

SUPPORTING INFORMATION

The Synergy between Electrochemical Substrate Oxidation and Oxygen Reduction Reaction to Enable Aerobic Oxidation

Supporting Information

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Experimental Procedures

1. Experimental Section

1.1 Materials and Methods

All the chemical reagents were purchased from commercial sources and used without further purification. Hydrazine hydrate (Hz) and Hydrazobenzene were obtained from Sigma Aldrich. Potassium hydroxide (KOH) was purchased from Merck. D₂O and Nafion were purchased from Sigma. CDCl₃ was purchased from Clearsynth, Carbon cloth was purchased from Eliteck. Deionized water (18.2 MΩ cm resistivity at 25 °C, purified using a Millipore system) was used as the solvent for all the reported electrochemical experiments.

1.2 Material Characterization

The electrode surface characterization was performed by Scanning Electron Microscopy (SEM) with Jeol JSM7600F instrument and Powder X-Ray Diffraction (PXRD) with Bruker D8 DISCOVER instrument. The oxidation state of Fe was determined by X-ray photoelectron spectroscopy (XPS) with model AXIS SUPRA C332905/01. Fe content in the sample was measured with inductively coupled plasma optical emission spectroscopy (ICP-OES) with Model Nexion 2000B ICP-MS. For it, 1 mg of the catalyst was digested in 24 mL aqua-regia for 72 hours at 50 °C and later the sample was diluted 30 times with deionized water for ICP-OES measurement. The total Fe present in the 1mg Fe PANI/C powder sample is 0.01524 mg. Fe content of pre- and post-electrolysis samples deposited on a carbon cloth was also determined by ICP-OES and given in the following table:

Table S1. Calculation of Fe content of pre- and post-electrolysis samples by ICP-OES per mg of Fe PANI/C.

SL No.	Sample	Fe content (mg)
1	Pre-electrolysis, Electrode	0.013
2	Post-electrolysis, Electrode	0.007
3	Post-electrolysis, Electrolyte	0.004*

* per mL of electrolyte

1.3 Electrochemical Measurements

All the measurements were performed in a three-electrode system using a Metrohm Autolab PGSTAT 101 potentiostat. Ag/AgCl (saturated KCl) and a Pt wire were used as the reference and counter electrodes, respectively. All the potentials were converted to the normal hydrogen electrode (NHE) scale:

$$E_{\text{NHE}} (\text{V}) = E_{\text{Ag/AgCl}} + 0.197 \quad (\text{Equation S1})$$

or to a reversible hydrogen electrode (RHE) scale using the Nernst equation at room temperature:

$$E_{\text{RHE}} (\text{V}) = E_{\text{Ag/AgCl}} + 0.0592 \times \text{pH} + 0.197 \quad (\text{Equation S2})$$

The scan rate was kept at 5 mV s⁻¹ for cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements. Constant current electrolysis was performed at 5 mA cm⁻² for the conversion at room temperature and constant stirring in an undivided cell with a carbon cloth as the working electrode. For catalyst ink preparation, 5 mg of the catalyst and 10 μL Nafion were mixed into 1000 μL IPA and sonicated for an hour. 20 μL of this ink solution was deposited on a glassy carbon electrode for analytical purpose and for electrolysis and product analysis, 8 mg of the catalyst with 20 μL Nafion were mixed into 1000 μL IPA and deposited on 1 cm X 1 cm carbon cloth and kept it for drying for one an hour before starting the electrochemical measurements.

0.1 M phosphate buffer adjusted to pH 7 - 12 was used as an electrolyte and for pH 14 and pH 13, 1 M KOH and 0.1 M KOH were used, respectively.

% Faradaic yield (FY) was determined from the following equations

$$\text{FY} (\%) = \frac{\text{Moles of N}_2 \text{ formed} \times 96,485 \text{ C mol}^{-1} \times 4}{\text{Total charge passed}} \times 100 \%$$

Electrochemical active surface area (ECSA) was determined from the following equation ^[1].

$$\text{ECSA} = (C_{\text{dl}}/C_s) \times A_{\text{geo}} \quad (\text{Equation S3})$$

Where, the double layer capacitance, C_{dl} is determined from Figure S6, Specific capacitance, C_s = 0.04 mF cm⁻² and A_{geo} is the geometric surface area of the electrode (0.07 cm²).

Turnover Frequency (TOF) was determined using the following equation ^[2].

$$\text{TOF} = j \times A / (4F \times m) \quad (\text{Equation S4})$$

where, j is the current density, 0 < log(j) < 1, j is recorded at 5 mV/s scan rate, A is the geometric area of glassy carbon electrode (0.07 cm²), F is the Faraday constant, m is the no. of moles of respective catalyst used.

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1.4 Product Analysis

The product yields for aerobic oxidation were obtained through NMR (Bruker Avance III, 500 MHz) having dioxane as an internal standard in D₂O. *Hydrogen and Nitrogen evolution measurements*: The amount of produced hydrogen in the reactor headspace was analyzed using a gas chromatograph (CIC-Dhruva) equipped with a thermal conductivity detector (TCD).

1.5 Aerobic Oxidation

0.02 mmol Hydrazobenzene was taken with 7.5 wt% of the catalyst in 2 mL DMF + H₂O mixture and 10 mM OH⁻ in O₂ saturated environment for 4 hours at room temperature. The reaction was monitored by TLC. After completion, the product was extracted using DCM, and the yield was calculated from ¹H NMR taking dioxane as the internal standard.

