Electronic supplementary information (ESI)

Electrocatalytic nitrogen reduction to ammonia at low potential using a phenalenyl-based iron (III) complex

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SI 1: Electrochemical set up

The CHI 760E electrochemical workstation serves as the site for all electrochemical studies. All electrochemical NRR processes were performed in three electrochemical setup (H-type cell) using 0.1 N HCl electrolyte solution. Ag/AgCl (saturated in 3 N KCl), Pt wire, and Fe(PLY)$_3$ loaded glassy carbon electrode (GCE) were used as reference electrode, the counter electrode, and the working electrode, respectively. The catalyst mass (4.5 mg cm^{-2}) was loaded on the working electrode. The following equation was used to convert all potentials from Ag/AgCl to the reversible hydrogen electrode (RHE): E (vs. RHE) = E (vs. Ag/AgCl) + 0.197 V + (0.059 V x pH).

SI 2: Catalyst ink preparation

Catalyst ink solution was made by mixing 3.5 mg of Fe(PLY)$_3$ with 100 µL 2-propanol and 10 µL Nafion 117 solution in a vial. To create a homogenous solution mixture, the mixture was sonicated for two minutes and then further vortexes for 10 min. Finally, 10 µL of the prepared

catalyst was loaded on glassy carbon electrode (GCE) with a 0.071 cm^2 cross section and dried for 6 hours at 60 ^{o}C.

SI 3: Isotope labelling experiments by ^{1}H NMR method

After the electrochemical NRR process, an experiment with isotopic labelling is conducted to confirm the source of the nitrogen in ammonia in the electrolyte solution. The experiment was conducted in 0.1 N HCl electrolyte while $^{15}N_2$ gas (98 atom% ^{15}N, Sigma-Aldrich) was continuously purged. After nearly 10 hours of NRR process at a potential of –0.2V (versus RHE) the electrolyte solution was further concentrated using a distillation setup. ^{1}H–NMR (Bruker 600 MHz, USA) was conducted to find ammonia in an electrolyte solution utilizing an internal standard of d^6-DMSO (Sigma–Aldrich).

SI 4: Determination of ammonia (NH$_3$) by UV–vis spectrophotometer

After two hours of the nitrogen reduction reaction (NRR) process employing the Fe(PLY)$_3$ catalyst, the presence of ammonia in the electrolyte solution was determined using the Indophenol blue method by a UV-vis spectrophotometer. Three different stock solutions have to be used in order to calculate the ammonia content. 4 g of NaOH, 5 g of salicylic acid, and 5 g of trisodium citrates were combined with 100 mL of water to create Solution-A. 4.7 mL of NaOCl solution is mixed with 45.3 mL of distilled water to create Solution-B. 50 mL of water and 0.5 g of sodium nitroprusside were combined to create Solution-C. After that, 2 mL of electrolyte solutions/standard solutions were mixed with 2 mL of Solution–A, 1 mL of Solution–B, and 0.2 mL of Solution–C and the mixture solutions were then incubated for two hours in a dark environment.

After that all UV measurements were carried out. Using the same indophenol blue procedure described above, a standard series calibration of NH$_4$Cl was constructed with adjusting the different concentrations (in mg/L or ppm) to determine the ammonia concentration in the electrolyte solution. For every standard concentration series, the highest absorbance peak occurred at 660 nm. When plotting several known concentrations against absorbance a straight line curve was seen with an R^2 value of 0.999.

SI 5: Determination of ammonium ions by Ion Chromatography

After the all electrochemical nitrogen reduction reaction (NRR) to ammonia, the concentration of ammonia was calculated using ion chromatography technique (Eco IC Metrohm). A cationic column (Metrosep C 6 - 150/4.0) was used at room temperature with an eluent flow rate of 0.9 mL/min. The eluent consists of 1.7 mmol/L nitric acid. The end of the retention time was set to 20 min and the peak of ammonia occurred at about 6.4 min with a pressure of 7.55 MPa.

