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Supporting Information

Achieving high-efficient oxygen reduction reaction via a molecular Fe single atom catalyst

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Experimental Section:

Materials:

Iron (II) Phthalocyanine (98%, purified by sublimation) and 2,4-Dihydroxybenzoic acid (97%, Alfa Aesar) were used without any further purification. Ethylenediamine and ethanol were purchased from Sinopharm Chemical Reagent Co. LTD. Polyethylene-polypropylene glycol and methenamine were made by MACKLIN. Dupont Nafion 117 solution (5 wt. %) were purchased by Shanghai Chuxi Industrial Co. LTD.

Synthesis of DMC:

2,4-Dihydroxybenzoic acid (3.08g), ethylenediamine (0.6g), methenamine (0.934g) and 3.5g of polyethylene-polypropylene glycol were dissolved in aqueous solution (80 ml) with stirring until the mixture is transparent. And then pour the mixed solution into the reactor which was placed in an oven at 130 °C for 2h. After the reactor cooled naturally to room temperature, we used deionized water washing the product for three times and finally dried at 70 °C under vacuum for overnight.

Synthesis of DMC-FePc:

Typically, DMC (500mg) and FePc (15mg) were dissolved in 30 ml and 10 ml ethanol respectively and ultrasound was performed on each of them for 12h. And then they were mixed with ultrasound for 6 hours after the mixture were dispersed evenly. At last, the solution was stirred for 6h at 50 °C. The obtained product were washed with ethanol for three times and finally dried at 60 °C under vacuum for overnight and then the synthesized precursors were heated to 900 °C for 3 h under a flow N_2 gas.

Preparation of Working Electrode:

5 mg of samples and 50 μL of Dupont Nafion 117 solution (5 wt.%) were added in ethanol (300 μL) and water (700 μL), followed by sonicated for 30 minutes to get a homogeneous suspension. Then, 15 μL of the catalyst was loaded onto a rotation ring disk electrode (RRDE).

Electrochemical Measurement.

All the electrochemical measurements were carried out in a conventional three-electrode system. The rotating disk electrode (RDE) with a glassy carbon, Ag/AgCl and a platinum wire were used as the working, reference and counter electrode, respectively. All potentials were adjusted to the reversible hydrogen electrode (RHE) using this equation, E (vs. RHE) = E (vs. Ag/AgCl) + 0.059 × pH + 0.197 V. The cyclic voltammetry (CV) tests were measured in N_2 and O_2-saturated 0.1 M KOH solution. LSV were conducted in O_2-saturated 0.1 M KOH at different rotation rates with a sweep rate of 10 mV s^{-1}.

The electron transfer number (n) was obtained by Koutecky-Levich equation:

$$\frac{1}{J}=\frac{1}{J_K}+\frac{1}{J_L}=\frac{1}{B\omega^{\frac{1}{2}}}+\frac{1}{J_K}$$

$$B=0.62nFC_0D_0^{\frac{2}{3}}V^{-\frac{1}{6}}$$

where J, J_K and J_L are the measured current density, the kinetic and diffusion-limiting current densities, ω is the angular velocity, n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant (96485 C mol^{-1}), C_0 is the bulk concentration of O_2 (1.2×10^{-6} mol cm^{-3}), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH (1.9×10^{-5} cm^2 s^{-1}), and V is the kinematic viscosity of the electrolyte (0.01 cm^2 s^{-1}).

The following equations are used to calculate the hydrogen peroxide yield (H_2O_2 %) and the electron transfer number (n):

$$H_2O_2\% = 200\frac{i_R/N}{i_D+i_R/N}$$

$$n = 4\frac{i_D}{i_D+i_R/N}$$

where i_D is the disk current, i_R is the ring current, N is determined to be 0.37.

Characterizations:

The all synthesized samples were studied by transmission electron microscope (TEM, JEM-F200), aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The structure of samples was performed by X-ray diffraction (XRD, Rigaku, Cu Kαradiation) and Raman spectra

(Witec Alpha 300). The X-ray photoelectron spectroscopy (XPS) were performed at the photoemission end-station at beamline BL10B using Al K Alpha (1486.7 eV). The XAS spectra was performed in the National Synchrotron Radiation Laboratory (Infrared spectroscopy and microspectroscopy, MCD endstation, NSRL), Shanghai synchrotron radiation facility (SSRF, BL14W1) and Beijing synchrotron radiation facility (BSRF, 1W1B). The XAFS data was analyzed by ATHENA and ARTEMIS software containing FEFF package. The R space spectra of Fe K-edge was fitted by using standard FePc as counterpart.