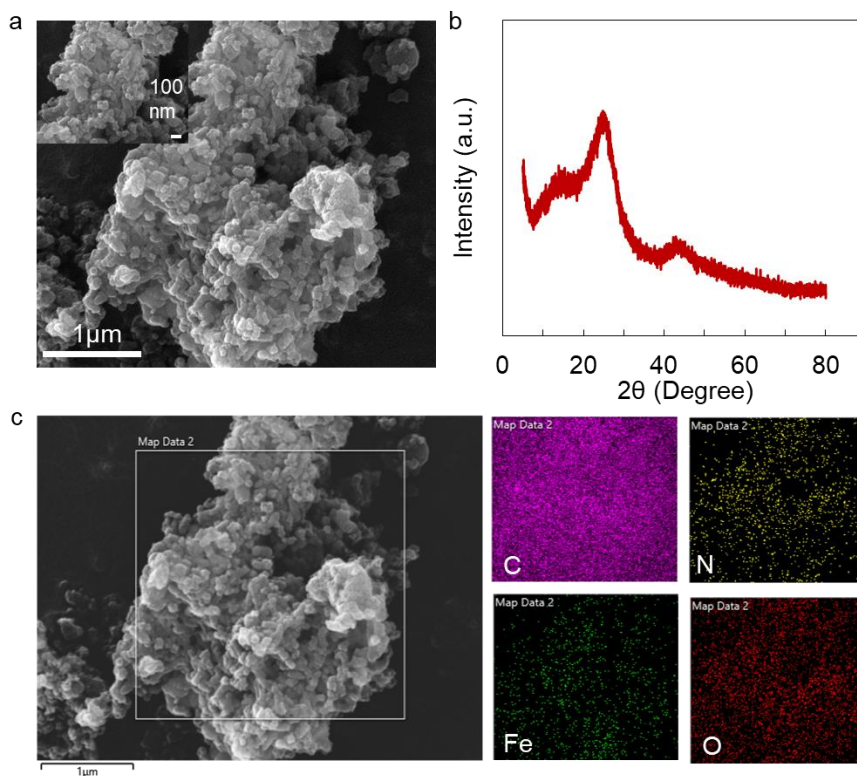


Figure S1A. a) SEM image; b) PXRD; and c) EDS analysis of the Fe PANI/C powder (C: pink, N: yellow, Fe: green, O: red).

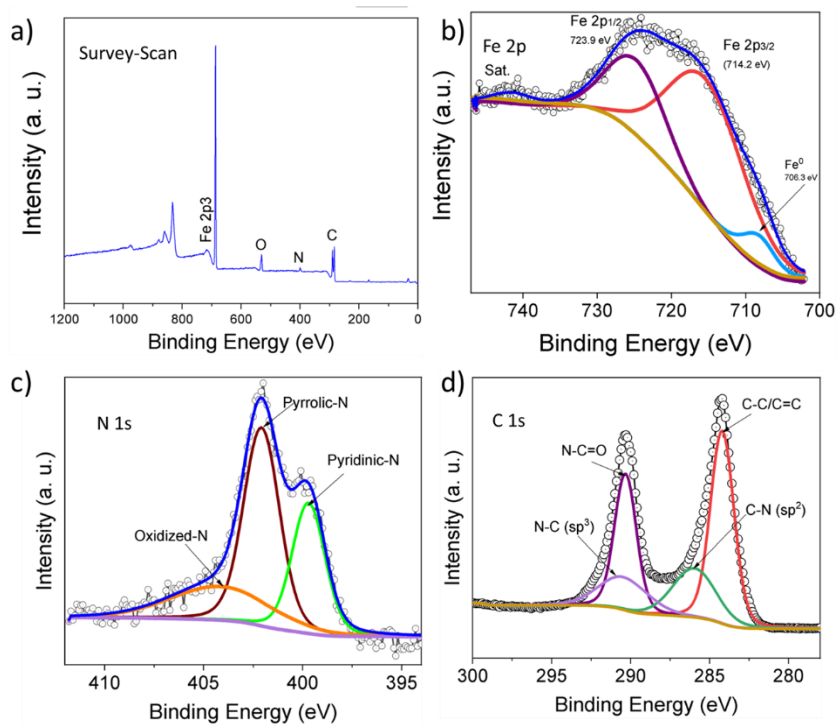


Figure S1B. XPS spectra of Fe PANI/C; Survey spectra (a), Fe (b), N (c), C (d).

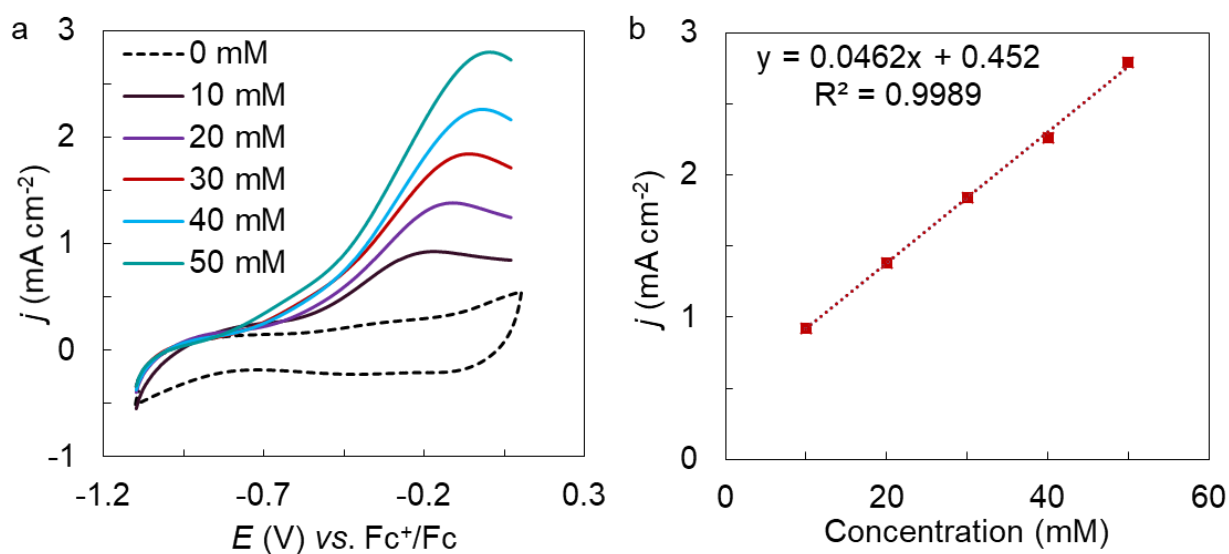


Figure S2. a) Hz concentration dependence LSVs; b) Plot of HzOR current vs. Hz concentration: Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively; (1:1 DMF + H_2O) mixture. Scan rate = 5 mV s^{-1} .

