Supplementary Material

Enhanced Electrocatalytic Nitrogen Reduction on a Three-Dimensional Cu_3P/SnP@CF Catalyst through a Multi-Site Synergistic Effect between the Heterointerface and Phosphorus Vacancies

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S1. Experimental section

S1.1 Chemicals

$CuSO_4$、$SnSO_4$、K_2SO_4 were purchased from Sinopharm Chemical Reagent Co., Ltd., H_2SO_4 was purchased from Shanghai Aladdin Biochemical Technology Co. None of the chemicals were further decontaminated.

S1.2. Catalyst Characterization.

Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) elemental mapping images were obtained by the JEOL JSM 7800F instrument. Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were obtained using a FEI Tecnai G2F30 S-Twin transmission electron microscope. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were collected by Bruker-D8 Advance and Thermo Scientific K-Alpha, respectively. The C 1s peak at 284.80 eV was used as an energy reference for all binding energies. The PL spectra was obtained by using a FLS 980 fluorescence spectrophotometer at room temperature.

S1.3. Electrochemical NRR measurement

The electrocatalytic nitrogen reduction reaction was carried on an H-type electrolytic cell at ambient temperature and pressure (all electrochemical reactions were carried out on a CHI604E electrochemical workstation), in which the electrolytic cell was separated by a Nafion 117 membrane, which needs to underwent pre-treatment before use consisting of sonication in 5 % H_2O_2, deionized water, 0.5 M H_2SO_4, and deionized water for 20 minutes each, followed by treatment with deionized water at 80 °C for more than 12 hours. Before electrochemical testing, the cathode chamber's electrolyte underwent a 30-minute purge with N_2.

S1.4. Determination of NH_3 and N_2H_4

The concentration of produced NH_3 was determined using the indophenol blue method. Specifically, 2 mL of the post-test solution was taken from the cathodic chamber and added to 2 mL of a 1.0 M NaOH solution containing $C_7H_6O_3$ and $C_6H_5Na_3O_7 \cdot 2H_2O$. Subsequently, 1 mL of NaClO (0.05 M) and 0.2 mL of $Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$ were added sequentially. After allowing the mixture to stand in the dark for 2 hours, the concentration of NH_3 was measured by UV-Vis spectroscopy at a wavelength of 655 nm. The concentration-absorbance curve was calibrated using a standard NH_4Cl solution, as illustrated in Fig. S2.

N_2H_4 as a byproduct in the nitrogen reduction reaction for ammonia synthesis, which affect the efficiency of ammonia synthesis, therefore, its concentration is measured during the tests. The concentration of N_2H_4 in the electrolyte was determined using the standard Watt and Chrisp method. A color reagent was prepared by mixing $C_9H_{11}NO$ (5.99 g), HCI (30 mL), and C_2H_5OH (300 mL). In detail, 5 mL of the electrolyte was taken from the electrochemical reaction cell and added to 5 mL of the prepared color reagent, then stirred for 10 minutes at 25 °C.

S1.5. Density functional theory (DFT) calculations

The density functional theory (DFT) calculations were carried out with the VASP code[1]. The Perdew–Burke–Ernzerhof (PBE) functional within generalized gradient approximation (GGA)[2] was used to process the exchange–correlation, while the projectoraugmented-wave pseudopotential (PAW)[3] was applied with a kinetic energy cut-off of 500 eV, which was utilized to describe the expansion of the electronic eigenfunctions. The vacuum thickness was set to be 20 Å to minimize interlayer interactions. The Brillouin-zone integration was sampled by a Γ-centered 5 × 5 × 1 Monkhorst–Pack k-point. All atomic positions were fully relaxed until energy and force reached a tolerance of 1×10^{-5} eV and 0.03 eV/Å, respectively. The dispersion corrected DFT-D method was employed to consider the long-range interactions[4].

The adsorption energy (E_{ads}) of a complex formed between two molecules, A and B, can be calculated using the following equation:

$E_{ads} = E_{complex} - (E_A + E_B)$

Where: $E_{complex}$ is the total energy of the molecular complex of A and B.

E_A and E_B are the total energies of isolated molecules A and B, respectively.

The Gibbs free energy change (ΔG) was calculated by computational hydrogen electrode (CHE) model as follows:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \qquad (1)$$

where ΔE is the reaction energy obtained by the total energy difference between the reactant and product molecules absorbed on the catalyst surface and ΔS is the change in entropy for each reaction, ΔZPE is the zero-point energy correction to the Gibbs free energy. T represents room temperature (298.15 K).