A standard calibration curve of ammonium ions using ammonium chloride (Merck) were done with varying the ammonium concentrations of 0.0, 0.2, 0.4, 0.6, 0.8, and 1 μg /mL (or ppm). A straight line curve was observed after plotting (origin software) the peak area (y–axis) vs retention time (x–axis) getting from standard calibration curves. It was shown that the linear correlation (y = 0.13914x + 0.00376, R^2 = 0.997) between the retention time and peak area at different concentration of ammonium ions.

SI 6: Determination of hydrazine

If any hydrazine is found in the electrolyte solution following the electrochemical NRR process, it can be found by the Watt and Chrisp method using a UV-vis spectrophotometer.[1] A mixture of 5.99 g of para–dimethylaminobenzaldehyde, 30 mL of concentrated HCl, and 300 mL of ethanol was used to create the colour solution.

A standard stock solution of hydrazine was made in parallel at concentrations of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 μg mL^{-1}. Then, 4 mL of the colouring solution was combined with 1 mL of the standard solution sample in a vial. For all standard solutions, the highest absorption peak occurred at about 455 nm during the UV-vis analysis. When plotting absorbance against various concentrations, a smooth straight line was seen (y = 0.79817 x + 0.21278; R^2 = 0.998).

SI 7: Determination of NO_x contaminants

After two hours of nitrogen reduction reaction (NRR) process utilising Fe(PLY)$_3$ catalyst, presence of any NO_x contaminants in the electrolyte solution can be measured using N-(-1-naphthyl)-ethylenediamine dihydrochloride by UV-vis spectrophotometer. It was necessary to use a colour stock solution to identify the NO_x contaminants. 5 mg of N-(-1-naphthyl)-ethylenediamine dihydrochloride, 0.5 g of sulfanilic acid, and 5 mL of acetic acid were combined with 95 mL of water to made the colour solution.

In parallel, a standard NO_x ($NaNO_2$) solution with various concentrations was made (0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 µg mL^{-1}). Then 1 mL of the standard solution and 4 mL of the colouring solution were combined, and it was left to sit for 15 minutes. For all varieties of standard solutions, the highest absorption peak was seen at 550 nm during UV-vis experiments. When plotting absorbance with varying concentrations, a linear straight line (y = 0.197 x + 0.00433) was found with an R^2 value of 0.999.

SI 8: Ammonia yield rate and Faradaic efficiency calculation:

In order to determine the Faradaic efficiency and ammonia yield rate or production rate using the NRR method, the following equations were employed:

$$R_{NH_3} = \frac{(C_{NH_3} \times V)}{(m_{cat} \times t)} \qquad \text{............... (1)}$$

Where, C is the concentration of ammonia (NH_3) produced in the electrolyte solution, V is the volume (in mL) of the electrolyte solution, t is the total reduction time (in seconds), and m is the mass of the catalyst loaded on the working electrode.

$$FE (\%) = \frac{(3 \times F \times C_{NH_3} \times V)}{(17 \times Q)} \text{ X } 100\% \qquad \text{............... (2)}$$

Where, F is the Faraday constant (96,485 C/mol), C is the concentration of ammonia (NH_3) produced in the electrolyte solution, V is the volume (in mL) of the electrolyte, and Q is the total charge passing through the electrode.

SI 9: Electrochemical active area calculation:

We calculated the ECSA value as mentioned in the equation below:

Double layer capacitance = C_{dl} = 0.6 mF/cm^2 (from CV data)

