

Electronic Supplementary Information for

**Phosphorus incorporation accelerates ammonia  
electrosynthesis over mesoporous Au film**

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## Experimental section

**2.1. Chemicals and Materials.** Polystyrene-*b*-poly(ethylene oxide) (PS<sub>18000</sub>-*b*-PEO<sub>7500</sub>) was purchased from Polymer Source Inc. Ethanol (C<sub>2</sub>H<sub>5</sub>OH), concentrated hydrochloric acid (HCl) sodium hydroxide (NaOH), *p*-dimethylaminobenzaldehyde (*p*-C<sub>9</sub>H<sub>11</sub>NO), hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O), sodium hypochlorite solution (NaClO), chloroauric acid (HAuCl<sub>4</sub>), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), tetrahydrofuran (THF), sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>), and sodium salicylate (C<sub>7</sub>H<sub>5</sub>NaO<sub>3</sub>) were purchased from Aladdin. Sodium nitroferricyanide dihydrate (C<sub>5</sub>FeN<sub>6</sub>Na<sub>2</sub>O·2H<sub>2</sub>O) and ammonium chloride (NH<sub>4</sub>Cl) were purchased from MACKLIN Inc. Pluronic F127 were purchased from Sigma-Aldrich. Carbon paper and Nafion 117 membranes were ordered from Shanghai Hesen Electric Co., Ltd.

**2.2. Synthesis of mAuP/NF.** In a typical synthesis, 10 mg of PS<sub>18000</sub>-*b*-PEO<sub>7500</sub> was dissolved in 3 mL of THF under sonication, followed by adding 1.5 mL of ethanol. Then, 2 mL of HAuCl<sub>4</sub> (20 mM) and 1 mL of NaH<sub>2</sub>PO<sub>2</sub> (12 mM) aqueous solutions were sequentially mixed with above solution. A piece of clean Ni foam (1 × 2 cm) was added into the above solution for 20 min at room temperature. Finally, the product was collected by fully washing with ethanol, and stored in the ethanol for further characterization.

**2.3. Characterizations.** Scanning electron microscopy (SEM, ZEISS SUPRA 55) was performed to observe the morphology and structure of the samples using a ZEISS SUPRA 55 at the accelerating voltage of 5 kV. Transmission electron microscope (TEM) images were carried out on JEOL JEM-2010 apparatus operating at 200 kV. X-ray diffraction (XRD) pattern of samples was performed by Bruker D8 ADVANCE X-ray powder diffractometer. The atomic valence of samples was detected by X-ray photoelectron spectroscopy (XPS, ESCALAB MK II spectrometer). Nitrogen temperature-programmed desorption (N<sub>2</sub>-TPD) experiments were conducted on a Micromeritics

AutoChem 2910 chemisorption analyzer. Before N<sub>2</sub>-TPD experiments, the samples were purified by the thermal treatment at 100 °C under He gas for 30 min. After cooling down to 40 °C, the samples adsorbed nitrogen for 30 min, then the temperature was programmed to 650 °C with the heating rate of 10 °C min<sup>-1</sup> in the He atmosphere.

**2.4. Electrochemical measurements.** All the electrochemical measurements were performed by CHI 760E potentiostat using a typical three-electrode cell separated by Nafion 211 membrane, in which the obtained mAUP/NF was employed as the working electrode, Ag/AgCl electrode (saturated KCl) as the reference electrode and graphite rod as the counter electrode. Before the N<sub>2</sub> reduction measurements, electrolyte (0.1 M Na<sub>2</sub>SO<sub>4</sub>) was bubbled with N<sub>2</sub> for 30 min. The current density was normalized to the geometric area of Ni foam, and all potentials in this work were recorded on the reversible hydrogen electrode (RHE).

