Supporting information

Tailoring Molecular Architectures of Fe Phthalocyanine on Nanocarbon Supports for High Oxygen Reduction Performance

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1. SEM image of FePc precursor before ball billing

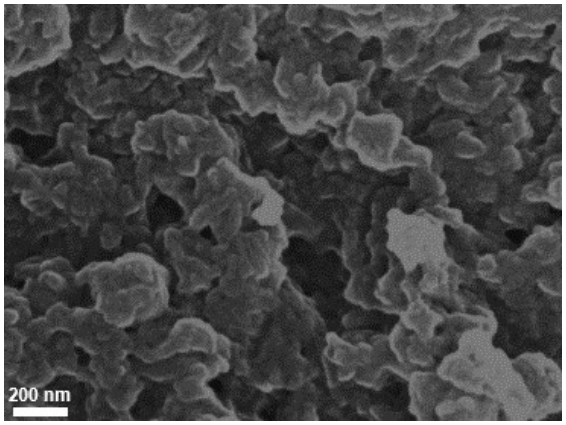

Fig. S1 SEM image of FePc precursor before ball-billing.

2. Additional electron microscopy images of FePc/Carbon composites

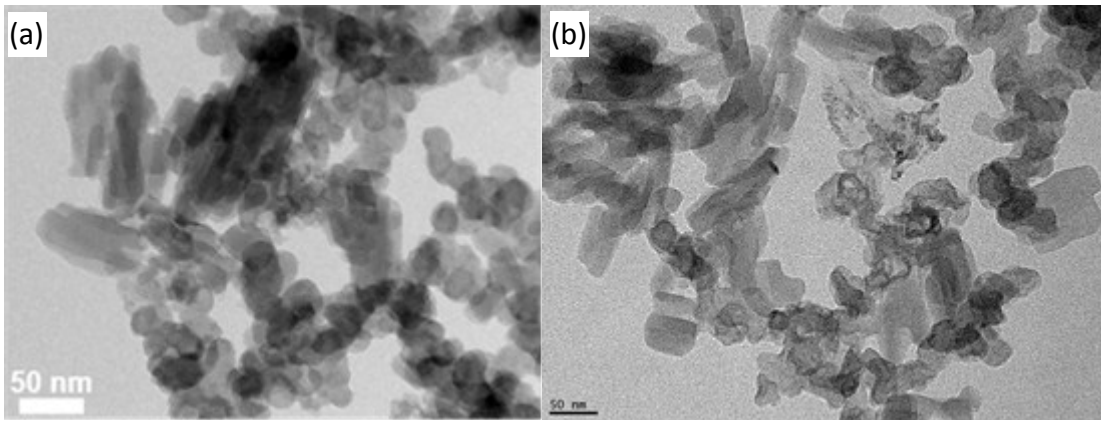

Fig. S2 TEM images of (a) FePc/CB-XC72 of 1:1 mass ratio and FePc/CB-EC600 of 4:1 mass ratio.

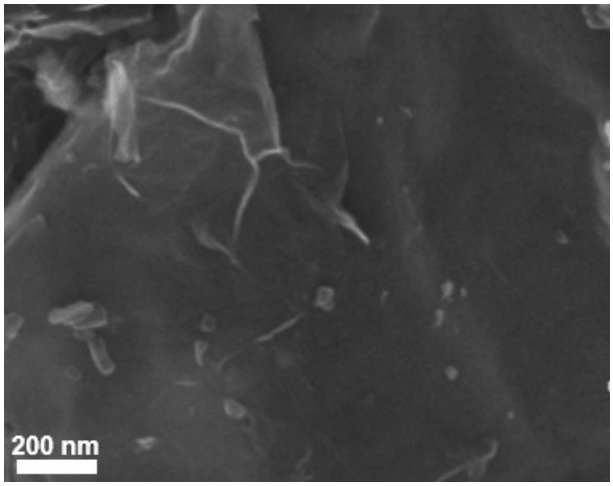

Fig. S3 SEM image of FePc/GS of 1:4 mass ratio.

