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-\textit{b}-poly(ethylene oxide) (PS_{18000-\textit{b}-PEO_{7500}}) was purchased from Polymer Source Inc. Ethanol (C_{2}H_{5}OH), concentrated hydrochloric acid (HCl) sodium hydroxide (NaOH), \textit{p}-dimethylaminobenzaldehyde (\textit{p}-C_{9}H_{11}NO), hydrazine monohydrate (N_{2}H_{4} \cdot H_{2}O), sodium hypochlorite solution (NaClO), chloroauric acid (HAuCl_{4}), sodium sulfate (Na_{2}SO_{4}), tetrahydrofuran (THF), sodium hypophosphite (NaH_{2}PO_{2}), and sodium salicylate (C_{7}H_{5}NaO_{3}) were purchased from Aladdin. Sodium nitroferricyanide dihydrate (C_{5}FeN_{6}Na_{2}O \cdot 2H_{2}O) and ammonium chloride (NH_{4}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_{18000-\textit{b}-PEO_{7500}} was dissolved in 3 mL of THF under sonication, followed by adding 1.5 mL of ethanol. Then, 2 mL of HAuCl_{4} (20 mM) and 1 mL of NaH_{2}PO_{2} (12 mM) aqueous solutions were sequentially mixed with above solution. A piece of clean Ni foam (1 \times 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_{2}-TPD) experiments were conducted on a Micromeritics...
AutoChem 2910 chemisorption analyzer. Before N₂-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⁻¹ 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 N₂ reduction measurements, electrolyte (0.1 M Na₂SO₄) was bubbled with N₂ 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.¹ In detail, 500 μL coloring solution (0.4 M C₇H₆O₃ + 0.32 M NaOH), 50 μL 0.75 M NaOH and 50 μL NaClO (ρCl = 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 NH₄Cl solutions of known concentration as standards. The NH₃ yield (r₉H₃) and Faradaic efficiency (FE) were evaluated from following equations:

\[
r_{NH₃} = (c_{NH₃} \times V) / (t \times m) \quad (1)
\]

\[
FE = 3F \times n_{NH₃} / Q \quad (2)
\]

where \(c_{NH₃} \) (μg mL⁻¹) is the NH₃ concentration, \(V\) (mL) is the electrolyte volume, \(t\) (h) is the electrolysis time, \(m\) (mg) is the loading catalyst mass, \(F\) (96485 C mol⁻¹) is the Faraday constant, \(n_{NH₃}\) (mol) is the mole of produced NH₃ and \(Q\) (C) is the total quantity of applied electricity.
N$_2$H$_4$ was detected using the Watt and Chrisp method.$^2$ The mixture of ethanol (300 mL), HCl (30 mL) and $p$-C$_9$H$_{11}$NO (5.99 g) was first prepared as color reagent. To detected N$_2$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 N$_2$H$_4$ was evaluated using a standard N$_2$H$_4$ calibration curve.

2.6 Detection of NO$_3^{-}$ ion. The NO$_3^{-}$ ions were detected according to the reported literature.$^3$ The standard solutions of NO$_3^{-}$ ions were prepared as follows.

1) 100 µg mL$^{-1}$ stock: 0.1 g of pre-dried KNO$_3$ was added into 1 L of deionized water.

2) 5 µg mL$^{-1}$ stock: 5 mL of the above 100 µg 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 µg mL$^{-1}$ standard solutions were finally obtained.

The concentration of the NO$_3^{-}$ in Na$_2$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 NO$_3^{-}$ was measured using UV-vis spectrophotometer. The standard curve for 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)$^{4,5}$ 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 2×2, 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\(^{-1}\). 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:

\[
\varepsilon_d = \frac{\int_{\varepsilon}^{\infty} n_d(\varepsilon) \varepsilon \, d\varepsilon}{\int_{-\infty}^{\infty} n_d(\varepsilon) \, d\varepsilon}
\]  

(3)
Fig. S1 Possible reactions involved in the synthesis of Au-P alloy.

\[
\begin{align*}
\text{H}_2\text{PO}_2^- + \text{AuCl}_4^- & \rightarrow \text{Au} + \text{H}_2\text{PO}_3^- \quad (1) \\
\text{Ni} + \text{AuCl}_4^- & \rightarrow \text{Au} + \text{Ni}^{2+} \quad (2) \\
\text{H}_2\text{PO}_2^- \xrightarrow{\text{Au}} \text{AuP} \quad (3)
\end{align*}
\]

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 NH$_4^+$ ions after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH$_3$ concentrations.
Fig. S6 The comparison of calculated NH$_3$ yields and FEs for mAuP/NF and mAu/NF at selected potentials.