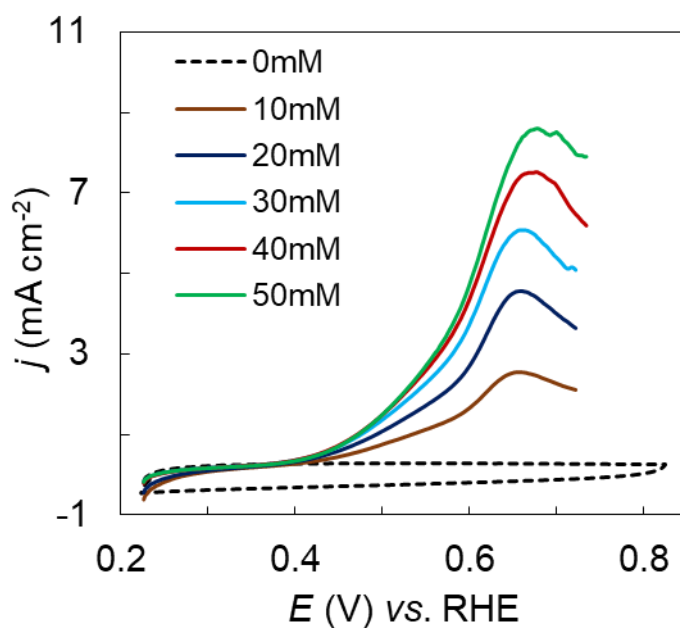


Figure S3. Concentration dependence of electrochemical HzOR in 1M KOH. Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively. Scan rate = 5 mV s^{-1} .

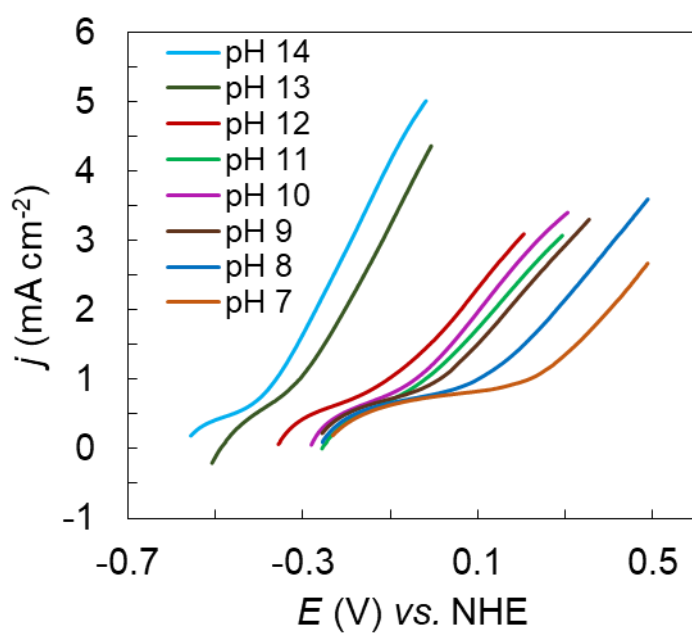


Figure S4. pH dependence for electrochemical HzOR from pH 14 to pH 7. Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively. Scan rate = 5 mV s^{-1} .

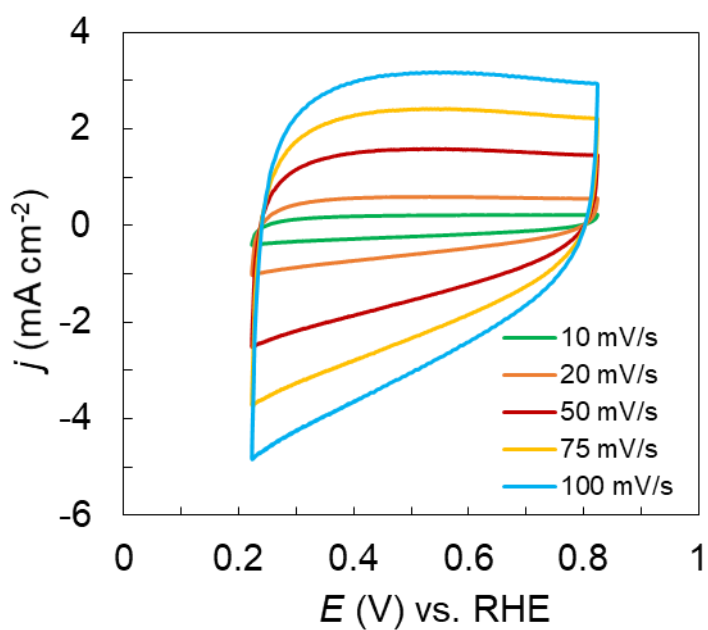


Figure S5. Scan rate-dependent CVs in the non-Faradaic region in 1 M KOH. Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively.

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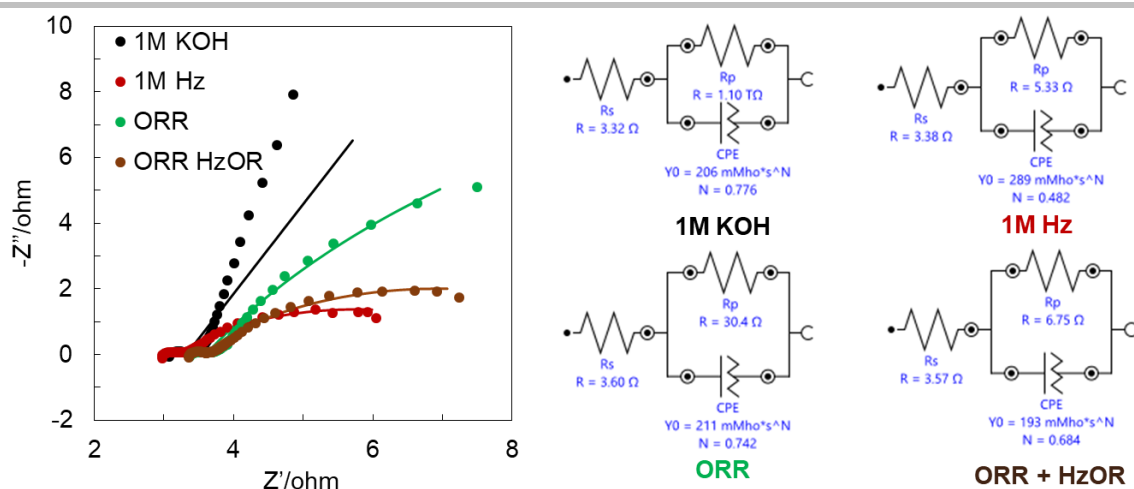