In general specific capacitance for a flat surface = C_s = 40 µF/cm^2

Roughness factor (R_f) = C_{dl} / C_s = {(0.6 mF/cm^2) / (40 µF/cm^2)} = 15

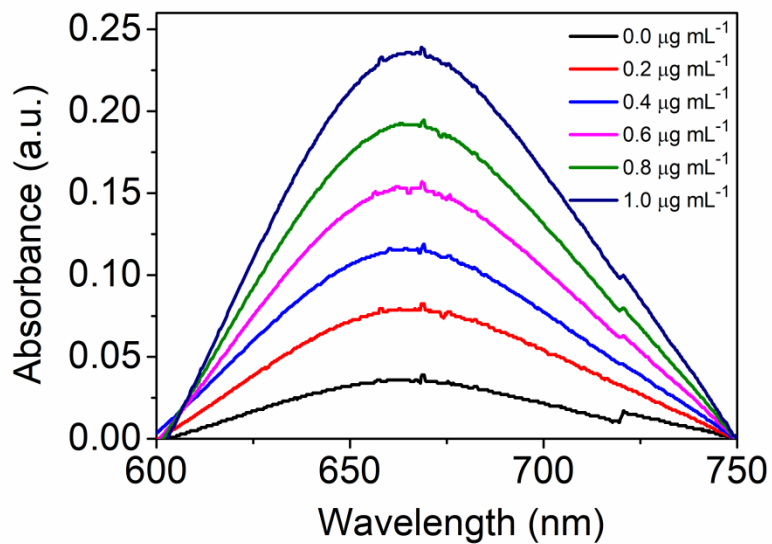ECSA = R_f x Geometric surface area = 15 x 0.071 cm^2 = 1.06 cm^2.

Fig. S1: UV–vis absorption spectra of different series concentration of ammonia

Standard ammonia calibration
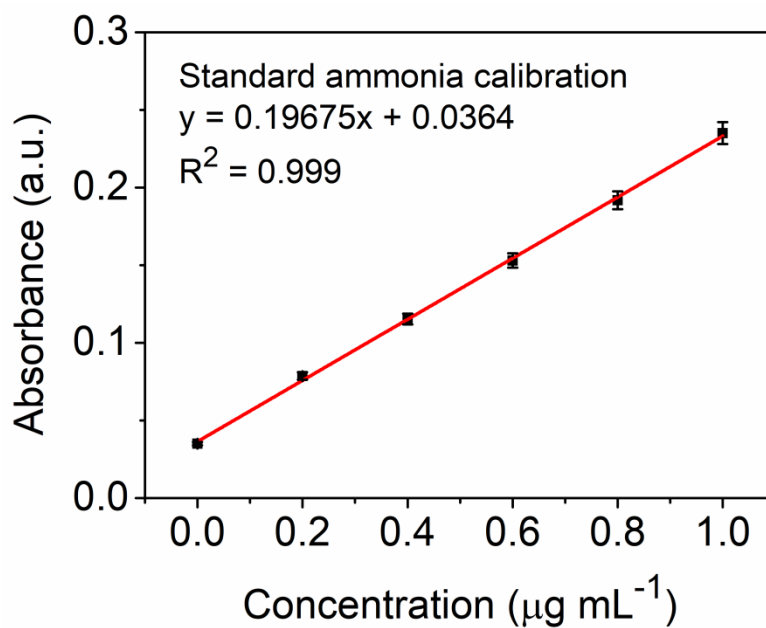$y = 0.19675x + 0.0364$
$R^2 = 0.999$

