## **Electronic Supplementary Information**

## Effect of nanoparticle composition on oxygen reduction reaction activity of Fe/N-C catalysts: a comparative study

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**Fig. S1** FTIR spectra of GO, PDA-rGO and Fe-PDA-rGO. The characteristic adsorption bands of GO (1634, 1057 and 1729 cm<sup>-1</sup>) and PDA (1509 cm<sup>-1</sup>) could be observed in the Fe-PDA-rGO precursor. The peak at 670 cm<sup>-1</sup> corresponds to the Fe-O bond, indicating the coordination between Fe ion and catechol group in Fe-PDA-rGO precursor.



Fig. S2 SEM image (a) and corresponding N (b), O (c) and Fe (d) EDS mapping images of Fe/Fe<sub>3</sub>O<sub>4</sub>@ N-G.



Fig. S3 Nitrogen sorption isotherm plot (inset: BJH pore size distribution) of Fe<sub>x</sub>N@N-G (a),

 $Fe/Fe_3O_4@N-G$  (b), and  $Fe_3C@N-G$  (c).



Fig. S4 Raman spectra of three catalysts.



Fig. S5 XPS survey spectrum (a) and Fe 2p (b) spectra of three catalysts.



**Fig. S6** LSV curves at different rotating rates and corresponding K-L plots of Fe<sub>x</sub>N@N-G (a, b) and Fe<sub>3</sub>C@N-G (c, d).



Fig. S7 EIS of three catalysts at a potential of 0.90 V (vs. RHE). Inset shows the electrical equivalent circuit used to simulate the Nyquist plots, where  $R_s$  is the electrolyte resistance,  $R_{ct}$  is the charge-transfer resistance, and  $C_{dl}$  represents the double-layer capacitance.



Fig. S8 LSV curves of Fe/Fe<sub>3</sub>O<sub>4</sub>@N-G before and after pickling at a rotation rate of 1600 rpm and

sweep rate of 5 mV s<sup>-1</sup>.



Fig. S9 Amperometric curves of Fe/Fe<sub>3</sub>O<sub>4</sub>@N-G and commercial Pt/C at 0.69 V (vs. RHE) in

 $O_2$ -saturated 0.1 M KOH solution.  $J_0$  is defines as the initial current density.



**Fig. S10** (a) CV curves of Fe/Fe<sub>3</sub>O<sub>4</sub>@N-G in O<sub>2</sub>-saturated 0.1 M KOH solution with and without methanol; (b) amperometric curves of Fe/Fe<sub>3</sub>O<sub>4</sub>@N-G and commercial Pt/C at 0.69 V (vs. RHE) in O<sub>2</sub>-saturated 0.1 M KOH solution. The arrows indicate the addition of 0.5 M methanol into the electrolyte.