Figure S6. Impedance spectra of Fe PANI/C in 1M KOH (black), after the addition of 1M Hz (red), ORR (green), ORR + HzOR (brown) Experimental conditions: $1 \times 1 \text{ cm}^2$ carbon cloth, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively. Corresponding equivalent circuit diagrams are also provided.

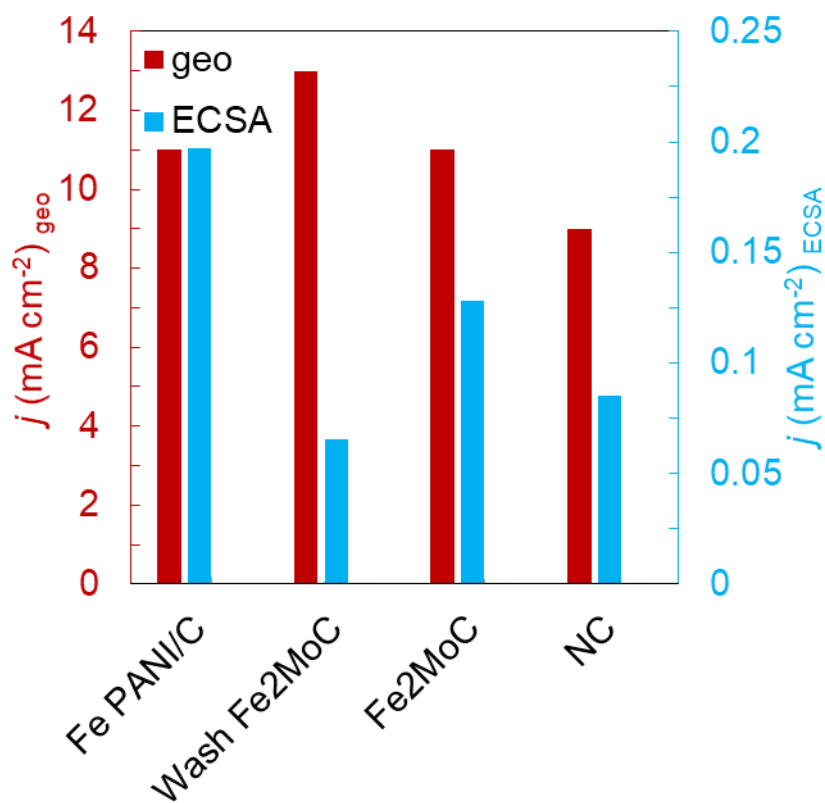


Figure S7. Comparison of catalytic current (peak maxima) normalized with the geometric area (red) and electrochemical active surface area (ECSA) (blue) for HzOR by Fe PANI/C and its comparison with literature reported Fe-based catalysts.³

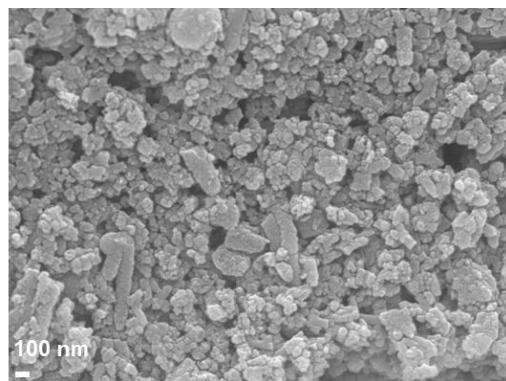


Figure S8. SEM image of the Fe PANI/C on carbon cloth before the electrolysis.

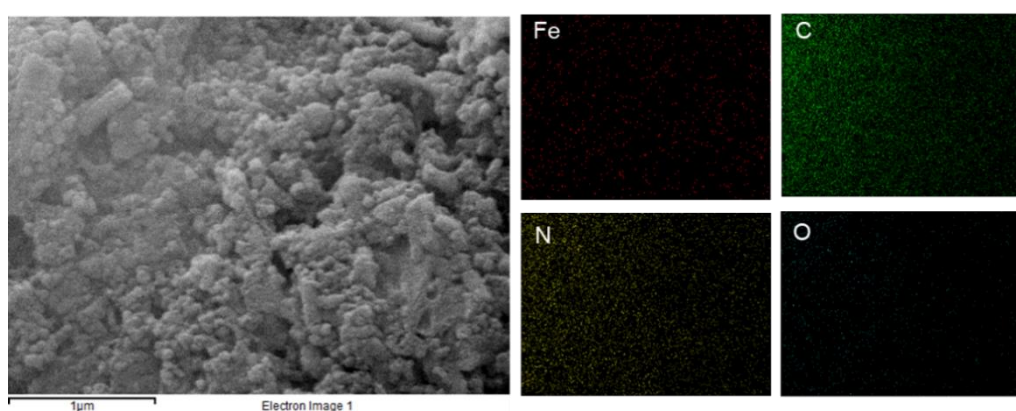


Figure S9. EDS analysis showing the uniform distribution of all elements of Fe PANI/C (Fe: red, C: green, N: yellow, O: cyan) on carbon cloth before the electrolysis.

