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"Spontaneous bubble-template" assisted and metal-polymeric frameworks derived N/Co dual-doped hierarchically porous carbon/Fe_3O_4 nanohybrids: superior electrocatalyst for oxygen reduction reaction in biofuel cells

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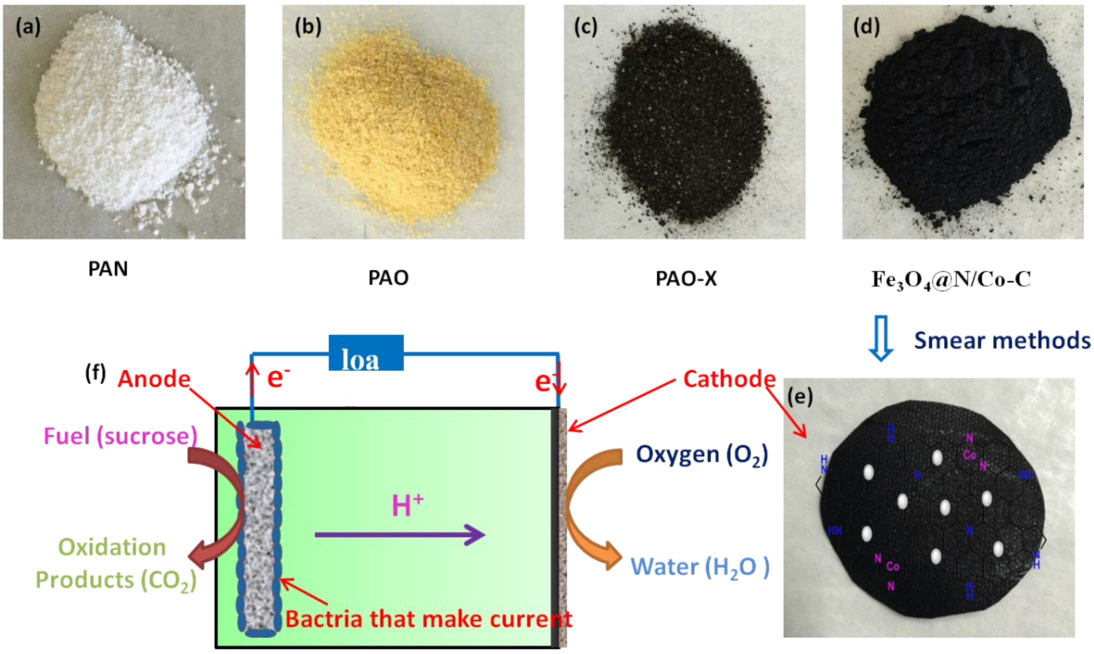

Fig.S1 (a) Polyacrylonitrile (PAN), (b) Polyacrylamidoxime (PAO), (c) metal-polymeric frameworks (PAO-X, X=Fe or Co), (d) Fe_3O_4@N/Co-C, (e) air-cathode of MFCs and (f) the configuration and working principles of MFCs.

