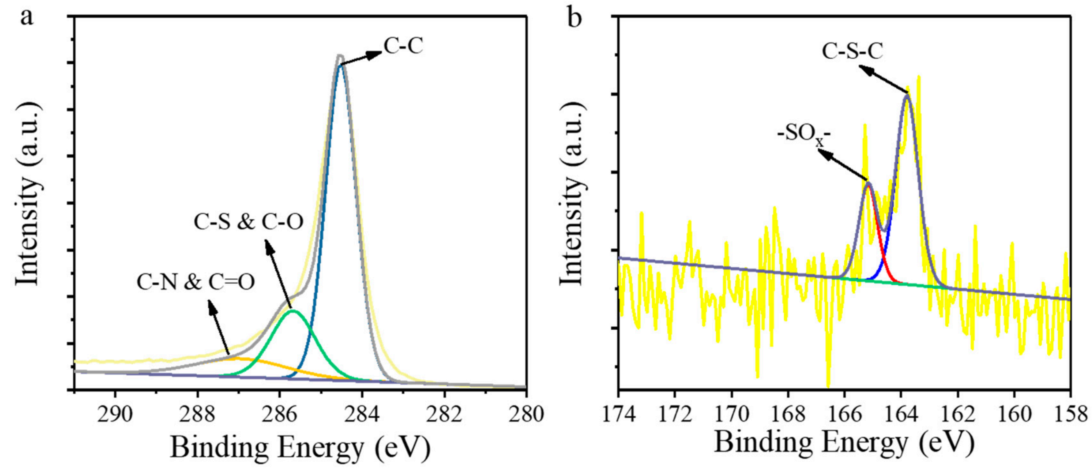

Figure S1. XPS spectra of C 1s (a) and S 2p (b) for Fe-N/Fe_3C/Fe/C-800

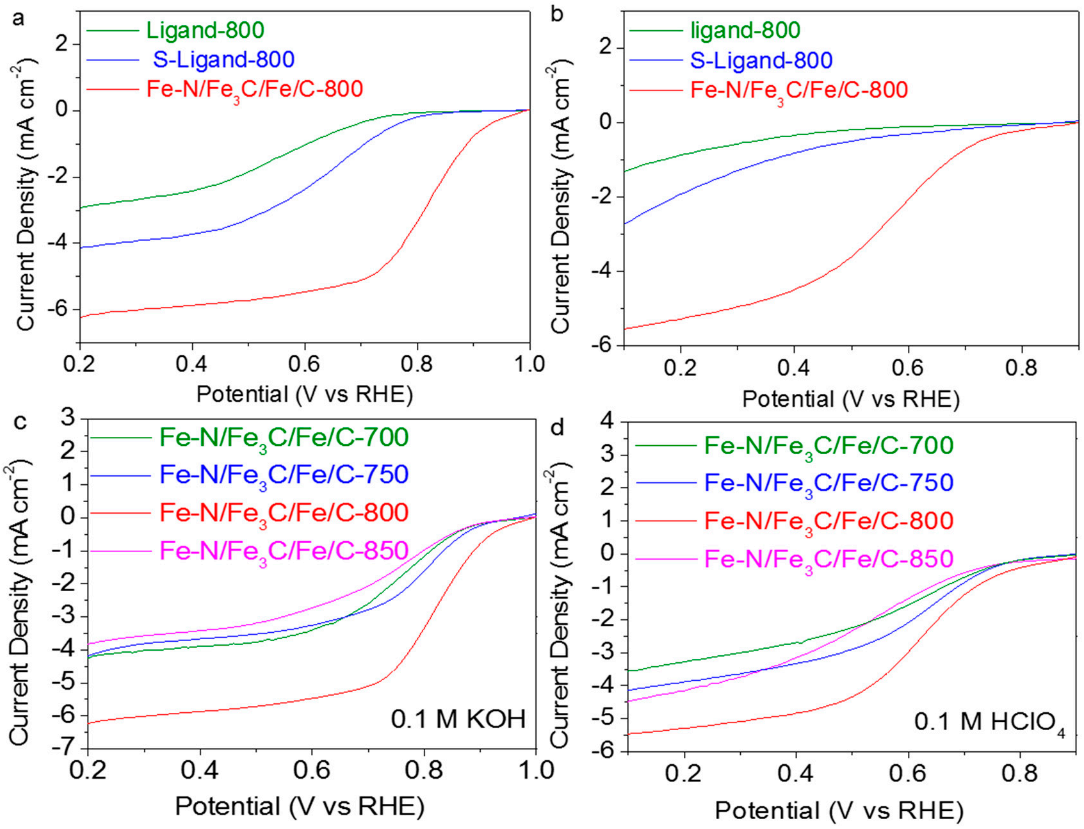

Figure S2. Linear sweeping voltammograms for oxygen reduction reaction at 1600 rpm. (**a**) Ligand-800, S-Ligand-800, and Fe-N/Fe_3C/Fe/C-800 in 0.1 M KOH. (**b**) Ligand-800, S-Ligand-800, and Fe-N/Fe_3C/Fe/C-800 in 0.1 M $HClO_4$. (**c**) Fe-N/Fe_3C/Fe/C catalysts with different pyrolyzing temperatures in 0.1 M KOH. (**d**) Fe-N/Fe_3C/Fe/C catalysts with different pyrolyzing temperatures in 0.1 M $HClO_4$.

