

Supporting Information

Ambient N₂ reduction to NH₃ electrocatalyzed by FeP-Fe₃O₄ nanospheres

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Experimental section

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (purity 98.5%) and Na_2SO_4 (purity 97%) were purchased from Xilong Scientific Co., Ltd. NaNO_3 (purity 99%) was purchased from J&K Scientific, NH_4Cl (AR), $\text{CH}_3\text{CH}_2\text{OH}$ (purity 99%), CH_3CN (purity 99%), $\text{C}_3\text{H}_8\text{O}$ (purity 99%) were purchased from sino-pharm, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (purity 98%) was purchased from Fuchen Tianjin Chemical Reagent Co., Ltd. NaClO (50 wt.% aq.), $p\text{-C}_9\text{H}_{11}\text{NO}$ (AR) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. $\text{C}_7\text{H}_5\text{O}_3\text{Na}$ (purity 99.5%), Nafion 117 mixture solution (5wt.%), $\text{C}_5\text{H}_4\text{FeN}_6\text{Na}_2\text{O}_3$ (purity 99%), $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (80 wt.%), were purchased from Beijing InnoChem, N_2 (purity 99.999%), Ar (purity 99.999%), Ar and H_2 ($\text{Ar} + 5\% \text{H}_2$) were purchased from Beijing Millennium Capital Gas Co., Ltd. All chemicals were used as received without further purification. Deionized water was used throughout the experiments.

Synthesis of Fe_2O_3 nanospheres. Preparation of Fe_2O_3 using a one-step solvothermal process: Ferric nitrate nonahydrate (1.55 g, 3.84 mmol) and sodium nitrate (1.0g, 11.76 mmol) were mixed in a binary solution containing 18 mL of ultrapure water and 30 mL of anhydrous ethanol. The resulting mixture was irradiated in an ultrasonic bath for 5 min at room temperature followed by magnetically stirring until a yellow clear solution was formed. To this mixture, 24 mL of acetonitrile was added and it was stirred for additional 30 min. The resulting solution was transferred to the inner lining of 100 mL reactor. The reactor was then placed in an oven and heated at 180°C for 16 h. After cooling to room temperature, it was centrifuged and the solid was washed 5mL acetonitrile, 5mL ultra-pure water, and 5 mL anhydrous ethanol, three

times each. The read solid was dried under vacuum at 80°C for 12 hours.¹

Synthesis of FeP-Fe₃O₄ and Fe₃O₄. FeP-Fe₃O₄ was prepared by a one-step thermal reduction method, and a brief description of the preparation method is as follow: Ground powdered Fe₂O₃ (100 mg, 0.625 mmol) was placed on one end of a quartz porcelain boat and sodium hypophosphite (500 mg, 5.68 mmol) powder was placed on the other end of the boat. The quartz porcelain boat was heated at 400°C for 2 h in Ar. After cooling to room temperature, the obtained black powder was FeP-Fe₃O₄. The Fe₃O₄ was obtained from ground powdered Fe₂O₃ (100 mg, 0.625 mmol) in the absence of sodium hypophosphite by applying 5% H₂/Ar. The working electrodes loaded with FeP-Fe₃O₄ and Fe₃O₄ catalysts on carbon paper (CP) were recorded as FeP-Fe₃O₄/CP and Fe₃O₄/CP, respectively.^{2,3}

Characterizations. X-ray diffraction (XRD) study was carried out on a D/MAX-TTRIII (CBO) with Cu K α radiation ($\lambda = 1.542 \text{ \AA}$). Scanning electron microscopy (SEM) was performed using a Hitachi S4800 scanning electron microscope. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies were performed using a Tecnai G2 F20 S-TWIN. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging and energy-dispersive X-ray spectrometer (EDS) elemental mapping were conducted on a JEM-ARM 200F. X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB 20 Xi XPS system. Ultraviolet-visible (UV-vis) spectra were carried out on a SHIMADZU UV-2700 UV-vis spectrophotometer. The BET analysis was performed with a specific surface area and porosity analyzer model ASAP 2420-4 for nitrogen

adsorption and desorption experiments. The degassing treatment temperature was 200°C and the isothermal curve testing temperature was -196°C.