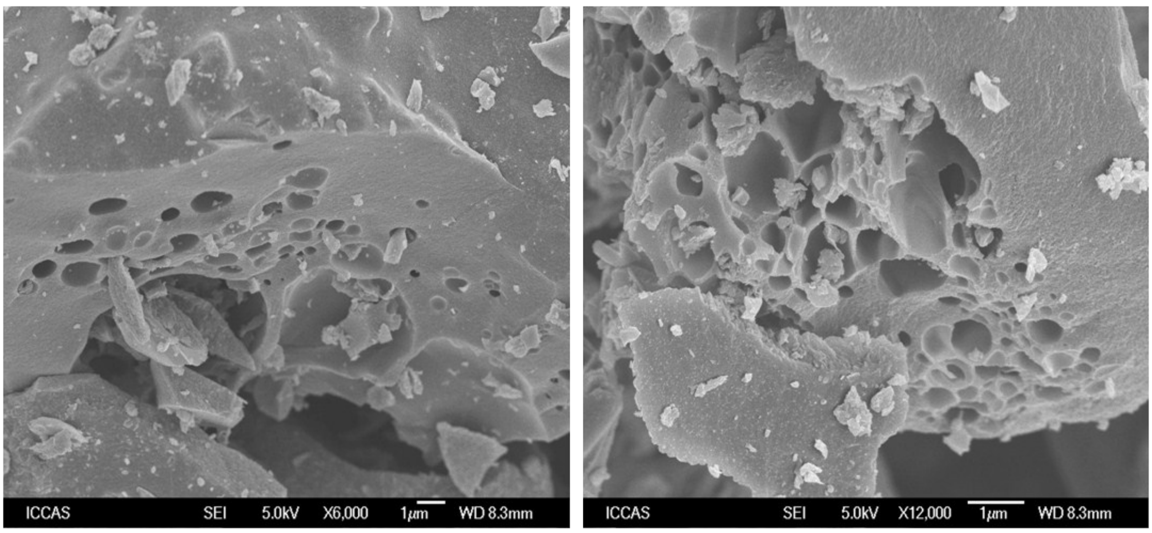

Fig.S2 The SEM images of carbon derived from PAN by carbonization

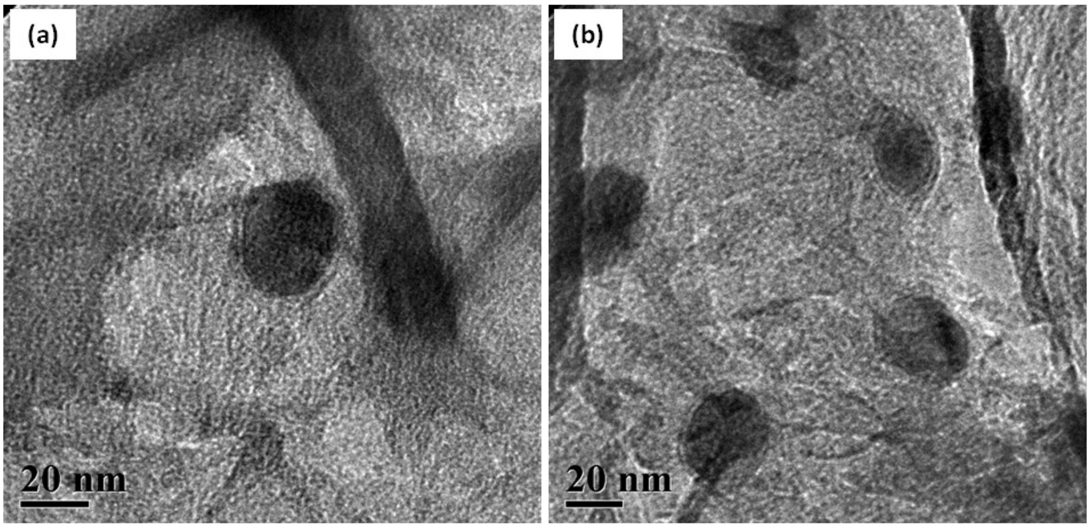

Fig.S3 The TEM images of Fe_3O_4@N-C (a) and Fe_3O_4@N/Co-C (b).