Computational Methods:

All calculations were performed via the Vienna ab initio simulation package based on the density functional theory (DFT). Generalized gradient approximation with spin polarized Perdue-Burke-Ernzerhof (PBE) functional was adopted to describe the exchange-correlation potential.[1] The projector augmented wave (PAW) potential was used to consider the interactions between electron and ions.[2] The plane wave cutoff energy was set to be 450 eV. During the calculation process, all atoms were fully relaxed until the energy convergence accuracy reached to 10^{-4} eV per atom and the interaction force is less than 0.02 eV/Å. A vacuum spacing of 15 Å was employed to isolate the surfaces. Gamma-point-only grid was used for the brillouin zone sampling.

The Gibbs free energy for each step of ORR can be calculated with the following equation[3]:

$$\Delta G = \Delta \mathrm{E} + \Delta \mathrm{ZPE} - \mathrm{T}\Delta \mathrm{S}$$

where ΔE is the reaction energy obtained by the DFT calculations, ΔZPE is the zero-point energy changes during the reaction, while TΔS determines the variation of entropy.

The adhesive energy was computed with $E_{ad}=E_{Graphene\text{-}FePc/DMC\text{-}FePc} - E_{Graphene/DMC} - E_{FePc}$, where $E_{Graphene/DMC}$, E_{FePc} and $E_{Graphene\text{-}FePc/DMC\text{-}FePc}$ represent the energies of the Graphene/DMC, FePc molecule and the hybrid systems.

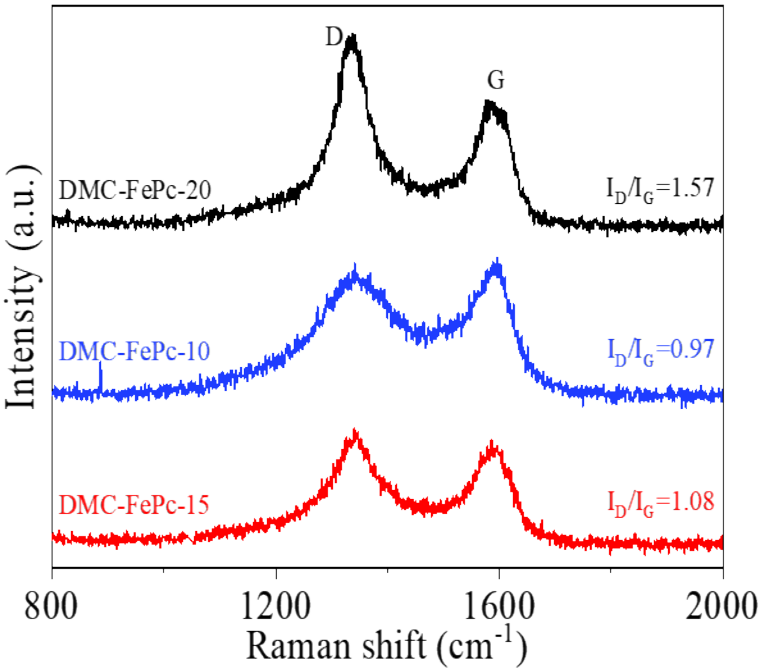

Figure S1. Roman spectra of different samples.