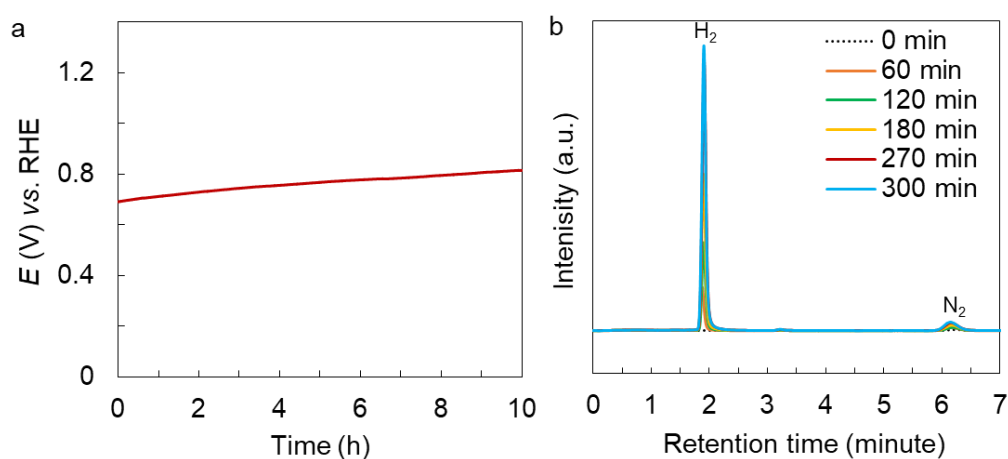


Figure S10. a) Constant current electrolysis graph for 10 hours in 1M KOH with 1M Hz; b) Time-dependent gas chromatography (GC trace) observed from the headspace of gas generated during electrolysis of 1M Hz in 1M KOH with Fe PANI/C showing a gradual increment in the peak intensity for both H_2 and N_2 .

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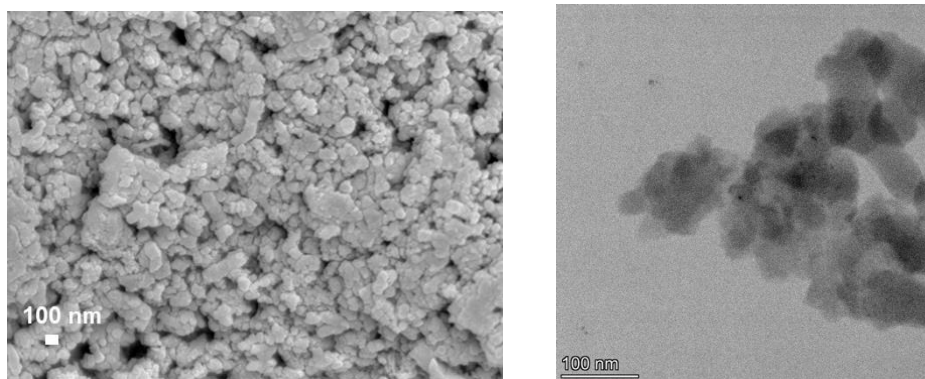


Figure S11. SEM (left) and TEM (right) images of the Fe PANI/C on carbon cloth after the electrolysis of HzOR.

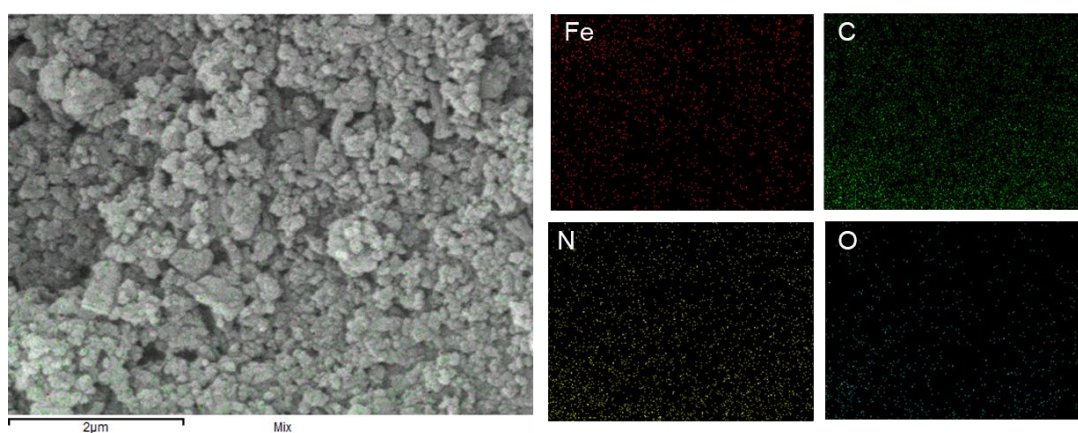


Figure S12. EDS analysis showing the uniform distribution of all elements of Fe PANI/C (Fe: red, C: green, N: yellow, O: cyan) on carbon cloth after the electrolysis of HzOR.

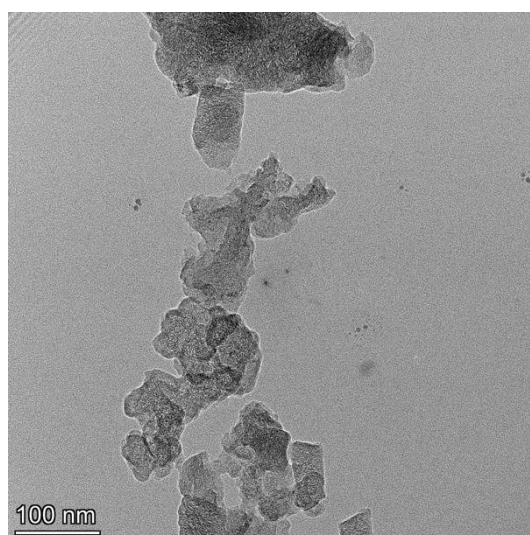


Figure S13A. TEM image of the Fe PANI/C on carbon cloth after the ORR electrolysis.

