

Supplementary Information

Iron phthalocyanine and nitrogen-doped graphene composite as novel non-precious catalyst for oxygen reduction reaction

*Chenzhen Zhang, Rui Hao, Han Yin, Fei Liu and Yanglong Hou**

Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China.

E-mail: hou@pku.edu.cn

1. Experimental details

1.1 Materials preparation

Iron(II) phthalocyanine (96 %) and cobalt(II) phthalocyanine were purchased from Alfa Aesar and used without further purification.

Graphite oxide was prepared by a modified Hummers method.¹ In a typical procedure, 1g of natural graphite power, 0.5 g of NaNO₃, and 23 mL of H₂SO₄ were stirred together in an ice bath for 24 h. Under vigorous agitation, 3 g of KMnO₄ was slowly added, and the mixture was transferred to a 35-40 °C water bath and kept there for 0.5 h. Next, 46 mL of water was gradually added, and the solution was stirred for 15 min. Finally, the solution was diluted with 140 mL of water and treated with 5 mL of 30 % H₂O₂. The resultant solid was collected by filtration, washed with 5 % HCl solution and water, and then dried in a vacuum oven at 70 °C overnight.

Nitrogen-doped graphene (NG) was synthesized according to our previous method.² 30 mg of graphene oxide (GO) was added in 5 mL of water and sonicated for 0.5 h. Next, 30 mL of ammonia solution (25 wt% in water) was added, and the mixture was transferred into a 50-mL autoclave and maintained at 200 °C for 12 h. The black solid was washed with 0.1 M HCl solution and then washed repeatedly with water and ethanol. The final product was collected by centrifugation and dried at 60 °C overnight under vacuum. The as-synthesized NG consists of ~4 layers confirmed by TEM, AFM, and Raman spectroscopy measurements, and its nitrogen content is ~10 at% measured by XPS.

Reduced graphene oxide (rGO) was synthesized by a common reduction approach. 80 mL of GO dispersion (1 mg mL⁻¹) was mixed with 0.4 mL of N₂H₄ H₂O, and 40 mg of NaOH was then added to adjust the pH value of the solution to 10. The mixture was stirred in an oil bath at 95 °C under a water-cooled condenser for 1 h. After reduction, the product was filtered and washed with water, and

finally dried at 60 °C under vacuum.

FePc/GX composites were synthesized as follows. 20 mg of FePc and 10 mg of GX (GX=NG, GO, and rGO) were dispersed in ethanol (1 mg mL⁻¹) separately and sonicated for 15 min. After well dispersion, both solutions were mixed and the mixture was then sonicated for 1 h. The final products were collected after centrifugation and dried at 60 °C under vacuum.

1.2 Sample characterizations

Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai F20. X-ray diffraction (XRD) patterns were performed on a Philips X'Pert Pro diffractometer with Cu K α ($\lambda=1.5405$ Å) radiation. Fourier transform infrared (FTIR) spectra were collected using a Nicolet ECTOR22 FTIR spectrometer. Raman spectroscopy measurements were performed on a Renishaw 1000 Raman imaging microscope system with an excitation wavelength of 632.8 nm. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an Axis Ultra (Kratos Analytical Ltd.) imaging photoelectron spectrometer using a monochromatized Al K α anode, and the C1s peak at 284.8 eV was taken as an internal standard. Thermogravimetric analysis (TGA) curves were recorded by Q50TGA under N₂ with a heating rate of 10 °C/min.

Electrochemical measurements were carried out on a CHI 760C electrochemical workstation with a three-electrode system. The glassy carbon electrode (diameter 5 mm) was used as working electrode, a Pt foil electrode and an Ag/AgCl with saturated KCl solution electrode as counter and reference electrode, respectively. For the electrode preparation, the suspension of FePc/NG and other catalysts in ethanol (1 mg mL⁻¹) was prepared by introducing a predetermined amount of the corresponding catalyst sample in ethanol under sonication. A 10 μ L portion of catalyst suspension was then dropped onto the electrode using a microsyringe, followed by dropping 5 μ L of Nafion solution in ethanol (0.1 wt%) as a binder.