Fig. S7 (a) UV-Vis absorption spectra of various N$_2$H$_4$·H$_2$O concentrations after color development for 10 min temperature. (b) Calibration curve for estimation of N$_2$H$_4$·H$_2$O concentration.
Fig. S8 (a) The UV-Vis absorption spectra and (b) corresponding yield of $N_2H_4$ at selected potentials.

Fig. S9 Calibration for nitrate determination. (a) UV-vis spectra for various concentrations of KNO$_3$. (b) Calibration curve used for calculating the concentration of nitrate.
Fig. S10  (a) UV-vis adsorption spectra for determining the concentration of NO$_3^-$ in Na$_2$SO$_4$. (b) The concentration of NO$_3^-$ in various concentrations of Na$_2$SO$_4$.

Fig. 11 UV-vis absorption spectra of the electrolytes stained with indophenols indicator under different conditions.
**Fig. S12** $^{15}$N isotope labeling experiment. $^1$H NMR spectra for the post-electrolysis 0.1 M Na$_2$SO$_4$ electrolytes with $^{15}$N$_2$, $^{14}$N$_2$ as the feeding gas. Also shown are the spectra for $^{15}$NH$_4^+$ and $^{14}$NH$_4^+$ standard samples.

**Fig. S13** (a) SEM and (b) TEM images of mAuP/NF after long-term stability test.
**Fig. S14** N$_2$-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.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH$_3$ yield</th>
<th>FE</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>mAuP/NF</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>36.52 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>20.32%</td>
<td>This work</td>
</tr>
<tr>
<td>Au flowers</td>
<td>0.1 M HCl</td>
<td>25.57 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>6.05%</td>
<td>6</td>
</tr>
<tr>
<td>Au$<em>{1}$Co$</em>{1}$@GO</td>
<td>0.1 M K$_2$SO$_4$</td>
<td>36.82 µg h$^{-1}$ mg$_{\text{cat}}^{-1}$</td>
<td>22.03%</td>
<td>7</td>
</tr>
<tr>
<td>mAu$_3$Pd/NF</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>24.02 µg h$^{-1}$ mg$_{\text{cat}}^{-1}$</td>
<td>10.54%</td>
<td>8</td>
</tr>
<tr>
<td>Au@Fe$_3$O$_4$ NPs</td>
<td>0.1 M KOH</td>
<td>21.42 µg h$^{-1}$ mg$_{\text{cat}}^{-1}$</td>
<td>4.5%</td>
<td>9</td>
</tr>
<tr>
<td>Au/WO$_{3-x}$</td>
<td>0.1 M KOH</td>
<td>23.15 µg h$^{-1}$ mg$_{\text{cat}}^{-1}$</td>
<td>14.72%</td>
<td>10</td>
</tr>
<tr>
<td>pAu/NF</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>9.42 µg h$^{-1}$ mg$_{\text{Pd}}^{-1}$</td>
<td>13.36%</td>
<td>11</td>
</tr>
<tr>
<td>Au/C</td>
<td>0.1 M KOH</td>
<td>17.49 µg h$^{-1}$ cm$^{-2}$</td>
<td>5.79%</td>
<td>12</td>
</tr>
<tr>
<td>Au HNCs</td>
<td>0.5 M LiClO$_4$</td>
<td>3.90 µg h$^{-1}$ cm$^{-2}$</td>
<td>30.2%</td>
<td>13</td>
</tr>
<tr>
<td>Au nanorods</td>
<td>0.1 M KOH</td>
<td>1.65 µg h$^{-1}$ cm$^{-2}$</td>
<td>8.9%</td>
<td>14</td>
</tr>
</tbody>
</table>
References