**2.5. Production determination.** The production of ammonia was measured by the indophenol blue method.<sup>1</sup> In detail, 500 μL coloring solution (0.4 M C<sub>7</sub>H<sub>6</sub>O<sub>3</sub> + 0.32 M NaOH), 50 μL 0.75 M NaOH and 50 μL NaClO (ρ<sub>Cl</sub> = 4–4.9) were first mixed with 4 mL electrolyte, which was kept in dark for 1 h. Then the ammonia was detected from the mixed solution by ultraviolet-visible (UV-vis) spectrophotometer at a wavelength of 680 nm. The concentration-absorbance curve was obtained to quantify the ammonia amount by using NH<sub>4</sub>Cl solutions of known concentration as standards. The NH<sub>3</sub> yield ( $r_{\text{NH}_3}$ ) and Faradaic efficiency (FE) were evaluated from following equations:

$$r_{\text{NH}_3} = (c_{\text{NH}_3} \times V) / (t \times m) \quad (1)$$

$$\text{FE} = 3F \times n_{\text{NH}_3} / Q \quad (2)$$

where  $c_{\text{NH}_3}$  (μg mL<sup>-1</sup>) is the NH<sub>3</sub> concentration,  $V$  (mL) is the electrolyte volume,  $t$  (h) is the electrolysis time,  $m$  (mg) is the loading catalyst mass,  $F$  (96485 C mol<sup>-1</sup>) is the Faraday constant,  $n_{\text{NH}_3}$  (mol) is the mole of produced NH<sub>3</sub> and  $Q$  (C) is the total quantity of applied electricity.

$\text{N}_2\text{H}_4$  was detected using the Watt and Chrisp method.<sup>2</sup> The mixture of ethanol (300 mL), HCl (30 mL) and *p*- $\text{C}_9\text{H}_{11}\text{NO}$  (5.99 g) was first prepared as color reagent. To detect  $\text{N}_2\text{H}_4$ , the aqueous solution (5 mL) and color reagent (5 mL) were mixed for 10 min, followed by UV-vis determination at a wavelength of 457 nm. The  $\text{N}_2\text{H}_4$  was evaluated using a standard  $\text{N}_2\text{H}_4$  calibration curve.

**2.6 Detection of  $\text{NO}_3^-$  ion.** The  $\text{NO}_3^-$  ions were detected according to the reported literature.<sup>3</sup> The standard solutions of  $\text{NO}_3^-$  ions were prepared as follows.

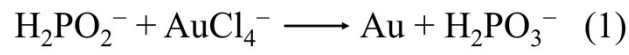
- 1) 100  $\mu\text{g mL}^{-1}$  stock: 0.1 g of pre-dried  $\text{KNO}_3$  was added into 1 L of deionized water.
- 2) 5  $\mu\text{g mL}^{-1}$  stock: 5 mL of the above 100  $\mu\text{g mL}^{-1}$  stock was mixed with deionized water to 100 mL.
- 3) The 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 mL solutions were separately added into the test tubes, which was mixed with deionized water to 5 mL, and 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0  $\mu\text{g mL}^{-1}$  standard solutions were finally obtained.

The concentration of the  $\text{NO}_3^-$  in  $\text{Na}_2\text{SO}_4$  solution can be determined by UV-vis spectrophotometer at the wavelength of 220 nm. In a typical procedure, 5 mL of electrolytes were added to the test tubes followed by addition of 0.1 mL of 1.0 M HCl. After shaking up and standing for 5 min, the concentration of  $\text{NO}_3^-$  was measured using UV-vis spectrophotometer. The standard curve for  $\text{NO}_3^-$  determination was plotted using the standard solutions.

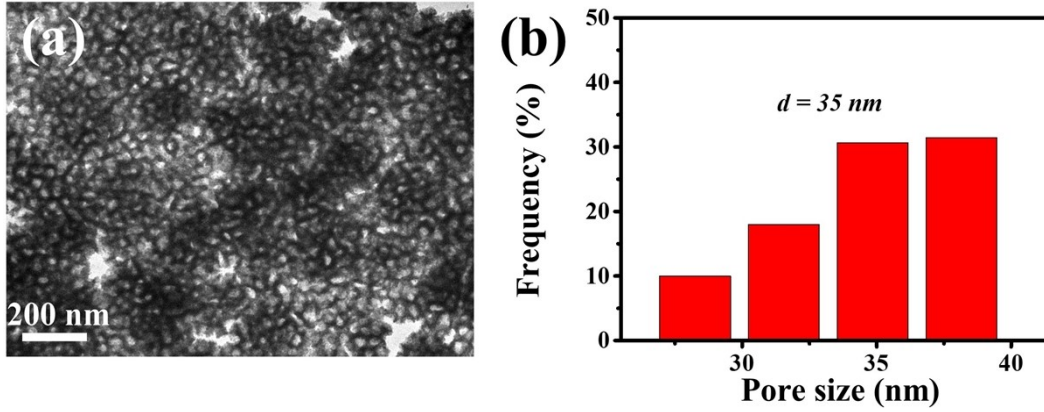
**2.7 The calculation of the d-band center.** All density functional theory calculations were performed with Vienna Ab Initio Simulation Package (VASP).<sup>4,5</sup> The basis set for the electronic wave functions was plane wave below a 500 eV energy cutoff. The Au(111) model was obtained by expanding monomer  $2 \times 2$ , and AuP(111) was obtained by placing P atoms in octahedral gap on the basis of Au(111) model. We use a Fermi smearing of electronic occupations with a width of 0.2 eV

