

Electronic Supplementary Information (ESI)†

Iron phthalocyanine integrated with boron-doped reduced graphene oxide for the highly selective four-electron oxygen reduction: An experimental study

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Experimental section

Chemicals

Graphite flakes were purchased from Sigma-Aldrich, India. Boric acid (H_3BO_3), ethanol ($\text{C}_2\text{H}_5\text{OH}$), and potassium permanganate (KMnO_4) were purchased from Qualigens. Potassium hydroxide (KOH) and methanol were obtained from SRL. Sulfuric acid (H_2SO_4), orthophosphoric acid (H_3PO_4), and *N, N* dimethylformamide (DMF) were purchased from S.D Fine Chemicals (India). Hydrogen peroxide (H_2O_2) was purchased from Merck, India.

Instrumentation

All electrochemical studies were done on CH Instruments (CHI-660C), USA and Squidstat potentiostats (Admiral Instruments, USA) with a three-electrode system. Glassy carbon rotating disc electrode (GC_{RDE}) is used as a working electrode for the study of activity and the kinetics of ORR. Rotating ring disc electrode with glassy carbon disc and gold ring (GC_{RRDE}) is used to study the four-electron selectivity of the materials. The surface area of GC_{RDE} is 0.196 cm^2 and the area of the disc and ring of GC_{RRDE} is 0.238 and 0.236 cm^2 , respectively. (The disc diameter of GC_{RRDE} is 5.5 mm and the ring's outer and inner diameters are 8.5 and 6.5 mm .) A saturated calomel electrode (SCE) is used as a reference electrode. A platinum wire and 0.1 M KOH ($\text{pH} = 13$) are used as a counter electrode and the electrolyte, respectively. Powder X-ray diffraction (XRD) patterns were obtained from Bruker D8 Advance X-ray diffractometer using $\text{Cu-} \alpha$ radiation (0.1541 nm) with a scan rate of 2 degrees per minute. Raman spectroscopy studies were done on Renishaw micro-Raman spectroscope using a (50%) 532 nm solid-state diode laser source in the range of $500\text{-}3000 \text{ cm}^{-1}$. FT-IR spectra were recorded over the range of $400\text{-}4000 \text{ cm}^{-1}$ on a Perkin Elmer spectrophotometer using the KBr pellet method. Transmission electron

microscopy (TEM) images were captured from a TECNAI 20 G² microscope operated at 200 kV. Scanning electron microscopy (SEM) images with energy dispersive X-ray (EDAX) elemental mapping analyses were carried out by SEM VEGA 3TESCAN and operated at 30 kV. X-ray photoelectron spectroscopy (XPS) data of different elements were recorded on Physical Electronics, PHI 5000VersaProbe III. The formulas used are given in Equations S1 and S2.

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \times \text{pH} + 0.241 \text{ V} \quad \dots(\text{S1})$$

(To convert the observed potentials with respect to a reversible hydrogen electrode (RHE) scale)

The Koutecky-Levich (K-L) equation is as follows

$$j^{-1} = j_{\text{K}}^{-1} + j_{\text{L}}^{-1} = \omega^{-1/2} B^{-1} + j_{\text{K}}^{-1} \quad \dots(\text{S2})$$

j = observed current density, $j_{\text{K}} = (kC_0nF)$ kinetic current density, ω = angular rotation of the electrode, $B = (0.62C_0nF\nu^{1/6}D^{2/3})$ = Levich constant. The other symbols have the usual meaning and are produced from literature.¹

To calculate the number of electrons and percentage of H₂O₂ produced using the RRDE experiment (Equations S3 and S4) disk electrode was scanned in the potential of ORR region (1.1 to 0.2 V vs RHE) and the disk current is denoted as (I_{D}) and ring electrode was kept at 1.5 V vs RHE and ring current is denoted as I_{R} . The collection efficiency (N) of the RRDE ring electrode is 0.3.²

$$\text{Number of electrons} = 4 \times I_{\text{D}} / (I_{\text{D}} + (I_{\text{R}}/N)) \quad \dots(\text{S3})$$

$$\% \text{ H}_2\text{O}_2 \text{ produced} = [(I_{\text{R}}/N) / (I_{\text{D}} + (I_{\text{R}}/N))] \times 200 \quad \dots(\text{S4})$$

