Supporting Information

Interfacial N-Cu-S Coordination Mode of CuSCN/C$_3$N$_4$ with Enhanced Electrocatalytic Activity for Hydrogen Evolution

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Experimental section:

1、 Estimation of electrochemically active surface areas ($A_{echem}$)

Based on previous reports, cyclic voltammetry (CV) could be carried out in neutral media to probe the electrochemical double-layer capacitance ($C_{dl}$) of various samples at non-Faradaic overpotentials as the means for estimating the $A_{echem}$ of samples. Accordingly, a series of CV measurements were performed at various scan rates (4 mV s$^{-1}$, 8 mV s$^{-1}$, 12mV s$^{-1}$, 16 mV s$^{-1}$, etc.) in 0.1 to 0.2 V vs. RHE range, and the sweep segments of the measurements were set to 10 to ensure consistency. By plotting the difference in current density ($J$) between the anodic and cathodic sweeps ($J_{anodic} - J_{cathodic}$) at 0.15 V vs. RHE against the scan rate, a linear trend was observed. The slope of the fitting line is found to be equal-to-twice the geometric $C_{dl}$, which is proportional to the $A_{echem}$ of the materials. Therefore, the $A_{echem}$ of different samples can be compared with one another based on their $C_{dl}$ values. However, it should be noted that this comparison makes sense only when the measurements of materials were carried out under the same conditions.

2、 Measurements of electrochemical impedance spectroscopy (EIS)

EIS studies were performed under operating conditions (i.e., at a cathodic bias that drives rapid hydrogen evolution) at -0.17 V vs. RHE with an applied sinusoidal voltage at amplitude of 5 mV while sweeping the frequency from 100 kHz to 0.01 Hz. The impedance data were then fitted, and the geometric values of series resistance ($R_s$) and charge transfer resistance ($R_{ct}$) were measured.

3、 TOF calculation

To calculate the per site turnover frequency (TOF), we used the following formula:

$$TOF = \frac{\text{number of total hydrogen turnovers/cm}^2 \text{ of geometric area}}{\text{number of active sites/cm}^2 \text{ of geometric area}}$$

The total number of hydrogen turnovers was calculated from the current density according to:
\[
\text{no. of } H_2 = \\
\left( \frac{mA}{cm^2} \right) \left( \frac{1C^{-1}}{1000 mA} \right) \left( \frac{1 \text{ mol of } e^{-}}{96485.3 C} \right) \left( \frac{1 \text{ mol of } H_2}{2 \text{ mol of } e^{-}} \right) \left( \frac{6.022 \times 10^{22} \text{ } H_2 \text{ molecules}}{1 \text{ mol } H_2} \right)
\]
\[
= 3.12 \times 10^{15} \frac{H_2/s}{cm^2} \text{ per } mA/cm^2
\]

Because the interfacial coordinated N-Cu-S can act as the catalytically active species for CuSCN/C\textsubscript{3}N\textsubscript{4}, therefore, the surface low-coordinated Cu ions of CuSCN were considered to be the catalytically active species for CuSCN/C\textsubscript{3}N\textsubscript{4} and pure CuSCN. On the basis of the electrochemical active surface area together with the unit cell (volume of 139.87 \text{ Å}^3) of the CuSCN crystal structure in the cases of CuSCN/C\textsubscript{3}N\textsubscript{4} and pure CuSCN, a similar approach was used to estimate TOF for them. Active sites per real surface area:

\[
\text{Active sites}_{\text{CuSCN/C3N4}} = \text{Active sites}_{\text{CuSCN}} = \left( \frac{2 \text{ atom/unit cell}}{139.87 \text{ Å}^3 / \text{unit cell}} \right) = 5.89 \times 10^{14} \times \text{ atoms cm}^{-2}
\]

\[
\text{TOF} = \frac{(3.12 \times 10^{15} \frac{H_2/s}{cm^2} \text{ per } mA/cm^2)}{\text{surface sites} \times A_{\text{chem}} \times |j|}
\]

Figure S1. Raman spectra of C\textsubscript{3}N\textsubscript{4} and CuSCN/C\textsubscript{3}N\textsubscript{4}
**Figure S2.** C 1s XPS spectra of CuSCN/C$_3$N$_4$ and pure CuSCN taken after synthesis.

**Figure S3.** SEM images of pure CuSCN.

**Figure S4.** HRTEM images of a) CuSCN/C$_3$N$_4$ and b) pure CuSCN. c-g) elemental mappings of pure CuSCN.
**Figure S5.** Optimized structure CuSCN coupled with one-layer C\textsubscript{3}N\textsubscript{4} shell.

**Figure S6.** Calculated charge-density differences of CuSCN coupled with three-layer C\textsubscript{3}N\textsubscript{4} shells. The isosurface value of the colour region is 0.6 e Å\textsuperscript{3}. The green and yellow regions refer to increased and decreased charge distributions. Blue, red, brown and white represent Cu, S, C, and N atoms, respectively.
Figure S7. Electrical equivalent circuit model for fitting the EIS response of hydrogen evolution reaction on CuSCN/C$_3$N$_4$, pure CuSCN, CuS, and C$_3$N$_4$ electrodes, where $R_s$ is series resistance, $R_{ct}$ at low frequency denotes charge transfer resistance, $R_p$ at high frequency region relates to the surface roughness of the material, and the double-layer capacitance ($C_{dl}$) is represented by the elements CPE1 and CPE2.