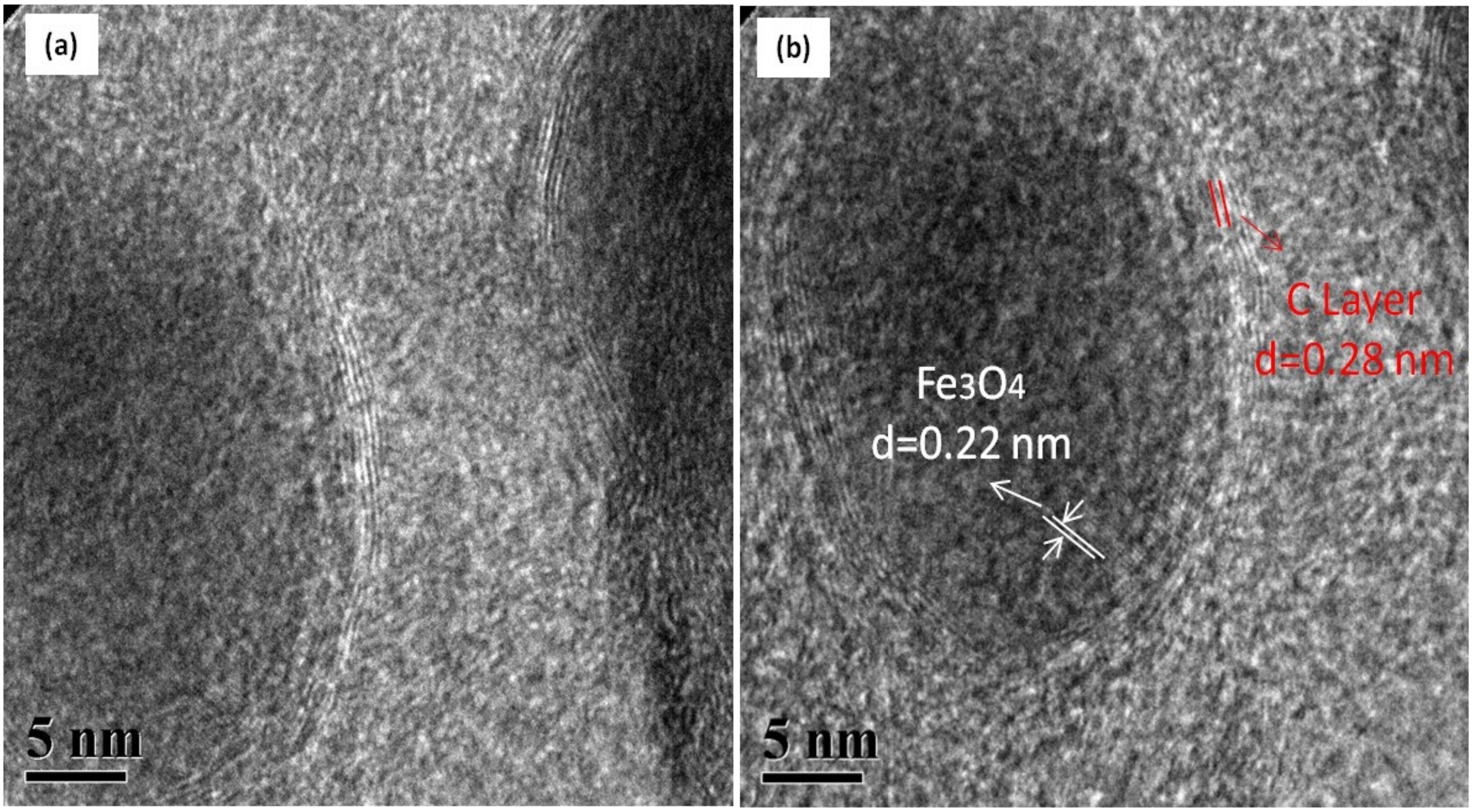

Fig. S4 The high-resolution TEM images of Fe_3O_4@N/Co-C

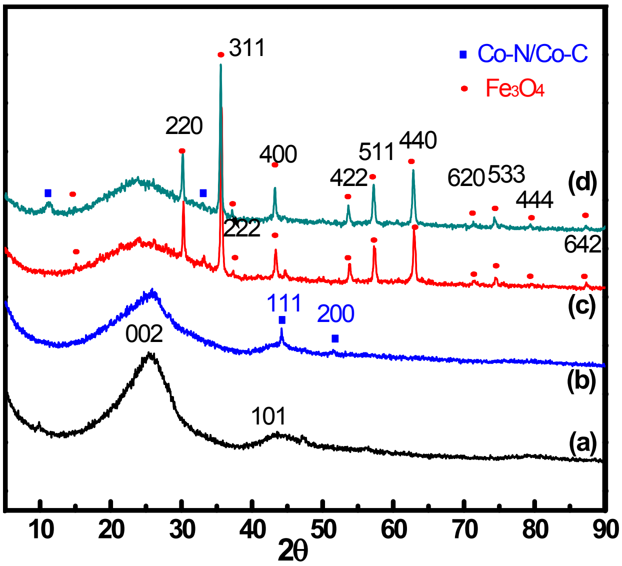

Fig. S5 The XRD patterns of (a) N-C, (b) N/Co-C, (c) Fe_3O_4@N-C and (d) Fe_3O_4@N/Co-C.

Matsuda's equation:

$$i_p = 0.4464 \times 10^{-3} n^{3/2} F^{3/2} A (RT)^{-1/2} D_R^{1/2} C_R^{*} \nu^{1/2} \qquad \text{Eq. S1}$$

where i_p is the peak current (A), n = 1 is the number of electrons transferred, F = 96487C mol^{-1} e^- Faraday's