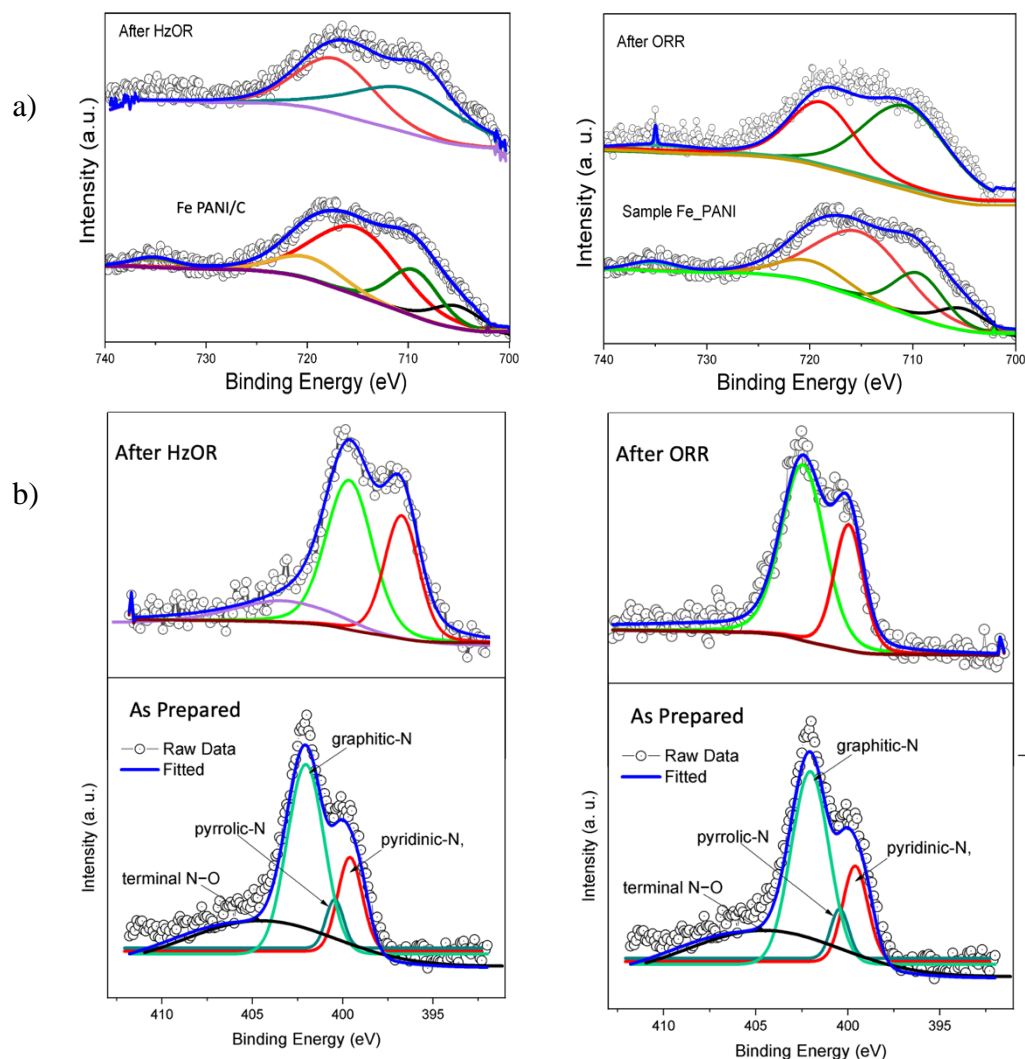


Figure S13B. Comparative XPS before and after catalysis for a) Fe and b) N of Fe PANI/C.

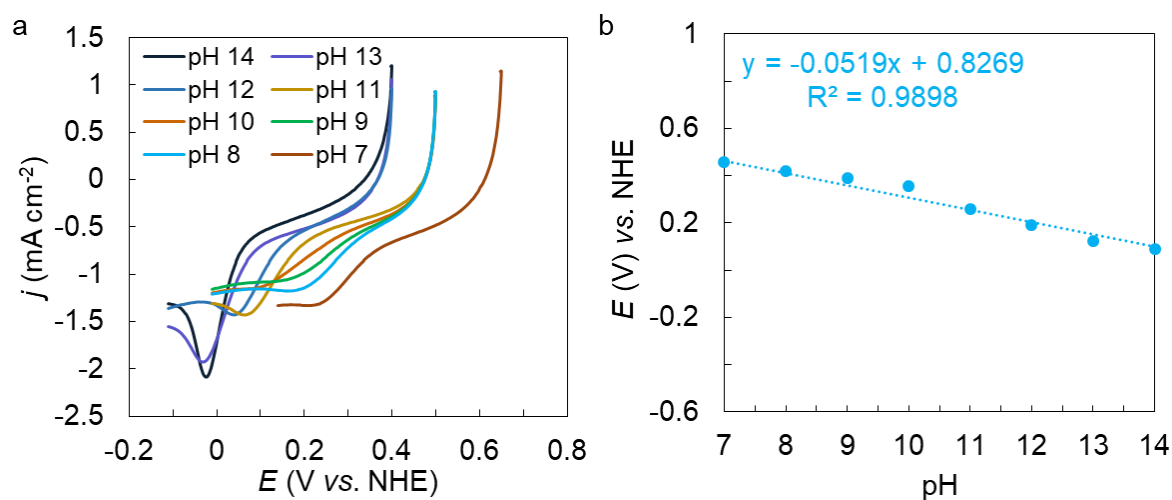


Figure S14. a) pH-dependent electrochemical ORR from pH 14 to pH 7; b) E vs. pH plot for ORR with a slope of 51.9 mV pH^{-1} indicating $1\text{H}^+ / 1\text{e}^-$ process. Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively. Scan rate = 5 mV s^{-1} .