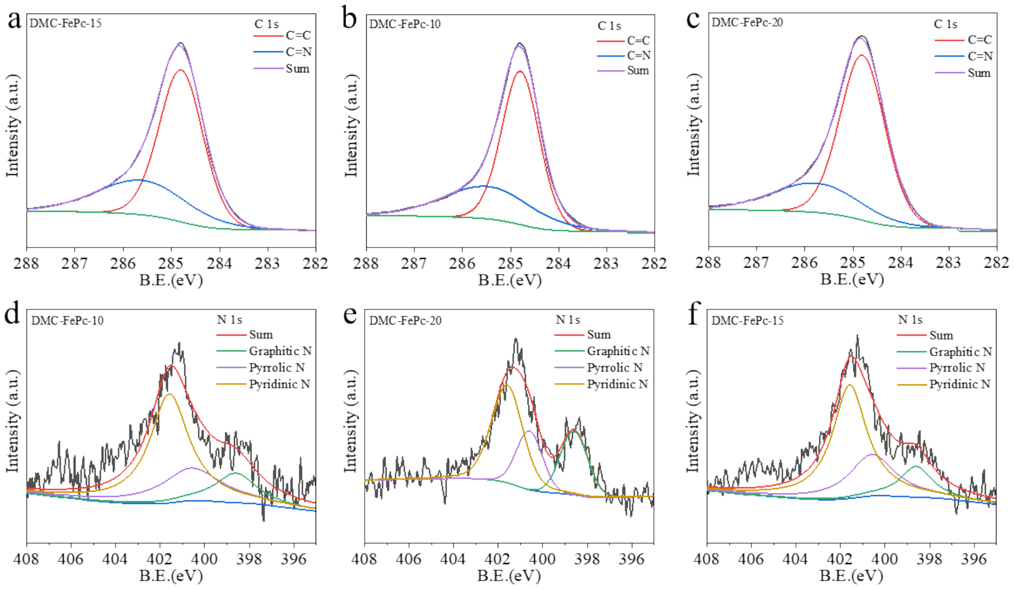

Figure S2. XPS spectra for the (a), (b), (c) C 1s, and (d),(e),(f) N 1s regions of DC-FePc-n, respectively.

The graphitic-N of DMC-FePc-10, DMC-FePc-15, and DMC-FePc-20 were calculated as 16.14%, 14.292%, and 26.263%. The pyridinic-N of DMC-FePc-10, DMC-FePc-15, and DMC-FePc-20 were calculated as 26.27%, 27.67%, and 22.96%. The pyrrolic-N have been calculated as 57.59%, 58.03%, and 50.77%, respectively.

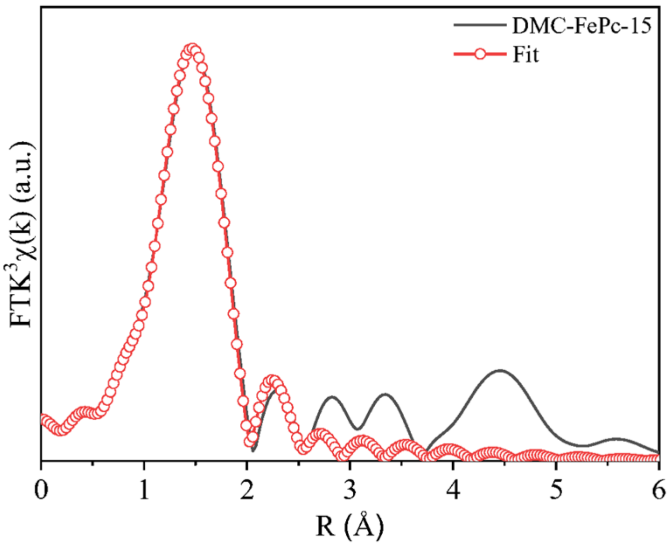

Figure S3. EXAFS fitting curve in R space of DMC-FePc-15

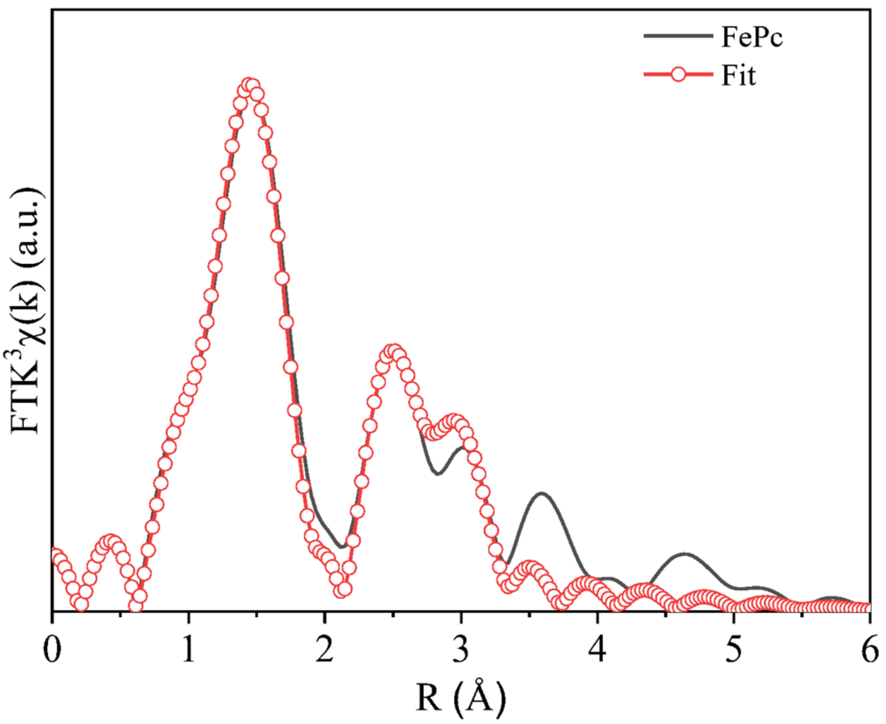

Figure S4. EXAFS fitting curve in R space of FePc.