constant, R = 8.314 J mol^{-1} K the gas constant, T = 308 K is the temperature, C_R^* = 0.005 mol L^{-1} the initial ferrocyanide concentration, ν = 0.05 V s^{-1} the scan rate. D_R is the diffusion coefficient of $K_4Fe(CN)_6$.

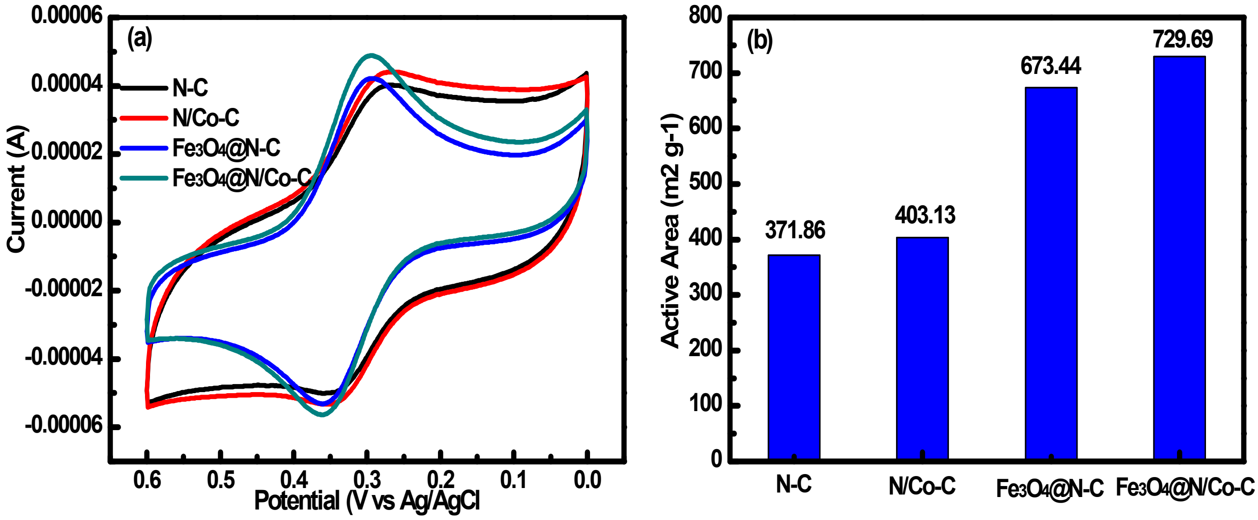

Fig. S6 Eletrochemical BET: (a) CV measured in ferrocyanide solution with different catalysts modified glass carbon eletrodes; (b) eletrochemical active area calculated by Matsuda's equation

