Supporting Information

Metal-Modified C₃N₁ Monolayer Sensors for Battery Instability Monitoring

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References
Computational section

For the original C₃N₁, Ag-C₂N₁, Cu-C₂N₁, PF₅, NO₂, NH₃, H₂O, C₂H₄, and C₂H₆, all structural optimization and electronic performance calculations are performed using DFT, based on Dmol³ code [1] under the Perdew-Burke-Ernzerhof functional, gradient approximation method correlation [2, 3], double precision number basis set polarization function is used to process atomic orbitals. The dispersion-corrected DFT method was selected based on Grimme vdW correction [4], which can accurately describe the interaction in all weak calculations. The global cut-off radius of real space is 4.9 Å, and the Monkhorst–Pack scheme is used to sample 3 × 2 × 1 k points in the Brillouin area to complete high-quality theoretical evaluation. In addition, the convergence tolerance of geometry optimization is 1 × 10⁻⁵ Ha for the total energy, 0.002 Ha/Å for the atomic force, and 0.005 Å for the highest displacement, respectively. The electron distribution and charge transfer were calculated using the Mulliken method [5]. To eliminate interactions between periodic images, use a 20 Å vacuum layer vertically to the Cu/Ag-C₂N₁ monolayer. The C-N bond length is 1.41 Å, the C-C bond length is 1.43 Å, and the maximum spacing of C-N-C-C is 2.83 Å in the initial C₃N₁ monolayer.
Details of thermodynamic calculation

These mainly include enthalpy, entropy, and the Gibbs free energy.

First, enthalpy (H) is calculated by

\[
H = H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + RT
\]

where \( H_{\text{trans}} \), \( H_{\text{rot}} \) and \( H_{\text{vib}} \) are the translation enthalpy, rotation enthalpy, and vibration enthalpy (kcal/mol), respectively. \( R \) and \( T \) are the ideal gas constant (8.314 J/mol/K) and the absolute temperature (K), accordingly. \( k \) is the Boltzmann constant, \( h \) is Planck's constant, and \( v_i \) is the vibrational frequency.

Second, entropy (S) is given by

\[
S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}}
\]

\[
= \frac{5}{2} R \ln T + \frac{5}{2} R \ln w - \frac{5}{2} \ln p - 2.3482
\]

\[
+ \frac{R}{2} \ln \left[ \frac{\pi^2 c_l A B C}{\sigma h h h (hc)^3} \right]
\]

\[
+ \frac{3}{2} R + R \sum_i \frac{h v_i / k T \exp \left( - h v_i / k T \right)}{1 - \exp \left( - h v_i / k T \right)}
\]

\[
- R \sum_i \ln \left[ 1 - \exp \left( - h v_i / k T \right) \right]
\]

Where \( S_{\text{trans}} \), \( S_{\text{rot}} \), and \( S_{\text{vib}} \) are the translation, rotation, and vibration entropies (cal/mol/K), accordingly. \( w \) is the molecular mass, \( p \) is the pressure, \( \sigma \) is the symmetry number, \( c \) is the molar concentration of the molecules, and \( I_{A} (B, C) \) is the moment of inertia.

Finally, the Gibbs free energy (G) (kJ/mol) is defined as

\[
G = E(0K) + H - T \cdot S
\]

where \( E(0K) \) is the zero-point energy (kcal/mol).
Details of diffusion performance calculation

From the point of view of gas motion (diffusion), the main energy barrier to be overcome in NO\(_2\) adsorption on the Ag-C\(_2\)N\(_1\) and Cu-C\(_2\)N\(_1\) monolayer was the gas diffusion energy barrier. The diffusion activation energy can be obtained by calculating the gas motion parameters according to molecular dynamics simulation with our previous work [6], and by this means, the energy barrier of NO\(_2\) adsorption on the Cu/Ag-C\(_2\)N\(_1\) monolayer can be well verified. Therefore, the mean-squared displacement (MSD) and diffusion coefficients (Ds) were used to investigate the diffusion properties of gases according to the Einstein diffusion law; these quantities were computed by the following equations.

\[
MSD(t) = \frac{1}{N} \sum_{i=1}^{N} \langle |r_i(t) - r_i(0)|^2 \rangle \tag{4}
\]

\[
D_s = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} \langle |r_i(t) - r_i(0)|^2 \rangle \tag{5}
\]

where \(N\) is the number of molecules, \(r_i(t)\) is the position of molecule when the time is \(t\), and \(r_i(0)\) is the initial position. According to Equations (4) and (5), the diffusion coefficients were calculated and are shown in Table S2 and S3.

