Supporting Information

Efficient Urea Synthesis via One-Step N–C–N Coupling: Strong Metal-Support Interaction-Driven Planar Cu Clusters on two-dimensional Mo₂C MXene

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COMPUTATIONAL DETAILS

The dissolution potential \( U_{\text{diss}} = U^\circ_{\text{diss(bulk)}} - E_f/\text{n} \) is a good parameter to evaluate the electrochemical stability of the catalyst, where \( U^\circ_{\text{diss(bulk)}} \), \( E_f \) and \( \text{n} \) are respectively the standard dissolution potential \( (U^\circ_{\text{diss(bulk)}}) \) of the bulk metal, the generation energy of the catalyst, and the number of electrons involved in the dissolution. To be specific, the standard dissolution potential for bulk metals uses the experimental standard dissolution potential of the metal atoms \( (U^\circ_{\text{diss(bulk)}}) \). For the generation energy, it can be calculated according to \( E_f = (E_{\text{Cu}_4/\text{Mo}_2\text{C}} - E_{\text{Mo}_2\text{C}} - 4 \times E_{\text{Cu}})/4 \), where \( E_{\text{Cu}_4/\text{Mo}_2\text{C}} \), \( E_{\text{Mo}_2\text{C}} \), and \( E_{\text{Cu}} \) are respectively the total energy per atom in the cluster system, \( \text{Mo}_2\text{C} \), and \( \text{Cu} \) metal. Taking \( \text{Cu}_4/\text{Mo}_2\text{C} \) as an example, with \( U^\circ_{\text{diss(bulk)}} \) of 0.34 V, the calculated \( E_f \) is \(-0.50\) eV. Therefore, its \( U_{\text{diss}} \) can be derived by:

\[
U_{\text{diss}} = [0.34 \text{ V} - (-0.50 \text{ eV})/2\text{e}] = 0.59 \text{ V}.
\]
**Table S1.** The computed Gibbs free energy changes (ΔG, eV) of each elementary step during urea synthesis on the Cu₄/Mo₂C. The preferable elementary step was marked in red.