Fig. S2: Calibration curve used for determination of ammonia concentration
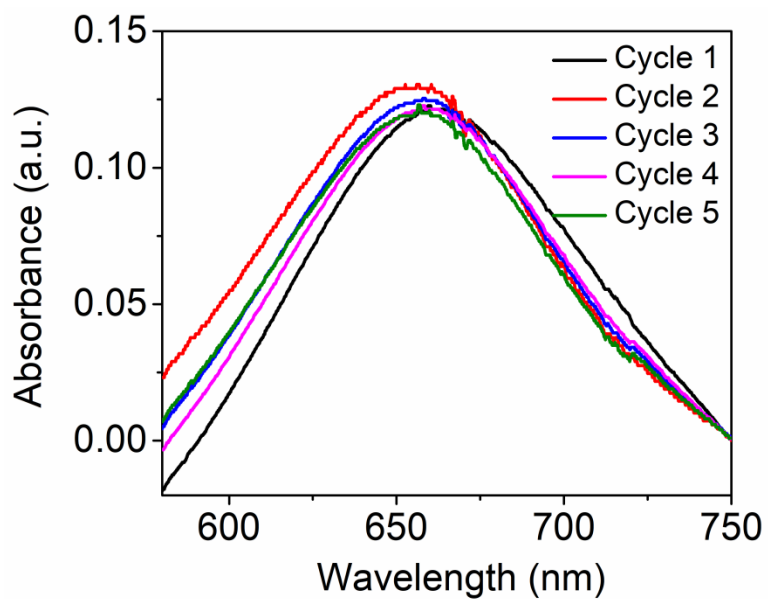
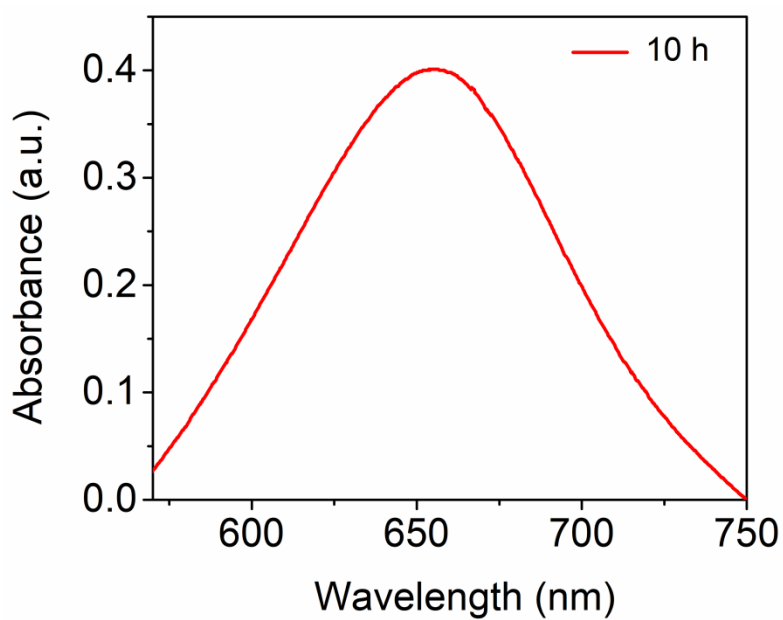**Fig. S3:** UV–vis absorption spectra for 5 cycle's @–0.2V for 2 h electrolysis

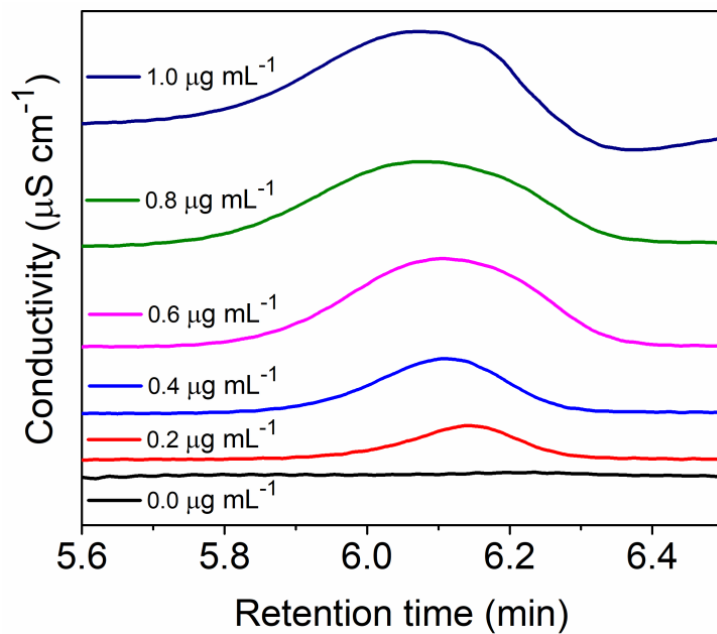
Fig. S4: UV–vis absorption spectra for 10h electrolysis