Synthesis of the materials

Graphene oxide (GO) was synthesized by the modified Hummers method. In this method, 1.0 g graphite powder was mixed with 6.0 g KMnO_4 and ground with a mortar and pestle. In a 500 mL beaker, 120.0 mL of concentrated H_2SO_4 was mixed with 13.0 mL of concentrated H_3PO_4 . The first mixture of graphite and KMnO_4 was slowly added to the beaker containing the acids and the temperature was maintained at 50 °C. The mixture was stirred magnetically for 4 h and then cooled to 3-5 °C using ice. To the ice-cold mixture, 5.0 mL H_2O_2 was added very slowly with string. The mixture was centrifuged at 10000 rpm for a few min and the material was washed with water until the pH of the washings became 7.0. The residue, graphene oxide (GO) was collected and dried at 40 °C.³⁻⁴ To prepare boron-doped reduced GO (B-RGO), 200.0 mg of boric acid is mixed with 50.0 mg of GO in a water-ethanol mixture (20.0, 8.0 mL respectively) and sonicated for 10 min and put in a Teflon-lined autoclave at 160 °C for 16 h. After cooling to room temperature, the materials were filtered and washed with ethanol and water.^{5,6} Immobilization of FePc on B-RGO was achieved by mixing 50.0 mg B-RGO and 5.0 mg FePc in 20.0 mL DMF and equilibrating for 24 h by continuous magnetic stirring. The formed product (FePc@B-RGO) was washed with water and DMF and dried at room temperature. In a similar way, FePc@RGO was also prepared, however, replacing B-RGO with RGO. The suspensions (5 mg in 1.0 mL DMF, *i.e.*, 0.5 %) of RGO, B-RGO, FePc@RGO, FePc@B-RGO, and Pt/C in DMF were prepared and sonicated for 45 min to modify the electrodes. The cleaned electrodes were coated with the respective suspensions to get the respective material-modified electrodes. The catalyst loadings for GC_{RDE} and GC_{RRDE} are approximately the same ($357 \mu\text{g}/\text{cm}^2$).

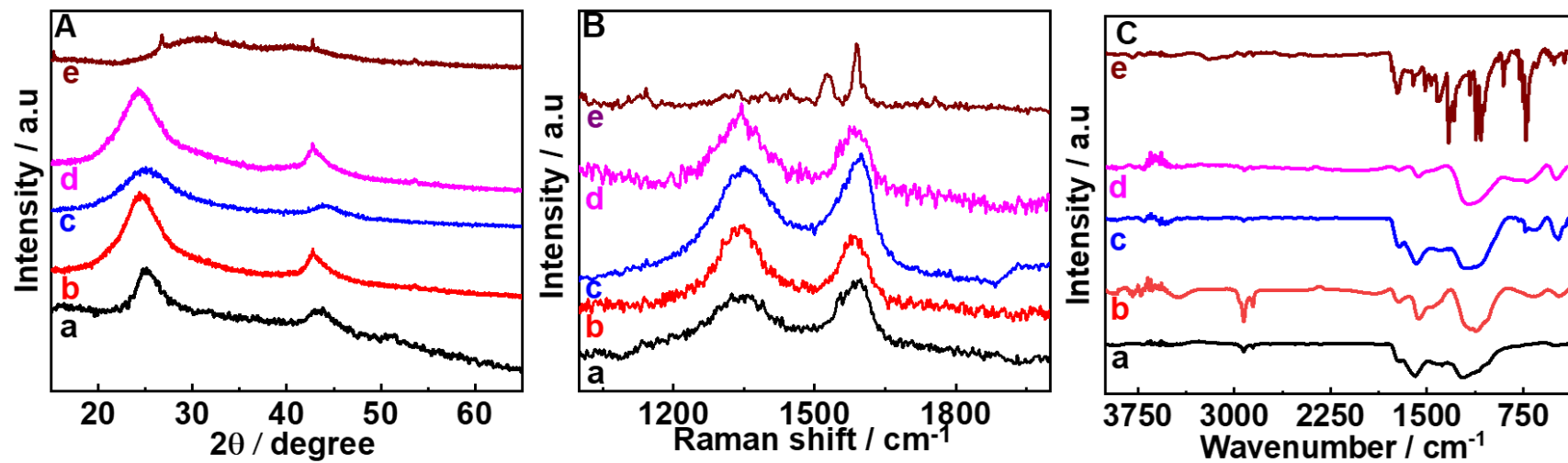


Fig. S1 Powder XRD patterns (A), Raman spectra (B), and FT-IR spectra (C) of RGO (a), B-RGO (b), FePc@RGO (c), FePc@B-RGO (d), and FePc (e).