2. Supplementary data

Table S1 XPS elemental analysis of FePc, NG, GO, rGO, FePc/NG, FePc/GO, and FePc/rGO samples.

Sample	C 1s (at%)	N 1s (at%)	O 1s (at%)	Fe 2p (at%)
FePc	77.95	17.90	1.76	2.38
NG	86.19	9.48	4.33	0
GO	65.54	0.89	32.31	0
rGO	92.28	1.46	6.26	0
FePc/NG	82.43	12.85	2.68	2.04
FePc/GO	79.48	12.44	6.20	1.88
FePc/rGO	81.71	12.47	3.82	2.00

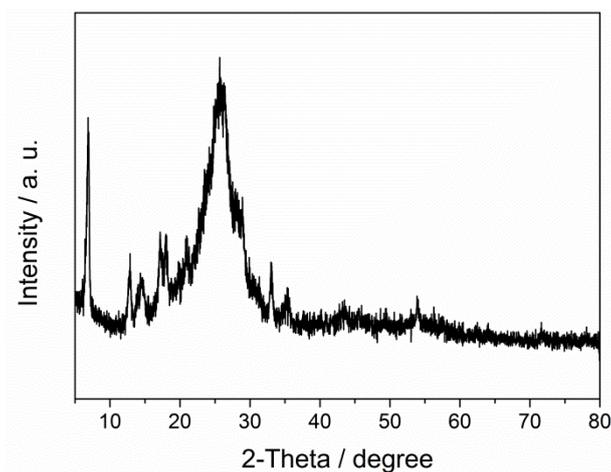


Fig. S1 XRD pattern of FePc/NG composite.

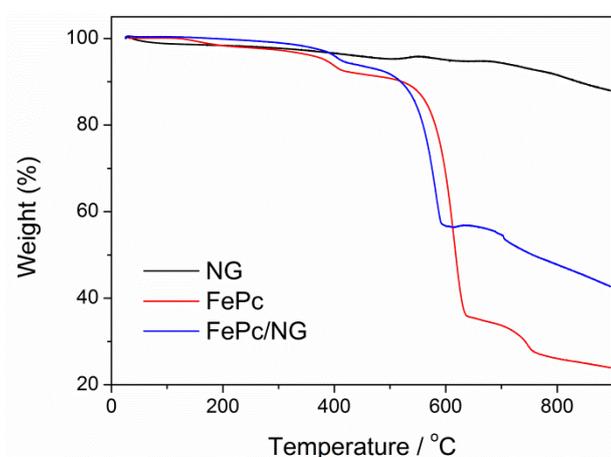


Fig. S2 TGA curves of NG, FePc, and FePc/NG composite. The weight percentage of FePc in FePc/NG is calculated to be about 70 wt%.