and Monkhorst-Pack mesh for the Brillouin zone sampling of (5, 5, 1). The structure relaxation is performed until the maximum force on each atom drops below 0.03 eV Å<sup>-1</sup>. When static calculations were performed, the K-point sampling was set to (10, 10, 1). The d-band center was obtained by the following formula:

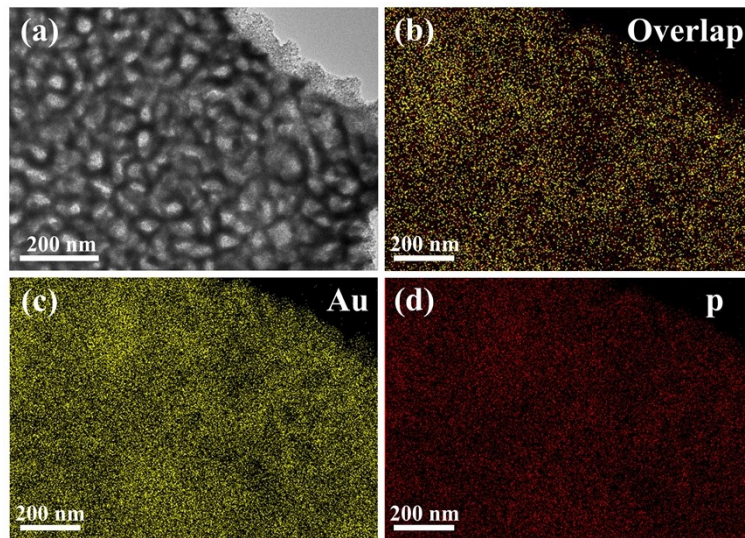
$$\varepsilon_d = \frac{\int_{-\infty}^{\infty} n_d(\varepsilon) \varepsilon d\varepsilon}{\int_{-\infty}^{\infty} n_d(\varepsilon) d\varepsilon} \quad (3)$$



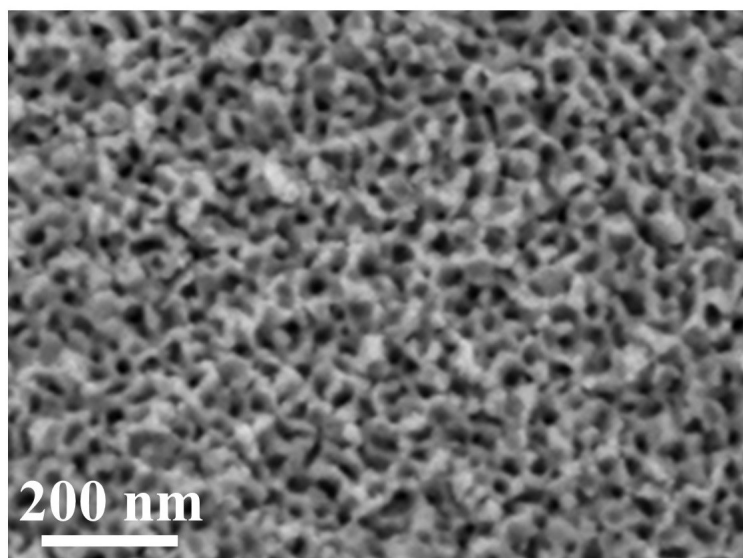
**Fig. S1** Possible reactions involved in the synthesis of Au-P alloy.