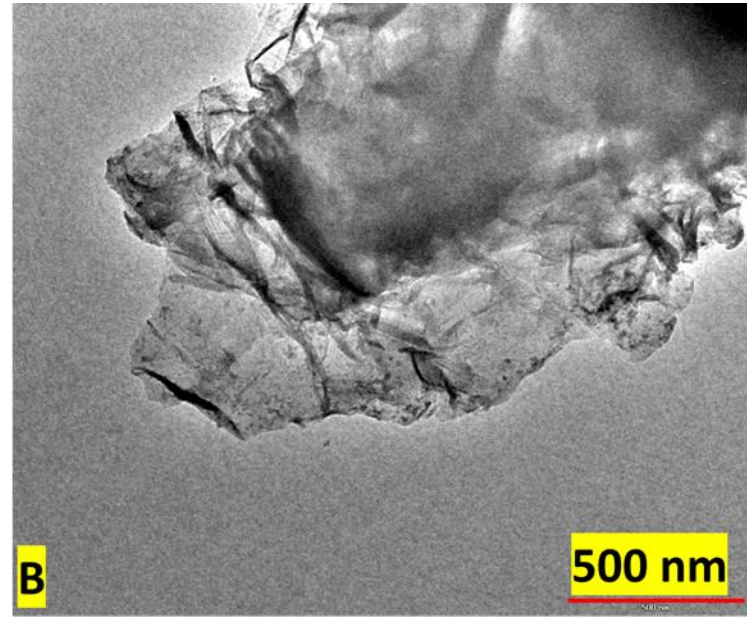
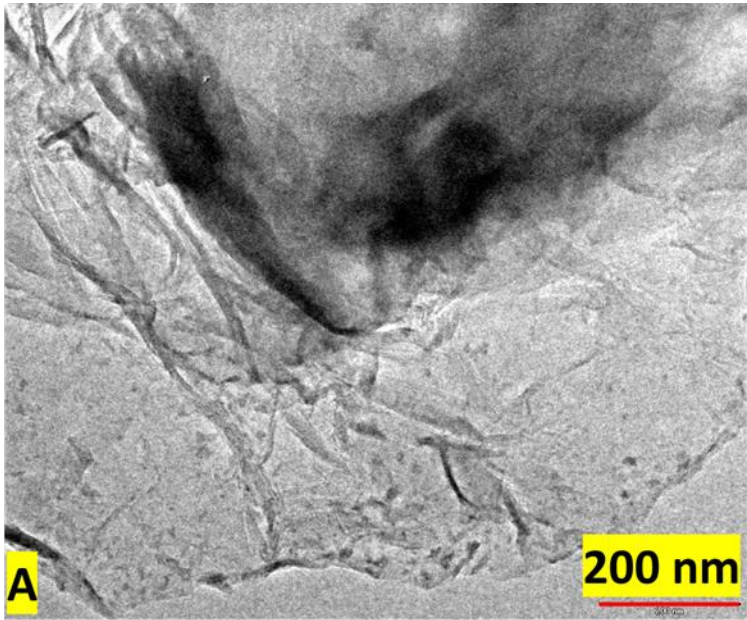


Fig. S2 TEM images of FePc@B-RGO at different magnifications (scale: 200 nm (A) and 500 nm (B)).