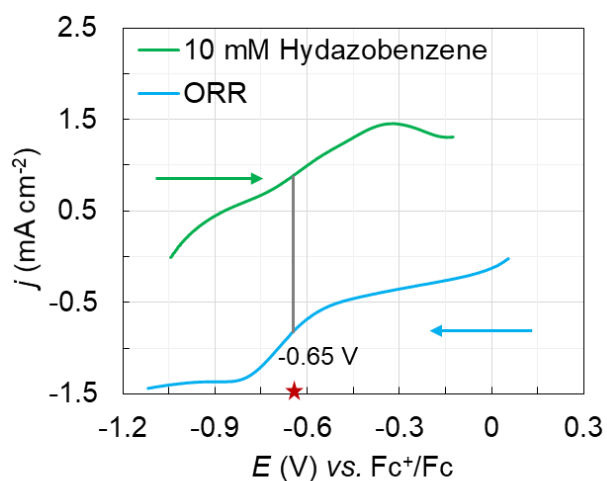


Figure S15. Independent polarization curve for 10 mM Hydrazobenzene oxidation (green), ORR (blue) with 10 mM OH⁻ in 1:1 DMF + H₂O mixture; The mixed potential (-0.65 V) is shown by the asterisk at the potential value where the current density for both the polarization curves are equivalent (grey line). Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively; Scan rate = 5 mV s⁻¹.

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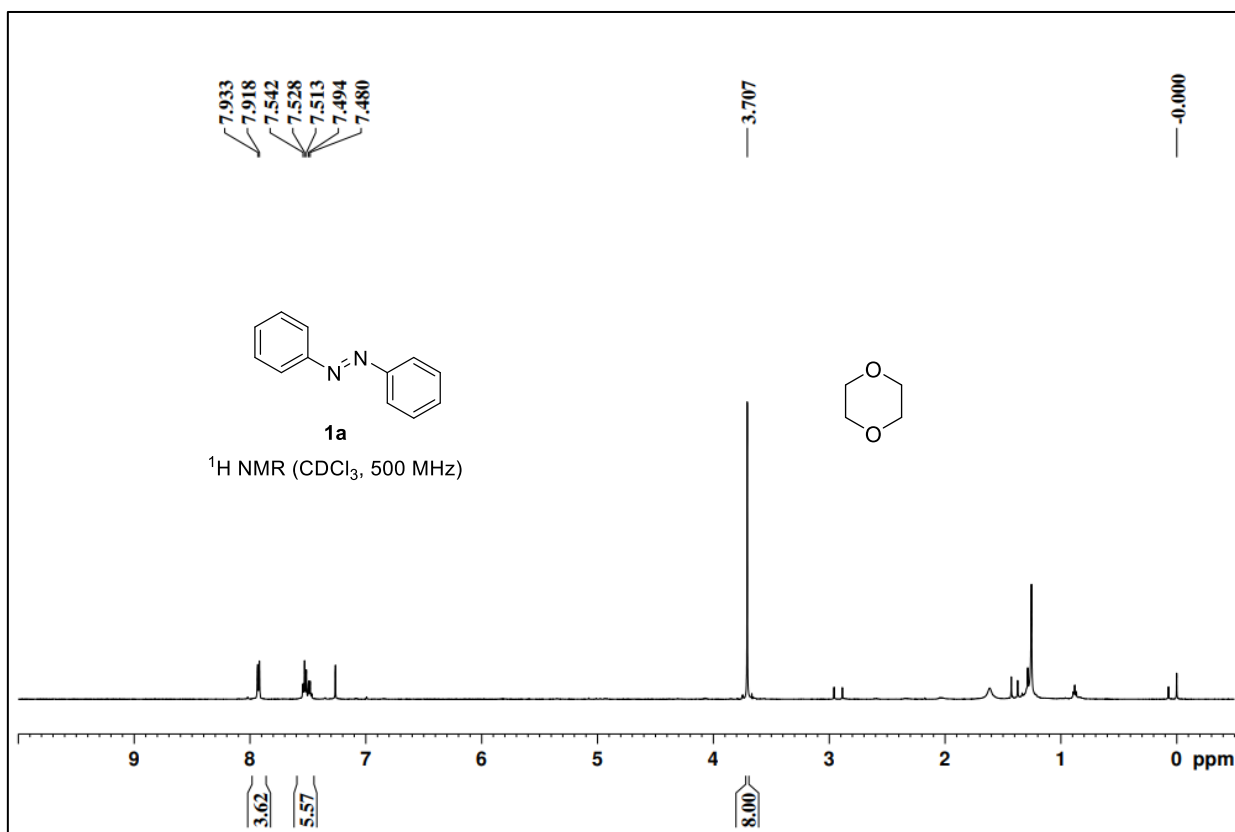


Figure S16. ^1H NMR (with internal standard dioxane) for azobenzene in CDCl_3 after the aerobic oxidation performed in DMF + H_2O mixture.

