Electronic Supplementary Information

NaCl Template-assisted Construction of CoP-MoP Heterostructured Electrocatalyst for Electrocatalytic Nitrogen Reduction

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S1. Electrodes preparation

The working electrodes were prepared by applying catalyst ink on carbon cloth (1 × 1 cm^2). Specifically, 5 mg of CoP-MoP-x sample were dispersed in a solvent mixture of 980 μL of ethanol and 20 μL of Nafion solution and sonicated for 30 min to form a homogeneous sample ink. A total of 100 μL of well-dispersed sample ink were applied on a clean carbon cloth surface. The prepared electrodes were dried at 60 °C overnight to completely remove the dispersant. The loading was ~500 μg • cm^{-2}.

S2. Indophenol blue method for for determining the yield of NH_3[1]

4 mL of the absorption solution were removed from the electrochemical vessel. Then, 0.5 mL of 1.0 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate was added to the absorption solution as a colorant, while 0.5 mL of 0.05 M NaClO as an oxidizing agent and 0.2 mL of 1 wt% sodium nitroferricyanide as a catalyst were added dropwise to the mixed solution. After stabilization for 2 h at room temperature and protected from light, an ultraviolet-visible spectrophotometer (UV-2600, Shimadzu) was used to measure the absorption spectra of the mixed solutions in the range of 500-800 nm. The standard fit curve showed a good linear relationship

between absorbance and NH_3 concentration ($y = 0.10116x + 0.00449$, $R^2 = 0.997$). The NH_3 yield (R_{NH_3}) was calculated by using the following equation (1):

$$R_{NH_3} = (C_{NH_3} \times V)/(t \times m) \quad (1)$$

where C_{NH_3} is the NH_3 concentration, V is the volume of the cathode electrolyte, t is the electrochemical reaction time, and m is the effective mass of catalyst involved in the reaction.

S3. Determination of FE

Assuming three electrons were needed to produce one NH_3 molecule, the Faraday efficiency (FE) in 0.1 M Na_2SO_4 could be calculated as the following equation (2):

$$FE = 3F \times C_{NH_3} \times V/(17 \times Q) \quad (2)$$

where F is the Faraday constant (96485 C mol^{-1}), C_{NH_3} is the NH_3 concentration, and Q is the total charge in the electrocatalytic process.

S4. Watt and Chrisp method for determining the concentration of N_2H_4[2]

Specifically, the color developer was obtained by mixing 5.99 g of p-dimethylaminobenzaldehyde, 30 mL of 0.1 M HCl, and 300 mL of ethanol. Then, 5 mL of absorbent were removed from the electrochemical vessel, added to 5 mL of color developer, and stirred at room temperature for 20 min. The absorption spectra were measured by UV-Vis spectrophotometer. The standard fit curve showed a good linear relationship between absorbance and N_2H_4 concentration ($y = 0.16781x + 0.00146$, $R^2 = 0.999$).

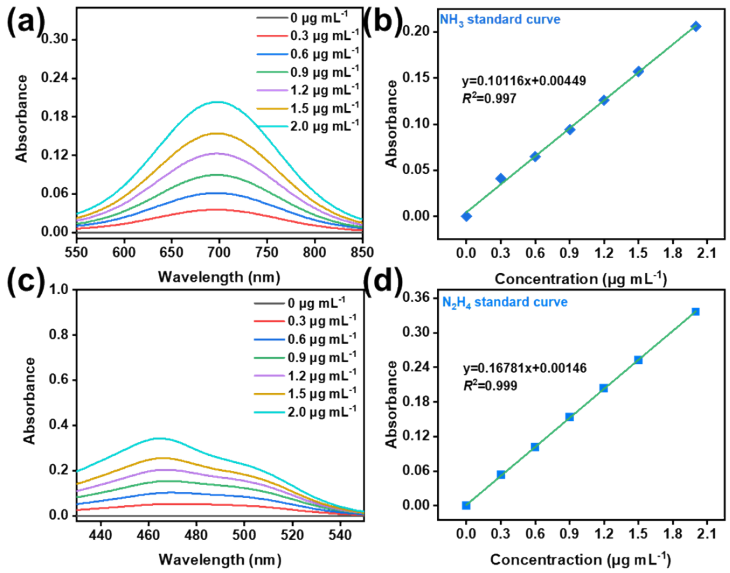

Fig. S1. (a) The UV-Vis absorption spectrum of NH_3 obtained using indophenol blue method and the (b) corresponding calibration curve. (c) The UV-Vis absorption spectrum of N_2H_4 obtained using Watt-Chrisp method and the (d) corresponding calibration curve.

References

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[2]. Zhou, S.; Yang, X.; Xu, X.; Dou, S. X.; Du, Y.; Zhao, J., Boron Nitride Nanotubes for Ammonia Synthesis: Activation by Filling Transition Metals. *J. Am. Chem. Soc.,* **2020,** *142* (1), 308-317.