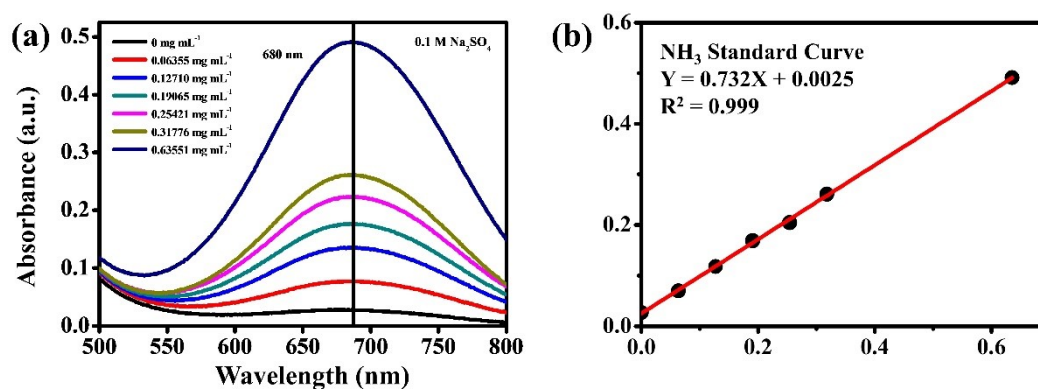
**Fig. S2** (a) TEM image and (b) pore size distribution of the mAuP film on Ni foam.



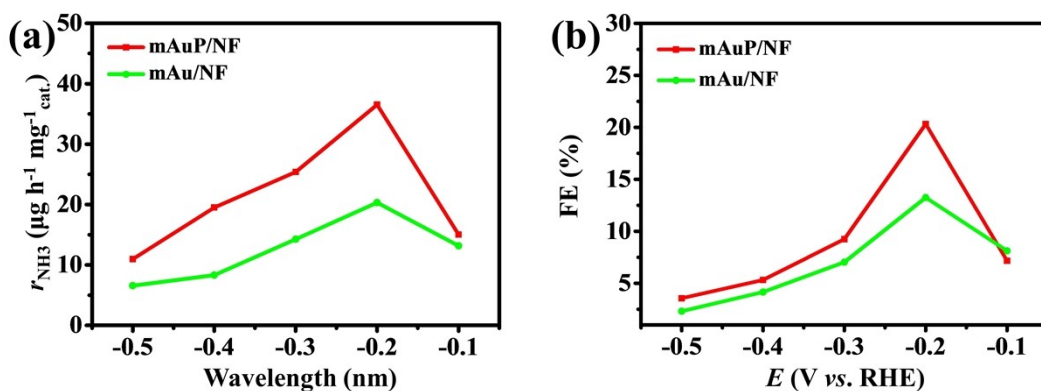
**Fig. S3** (a) HAADF-STEM image and (b-d) the element mapping images of the mAuP film.



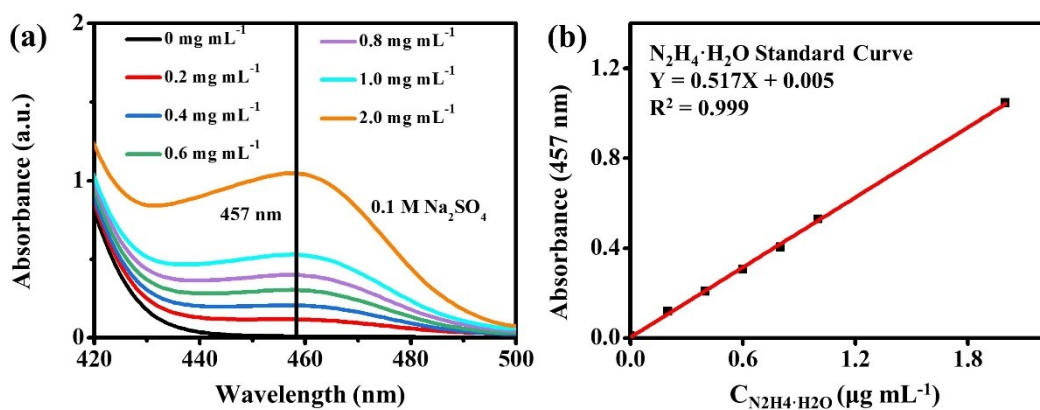
**Fig. S4** SEM image of the mAu/NF.