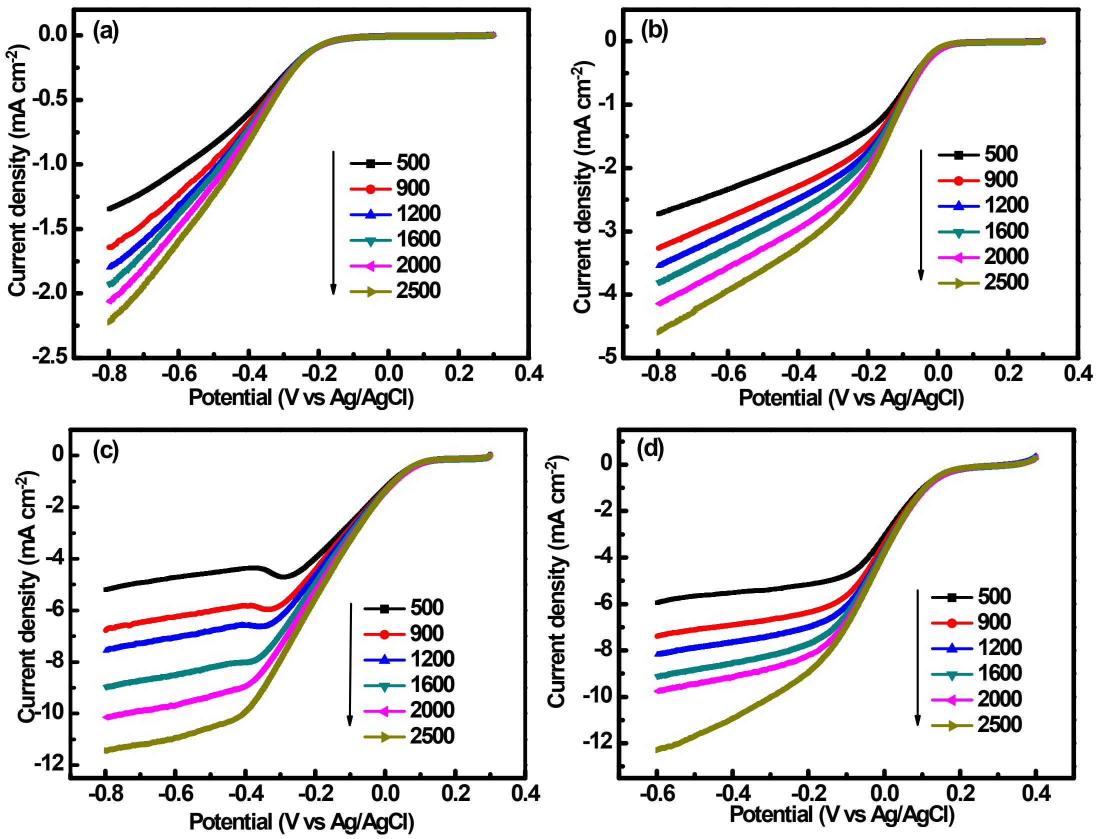

Fig. S7 LSV of N-C, N/Co-C, Fe_3O_4@N-C and Pt/C at different rotation speed from 500 to 2500 rpm min^{-1} in PBS solution.