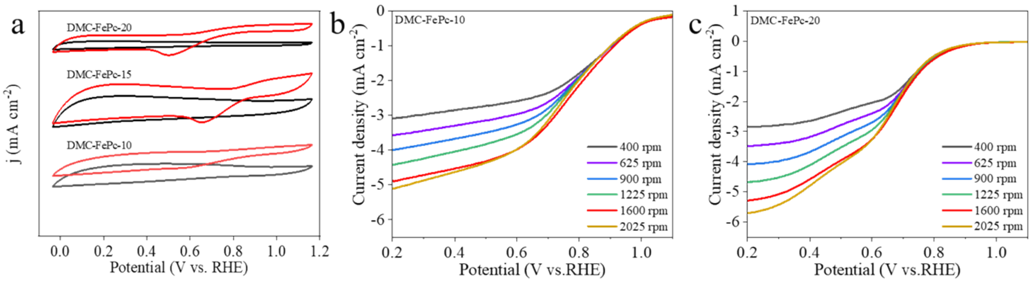

Figure S5. (a) ORR CV curves of DMC-FePc-n in O_2, N_2-saturated 0.1M KOH solution. (b), (c) LSV curves of DMC-FePc-10 and 20 at different rotating rates, respectively.

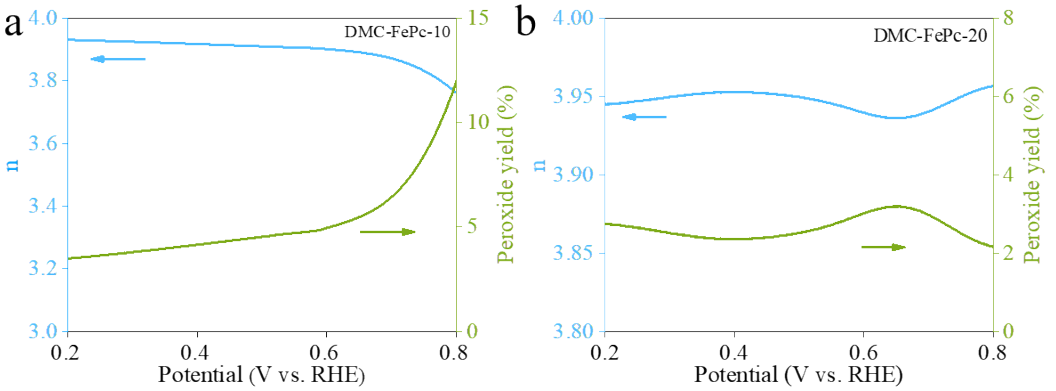

Figure S6. (a), (b) The electron transfer number (n) and peroxide yield value of DC-FePc-10 and 20 respectively.

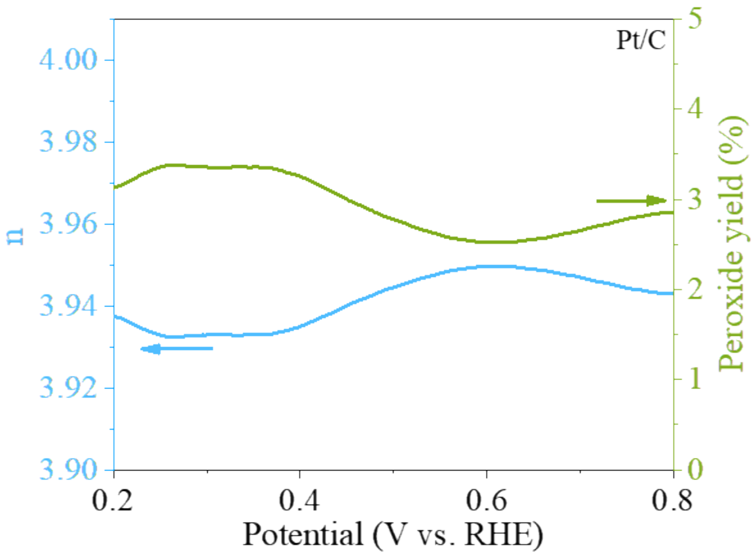

Figure S7. The electron transfer number (n) and peroxide yield value of commercial Pt/C in 0.1M KOH solution.

