**d-orbital coupling modulation of CuNi alloy for acetonitrile electrochemical reduction and in-situ hydrogenation behavior characterization**

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Materials and method

Materials chemicals

Cupric chloride (CuCl$_2$·2H$_2$O), acetonitrile (CH$_3$CN, 99.8%) were purchased from Shanghai Aladdin Bio-Chem Technology. Nickel Chloride (NiCl$_2$·6H$_2$O), Polyethylene glycol 2000 (PEG 2000), Dimethyl sulfoxide (DMSO) were purchased from Sinopharm Shanghai Chemical Reagent Company. Ammonium citrate dibasic (C$_6$H$_{14}$N$_2$O$_7$) was purchased from Shanghai yuanye bio-technology. Sodium hydroxide (NaOH), Sodium acrylate (C$_3$H$_3$O$_2$Na) were purchased from Shanghai Meryer chemical technology. Ethylamine (CH$_3$CH$_2$NH$_2$, 50% in H$_2$O), Diethylamine (C$_4$H$_{11}$N, 99.5%) were purchased from Shanghai Macklin Biochemical. Acrolein (C$_3$H$_4$O), Deuterium oxide (D$_2$O, 99.9% for NMR) were purchased from Energy Chemical. 3-Hydroxypropionitrile (C$_3$H$_5$NO) were purchased from TCI Shanghai. Carbon cloth (W0S1011) were purchased from CeTech, copper foam (GJYCU001) were purchased from Guangjiayuan. Ultrapure water (18.25 MΩ cm) was used in all experiments.

Pretreatment for substrates

Carbon clothes were first immersed into 1 M NaOH at 80 °C for 5 hours, then they were treated by aqua regia (1:1 mixture of H$_2$SO$_4$ and HNO$_3$) for 12 hours. Finally, they were kept in ultrapure water.

Copper foams were subjected to ultrasonication in ultrapure water for 5 min then were ultrasonicated in ethanol for 5 min. They were dried at 40 °C, then use them immediately.

Synthesis of catalysts

The electrodeposition experiments were carried out in solutions of 1.4 mM Cupric chloride, 0.6 mM Nickel Chloride, 6 mM Ammonium citrate dibasic, 5 ppm PEG2000. Two pieces of Carbon cloth were used as working electrode and counter electrode respectively, An Ag/AgCl electrode was used as reference electrode. To co-electrodeposit CuNi alloy, -4 V versus Ag/AgCl was first applied for 5 seconds then -3 V versus Ag/AgCl was applied for 2400 seconds. Cu and Ni controls were synthesized without Nickel Chloride and Cupric chloride respectively, but the total M$^{2+}$ (M is Cu or Ni) concentration was 2 mM. CuNi/CF was electrodeposited on copper foam, the concentration of electrolyte is in accordance with the above, but the time needed at -3 V vs. Ag/AgCl was extended to 4800s.

All of these catalysts were synthesized under 26 °C and kept in vacuum box.

Characterization

The morphology of catalysts was collected through scanning electron microscope (SEM, JEOL S-4800). The crystalline structure of catalysts was characterized by a Rigaku SmartLab-3kW Powder X-Ray Diffractometer (XRD) with Cu Kα radiation (λ = 1.540598 Å) operating at 30 kV and 30 mA. The dark-field image, element mappings, selected area electron diffraction and high-resolution TEM were all carried out by JEOL JEM-F200 transmission electron microscope (TEM). The chemical state
was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB250Xi) and soft X-ray absorption spectroscopy (sXAS, beamlines BL10B of the NSRL in Hefei, China). Raman spectra were collected through Horiba HR Evolution. The composition of CuNi alloy was detected by an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent, Agilent 5110). Characterization of acetonitrile reduction reaction liquid product was employed by nuclear magnetic resonance technique (NMR, Bruker BioSpin AG, AVANCE NEO 400) while the gas product analysis was carried out by gas chromatography (GC-2014 C). Operando synchrotron radiation FTIR measurements were made at the infrared beamline BL10B of National Synchrotron Radiation Laboratory (NSRL, China)