Electrochemical Measurements. The Shanghai Chenhua CHI660E electrochemical workstation with three-electrode system was used for all electrochemical tests in this work. The H-type electrolytic cell was chosen as the reaction device, in which the as-prepared FeP-Fe₃O₄ or CP was used as the working electrode (WE), a Hg/HgO electrode was used as reference electrode (RE) under alkaline conditions, Pt sheet electrode was used as the counter electrode (CE), and a Nafion 211 membrane was used to separate the cathode and anode. Ultra-pure N₂ (99.999%) or Ar (99.999%) was continuously passed into the electrolyte for at least 30 min before each test. The potentials were converted to RHE values by [Eq. 1](#)

$$E_{(\text{vs. RHE})} = E_{(\text{vs. Hg/HgO})} + 0.059 \times \text{pH} + 0.098 \text{ V} \quad (1)$$

Determination of NH₃. The salicylic acid method was used for the determination of NH₃ concentration.⁴ The standard linear fitting equation of the method was obtained by calibration of a series of solutions with known concentrations of NH₄Cl to ensure a good linearity ([Fig. S1](#)). The electrolyte was 0.1 M KOH + 0.1 M K₂SO₄ solution, and the standard linear fitting equation was $y = 0.4174x + 0.027$, $R^2 = 0.998$, where x is NH₄⁺ concentration, y is absorbance.

Determination of N₂H₄. The Watt and Chrisp method was used to assay the hydrazine hydrate concentration.⁵ The standard linear fitting equation for the method was obtained by calibrating a series of solutions with known concentrations of hydrazine hydrate to ensure a good linearity ([Fig. S2](#)). The electrolyte was a mixture of

0.1 M KOH + 0.1 M K₂SO₄ solution, and the standard linear fitting equation was $y = 0.1078x + 0.0348$, $R^2 = 0.998$, where x is N₂H₄ concentration, y is absorbance.

Graphics

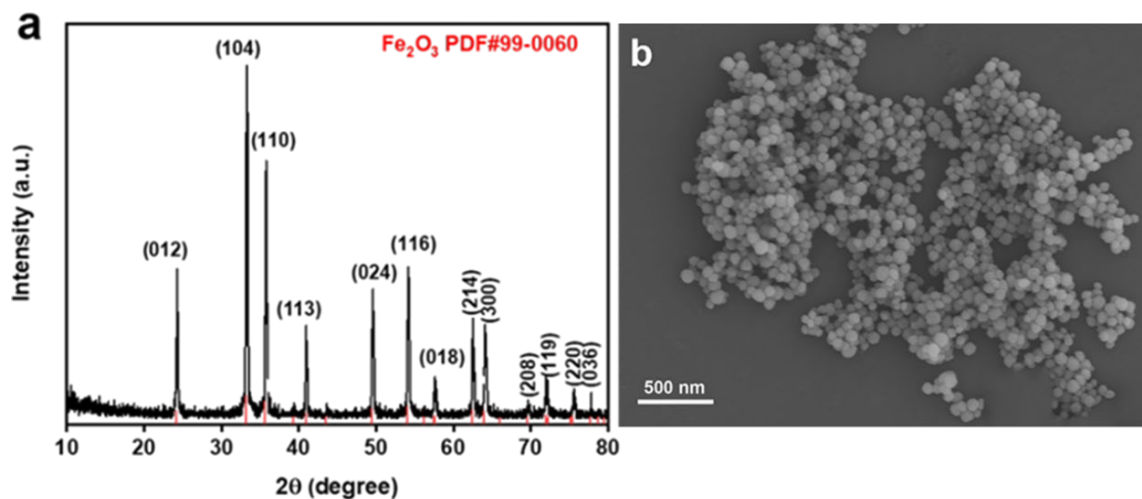


Fig. S1. (a) XRD pattern and (b) SEM images of Fe₂O₃ precursor.