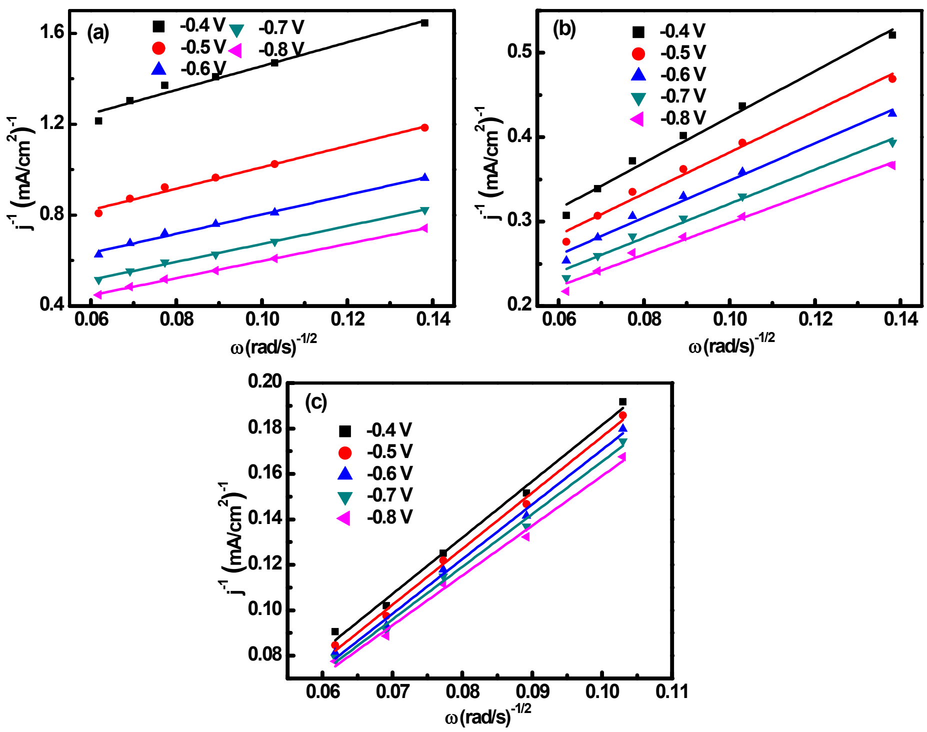

Fig. S8 The Koutecky–Levich plots measured by rotating disc electrode (RDE) in O_2-saturated PBS solution: N-C (a), N/Co-C (b) and Fe_3O_4@N-C (c).

Table S1 The catalysts with different Fe/Co ratio (mass ratio) and their eletrochemical active area.

Samples	ICP results		Fe:Co(wt/wt)	Active area	Carbon content
	Fe (wt %)	Co (wt %)		(m^2 g^{-1})	[a](wt %)
Fe_3O_4@N-C	8.66	0	non	673.44	84.44
Fe_3O_4@N/Co-C-1	8.14	0.41	19.85	702.38	81.80
Fe_3O_4@N/Co-C-2	7.25	0.64	11.33	729.69	82.29
Fe_3O_4@N/Co-C-3	5.97	0.95	6.28	594.38	82.51
Fe_3O_4@N/Co-C-4	5.03	1.27	3.96	503.12	82.78
Fe_3O_4@N/Co-C-5	4.32	1.59	2.72	466.62	83.26
N/Co-C	0	1.98	non	403.13	87.08
N-C	non	non	non	371.86	93.41
Pt/C	non	non	non	456.25	80

[a]Carbon content was calculated by combining ICP and XPS results.