**Electrochemical measurements**

The electrochemical experiments were carried out in a three-electrode electrochemical cell connected to a electrochemical workstation CHI 660E. Cathodic electrolyte is 1 M NaOH, anodic electrolyte is 1 M NaOH + 8 wt% acetonitrile, cathode and anode are separated by an anion-exchange membrane. The as-prepared catalysts on carbon cloth or copper foam serve as working electrode, mercuric oxide electrode (Hg/HgO) and a platinum sheet (1×2 cm²) electrode serve as reference and counter electrodes, respectively. The geometric surface area of catalyst deposited on carbon cloth and copper foam was 1 cm² and 0.5 cm², respectively. Linear sweep voltammetric (LSV) measurements were carried out at a scan rate of 5 mV s⁻¹. The potentials versus Hg/HgO were converted to RHE according the equation: E (RHE) = E (Hg/HgO) + 0.098 + 0.0591 × PH. 90 % IR compensation was applied for LSV measurements. Electric double layer capacitance is obtained by the cyclic voltammetry (CV) method with scan rate:20, 40, 60, 80, 100 mV s⁻¹. EIS measurements were conducted at 0.2 V vs. RHE and the range from 100 kHZ to 0.01 HZ.

**Products faradic efficiency measurements**

Using internal standard method to measure ethylamine faradic efficiency. Cathodic electrolyte was first applied a certain potential (in the range of -0.3 V to -0.8 V) for a while (the total quantity of electric charge is Q_total, and Q_total is more than 100 C). After reaction, 100 μL cathodic electrolyte was mixed with 900 μL ultrapure water. Then took out 500 μL such solution mixed with 40 μL internal standard (7.04 mM Dimethyl sulfoxide + 0.1 M NaOH) and 60 μL D₂O. This mixture was transferred to a nuclear magnetic resonance (NMR) sample tube and analyzed by ¹H NMR with 400 MHZ spectrometer. Dividing the peak area of CH₂ by the peak area of DMSO to get Peak Integration, then calculated the total ethylamine yield through internal standard curves (figure S15) and the total electric charges transferred to ethylamine is Q_ethylamine. The ethylamine faradic efficiency is Q_ethylamine/Q_total × 100%.

The ethylamine yield rate (mol cm⁻² h⁻¹) is $J \times FE_{ethylamine} \times 3600 \ s \div F \div 4$. $J$ is the total current density, $FE_{ethylamine}$ is the ethylamine faradic efficiency, $F$ is faradic constant, an acetonitrile molecule needs 4 electrons to be converted into an ethylamine molecule.

The H₂ faradic efficiency was measured by gas chromatograph. In the same way, we calculated the total electric charges transferred to H₂(Q_hydrogen), the H₂ faradic efficiency is Q_hydrogen/Q_total × 100%.
Theoretical calculations

Density Function Theory (DFT) Calculations: In this work, all DFT simulations were conducted using CASTEP code implemented in the Materials Studios package. The Perdew–Burke–Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) was used to conduct the electron exchange-correlation potential. We employed ultrasoft pseudopotentials, and the kinetic energy cutoff was set to 450 eV for the plane-wave basis set. The Brillouin zone integration was sampled with a $2 \times 2 \times 1$ Monkhorst–Pack mesh k-point. The energetic and force tolerances were set to $2 \times 10^{-5}$ eV/atom and 0.005 eV/Å. A CuNi (111) plane with a vacuum region of 15 Å along the Z-axis was constructed based on the XRD and HRTEM results for calculation, and we did the same things for Cu. The free energy ($\Delta G$) calculations of each elementary step were based on the standard hydrogen electrode model, which can be determined as

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

$\Delta E$ is the reaction energy, $\Delta S$ is the entropy change and $\Delta E_{ZPE}$ is the difference in zero-point energy.