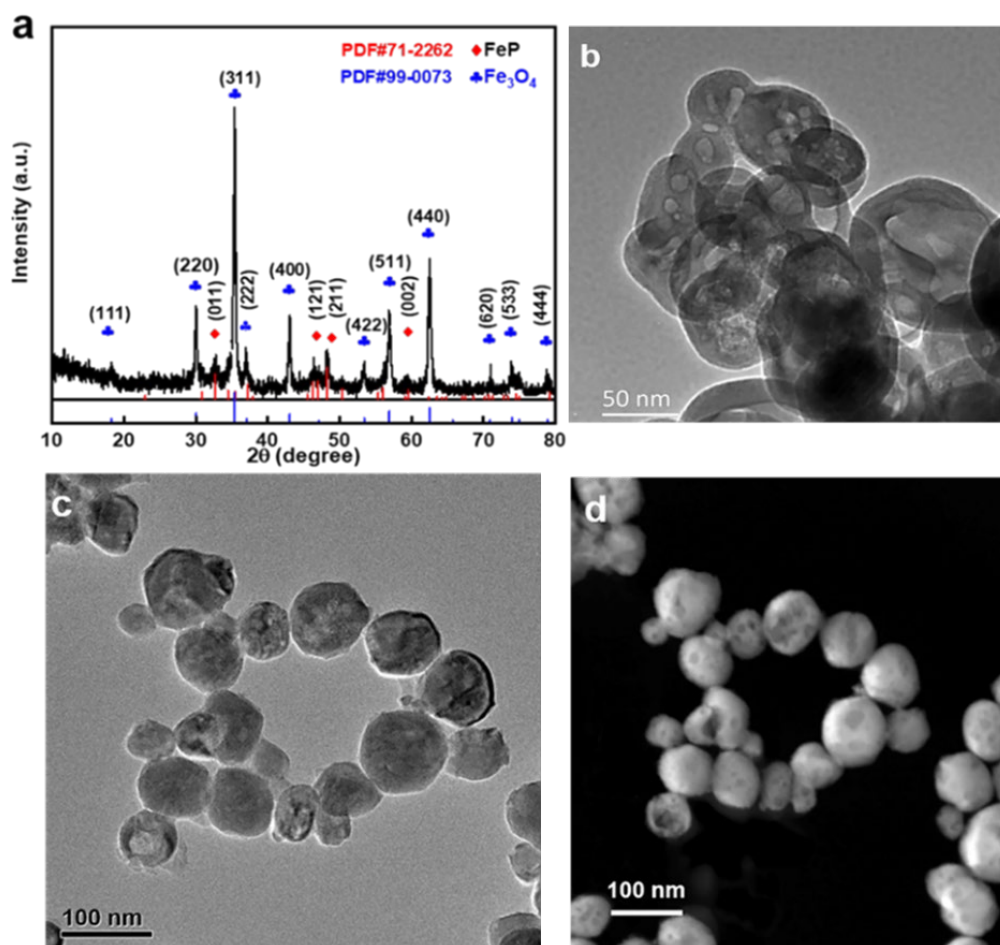


Fig. S2. (a) XRD pattern, (b-c) TEM images, (d) HAADF-STEM images of FeP-Fe₃O₄.