**Fig. S5** (a) UV-Vis curves of indophenol assays with  $\text{NH}_4^+$  ions after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of  $\text{NH}_3$  concentrations.

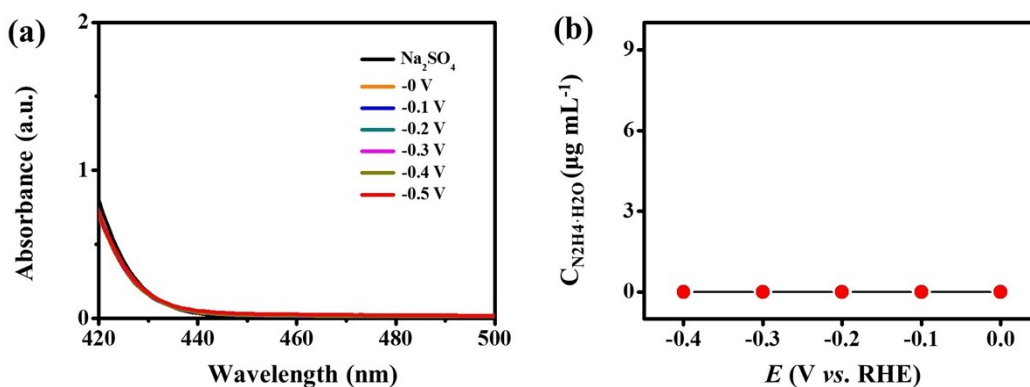


**Fig. S6** The comparison of calculated  $\text{NH}_3$  yields and FEs for mAuP/NF and mAu/NF at selected potentials.

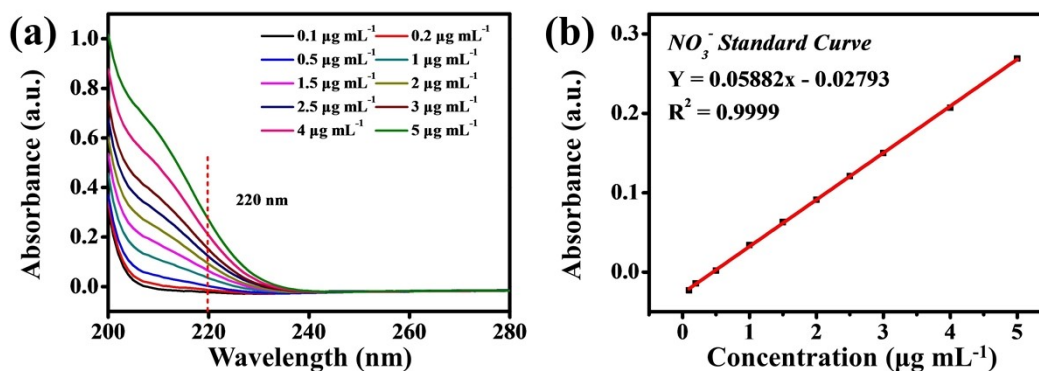


**Fig. S7** (a) UV-Vis absorption spectra of various  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  concentrations after color development for 10 min temperature. (b) Calibration curve for estimation of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  concentration.