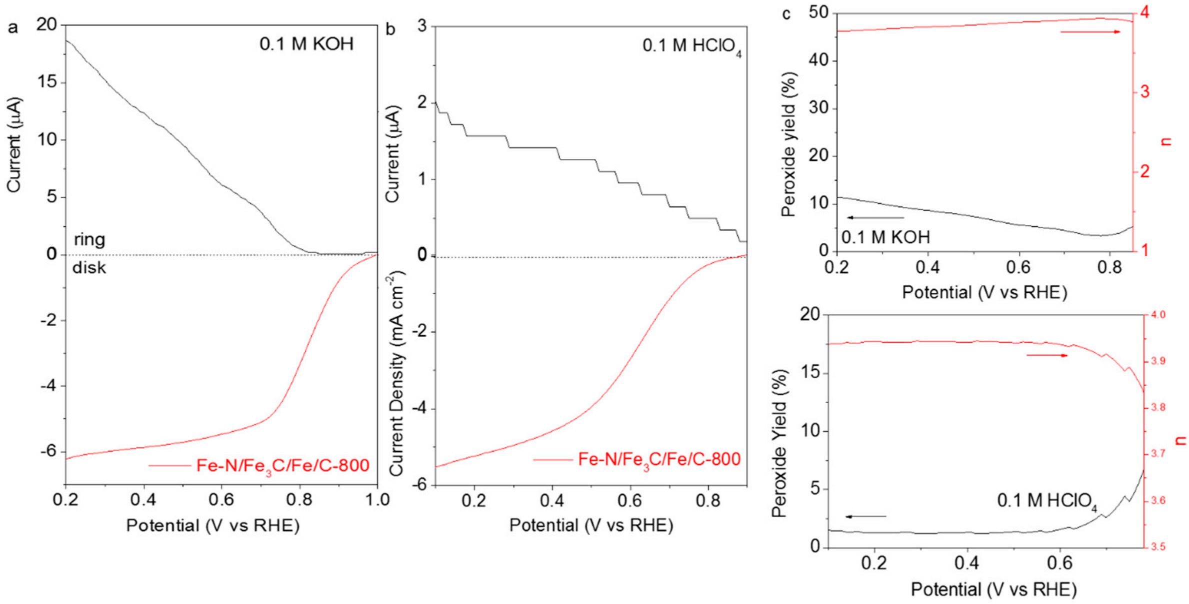

Figure S3. (**a**) , (**b**) Rotating ring-disk electrode voltammogram of Fe-N/Fe_3C/Fe/C-800 in O_2-saturated 0.1 M KOH and 0.1 M $HClO_4$ at 1600 rpm, respectively. (**c**) The electron transfer number (n) of Fe-N/Fe_3C/Fe/C-800 at different potentials and percentage of peroxide with respect to the total oxygen reduction products in 0.1 M KOH and 0.1 M $HClO_4$, respectively.

Reference:

[1] Chen L, Kim J, Ishizuka T, Honsho Y, Saeki A, Seki S, Ihee H, Jiang DL (2009) J Am Chem Soc 131:7287-7292