After a series of the diffusion coefficients, \(D_s\), of NO\(_2\) at different temperatures were obtained, the diffusion activation energy of NO\(_2\) could be calculated by means of the Arrhenius equation:

\[
D_s = D_0 \exp(-E'_a / RT) \tag{6}
\]

where \(E'_a\), \(A\), and \(R\) refer to the Arrhenius activation energy, the Arrhenius factor, and gas constant, respectively. Equation (6) can also be expressed as:

\[
\ln D_s = \ln A - E'_a / RT \tag{7}
\]

According to the data in Table S3 and Equation (7), the diffusion activation energy


$E'_a$ could be directly calculated from the slope of the fitted curve. Figure 6 shows the Arrhenius temperature dependence of the diffusion coefficients along with the activation energy for diffusion. Therefore, the energy barriers to be overcome in the process of NO$_2$ diffusion to the monolayer of Ag-C$_2$N$_1$ and Cu-C$_2$N$_1$ are 2.7 kJ/mol and 2.5 kJ/mol.
Figure S1. The energy fluctuations with time process for the *ab initio* molecular dynamics of Cu/Ag-C$_2$N$_1$ monolayer.
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<table>
<thead>
<tr>
<th>Gas</th>
<th>Cu-C$_2$N$_1$</th>
<th>Ag-C$_2$N$_1$</th>
</tr>
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<tbody>
<tr>
<td>C$_2$H$_4$</td>
<td>-0.09</td>
<td>-0.07</td>
</tr>
<tr>
<td>H$_2$O</td>
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<td>0.09</td>
</tr>
<tr>
<td>NO$_2$</td>
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<td>NH$_3$</td>
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<td>0.13</td>
</tr>
<tr>
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<td>0.06</td>
</tr>
<tr>
<td>PF$_5$</td>
<td>0.01</td>
<td>-0.91</td>
</tr>
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</table>
Table S2. Diffusion coefficient of six gases on the Cu/Ag-C$_2$N$_1$ monolayer at 300 K.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Cu-C$_2$N$_1$</th>
<th>Ag-C$_2$N$_1$</th>
</tr>
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<tbody>
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<td>C$_2$H$_4$</td>
<td>4.89</td>
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</tr>
<tr>
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<td>6.60</td>
</tr>
<tr>
<td>NO$_2$</td>
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<td>2.83</td>
</tr>
<tr>
<td>NH$_3$</td>
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<td>5.07</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
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<td>4.13</td>
</tr>
<tr>
<td>PF$_5$</td>
<td>4.39</td>
<td>3.72</td>
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Table S3. Diffusion coefficients of NO$_2$ on the Cu/Ag-C$_2$N$_1$ at different temperatures.

<table>
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<th>T (K)</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-C$_2$N$_1$</td>
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<td>3.12</td>
<td>3.37</td>
<td>4.44</td>
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<td>Ag-C$_2$N$_1$</td>
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<td>3.78</td>
<td>3.70</td>
<td>5.18</td>
<td>-</td>
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Table S4. The recovery time (s) of the gas on the Cu-C$_2$N$_1$.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>C$_2$H$_4$</th>
<th>H$_2$O</th>
<th>NO$_2$</th>
<th>NH$_3$</th>
<th>C$_2$H$_6$</th>
<th>PF$_5$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.0×10$^3$</td>
<td>1.9×10$^{53}$</td>
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<td>3.6×10$^{-9}$</td>
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<tr>
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<td>4.4×10$^{23}$</td>
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<td>8.8×10$^{-11}$</td>
</tr>
<tr>
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<td>1.2×10$^{-2}$</td>
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<td>2.4×10$^{-11}$</td>
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<tr>
<td>800</td>
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<td>6.6×10$^{-4}$</td>
<td>2.9×10$^{-8}$</td>
<td>1.6×10$^{-11}$</td>
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Table S5. The recovery time (s) of the gas on the Ag-C$_2$N$_1$.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>C$_2$H$_4$</th>
<th>H$_2$O</th>
<th>NO$_2$</th>
<th>NH$_3$</th>
<th>C$_2$H$_6$</th>
<th>PF$_5$</th>
</tr>
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<tbody>
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<td>1.9×10$^{48}$</td>
<td>1.4×10$^{10}$</td>
<td>5.8×10$^{-4}$</td>
<td>4.4×10$^5$</td>
</tr>
<tr>
<td>300</td>
<td>1.3×10$^{14}$</td>
<td>2.9</td>
<td>7.1×10$^{42}$</td>
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<td>9.5×10$^{-5}$</td>
<td>1.1×10$^4$</td>
</tr>
<tr>
<td>400</td>
<td>3.7×10$^{7}$</td>
<td>2.2×10$^{-3}$</td>
<td>1.4×10$^{29}$</td>
<td>1.3×10$^{3}$</td>
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<td>1.1</td>
</tr>
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<td>4.6×10$^{3}$</td>
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References