Figure S8. Plots used for evaluating the $C_{dl}$ of CuSCN/C$_3$N$_4$, pure CuSCN, CuS and C$_3$N$_4$.

Table S1. Local structure parameters around Cu in samples estimated by EXAFS
analysis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Shell</th>
<th>$R(\text{Å})^{[a]}$</th>
<th>$N^{[b]}$</th>
<th>$\sigma^2(10^{-3} \text{Å}^2)^{[c]}$</th>
<th>$\Delta E_0$ [eV]^{[d]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CuSCN</td>
<td>Cu-N</td>
<td>1.91</td>
<td>1.0</td>
<td>8.1</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>Cu-S</td>
<td>2.31</td>
<td>3.0</td>
<td>4.9</td>
<td>1.2</td>
</tr>
<tr>
<td>CuSCN/C$_3$N$_4$</td>
<td>Cu-N</td>
<td>2.07</td>
<td>1.1</td>
<td>8.3</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>Cu-S</td>
<td>2.29</td>
<td>3.0</td>
<td>4.6</td>
<td>2.7</td>
</tr>
</tbody>
</table>

[a] $R$ = distance between absorber and backscatter atoms; [b] $N$ = coordination number; [c] $\sigma^2$ = Debye-Waller factor; [d] $\Delta E_0$ = energy shift.

Table S2. Comparison of the electrocatalytic performance of CuSCN/C$_3$N$_4$ versus HER electrocatalysts reported recently.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte Solution</th>
<th>Current Density (j)</th>
<th>Overpotential at the Corresponding j</th>
<th>Stability</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSCN/C$_3$N$_4$</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>10 mA/cm$^2$</td>
<td>85 mV</td>
<td>20 h</td>
<td>This work</td>
</tr>
<tr>
<td>CuCo@NC</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>10 mA/cm$^2$</td>
<td>145 mV</td>
<td>8 h</td>
<td>[5]</td>
</tr>
<tr>
<td>NiCu@C</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>10 mA/cm$^2$</td>
<td>48 mV</td>
<td>3.3 h</td>
<td>[6]</td>
</tr>
<tr>
<td>Cu-CMP</td>
<td>1 M KOH</td>
<td>1 mA/cm$^2$</td>
<td>190 mV</td>
<td>_</td>
<td>[7]</td>
</tr>
<tr>
<td>CFP/NiCo$_2$O$_4$/CuS</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>10 mA/cm$^2$</td>
<td>72.3 mV</td>
<td>50 h</td>
<td>[8]</td>
</tr>
<tr>
<td>Cu$_2$S$_2$/MoS$_2$</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>10 mA/cm$^2$</td>
<td>133 mV</td>
<td>10 h</td>
<td>[9]</td>
</tr>
<tr>
<td>Cu$_3$P NW/CF</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>10 mA/cm$^2$</td>
<td>143 mV</td>
<td>25 h</td>
<td>[10]</td>
</tr>
<tr>
<td>Cu NDs/Ni$_3$S$_2$ NTs-CFs</td>
<td>1 M KOH</td>
<td>10 mA/cm$^2$</td>
<td>128 mV</td>
<td>30 h</td>
<td>[11]</td>
</tr>
<tr>
<td>Cu/Cu$_2$O</td>
<td>0.5 M KPi</td>
<td>8 mA/cm$^2$</td>
<td>~320 mV</td>
<td>_</td>
<td>[12]</td>
</tr>
</tbody>
</table>
Cu@NiFe LDH | 1M KOH | 10 mA/cm² | 116 mV | 48 h | [13]
Cu@CoSx/CF | 1M KOH | 10 mA/cm² | 134 mV | 200 h | [14]
N,P-doped GO | 0.5 M H₂SO₄ | 30 mA/cm² | 210 mV | 4 h | [15]
N,S-doped graphene | 0.5 M H₂SO₄ | 10 mA/cm² | 276 mV | _ | [16]
C₃N₄@N-doped graphene | 0.5 M H₂SO₄ | 10 mA/cm² | 240 mV | _ | [17]
TiO₂ NDs/Co NSNTs-CFs | 1.0 M KOH | 10 mA/cm² | 108 mV | 100 h | [18]
Mn doped CoSe₂ | 0.5 M H₂SO₄ | 10 mA/cm² | ~190 mV | 17 h | [19]

**Table S3.** The TOF values of CuSCN/C₃N₄ and pure CuSCN at the overpotential of 0.2 V vs. RHE.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSCN/C₃N₄</td>
<td>6.35</td>
</tr>
<tr>
<td>Pure CuSCN</td>
<td>1.36</td>
</tr>
</tbody>
</table>

**Table S4.** The ICP-OES measured values of Cu content for CuSCN/C₃N₄ and pure CuSCN in 0.5 M H₂SO₄ electrolyte after the chronoamperometric measurement for a 5, 10, and 20 h period.

<table>
<thead>
<tr>
<th>Period</th>
<th>Cu content in electrolyte for CuSCN/C₃N₄</th>
<th>Cu content in electrolyte for pure CuSCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 h</td>
<td>0.1 mg</td>
<td>0.7 mg</td>
</tr>
<tr>
<td></td>
<td>10 h</td>
<td>0.1 mg</td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>20 h</td>
<td>0.2 mg</td>
<td>2.3 mg</td>
</tr>
</tbody>
</table>

References