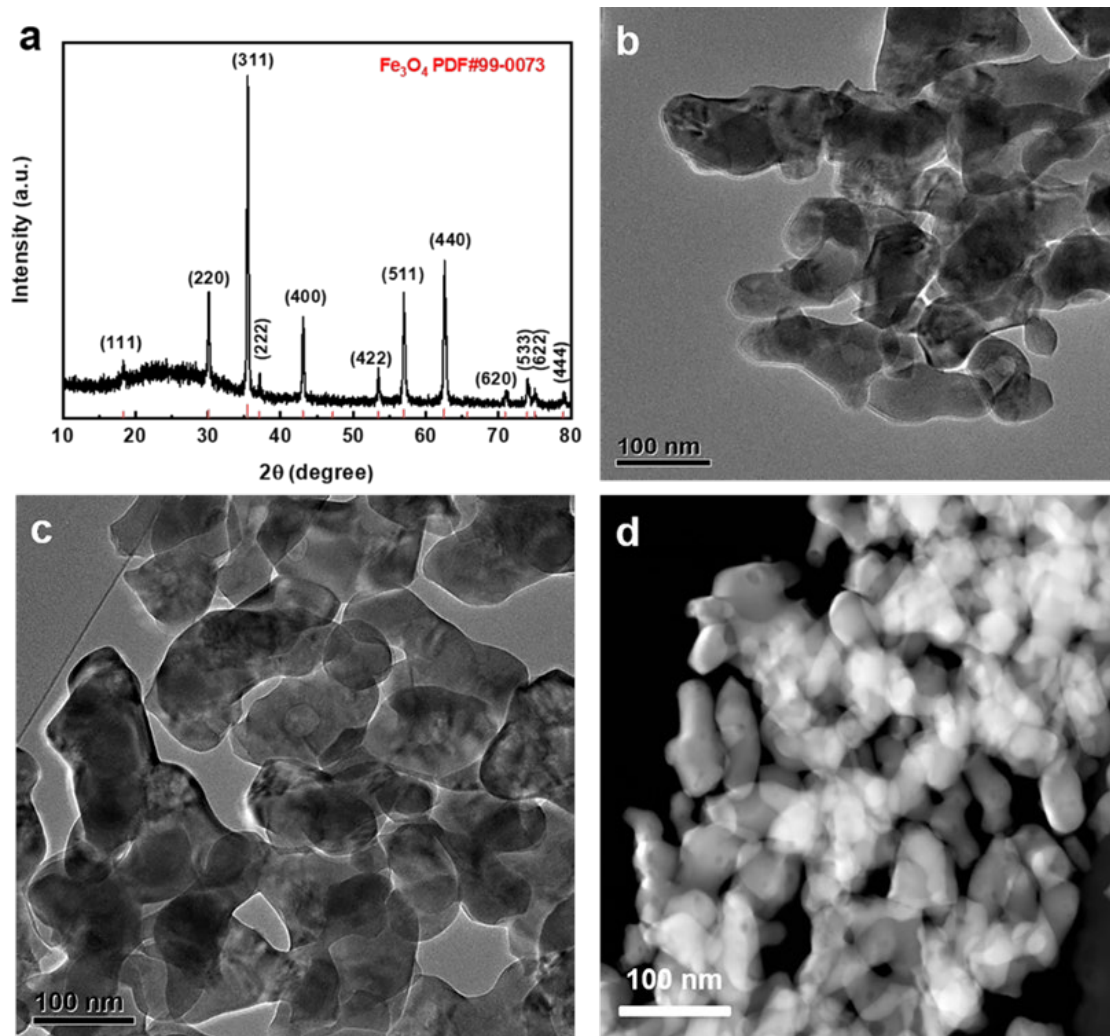


Fig. S3. (a) XRD pattern, (b-c) TEM images, (d) HAADF-STEM images of Fe₃O₄.

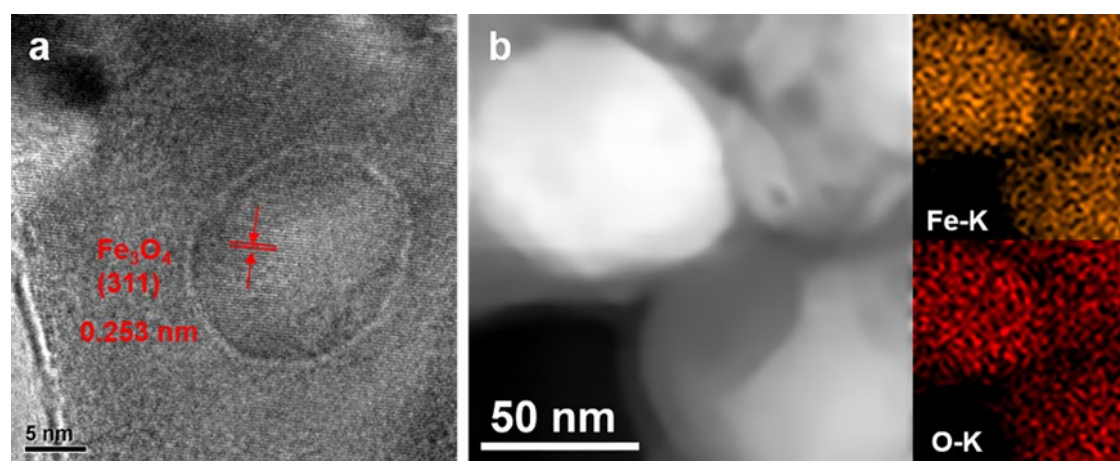


Fig. S4. (a) HRTEM image, (b) HAADF-STEM image and corresponding EDS element distribution map of Fe₃O₄.