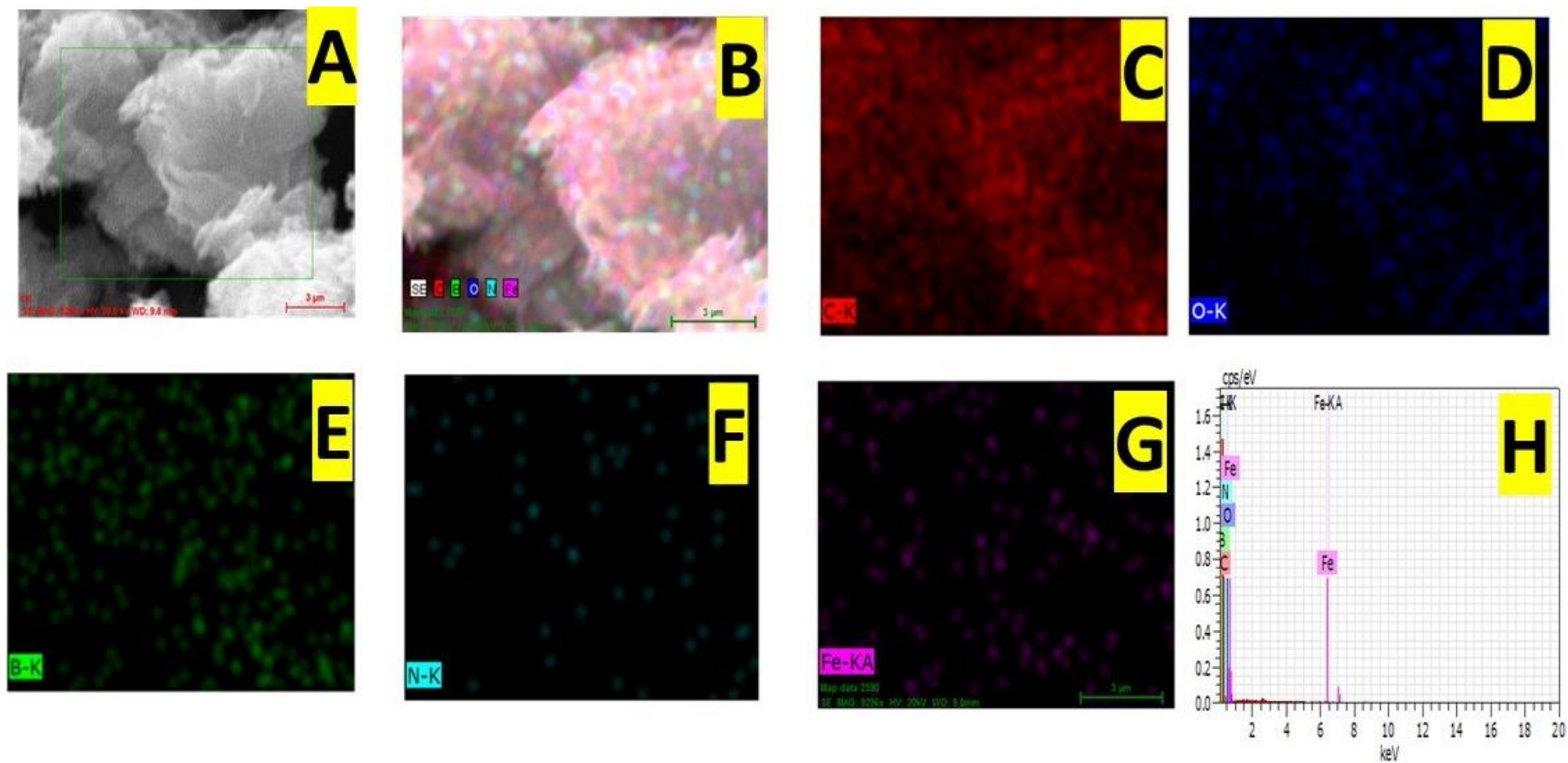


Fig. S3 SEM mapping images (A-G) and EDAX spectrum (H) of FePc@B-RGO.