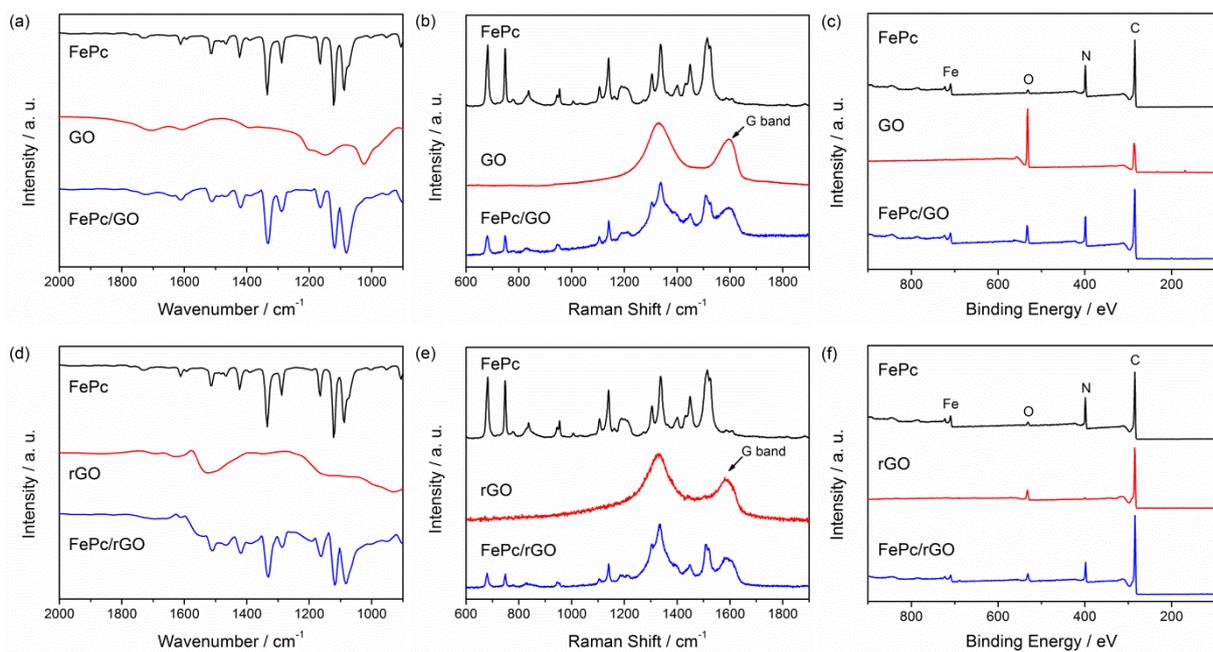


Fig. S3 FTIR, Raman, and XPS spectra of (a-c) FePc/GO composite and (d-f) FePc/rGO composite.

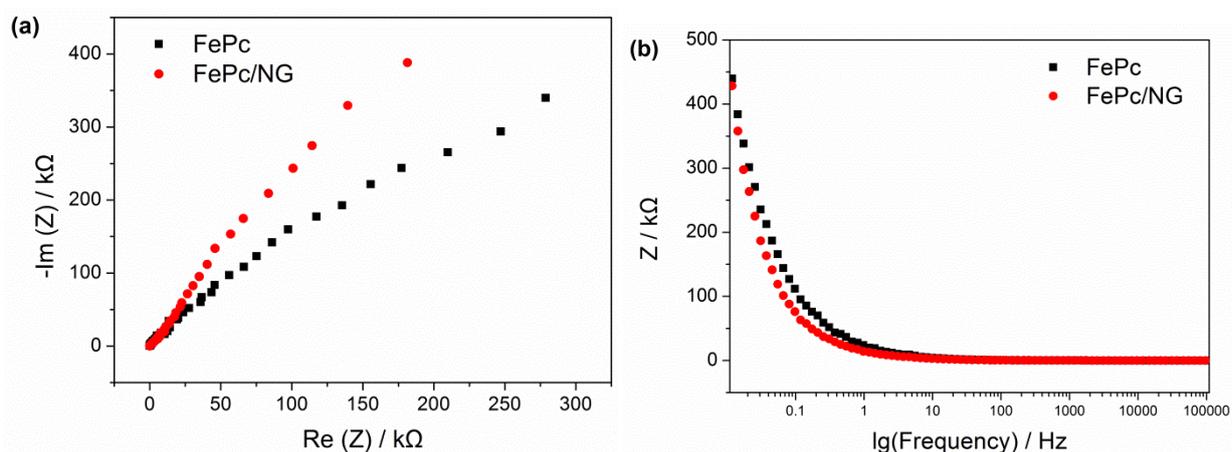


Fig. S4 (a) Nyquist and (b) Bode spectra of FePc and FePc/NG composite obtained by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 10 mHz.

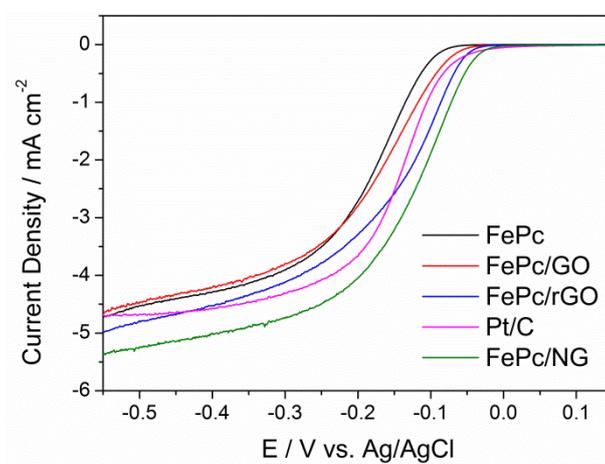


Fig. S5 LSV curves on the FePc, FePc/GO, FePc/rGO, Pt/C, and FePc/NG electrodes in an O_2 -saturated 0.1 M KOH at a scan rate of 10 mV s^{-1} .