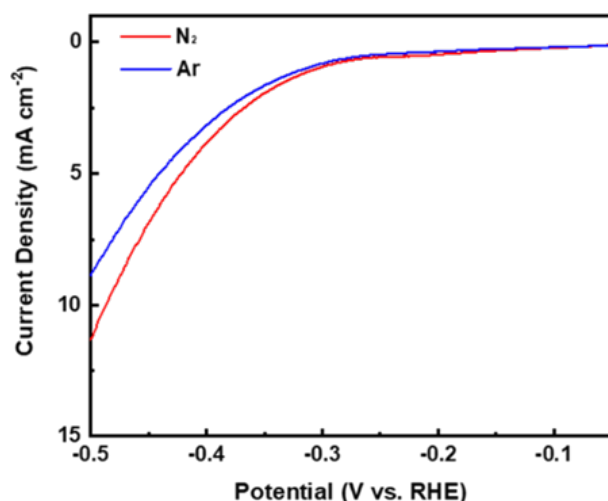


Fig. S5. LSV curves of FeP-Fe₃O₄ in the electrolyte at N₂ (red curve) saturation and Ar (blue curve) saturation at scanning rate of 10 mV s⁻¹.

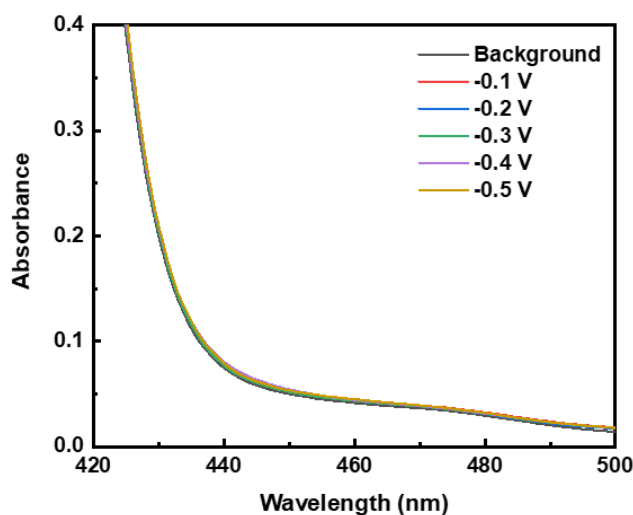


Fig. S6. UV-vis absorption results of 0.1M KOH + 0.1M K₂SO₄ electrolyte dyed with p-C₉H₁₁NO indicator for Fe-Fe₃O₄ before and after electrolysis at different potentials for 2 h.

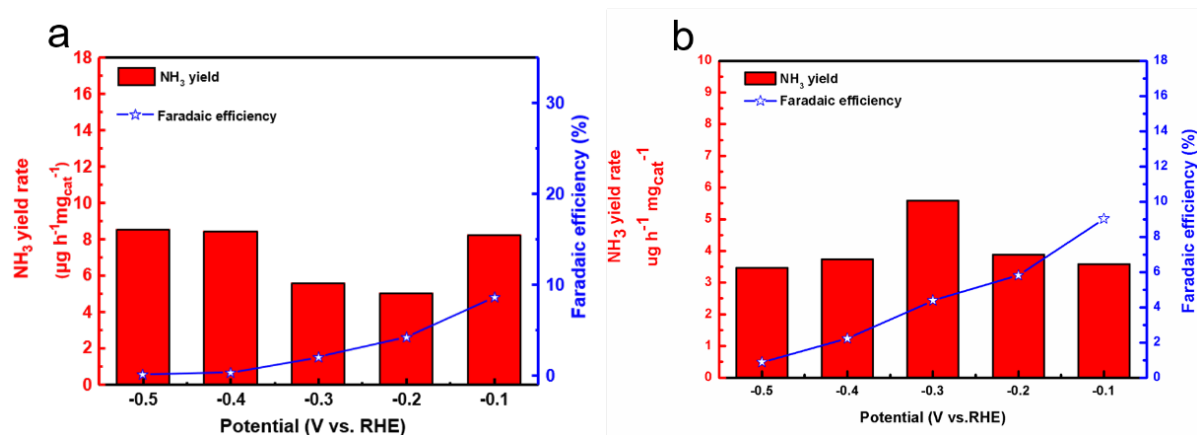


Fig. S7. NH₃ yield and Faraday efficiency of Fe₃O₄ (a) and Fe₂O₃ (b) in N₂-saturated electrolyte at different potentials.