We used a complete linear-synchronous-transitions (LST) and quadratic synchronous transitions (QST) approach for transition state searching.
**Figure S1.** SEM images of (a-c) Cu, (d-f) CuNi, (g-i) Ni

**Figure S2.** (a) The comparison of XRD patterns (no smooth) for Cu and CuNi alloy. (b) Corresponding line scan profiles of figure 1c. (c) Corresponding line scan profile of figure S3.

The results of line scan profiles and XRD is coherent. Meanwhile, DFT calculation exhibits that the lattice constant of Cu$_3$Ni$_4$ is $a=b=c=3.601$ Å which is 0.028 Å smaller than that of Cu ($a=b=c=3.629$ Å), and the difference of their (111) interplanar spacing is 0.016 Å.
Figure S3. SAED and HRTEM images of Cu

Compared with the SAED of CuNi (figure 1c), the pattern of Cu is more like spotty, which indicates that Cu is less polycrystalline than CuNi. XRD in figure 1b shows that the crystallite size of CuNi is smaller than that of Cu, which can explain the difference between the SAED of Cu and CuNi.
Figure S4. The XPS survey spectrum of Cu, Ni and CuNi

Figure S5. The C 1s XPS spectrum of (a) Cu, (b) CuNi and (c) Ni
Figure S6. (a) Cu 2p region and (b) Ni 2p region of XPS spectra spectrum for CuNi alloy, metallic Cu and Ni.

For Cu 2p spectra, both Cu $2p_{3/2}$ and Cu $2p_{1/2}$ can be fitted into two peaks which correspond to Cu$^{0}$ and Cu$^{+}$. Specifically, all fitted peaks of CuNi alloy show lower binding energy than that of Cu (the binding energy of each fitted peaks are presented in Table S2), which suggests that there are more electrons transferred from Ni to Cu atoms in CuNi. Ni $2p_{3/2}$ spectra can be fitted into three peaks and their satellite peaks. The peak at 853 eV belongs to Ni$^{0}$, while peaks at 854 eV and 856 eV are corresponded to Ni$^{2+}$. Ni$^{0}$ is dominant in both CuNi alloy and Ni. Compared with Ni, each fitted peaks of CuNi alloy has a positive shift, which means that Ni atoms in CuNi alloy lose electrons.
Figure S7. Synchrotron XAS spectra of (a) Cu L-edge and (b) Ni L-edge for CuNi alloy and CuNi alloy after Ar/H$_2$ annealing (at 350°C for 3 hours).

XAS spectra show that the L$_3$ edges of Cu and Ni both slightly shift to lower photon energy after Ar/H$_2$ annealing, which suggests that the electrodeposited CuNi alloy is mostly zero valent and that its surface has been slightly oxidized.
Figure S8. Raman spectra of CuNi/CC in air
Figure S9. Cyclic voltammograms for Cu (a), Ni (b) and CuNi/CC (c) in the non-Faradaic capacitive range. (d) The plots of ΔJ versus scan rates for Cu, Ni and CuNi/CC.
Figure S10. Total current density versus potential in 4 wt%, 8wt% and 12 wt% acetonitrile in 1 M NaOH on CuNi/CC catalyst.
Figure S11. $^1$H NMR spectra of standard ethylamine solution, standard acetonitrile solution and acetonitrile solution after ACNRR catalyzed by CuNi/CC.

Figure S12. The overall $^1$H NMR spectra of the electrolyte after ACNRR catalyzed by CuNi/CC.
Figure S13. $^1$H NMR spectra of standard ethylamine solution, and the mixture of ethylamine and diethylamine.