3. XPS analysis

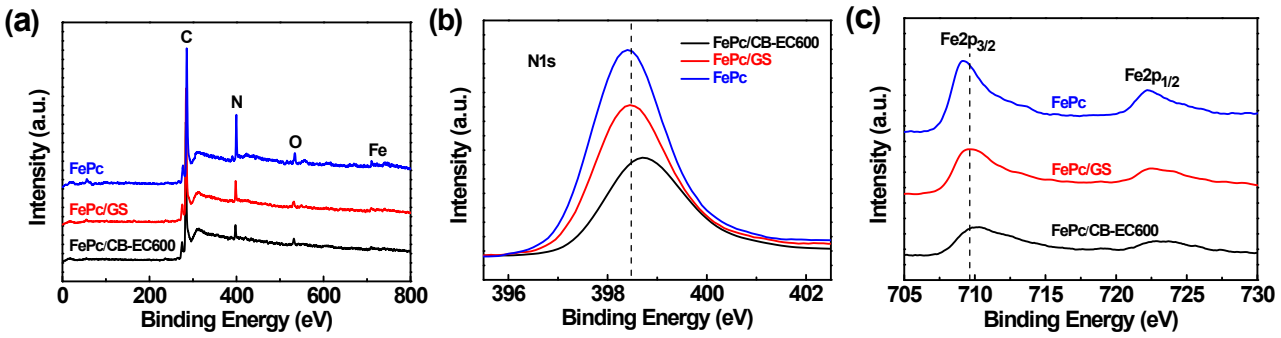

Fig. S4 XPS survey spectra of (a) a wide survey scan, (b) N1s narrow-scan, and (c) Fe2p narrow-scan of the FePc/CB-EC600, FePc/GS, and FePc.

The XPS broad scan spectra (Fig. S4a) indicated the existence of N and Fe in the FePc/CB-EC600 and FePc/GS composites. By integrating the XPS peaks for N, Fe, C and O and correcting the corresponding element sensitivity, the relative contents of various elements in the surface region of different samples were estimated. Table S1 lists the contents for N and Fe. It was found that the FePc/CB-EC600 composite had the lowest contents of N and Fe as compared with the FePc/GS composite and FePc, which indicated the highest dispersion of FePc in the FePc/CB-EC600 composite.

Table S1 N and Fe contents in various samples estimated from XPS analysis.

Samples	FePc/CB-EC600	FePc/GS	FePc
N 1s (at%)	5.1%	7.6%	12.5%
Fe 2p (at%)	1.0%	1.3%	1.9%