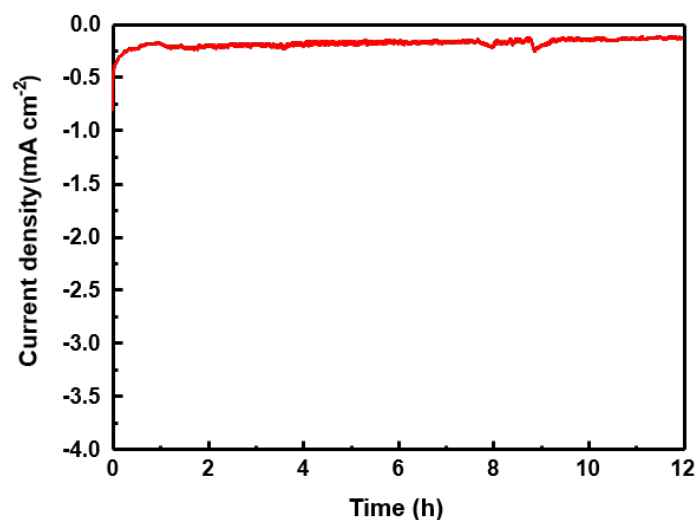


Fig. S8. Current density of FeP-Fe₃O₄ over time 12 h at -0.1 V.