Explanation:
The single peak at 2.703 ppm is the chemical shift of H atom in DMSO. The quartet at around 2.61 ppm is the chemical shift of H atom in -CH$_2$- while the triplet at around 1.02 ppm is the chemical shift of H atom in -CH$_3$.
The quartet of ethylamine doesn’t overlap with diethylamine, but their triplets are overlapped with each other, therefore, we used the quartet area to calculate ethylamine faradic efficiency.
Figure S14. Internal standard curve of ethylamine.
**Figure S15.** Current density versus the applied potential for ACNRR in 8 wt% acetonitrile in 1 M NaOH on Cu, Ni and CuNi/CC catalysts (no IR compensation).
Figure S16. $^1$H NMR spectra of electrolyte after 20-hour stability test.

\[
\text{CH}_3\text{CH}=\text{NH} + \text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CH}=\text{NCH}_2\text{CH}_3 + \text{NH}_3 \tag{1}
\]

\[
\text{CH}_3\text{CH}=\text{NCH}_2\text{CH}_3 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3 + 2\text{OH}^- \tag{2}
\]

In stability test, ethylamine concentration increased as time went by. Higher ethylamine concentration means higher chance for the combination of CH$_3$CH$_2$NH$_2$ and CH$_3$CH=NH. But the diethylamine yield is still very low, which suggests that CuNi has excellent catalytic selectivity for ethylamine in ACNRR.
Figure S17. The gas chromatogram spectra of the gas product towards ACNRR catalyzed by CuNi/CC.
Figure 18. v-t curve towards ACNRR at -20 mA cm$^{-2}$ for 20 hours

![v-t curve](image)

Figure S19. (a) XRD patterns of CuNi/CC and CuNi/CC after stability test. XPS spectra of CuNi/CC and CuNi/CC after stability test in (b) Cu 2p region and (c) Ni 2p region.

The XRD patterns show that no new phase appears after test. The XPS spectra exhibit that the binding energy of Cu has a slight negative shift, which comes from the reduction of Cu$_2$O.
Figure S20. LSV curves of Cu, Ni, CuNi/CC, CuNi/CF, Carbon cloth and copper foam towards ACNRR (a), and the corresponding Tafel slopes (b).
**Figure S21.** Stability test over 24h in H-type cell using CuNi/CF as the catalyst at a constant current density of 100 mA cm$^{-2}$ and ethylamine FE at 1h, 3h, 6h, 12h and 24h.

**Figure S22.** SEM images of (a) CuNi/CF and (b) CuNi/CF after stability test.
Figure 23. Ethylamine faradic efficiency of ACNRR at -100 mA cm$^{-2}$ catalyzed by CuNi/CF in different electrolyte.

From left to right:
- Electrolyte one is 1.95 M acetonitrile + 22.2 mM Sodium acrylate + 1 M NaOH.
- Electrolyte two is 1.95 M acetonitrile + 14.3 mM Acrolein + 1 M NaOH.
- Electrolyte three is 1.95 M acetonitrile + 11.3 mM 3-Hydroxypropionitrile + 1 M NaOH.
- Electrolyte four is 1.95 M acetonitrile + 11.3 mM 3-Hydroxypropionitrile + 14.3 mM Acrolein + 22.2 mM Sodium acrylate + 1 M NaOH.
Figure S24. $^1$H NMR spectra of ACN + AA electrolyte before and after ACNRR.

Figure S25. $^1$H NMR spectra of ACN + ACL electrolyte before and after ACNRR.

Figure S26. $^1$H NMR spectra of ACN + R(OH)CN electrolyte before and after ACNRR.
Figure S27. $^1$H NMR spectra of ACN + R(OH)CN + AA + ACL electrolyte before and after ACNRR.
Figure S28. The corresponding Tafel slopes towards LSV curves of ACNRR.
Figure S29. Nyquist plots of Cu, Ni and CuNi/CC at 0.2 V vs. RHE
**Figure S30.** Devices for in-situ SR-FTIR (a) and Raman (b) experiments.
Figure S31. (a) In-situ SR-FTIR spectra of CuNi towards O-H stretching vibration. The curves from top (deep read) to bottom (blue) are OCP, 0.2 V to -0.6 V vs. RHE respectively, -0.1 V per step. (b) Move all curves to the same starting points.
Figure S32. Gibbs free energy diagrams for $^*\text{CH}_3\text{CH}_2\text{NH}_2$ desorption on Ni (111)
Figure S33. (a) LSV curves of Cu and CuNi/CC towards HER. (b) The corresponding Tafel slopes.