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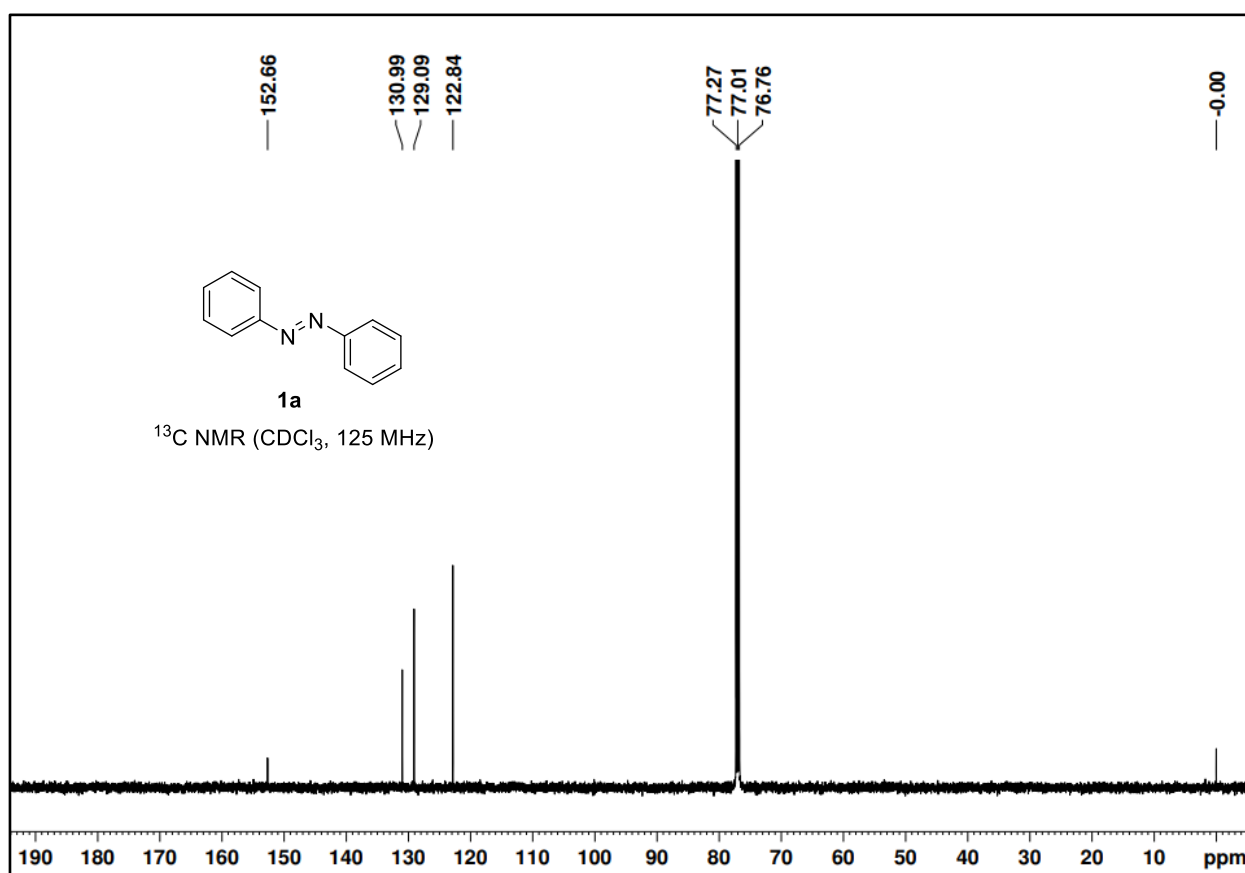
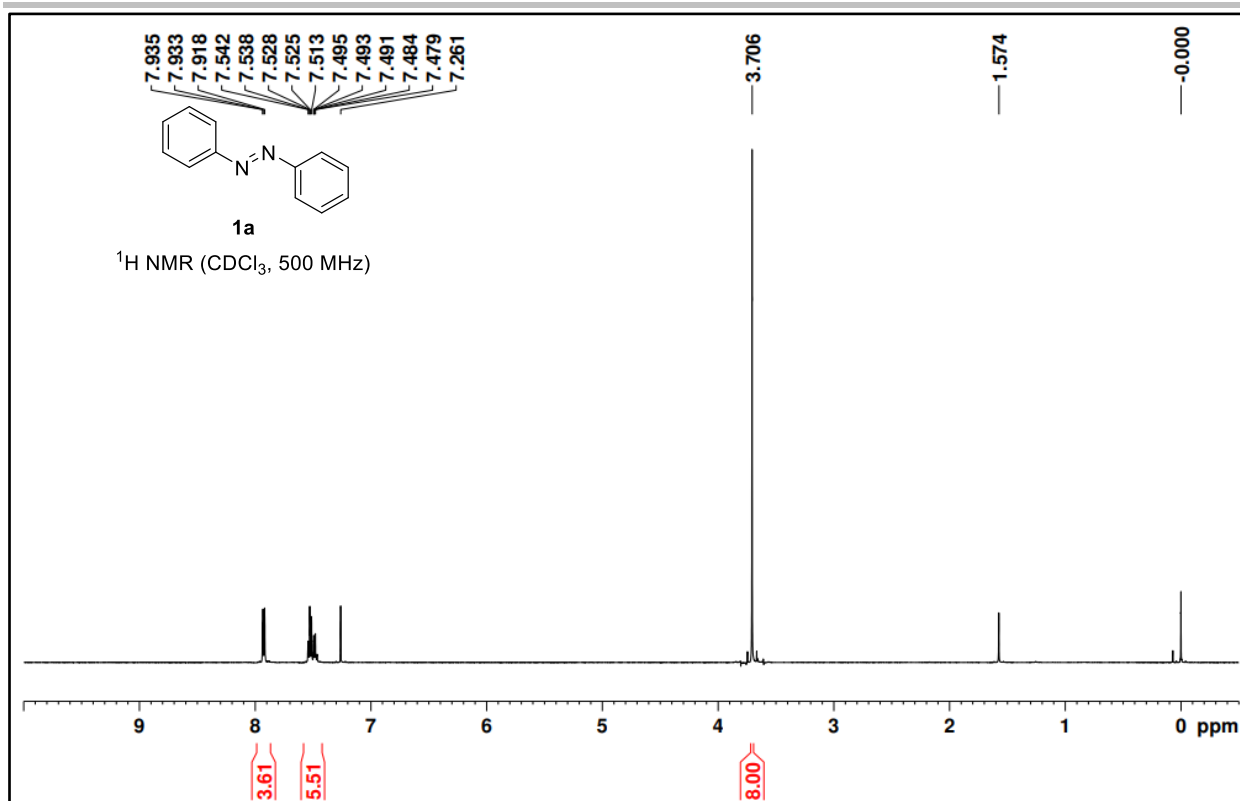


Figure S17. ¹H NMR (with internal standard dioxane), top and ¹³C NMR, bottom of azobenzene in CDCl₃ after the aerobic oxidation reaction performed in ethanol.

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1. N. Wang, X. Li, M. K. Hu, W. Wei, S. Zhou, Wu. H, T. X, Q. L. Zhu, *Appl.Catal. B.*, 2022, **316**, 121667.
2. L. Fagiolari, F. Zaccaria, F. Costantino, R. Vivani, C. K. Mavrokefalos, G. R. Patzke, A. Macchioni, *Dalton Trans.*, 2020, **49**, 2468-2476.
3. K. Ojha, E. M. Farber, T. Y. Burshtein, D. Eisenberg, *Angew. Chem., Int. Ed.* 2018, **57**, 17168-17172.