4. Koutecky-Levich analysis

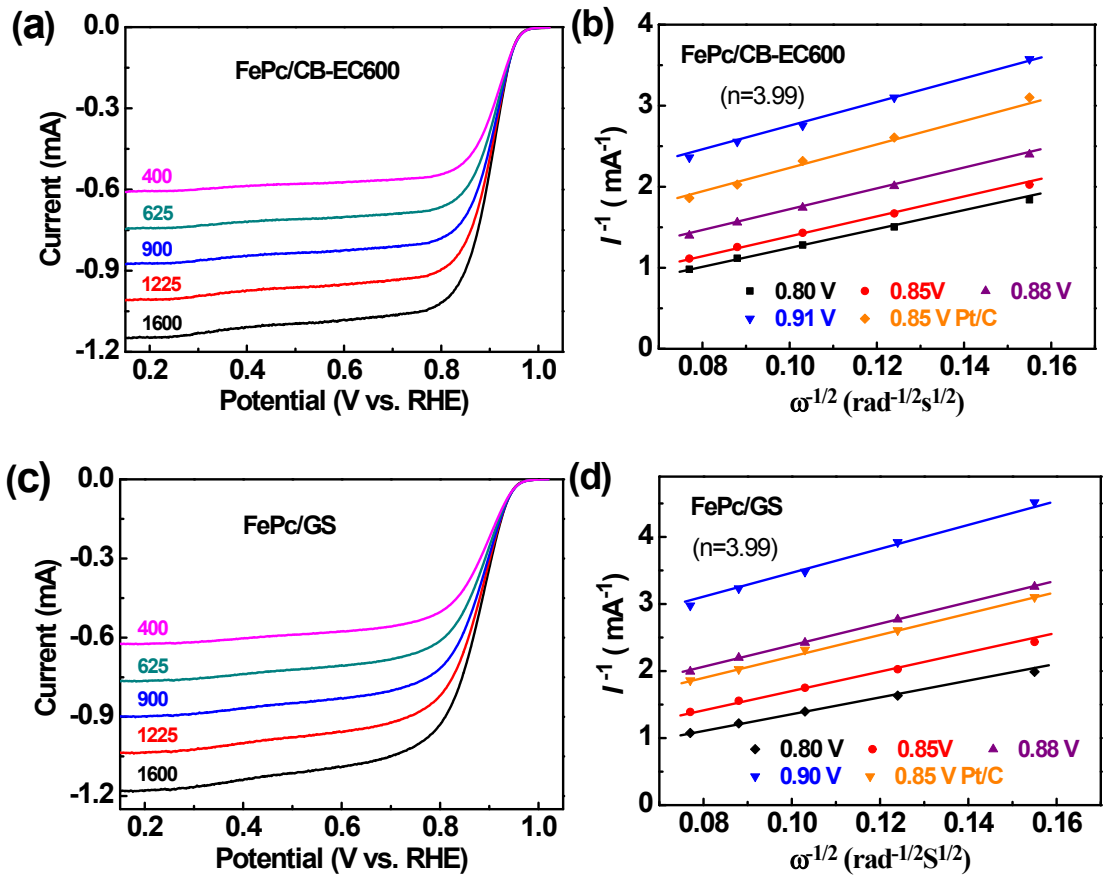

Fig. S5 ORR polarization curves obtained at different rotating rate in O_2-saturated 0.1 M KOH and the corresponding Koutecky-Levich plots for (a, b) FePc/CB-EC600 and (c, d) FePc/GS composite. The Koutecky-Levich plot for Pt/C at 0.85 V is given in (b) and (d) for comparison.

The electron transfer numbers (n) can be calculated using the Koutecky-Levich equation:

$$i^{-1}=i_k^{-1}+i_l^{-1}=i_k^{-1}+1/(0.62nFAD_{O2}^{2/3}\omega^{1/2}\upsilon^{-1/6}c_0) \quad \text{(Eq. S1)}$$

Where i is the current on the measured polarization curve; i_k is the kinetic current; i_l is the diffusion-limited current; F is the Faraday constant (96500 C mol^{-1}); A is electrode area (0.196 cm^{-2}); D_{O2} is the diffusion coefficient of O_2 in 0.1 M KOH solution (1.9×10^{-5} cm^2 s^{-1}); ω is the rotation rate (rad s^{-1}); υ is the kinetic viscosity of the water (0.01 cm^2 s^{-1}) and c_0 is bulk concentration of O_2 in

0.1 M KOH solution (1.2×10^{-6} mol cm^{-3}). The slope of the plot of reciprocal current (i^{-1}) versus the reciprocal square root of rotation rate ($\omega^{-1/2}$) gives *n* values according Eq. S1. One can see that the Koutecky-Levich plots for the two FePc composites at various potentials have very similar slopes to that for Pt/C. The calculated *n* values were ca. 3.99.