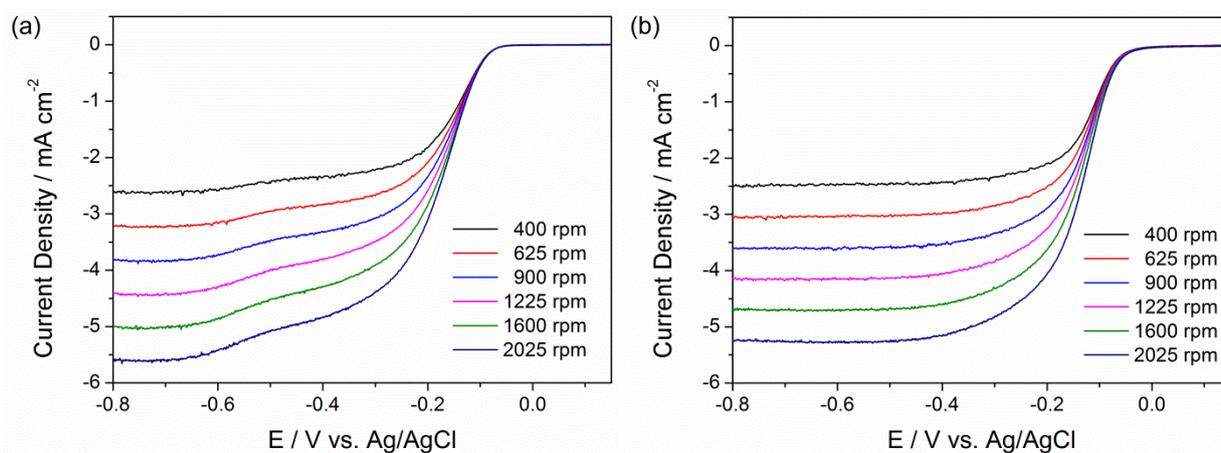


Fig. S6 RDE curves of (a) pure FePc and (b) Pt/C in O_2 -saturated 0.1 M KOH with different speeds at a scan rate of 10 mV s^{-1} .

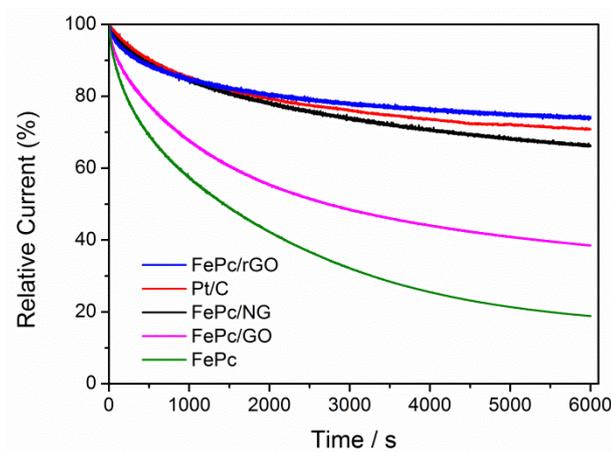


Fig. S7 Chronoamperometric responses (percentage of current retained vs. operation time) of ORR catalysts at -0.25 V in an O_2 -saturated 0.1 M KOH at a rotation speed of 1600 rpm.