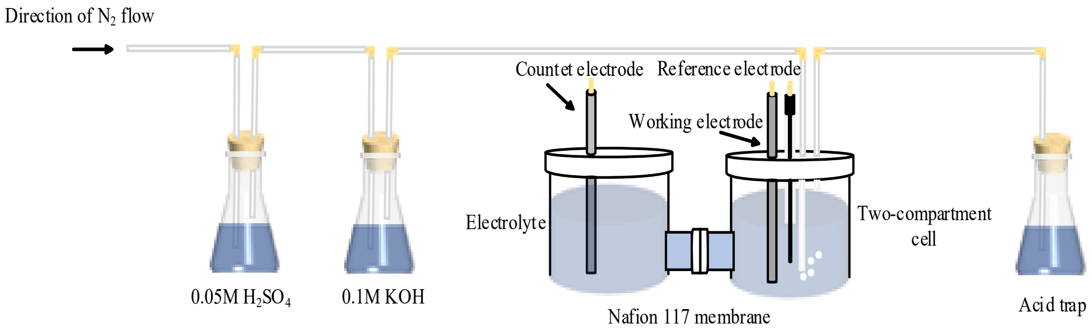

Fig. S1 Ammonia electrolysis device

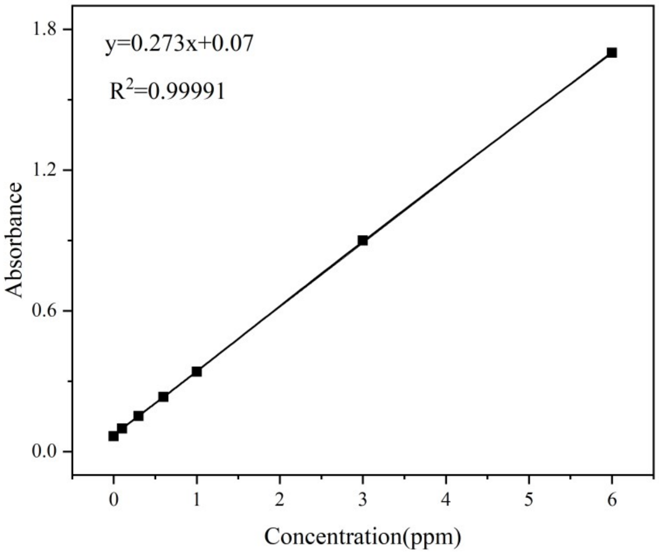

Fig. S2 standard curve of NH_4^+

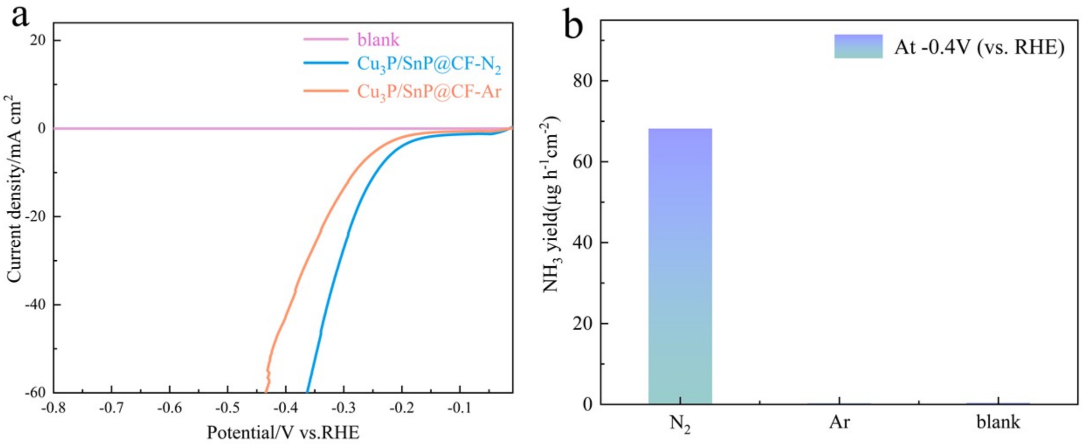

Fig. S3 (a) LSV curves in Ar- and N$_2$-saturated 1 M KOH solution and blank group, (b) Ammonia yield of catalysts in Ar- and N$_2$-saturated 1 M KOH solution and blank group

References

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