5. ORR activities of the pure carbon supports

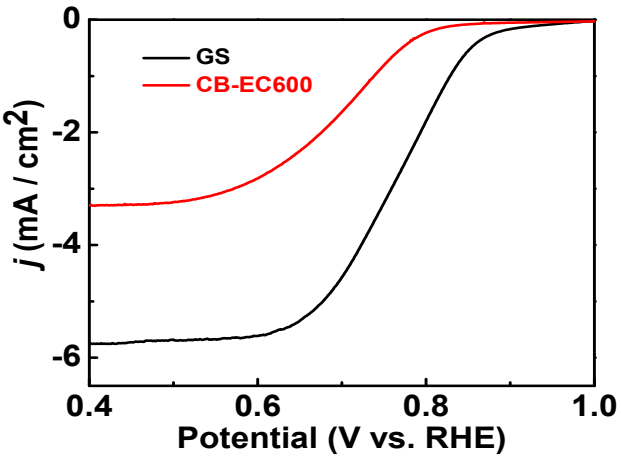

Fig. S6 ORR polarization curves of the pure GS and CB-EC600 obtained at the rotating rate of 1600 rpm in O_2-saturated 0.1 M KOH. Catalyst loading: 250 μg/cm^2.

6. Performance comparison of the different NPMCs

Table S2 Positive shift of $E_{1/2}$ for carbon-supported Me-N composites reported in recent works as compared with that of Pt/C in 0.1 M KOH solution.

Number	NPMCs	Positive shift of $E_{1/2}$	Refs.
1	FePc/Vulcan XC-72	~50 mV	[16] J. Phys. Chem. C / 2009
2	FePc-Py-CNTs	~35 mV	[17] Nat. Commun. / 2013
3	rGO/$(Co^{2+}$-THPP$)_7$	~ -120 mV	[18] Angew. Chem. Int. Ed. / 2013
4	(DFTPP)Fe-Im-CNTs	47 mV	[19] Angew. Chem. Int. Ed. / 2014
5	graphene-FePc	~50 mV	[20] ACS Catal. / 2013
6	FePc/CB-EC600	60 mV	This work

7. Effects of FePc/carbon mass ratios on the ORR performance

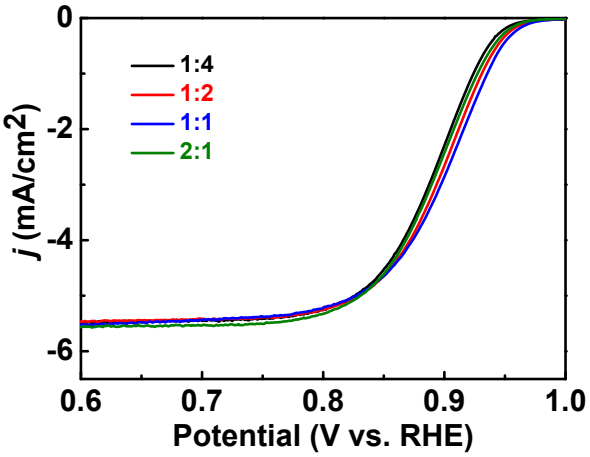

Fig. S7 ORR polarization curves of FePc/CB-EC600 composites with different FePc/carbon mass ratios. Catalyst loading: 0.1 mg/cm^2.

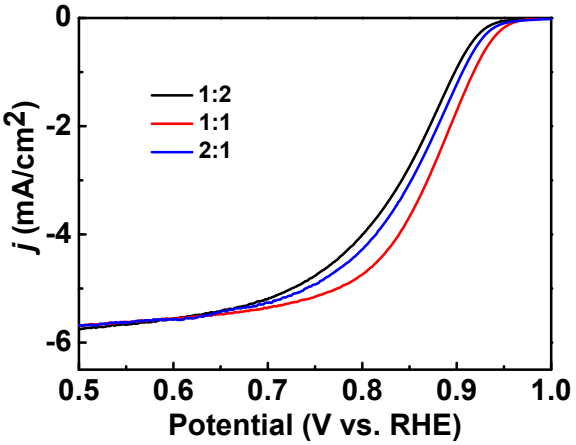

Fig. S8 ORR polarization curves for FePc/GS composites with different FePc/carbon mass ratios. Catalyst loading: 0.1 mg/cm^2.