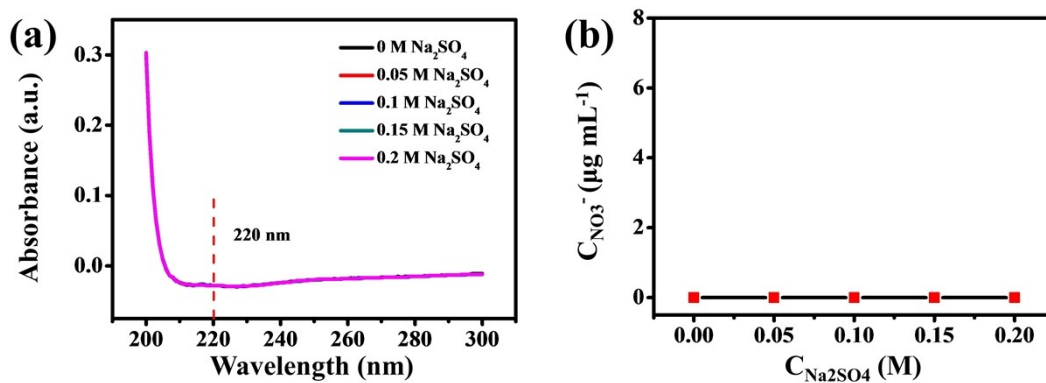




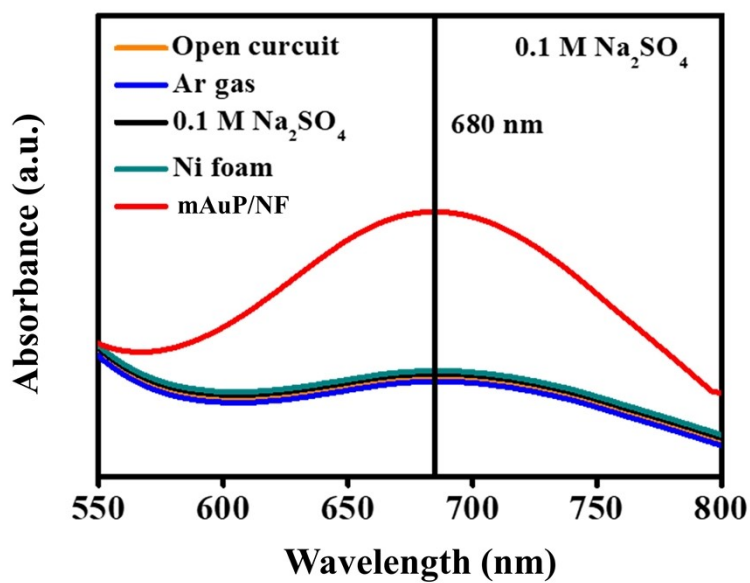
**Fig. S8** (a) The UV-Vis absorption spectra and (b) corresponding yield of  $\text{N}_2\text{H}_4$  at selected potentials.



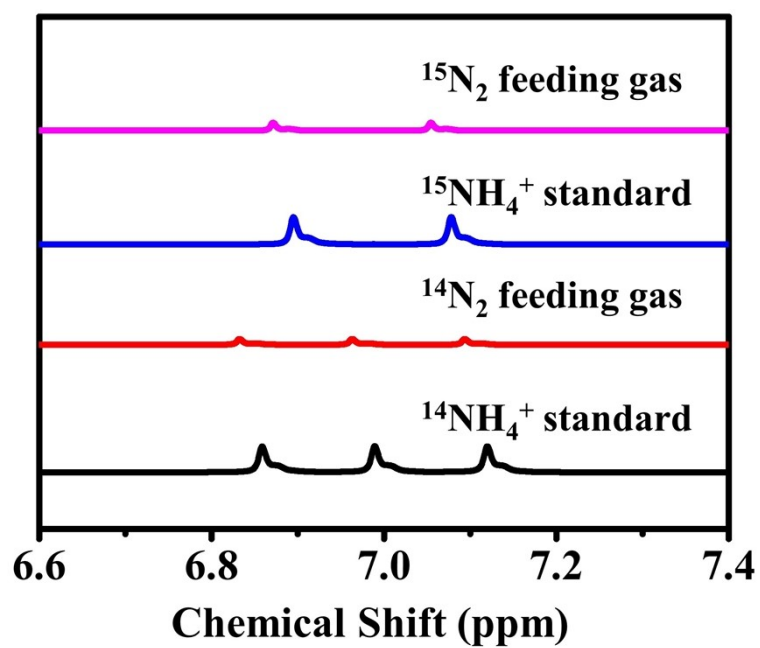
**Fig. S9** Calibration for nitrate determination. (a) UV-vis spectra for various concentrations of  $\text{KNO}_3$ . (b) Calibration curve used for calculating the concentration of nitrate.