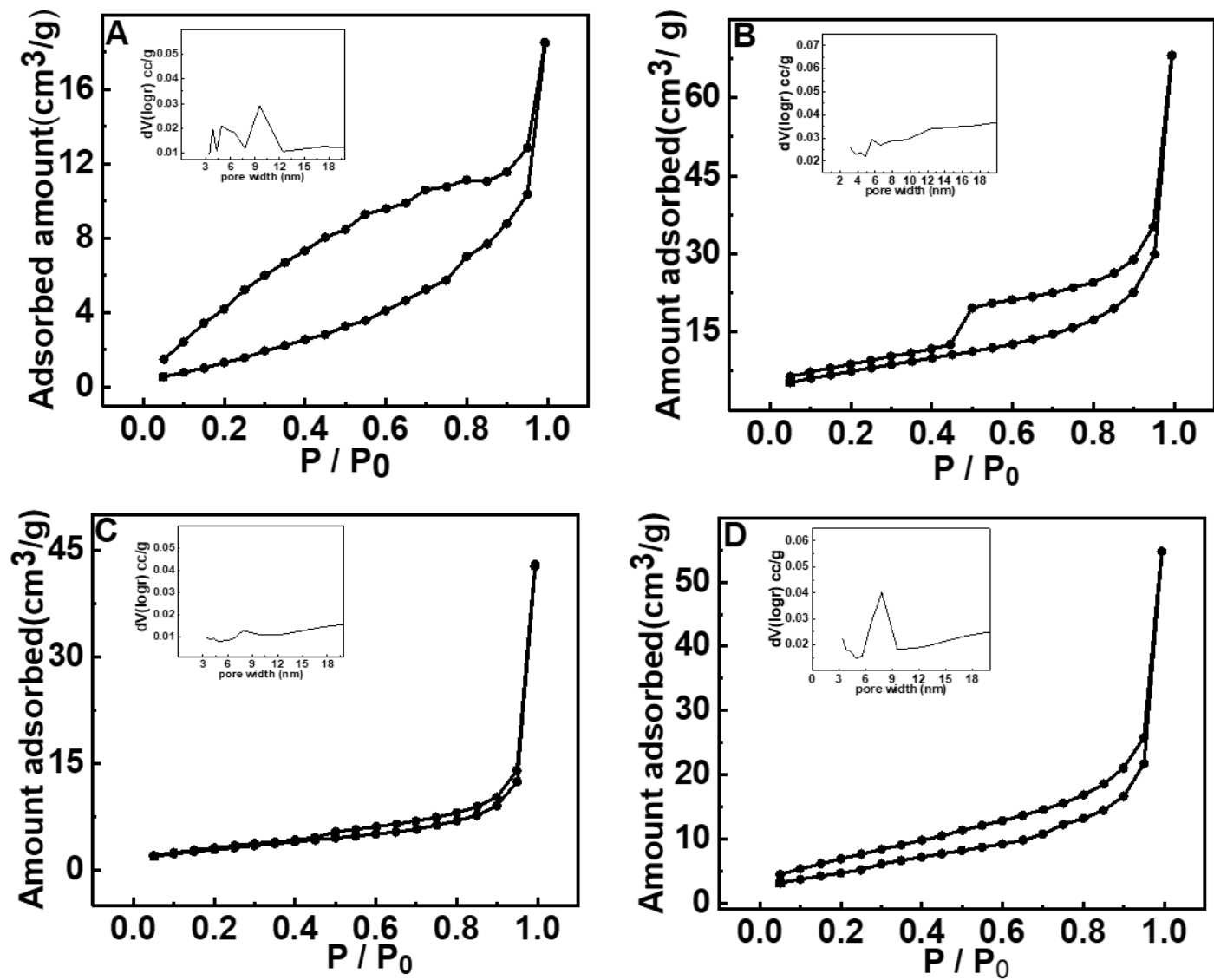


Fig. S4 N_2 adsorption-desorption isotherms of (A) RGO, (B) B-RGO, (C) FePc@RGO, and (D) FePc@B-RGO.