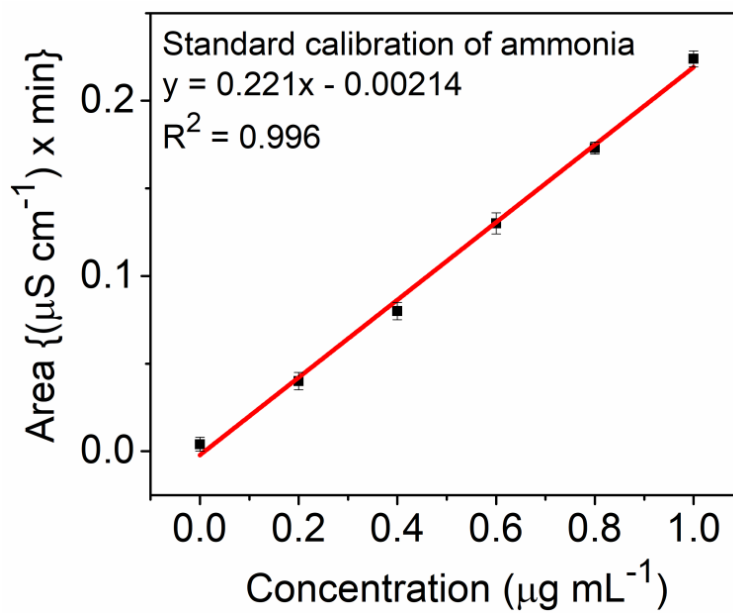**Fig. S5:** IC curve of different series concentration of ammonia

Standard calibration of ammonia
y = 0.221x - 0.00214
R^2 = 0.996

Fig. S6: IC calibration curve used for determination of ammonia concentration
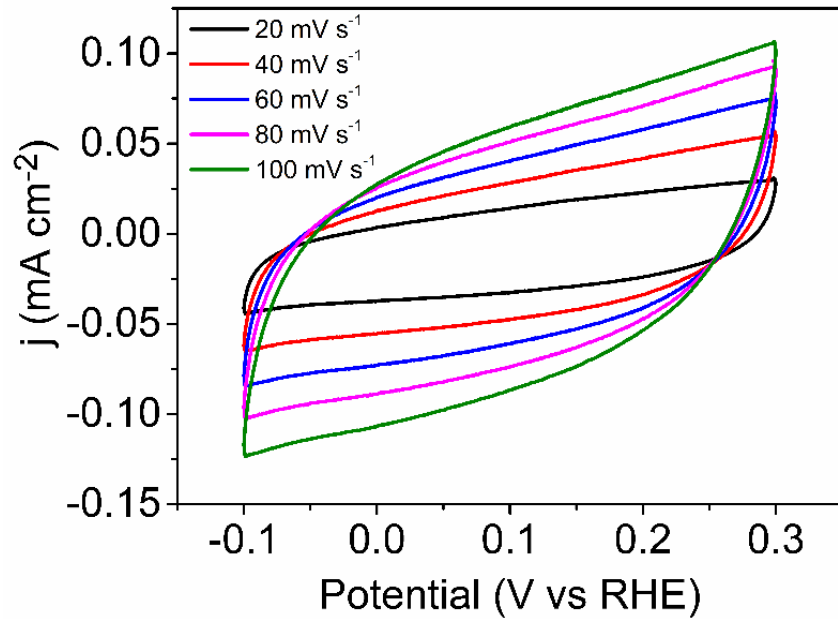
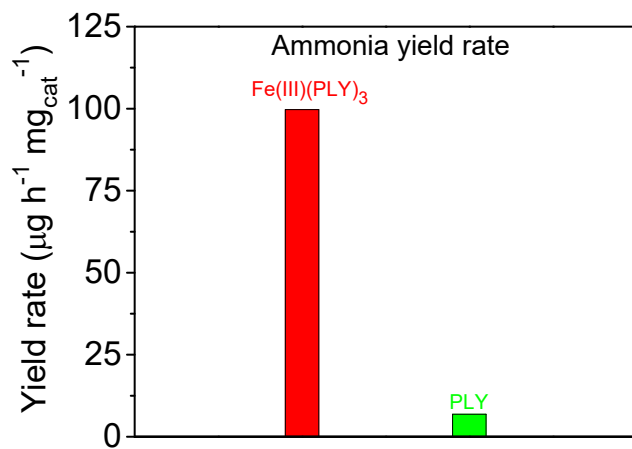**Fig. S7:** The cyclic voltammetry (CV) profiles at the different sweep rates