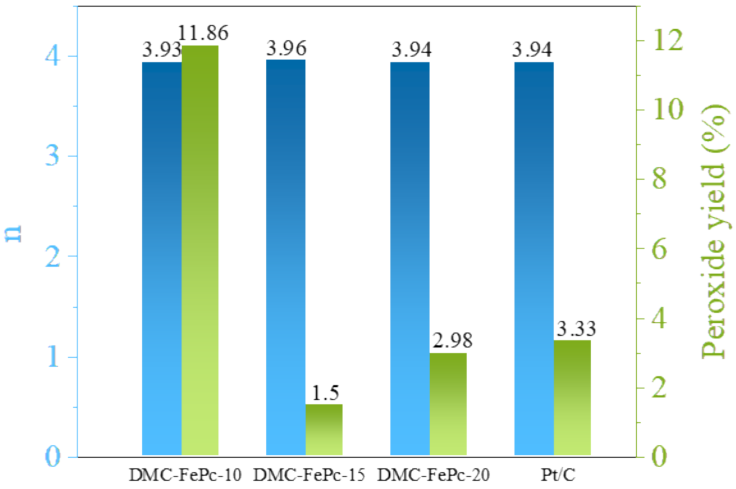

Figure S8. The overall comparison of commercial Pt/C and the prepared catalysts for the electron transfer number (n) and peroxide yield value.

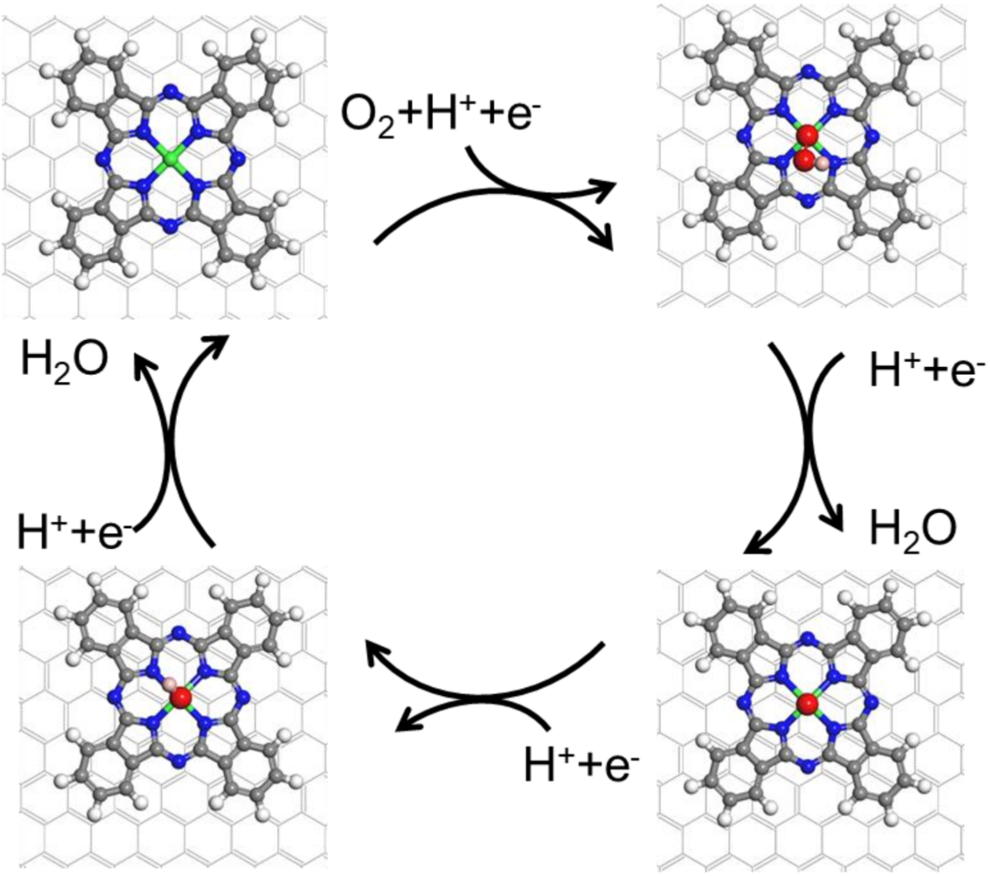

Figure S9. Optimized configurations at each intermediate step of ORR on Gr-FePc.

Table S1. EXAFS fitting parameters of FePc and DMC-FePc-15

Sample	Path	N	R(Å)	σ^2 (10^{-3} Å^2)
FePc	Fe-N	4	1.98	0.45
DMC-FePc-15	Fe-N/O	3.8	1.95	1.3

Here, N represents the coordination number, R represents the bond distance, σ^2 represents the Debye-Waller factor value. S_0^2 was fixed to from FePc fitting.

1. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
2. P. E. Blöchl, *Phys. Rev., B Condens. Matter*, 1994, **50**, 17953.
3. J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jonsson, *J. Phys. Chem. B*, 2004, **108**, 17886-17892.