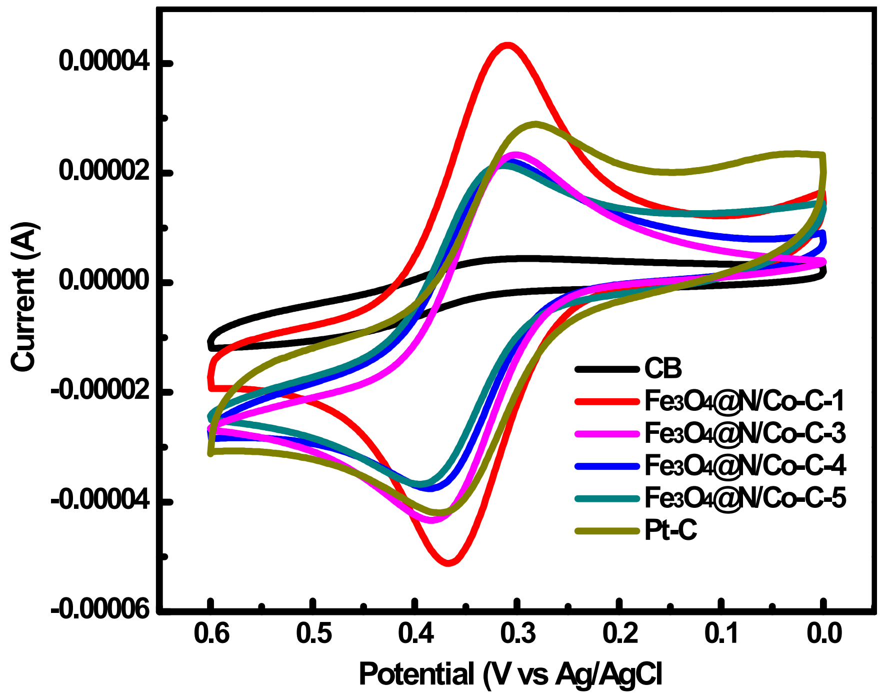

Fig. S9 Eletrochemical BET: CV measured in ferrocyanide solution with different catalysts modified glass carbon eletrodes.

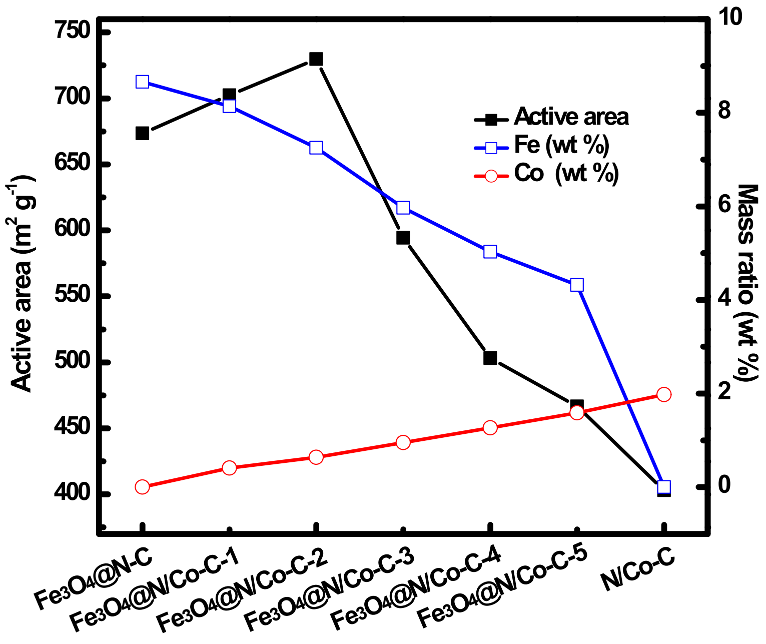

Fig. S10 The effect of Fe/Co ratio on the electrochemical active area.

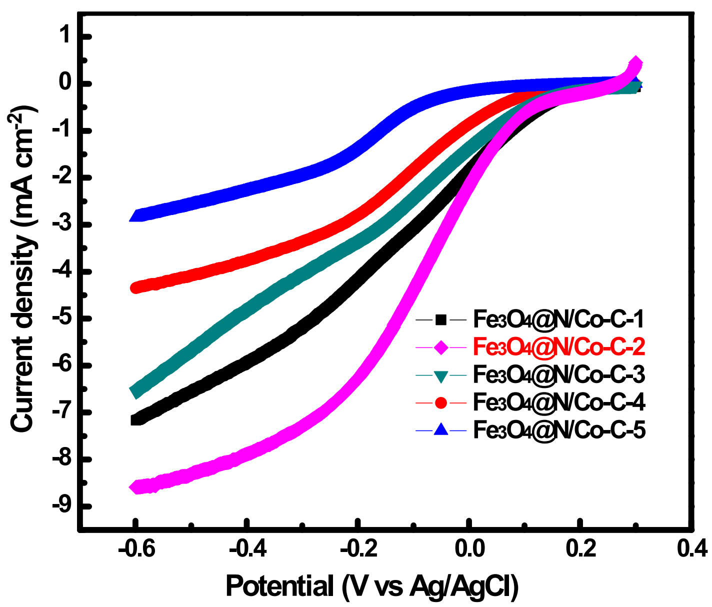

Fig. S11 LSV of Fe_3O_4@N/Co-C with different Fe/Co ratio at 1600 rpm min^{-1} in O_2-Saturated PBS solution.