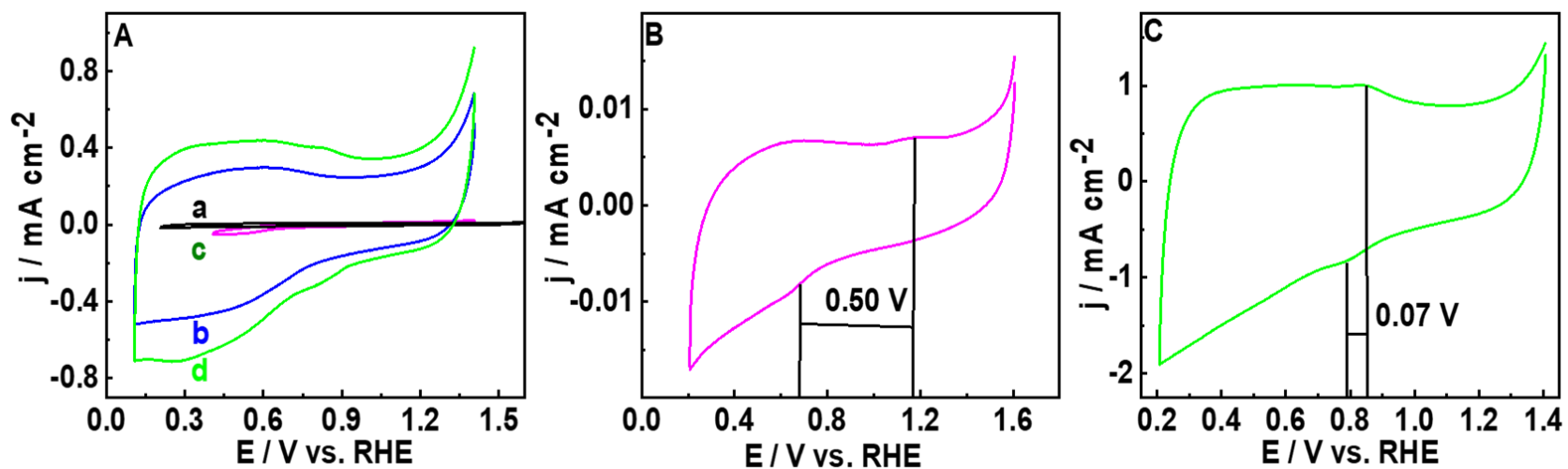


Fig. S5 CV responses of (a) RGO, (b) B-RGO, (c) FePc@RGO, and (d) FePc@B-RGO in N_2 saturated in 0.1 M KOH at 20 mVs^{-1} scan rate (A), CV responses of FePc@RGO (B), and FePc@B-RGO (C) recorded in N_2 saturated 0.1 M KOH at 50 mVs^{-1} scan rate.