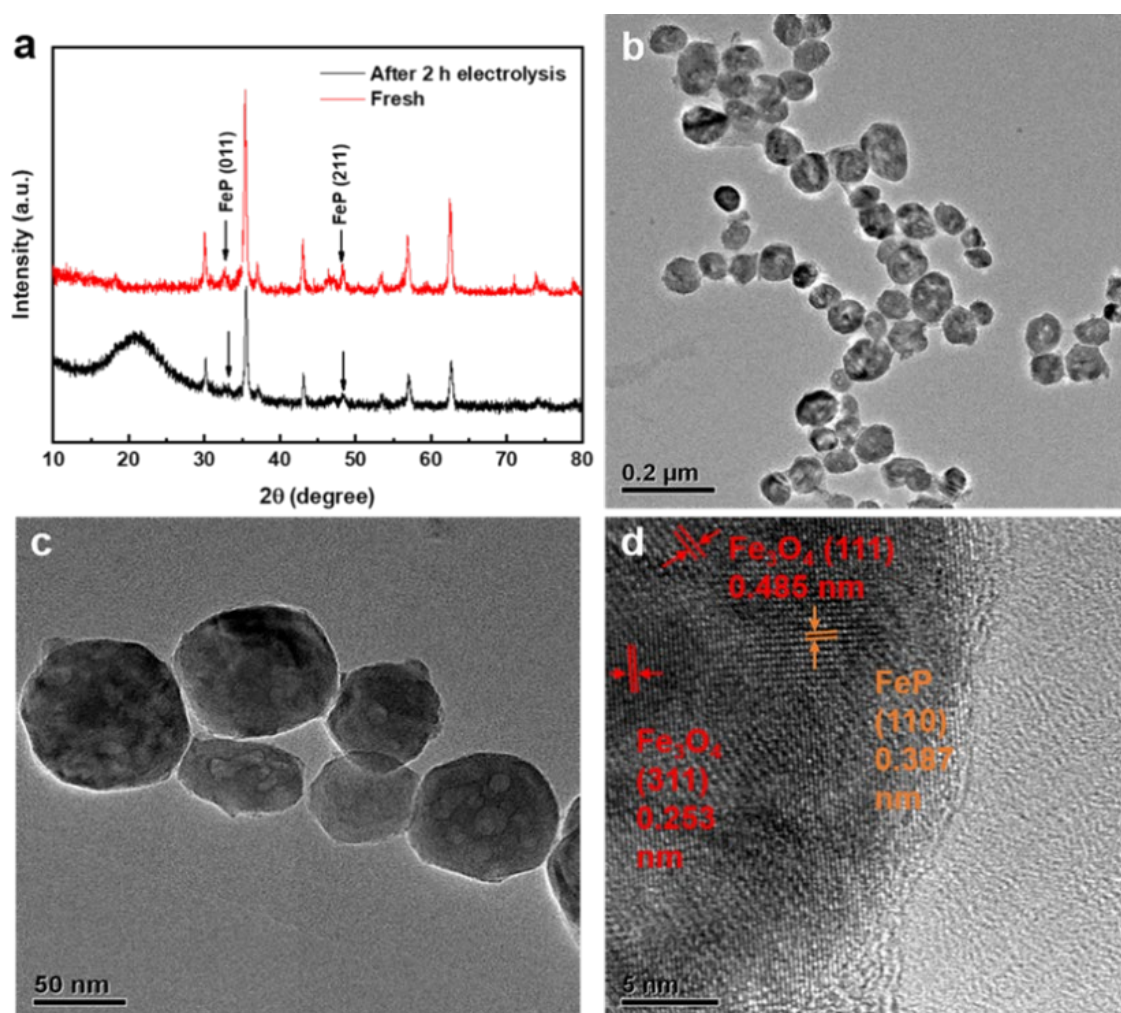


Fig. S9. (a) XRD comparison of FeP-Fe₃O₄ before and after 2 h eNRR test at -0.1 V, (b-c) TEM and (d) HR-TEM images of FeP-Fe₃O₄ after 2 h eNRR test at -0.1 V.

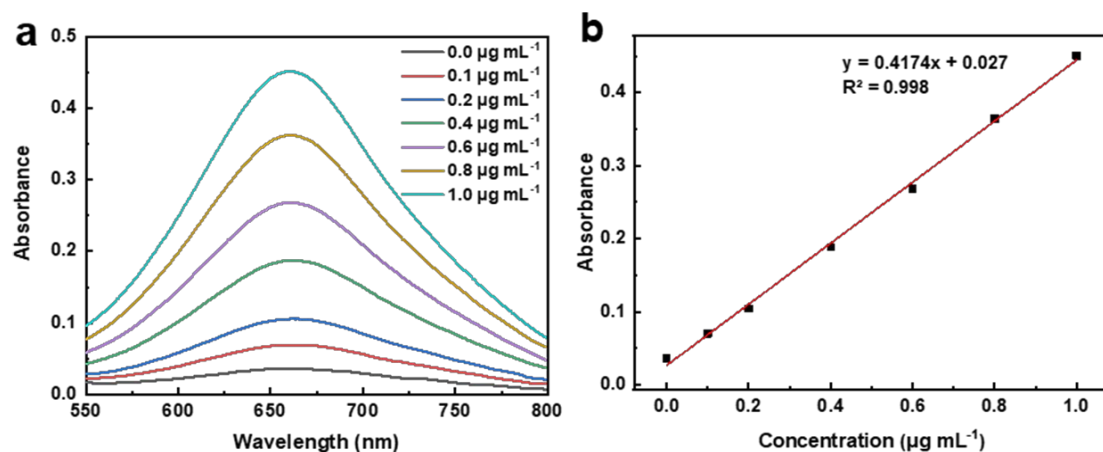


Fig. S10. (a) UV-vis absorption spectra of the electrolytes with various NH_4^+ concentrations after incubation in dark for 2 h, (b) The corresponding calibration curve utilized to determine NH_3 .

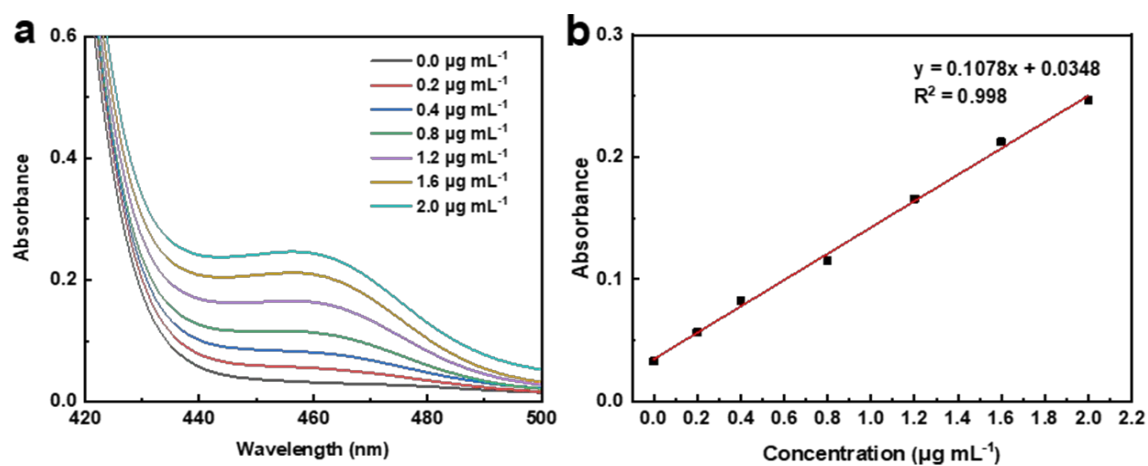


Fig. S11. (a) UV-vis absorption spectra of the electrolytes with various concentration of N_2H_4 , (b) The corresponding calibration curve utilized to determine N_2H_4 .

