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Supporting Information

3D Porous P-doped Cu-Ni Alloy for Atomic H* Enhanced

Electrocatalytic Reduction of nitrate to Ammonia

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Figure S1. SEM images of (a) $Cu_{0.05}$ /SSM, (b) Cu-Ni₁₀/SSM.



Figure S2. HRTEM images of Cu-Ni $_{10}$ /SSM.



Figure S3. XRD images of Cu-Ni_v/SSM.



Figure S4. (a-j) CA curves and UV-visible absorption spectrum of different applied potentials (-0.35, -0.3, -0.25, -0.2, and -0.15 V *vs.* RHE). Cyclic stability tests of Cu-Ni- P_{30} /SSM: (k) CA curves, (l) UV-visible absorption spectra.



Figure S5. (a) UV-visible absorption spectrum with different concentrations of NH_4Cl . (b) The standard curve and equation for ammonia.



Figure S6. (a) ¹H NMR spectra of a series of standard ${}^{15}NH_4^+$ solutions with different concentration. (b) The standard curve of integral area (${}^{15}NH_4^+$ -15N/C₄H₄O₄) against ${}^{15}NH_4^+$ -15N concentration. (c) ¹H NMR spectra of a series of standard ${}^{14}NH_4^+$ solutions with different concentration. (d) The standard curve of integral area (${}^{14}NH_4^+$ -14N/C₄H₄O₄) against ${}^{14}NH_4^+$ -14N/C₄H₄O₄) against ${}^{14}NH_4^+$ -14N/C₄H₄O₄)



Figure S7. PDOS of the Cu d orbitals in Cu (111).



Figure S8. (a) XRD images of $Cu_{0.05}/SSM$. (b) The XPS survey spectrum of $Cu_{0.05}/SSM$ (c) High-resolution Cu 2p XPS spectra of $Cu_{0.05}/SSM$. The water contact angle (d) Cu foil (e) Cu foam (d) $Cu_{0.05}/SSM$.

Optimization of electrodeposition conditions

The morphology and loading capacity of the catalyst are directly influenced by electrodeposition conditions, thereby impacting its catalytic activity. Therefore, the hydrogen bubble template method was employed under various conditions, including deposition time (100-500 s), deposition current density (600-2000 mA cm⁻²), Cu concentrations (0.03, 0.04, 0.05, 0.06, and 0.07 M) and Cu²⁺/Ni²⁺ ratios (1, 5, 10, 15 and 20). Specifically, the catalytic activity of the samples was evaluated using the limiting current density in LSV, and electrodeposition synthesis conditions were optimized following the control variable method. To investigate the impact of deposition time on catalytic activity, other electrodeposition conditions remained constant (electrodeposition solution: 0.04 M CuSO₄, 1 M NaCl, 1 M H₂SO₄; constant current: 2000 mA cm⁻²). The LSV analysis reveals that the limiting current density increases from 85 mA cm⁻² to 139 mA cm⁻² with an increase in deposition time from 100 s to 300 s (Figure S9a). With the increase in deposition time, the number of active sites and electrocatalytic activity both increased. However, when the deposition time was extended from 300 s to 500 s, a decrease in limiting current density was observed from 139 mA cm⁻² to 122 mA cm⁻². It was found that the Cu deposition layer was likely to fall off from the substrate when the deposition time was greater than 400 s. Therefore, an electrodeposition time of 300 s is deemed optimal. The deposition current density was investigated under a constant electrodeposition time of 300 s. It can be seen from Figure S9b that the optimal performance of the prepared electrocatalyst for NRA is achieved at a deposition current density of 1000 mA cm⁻², as indicated by the limit current densities in LSV of 144, 153, 161, 157, 150, 147, 143 and 141 mA cm⁻² respectively when the current density varies between 600 to 2000 mA cm⁻². In conclusion, the optimal conditions for preparing NRA catalyst are achieved at 1000 mA cm⁻² and 300 s. In addition, the effects of CuSO₄ concentration, Cu²⁺/Ni²⁺ ratio, and P concentration on the catalytic activity of NRA were also investigated. Under the same electrodeposition conditions (1 M NaCl, 1 M H₂SO₄; constant current: 1000 mA cm⁻²;

time: 300 s), as shown in Figure S9c, the series of samples were named Cu_x/SSM (where x represents the concentration of $CuSO_4$, x = 0.03, 0.04, 0.05, 0.06 and 0.07 M). The limiting current densities (112, 161, 199, 186, and 174 mA cm⁻², respectively) in LSV exhibited a "volcanic" distribution with the maximum value observed at Cu0.05/SSM. Based on this, the impact of Cu²⁺/Ni²⁺ ratios in the electrodeposition solution on the performance of NRA electrocatalysts was investigated. The LSV curves of Cu-Ni/SSM, Cu-Ni₅/SSM, Cu-Ni₁₀/SSM, Cu-Ni₁₅/SSM, and Cu-Ni₂₀/SSM exhibited a similar trend (Figure S9d). As the potential becomes more negative, the current density increases gradually and decreases after reaching the maximum value. This can be attributed to the occurrence of competitive HER. Specifically, Cu-Ni₁₀/SSM in the Cu-Ni_v/SSM samples reached the maximum current density (226 mA cm⁻²) at -0.26 V. As the potential becomes more negative, the coverage of *H on the catalyst surface increases, resulting in a competition between HER and NRA. Because the electron transfer number of HER is less than that required by NRA, the current density shows a gradual decreasing trend. As the potential becomes more negative, HER dominates the reaction. When the LSV potential of Cu-Ni₁₀/SSM exceeds -0.42 V, the current density gradually increases and exhibits slight fluctuations due to significant H₂ interference in proximity to the electrode surface. Therefore, the optimal Cu^{2+}/Ni^{2+} ratio in an electrodeposition solution is 1:10.



Figure S9. Effect of electrodeposition time (a) and electrodeposition current (b) on NRA activity of samples. Effect of $CuSO_4$ concentration (c) and Cu^{2+}/Ni^{2+} ratios (d) in electrodeposition solution on NRA activity.



Figure S10. 3D performance comparison diagram of this work with other electrocatalysts in recent literature.



Figure S11.(a) The calculated models of Cu-Ni-P₃₀. (b)~(h) Atomic structures of the reaction intermediates during the NRA on the Cu-Ni-P₃₀ surface.