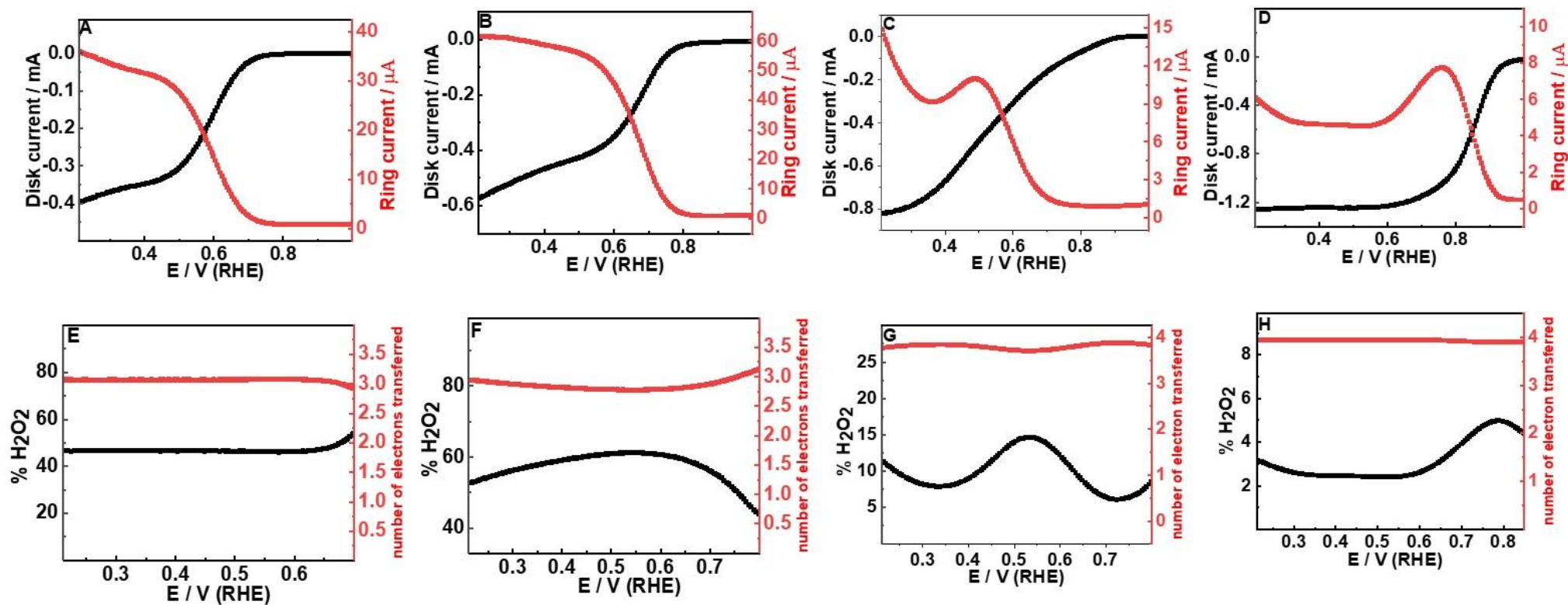


Fig. S6 LSV response of RGO (A), B-RGO (B), FePc@RGO (C), and Pt/C (D) in basic medium showing the disc current in the potential window of 0.0 to 1.0 V vs. RHE and ring current at an applied potential of 1.5 V vs. RHE and the corresponding plots (E-H, respectively) showing the percentage of H_2O_2 formed and the number of electrons transferred during the ORR.