Figure S34. The LSV curves of Cu, Ni and CuNi towards ACN reduction, no iR compensation.
Table S1. The market sizes and prices of acetonitrile and ethylamine

<table>
<thead>
<tr>
<th>Product</th>
<th>Market size ($, 2022)</th>
<th>Price ($/kg)</th>
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<tr>
<td>ethylamine</td>
<td>2,087.9 million [1]</td>
<td>10-100 [3]</td>
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Table S2. 111 Peak position in XRD curves of Cu, Ni and CuNi and their corresponding (111) interplanar spacings.

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<th>Catalyst</th>
<th>2θ</th>
<th>d_{111}</th>
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<tr>
<td>Cu</td>
<td>43.3°</td>
<td>2.09 Å</td>
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<tr>
<td>CuNi</td>
<td>43.5°</td>
<td>2.08 Å</td>
</tr>
<tr>
<td>Ni</td>
<td>44.7°</td>
<td>2.03 Å</td>
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Table S3. XPS peak splitting fitting results

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<tr>
<th>Catalyst</th>
<th>Cu² 2p_{3/2}</th>
<th>Cu² 2p_{1/2}</th>
<th>Cu⁺ 2p_{3/2}</th>
<th>Cu⁺ 2p_{1/2}</th>
<th>Ni⁰ 2p_{3/2}</th>
<th>Ni²⁺ 2p_{3/2} (1)</th>
<th>Ni²⁺ 2p_{3/2} (2)</th>
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<tbody>
<tr>
<td>Cu</td>
<td>933.0 eV</td>
<td>933.61 eV</td>
<td>952.94 eV</td>
<td>954.01 eV</td>
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<td></td>
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<tr>
<td>CuNi</td>
<td>933.04 eV</td>
<td>933.51 eV</td>
<td>952.84 eV</td>
<td>953.92 eV</td>
<td>853.55 eV</td>
<td>854.53 eV</td>
<td>856.56 eV</td>
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<tr>
<td>Ni</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>853.11 eV</td>
<td>853.99 eV</td>
<td>855.83 eV</td>
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Table S4. The FEethylamine and corresponding current density obtained by electrochemical ACNRR of various reported electrocatalysts.

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<th>Catalyst</th>
<th>Electrolyte</th>
<th>FEthylamine</th>
<th>Current density</th>
<th>Reference</th>
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<tr>
<td>CuNi alloy</td>
<td>1 M NaOH</td>
<td>97%</td>
<td>114 mA cm⁻²</td>
<td>This work</td>
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<tr>
<td></td>
<td>+ 8 wt% ACN</td>
<td>82.8%</td>
<td>602.8 mA cm⁻²</td>
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</tr>
<tr>
<td>Cu NPs</td>
<td>1 M NaOH</td>
<td>98.2%</td>
<td>10 mA cm⁻²</td>
<td>[5]</td>
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<tr>
<td></td>
<td>+ 8 wt% ACN</td>
<td>62.9%</td>
<td>600 mA cm⁻²</td>
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<tr>
<td>Cu nanoarrays/Cu foil</td>
<td>0.5 M KHCO₃+CO₂</td>
<td>94%</td>
<td>&lt; 40 mA cm⁻²</td>
<td>[6]</td>
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<tr>
<td></td>
<td>+ 0.5 M ACN</td>
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<td></td>
<td></td>
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<tr>
<td>CuNiO metallic aerogels</td>
<td>1 M NaOH</td>
<td>95.5%</td>
<td>19.4 mA cm⁻²</td>
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<td></td>
<td>+ 8 wt% ACN</td>
<td>~80%</td>
<td>72.9 mA cm⁻²</td>
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References

4  [Reference number]