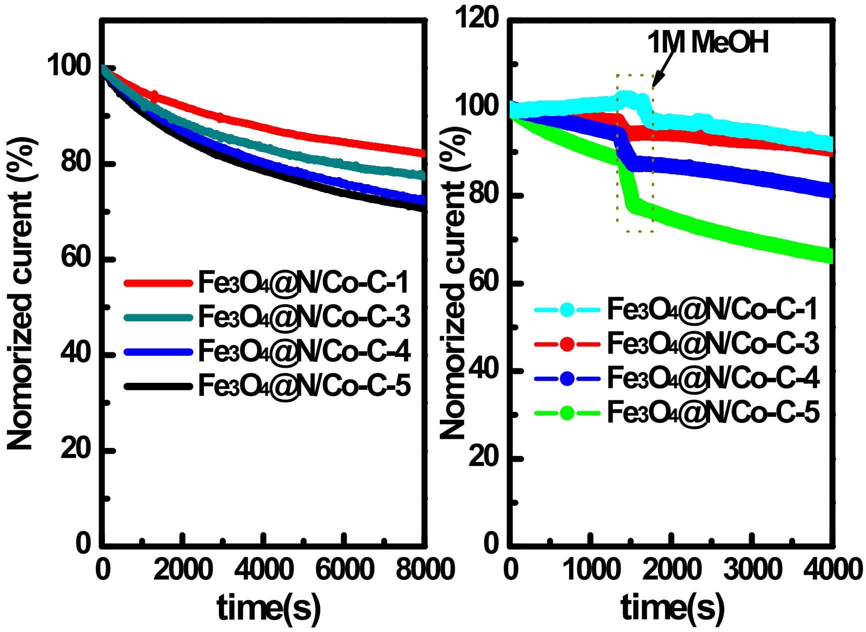

Fig. S12 The i-t curves (a) and the anti-toxic ability (b) of Fe_3O_4@N/Co-C with different Fe/Co ratio in O_2-Saturated PBS solution.

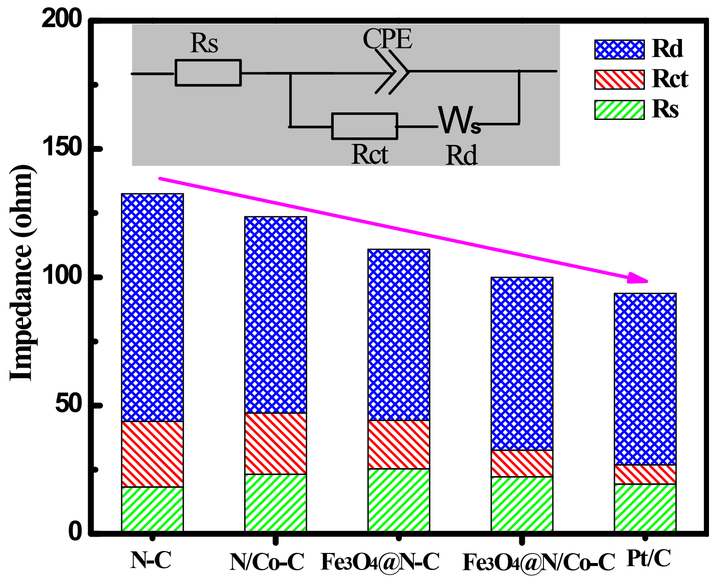

Fig. S13 The resistance composition of different catalysts (insert picture: characteristic equivalent electrocircuit).