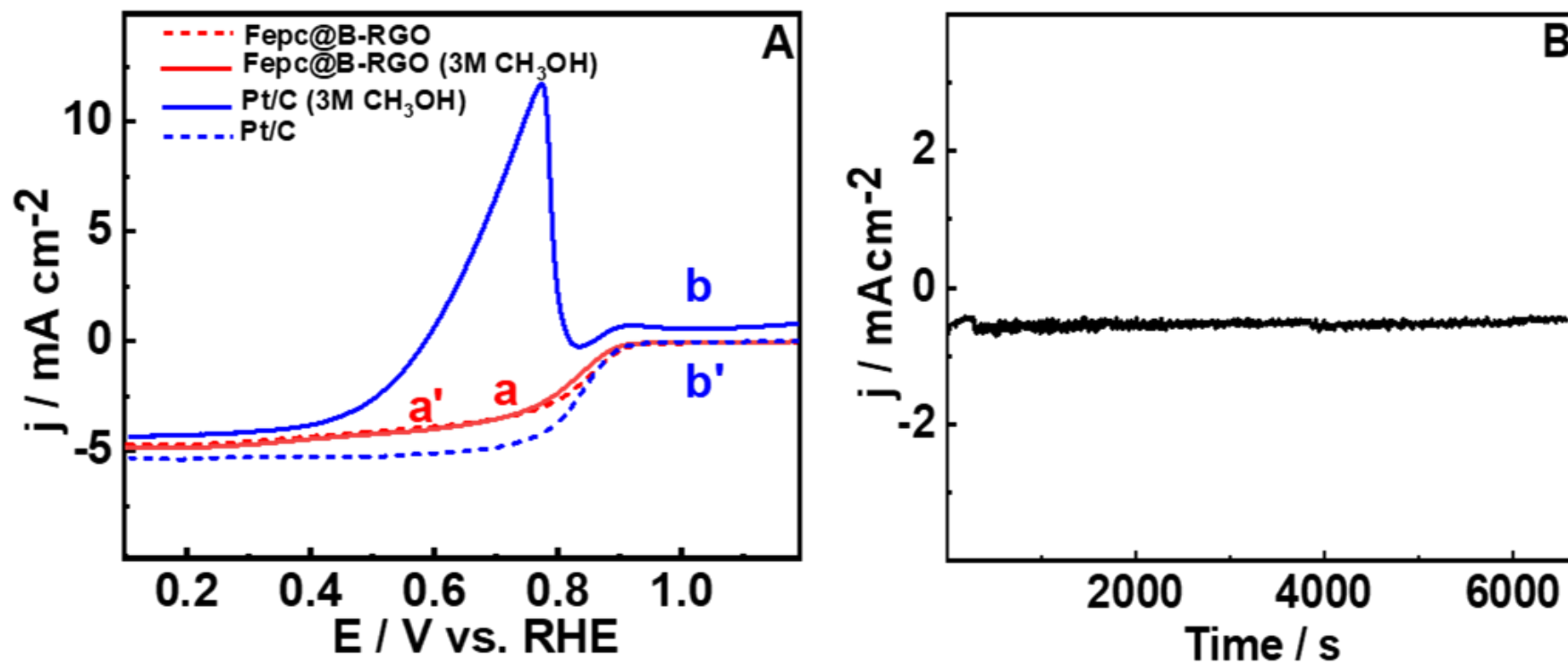


Fig. S7 (A) Methanol tolerance study: LSV responses of FePc@B-RGO (a, a') and Pt/C (b, b') before (a', b') and after (a, b) the addition of 3.0 M methanol. (B) Stability study: Amperometry response of FePc@B-RGO for 7200 s at -0.5 V (vs. SCE).

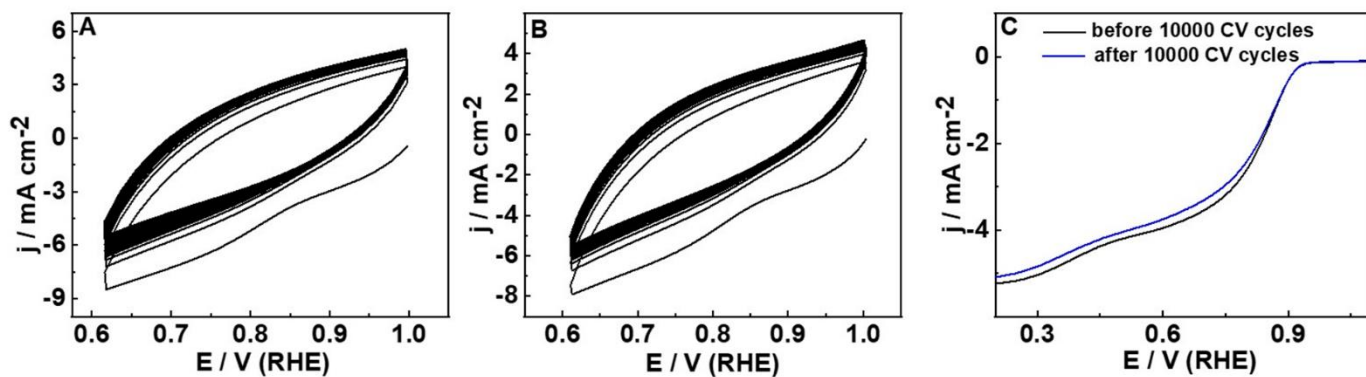


Fig. S8 CV response of FePc@B-RGO catalyst in O₂-saturated 0.1 M KOH for 7000 continuous cycles (A) and after a 10 min break, further 3000 CV cycles (B). LSV curves before and after 10,000 CV cycles (C) measured in O₂-saturated 0.1 M KOH with a scan rate of 5 mVs⁻¹ and at a rotation rate of 1600 rpm.

Table S1. Comparison of the ORR efficiency of FePc@B-RGO with other catalysts in terms of onset potential

Material	Support material	E_{onset} (RHE)	E_{1/2} (RHE)	References
FePc ^A	RGO ^E	0.90 V	-	S7
FePc	ERGO ^F	0.92 V	-	S8
FePc	NGA ^G	0.92 V	-	S9
FeTPPc ^B	Gr ^H	0.88 V	-	S10
TQFePc ^C	RGO/CB ^I	0.88 V	-	S11
FePc	CNT N ^J	0.95 V	0.84 V	S12
FePc(CP) ₄ ^D	Gr ^H	0.81 V	-	S13
FePc	B-RGO ^K	0.95 V	0.85 V	This work
FePc	MCN ^L	0.93 V	-	S14

^A Iron phthalocyanine; ^B Iron(II) tetrapyriddyloxyphthalocyanine; ^C Tetra-β-(8-quinolinoxy) iron phthalocyanine; ^D Iron(III) tetracumylphenoxy phthalocyanine; ^E Reduced graphene oxide; ^F Electrochemical reduced graphene oxide; ^G Nitrogen-doped graphene aerogel; ^H Graphene; ^I Carbon black; ^J Nitrogen-doped carbon nanotubes; ^K Boron-doped reduced graphene oxide; ^L Mesoporous carbon nitride.

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