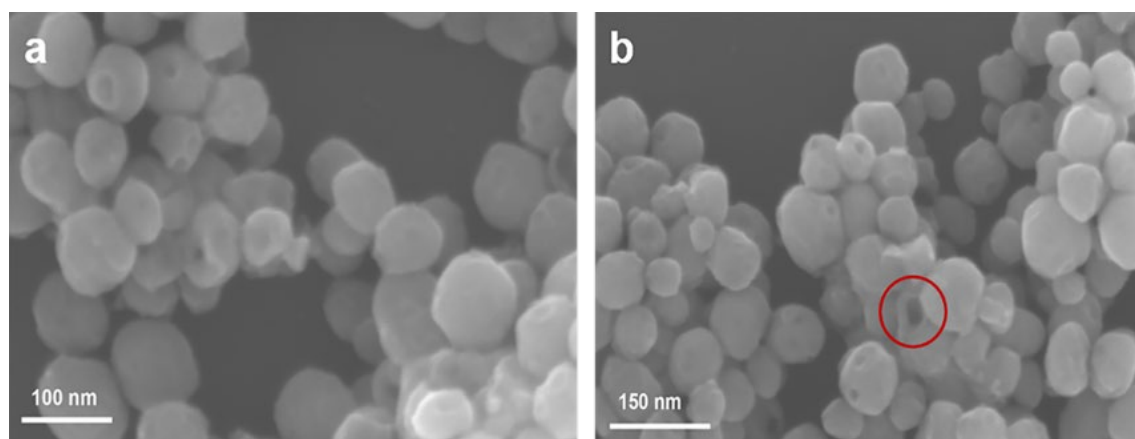


Fig. S12. SEM image of $\text{FeP-Fe}_3\text{O}_4$.

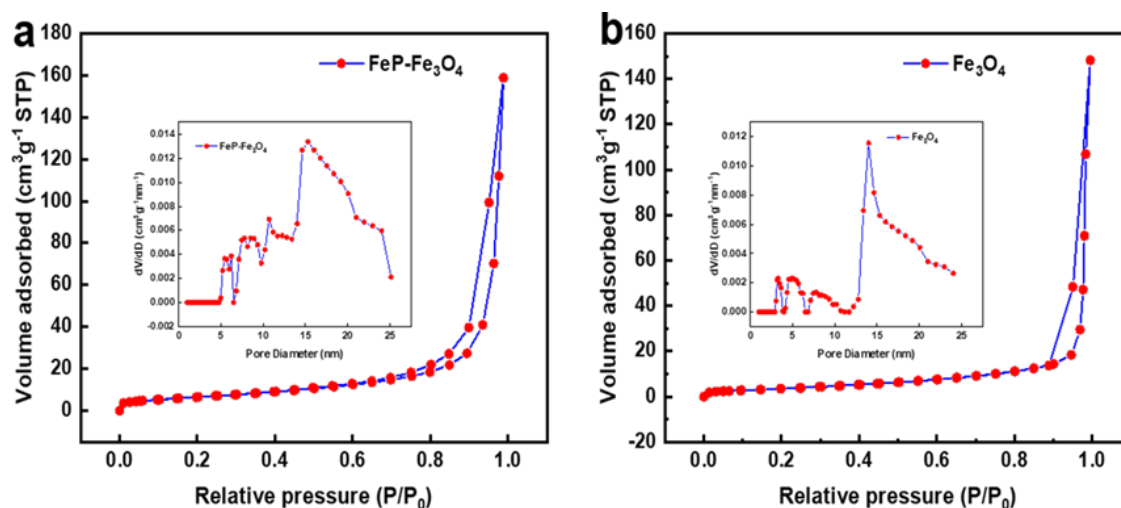


Fig. S13. BET isotherm of (a) FeP-Fe₃O₄ and (b) Fe₃O₄, illustrated with corresponding DFT aperture distribution.

Table S1 The atomic ratios of Fe, P, and O elements

Name	At. %	The ratio of each atom to the carbon atom	Content after removing the carbon atom (%)
C 1s	32.835	1	
Fe 2p	9.163	0.279	13.643
O 1s	47.804	1.456	71.174
P 2p	10.199	0.311	15.185

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