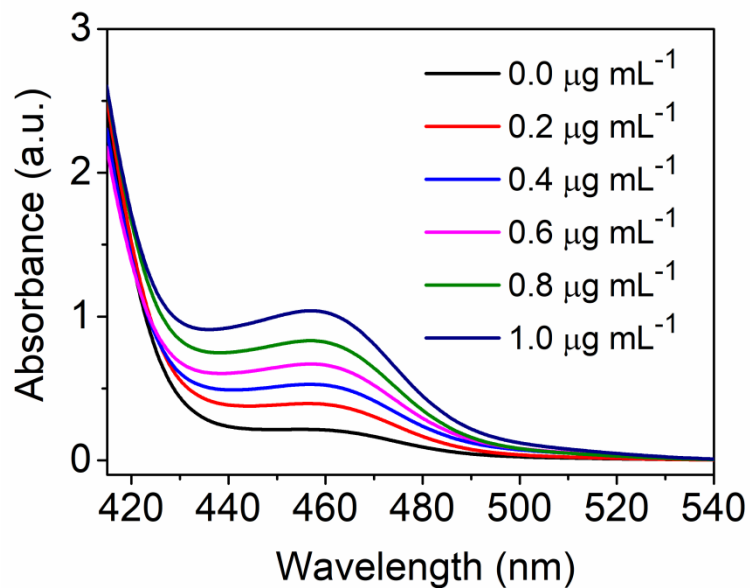**Fig. S8**: Comparison of ammonia yield rate of Fe(PLY)₃ and PLY system

Fig. S9: UV–vis absorption spectra of different N_2H_4 concentration

Hydrazine calibration
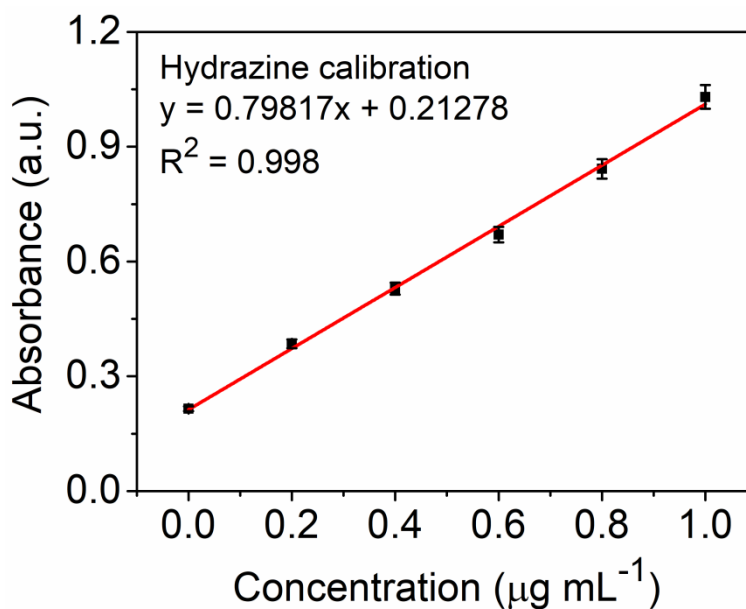y = 0.79817x + 0.21278
R^2 = 0.998