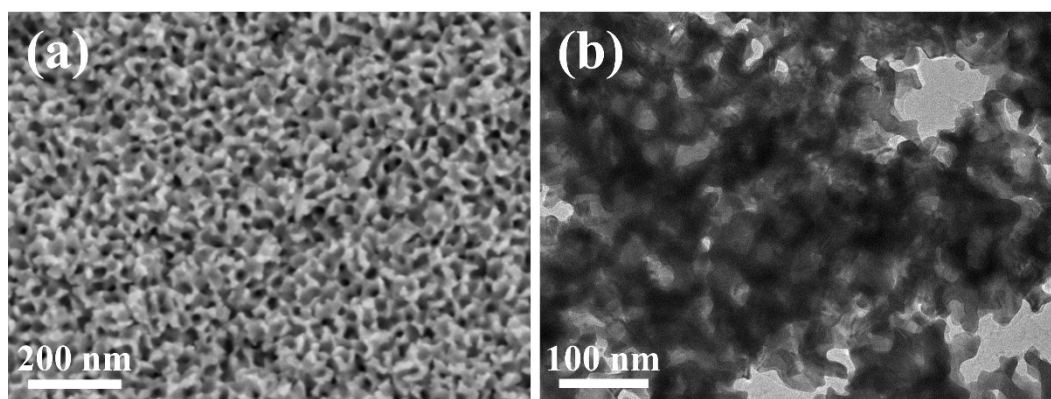
**Fig. S10** (a) UV-vis adsorption spectra for determining the concentration of  $\text{NO}_3^-$  in  $\text{Na}_2\text{SO}_4$ . (b) The concentration of  $\text{NO}_3^-$  in various concentrations of  $\text{Na}_2\text{SO}_4$ .



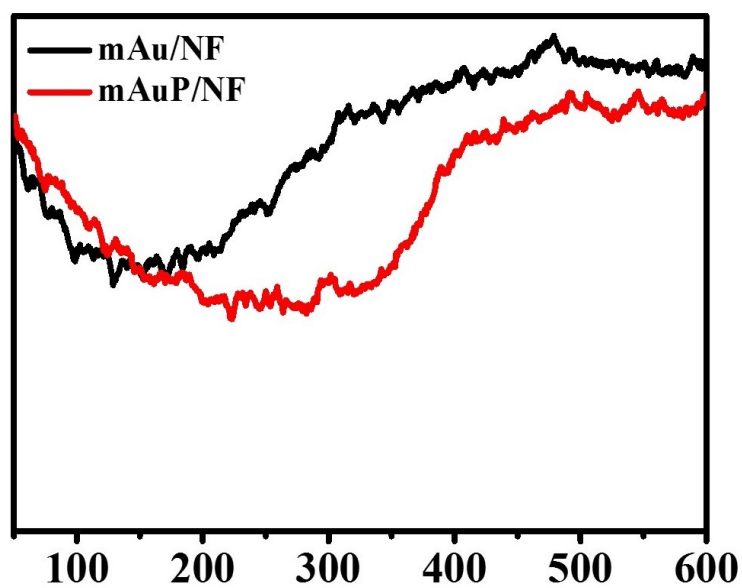
**Fig. 11** UV-vis absorption spectra of the electrolytes stained with indophenols indicator under different conditions.



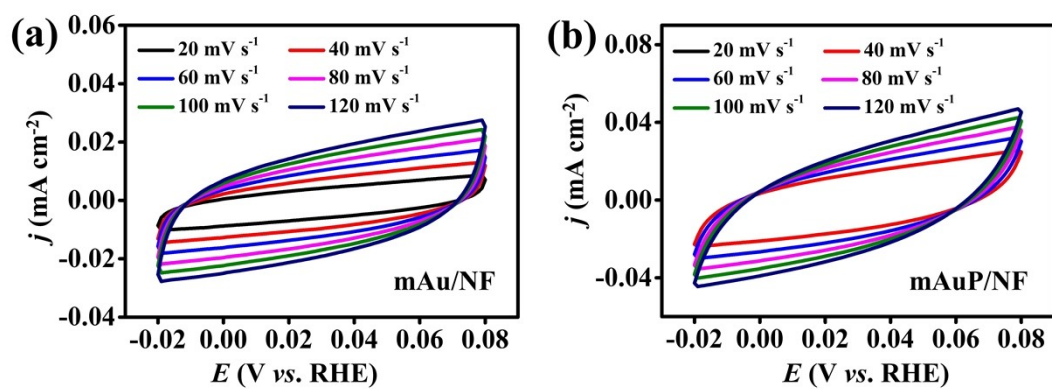
**Fig. S12**  $^{15}\text{N}$  isotope labeling experiment.  $^1\text{H}$  NMR spectra for the post-electrolysis 0.1 M  $\text{Na}_2\text{SO}_4$  electrolytes with  $^{15}\text{N}_2$ ,  $^{14}\text{N}_2$  as the feeding gas. Also shown are the spectra for  $^{15}\text{NH}_4^+$  and  $^{14}\text{NH}_4^+$  standard samples.