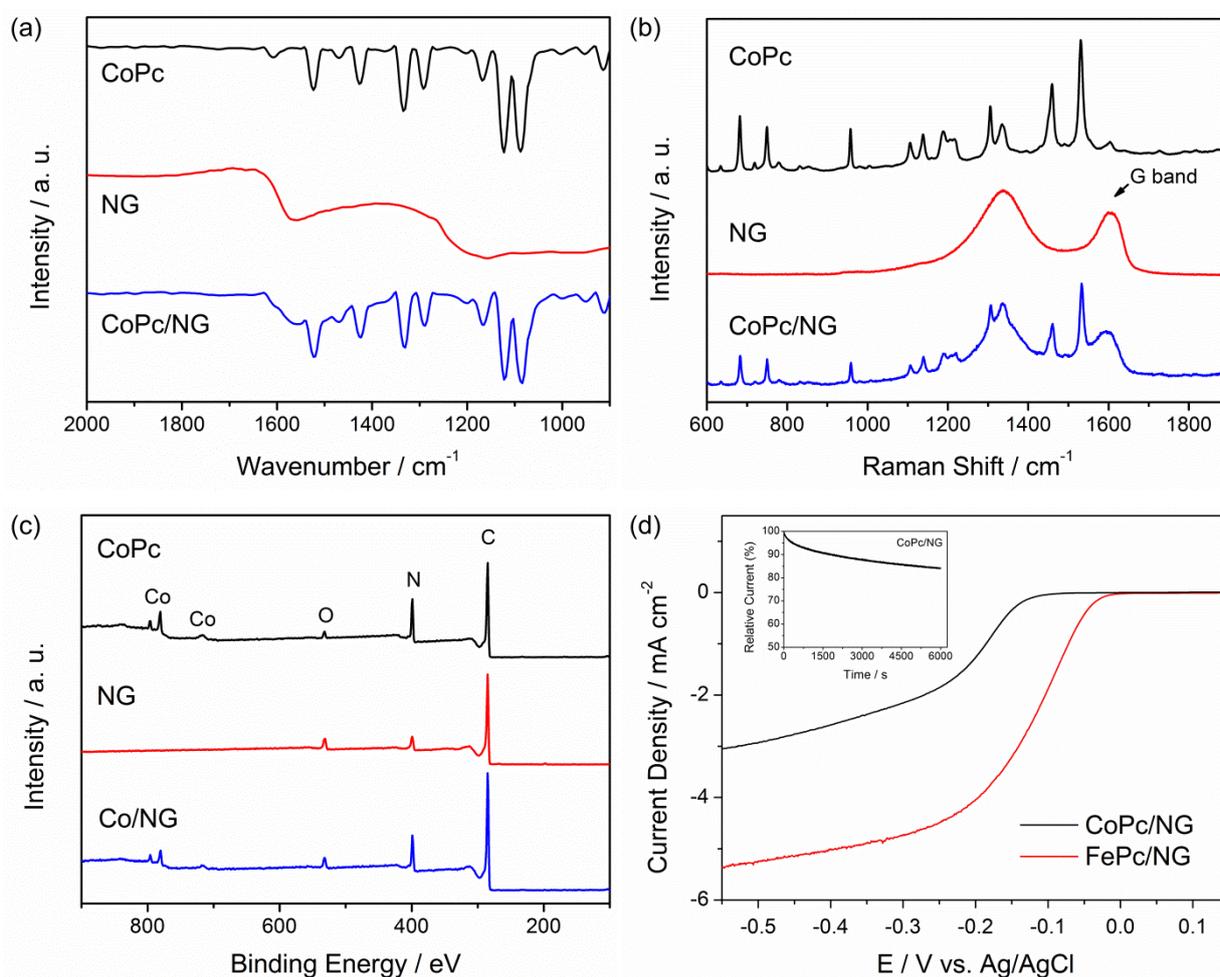


Fig. S8 (a) FTIR, (b) Raman, and (c) XPS spectra of CoPc, NG, and CoPc/NG composite. (d) LSV curves of on the CoPc/NG and FePc/NG electrodes in an O_2 -saturated 0.1 M KOH at a scan rate of 10 $mV\ s^{-1}$. Inset showing the $i-t$ curve of CoPc/NG composite at -0.25 V in an O_2 -saturated 0.1 M KOH at a rotation speed of 1600 rpm

References

[S1] W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

[S2] C. Zhang, R. Hao, H. Liao and Y. Hou, *Nano Energy*, DOI: 10.1016/j.nanoen.2012.07.021.