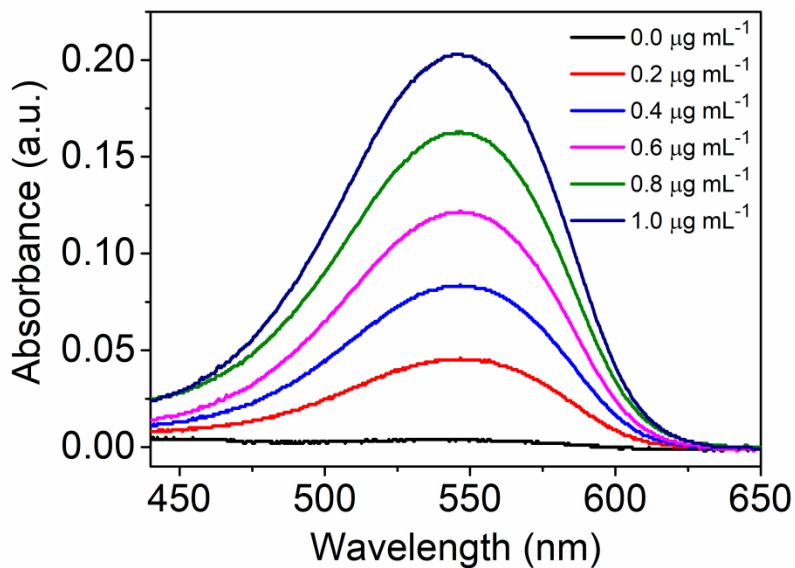**Fig. S10:** Calibration curve used for determination of N_2H_4 concentration

Fig. S11: UV–vis absorption spectra of NO_2^- of various concentration solutions
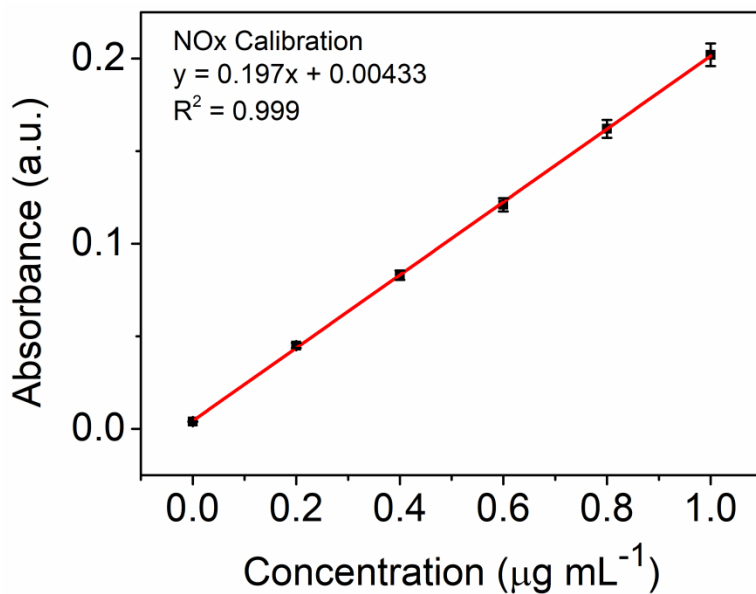

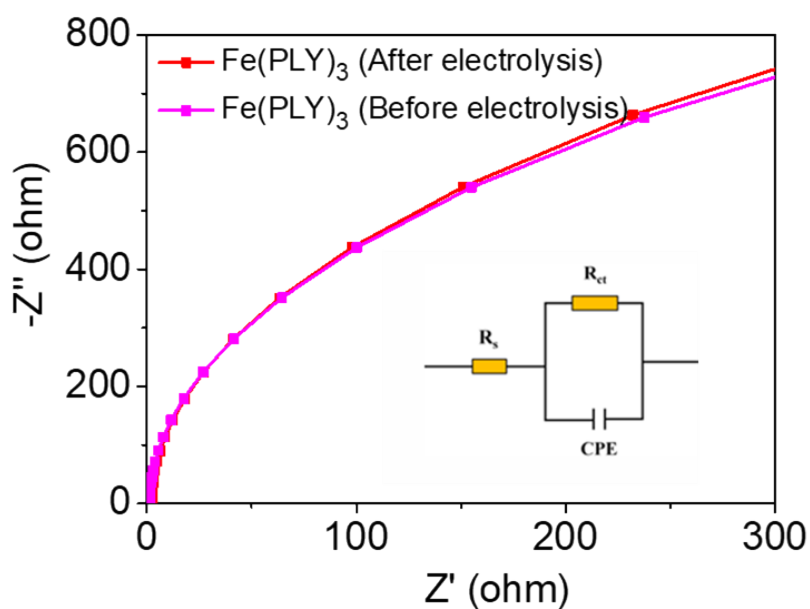**Fig. S12:** Calibration curve of $NaNO_2$ with the given concentrations