**Fig. S13** (a) SEM and (b) TEM images of mAuP/NF after long-term stability test.



**Fig. S14** N<sub>2</sub>-TPD curve of mAu/NF and mAuP/NF.



**Fig. S15** Cyclic voltammograms for different samples.

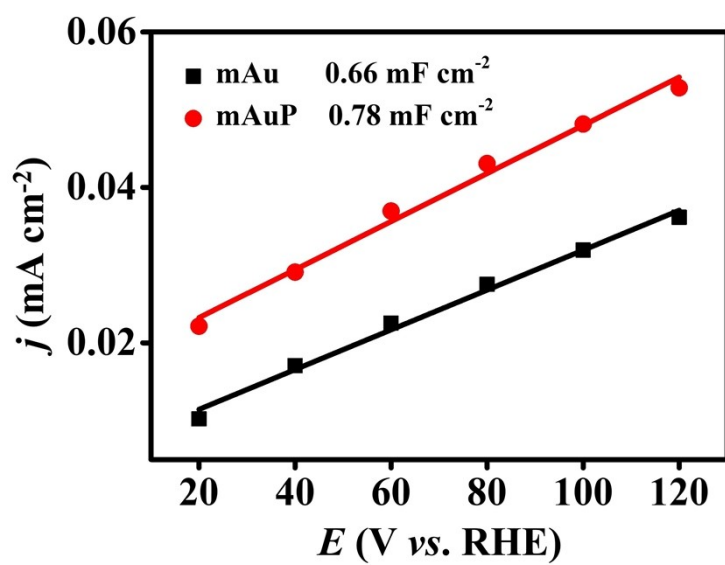


Fig. S16 Cyclic voltammograms for different samples

**Table S1.** Summary of the representative reports on electrocatalytic NRR at ambient conditions.

Catalyst	Electrolyte	NH <sub>3</sub> yield	FE	Ref.
<b>mAuP/NF</b>	<b>0.1 M Na<sub>2</sub>SO<sub>4</sub></b>	<b>36.52 μg h<sup>-1</sup> mg<sup>-1</sup><sub>cat.</sub></b>	<b>20.32%</b>	<b>This work</b>
Au flowers	0.1 M HCl	25.57 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	6.05%	6
Au <sub>1</sub> Co <sub>1</sub> @GO	0.1 M K <sub>2</sub> SO <sub>4</sub>	36.82 μg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	22.03%	7
mAu <sub>3</sub> Pd/NF	0.1 M Na <sub>2</sub> SO <sub>4</sub>	24.02 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	10.54%	8
Au@Fe <sub>3</sub> O <sub>4</sub> NPs	0.1 M KOH	21.42 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	4.5%	9
Au/WO <sub>3-x</sub>	0.1 M KOH	23.15 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	14.72%	10
pAu/NF	0.1 M Na <sub>2</sub> SO <sub>4</sub>	9.42 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>Pd</sub>	13.36%	11
Au/C	0.1 M KOH	17.49 μg h <sup>-1</sup> cm <sup>-2</sup>	5.79%	12
Au HNCs	0.5 M LiClO <sub>4</sub>	3.90 μg h <sup>-1</sup> cm <sup>-2</sup>	30.2%	13
Au nanorods	0.1 M KOH	1.65 μg h <sup>-1</sup> cm <sup>-2</sup>	8.9%	14

## References

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