Fig. S13: EIS plot of the catalyst

In the Nyquist plot, R_{ct} indicates charge transfer resistance (660 Ω), CPE indicates constant phase element (0.000042 F), and R_s indicates initial resistance due to solution and the value is 0.89 Ω.

Table S1: Comparison of the NRR activity with other electrocatalyst in aqueous solution at ambient conditions

Catalyst	Electrolyte	Potential (V vs. RHE)	NH$_3$ yield rate	FE (%)	References
a-Au/CeO$_x$–RGO	0.1 M HCl	−0.2 V	8.3 µg h^{-1} mg$^{-1}_{cat}$	10.10 %	Adv. Mater. 2017, 29, 1700001
Au-TiO$_2$	1 M HCl	−0.2 V	21.4 µg h^{-1} mg$^{-1}_{cat}$	8.11 %	Adv. Mater. 2017, 29, 1606550
PdCu Nanoparticles	0.5 M LiCl	−0.1V	35.7 µg h^{-1} mg$^{-1}_{cat}$	11.5 %	Angew. Chem. Int. Ed. 10.1002/anie.201913122
Nb$_2$O$_5$ nanofiber	0.1 M HCl	− 0.55 V	43.6 µg h^{-1} mg$^{-1}_{cat}$	9.26 %	Nano Energy, 2018, 52, 264-270
FePc/O-MWCNT	0.1 M HCl	− 0.3 V	36 µg h^{-1} mg$^{-1}_{cat}$	9.73 %	Chem. Commun. 2019, 55, 14111
TiO$_2$ NPs	0.5M LiClO4	−0.55V	21.31 µg h^{-1} mg$^{-1}_{cat}$	21.99 %	Adv. Mater. 2020, 2000299
MoSAs-Mo$_2$C/NCNTs	0.05M H$_2$SO$_4$	−0.25V	16.1 µg h^{-1} cm$^{-2}_{cat}$	7.1%	Adv. Mater. 2020, 2002177
FL-BP NSs	0.01M HCl	−0.6V	31.37 µg h^{-1} mg$^{-1}_{cat}$	5.07%	Angew. Chem. Int. Ed. 2019, 58, 2612

NiTe Nanocrystals	0.1M HCl	−0.1V	33.34 ± 0.70 µg h^{-1} mg^{-1}	$17.38 \pm 0.36\%$	Adv. Funct. Mater. 2020, 2004208
MoO$_2$/graphene hybrid	0.1M Na$_2$SO$_4$	−0.35V	37.4 µg h^{-1} mg^{-1}	6.6%	Catal. Sci. Technol., 2019,9, 4248-4254
α–CuPc	0.1 M HCl	−0.4 V	11.56 µg h^{-1} mg$^{-1}_{cat}$	6.29%	Catalysis Today, 2023, 423, 113905
Fe(III) (PLY)$_3$	**0.1 M HCl**	**−0.2V**	**99.7 µg h^{-1} mg$^{-1}_{cat}$**	**43.4%**	**This Work**

SI: References

[1]   Watt, G. W.; Chrisp, J. D. Spectrophotometric Method for Determination of Hydrazine. *Anal. Chem.* **1952**, *24*, 2006−2008.