<table>
<thead>
<tr>
<th>Elementary step</th>
<th>ΔG</th>
</tr>
</thead>
<tbody>
<tr>
<td>* + NO → NO*</td>
<td>-1.06</td>
</tr>
<tr>
<td>NO* + NO → NO* + NO*</td>
<td>-0.69</td>
</tr>
<tr>
<td>NO* + CO → NO* + CO*</td>
<td>0.04</td>
</tr>
<tr>
<td>NO* + H⁺ + e⁻ → NOH*</td>
<td>0.21</td>
</tr>
<tr>
<td>NO* + H⁺ + e⁻ → HNO*</td>
<td>-0.11</td>
</tr>
<tr>
<td>NO⁺ + NO⁺ + CO → NO⁺ + NO⁺ + CO⁺</td>
<td>-0.29</td>
</tr>
<tr>
<td>NO⁺ + NO⁺ + H⁺ + e⁻ → NOH⁺ + NO⁺</td>
<td>0.30</td>
</tr>
<tr>
<td>NO⁺ + NO⁺ + H⁺ + e⁻ → HNO⁺ + NO⁺</td>
<td>0.19</td>
</tr>
<tr>
<td>NO⁺ + NO⁺ → &quot;NO-NO⁺&quot;</td>
<td>0.21</td>
</tr>
<tr>
<td>NO⁺ + NO⁺ + CO⁺ → NO⁺-NO⁺ + CO⁺</td>
<td>-0.01</td>
</tr>
<tr>
<td>NO⁺ + NO⁺ + CO⁺ → NO⁺-CO⁺ + NO⁺</td>
<td>0.53</td>
</tr>
<tr>
<td>NO⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → N⁺⁺-NO⁺⁺ + CO⁺</td>
<td>-0.71</td>
</tr>
<tr>
<td>NO⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → HNO⁺⁺-NO⁺⁺ + CO⁺</td>
<td>1.14</td>
</tr>
<tr>
<td>NO⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NOH⁺⁺-NO⁺⁺ + CO⁺</td>
<td>0.63</td>
</tr>
<tr>
<td>NO⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NOH⁺⁺-HNO⁺⁺ + CO⁺</td>
<td>0.69</td>
</tr>
<tr>
<td>NO⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NOH⁺⁺-NO⁺⁺ + COH⁺</td>
<td>2.85</td>
</tr>
<tr>
<td>NO⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NOH⁺⁺-NO⁺⁺ + CHO⁺</td>
<td>1.01</td>
</tr>
<tr>
<td>N⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NH⁺⁺⁺-NO⁺⁺ + CO⁺</td>
<td>-1.06</td>
</tr>
<tr>
<td>N⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → N⁺⁺⁺-NOH⁺⁺ + CO⁺</td>
<td>1.58</td>
</tr>
<tr>
<td>N⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → N⁺⁺⁺-HNO⁺⁺ + CO⁺</td>
<td>-0.69</td>
</tr>
<tr>
<td>N⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → N⁺⁺⁺-NO⁺⁺ + COH⁺</td>
<td>2.58</td>
</tr>
<tr>
<td>N⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → N⁺⁺⁺-NO⁺⁺ + CHO⁺</td>
<td>1.13</td>
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<tr>
<td>NH⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NH₂⁺⁺⁺-NO⁺⁺ + CO⁺</td>
<td>0.36</td>
</tr>
<tr>
<td>NH⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NH⁺⁺⁺-NOH⁺⁺ + CO⁺</td>
<td>1.58</td>
</tr>
<tr>
<td>NH⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NH⁺⁺⁺-HNO⁺⁺ + CO⁺</td>
<td>0.67</td>
</tr>
<tr>
<td>NH⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NH⁺⁺⁺-NO⁺⁺ + COH⁺</td>
<td>2.52</td>
</tr>
<tr>
<td>NH⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NH⁺⁺⁺-NO⁺⁺ + CHO⁺</td>
<td>0.98</td>
</tr>
<tr>
<td>NH₂⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NH₂⁺⁺⁺-NO⁺⁺ + CO⁺</td>
<td>-0.05</td>
</tr>
<tr>
<td>NH₂⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NH₂⁺⁺⁺-NOH⁺⁺ + CO⁺</td>
<td>0.26</td>
</tr>
<tr>
<td>NH₂⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NH₂⁺⁺⁺-HNO⁺⁺ + CO⁺</td>
<td>1.67</td>
</tr>
<tr>
<td>NH₂⁺⁺⁺-NO⁺⁺ + CO⁺ + H⁺ + e⁻ → NH₂⁺⁺⁺-NO⁺⁺ + COH⁺</td>
<td>0.97</td>
</tr>
<tr>
<td>Reaction</td>
<td>ΔG (kJ/mol)</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NOH}^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_3\text{(g)} + \text{NH}_2^<em>\text{-CO} + \text{NH}_2^</em> )</td>
<td>-1.07</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_3\text{(g)} + \text{NH}_2^<em>\text{-NOH}^</em> + \text{CO}^* )</td>
<td>-0.61</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CO}^* )</td>
<td>1.60</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CH}_2^* )</td>
<td>0.97</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CHO}^* )</td>
<td>-1.07</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CHO}^* )</td>
<td>-0.61</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CH}_2^* )</td>
<td>1.60</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NH}_2^</em> + \text{CHO}^* )</td>
<td>0.97</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NOH}^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-N}^</em> + \text{CO}^* )</td>
<td>-1.14</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NOH}^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-N}^</em> + \text{CO}^* )</td>
<td>-0.14</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NOH}^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NOH}^</em> + \text{CO}^* )</td>
<td>2.39</td>
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<td>( \text{NH}_2^<em>\text{-NOH}^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NOH}^</em> + \text{CHO}^* )</td>
<td>0.93</td>
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<tr>
<td>( \text{NH}_2^<em>\text{-N}^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NH}^</em> + \text{CO}^* )</td>
<td>-0.85</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-N}^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-N}^</em> + \text{CO}^* )</td>
<td>2.57</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-N}^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NH}^</em> + \text{CHO}^* )</td>
<td>0.95</td>
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<tr>
<td>( \text{NH}_2^<em>\text{-NH}^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NH}^</em> + \text{CO}^* )</td>
<td>-0.11</td>
</tr>
<tr>
<td>( \text{NH}_2^<em>\text{-NH}^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NH}^</em> + \text{CO}^* )</td>
<td>2.38</td>
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<tr>
<td>( \text{NH}_2^<em>\text{-NH}^</em> + \text{CO}^* + H^+ + e^- \rightarrow \text{NH}_2^<em>\text{-NH}^</em> + \text{CHO}^* )</td>
<td>3.79</td>
</tr>
</tbody>
</table>
Fig. S1. (a) Top and side views of the optimized Mo$_2$C structure. (b) The planar and three-dimensional structures of the isolated Cu$_n$ clusters, as well as their respective relative energies ($\Delta E$).
\( \text{Cu}_1/\text{Mo}_2\text{C} \quad \text{Cu}_2/\text{Mo}_2\text{C} \quad \text{Cu}_3/\text{Mo}_2\text{C} \)

(a)

\[ \Delta E = 0.00 \text{ eV} \]

\[ \Delta E = 1.52 \text{ eV} \]

\[ \Delta E = 0.00 \text{ eV} \]

\[ \Delta E = 5.67 \text{ eV} \]
Fig. S2. The optimized configurations for (a) Cu₁, Cu₂, and Cu₃ and (b) Cu₄, Cu₅, Cu₆, and Cu₇ clusters with three-dimensional and planar structures anchored on the Mo₂C substrate and their relative energy difference (ΔE).
Fig. S3. The kinetic processes and the corresponding barrier for (a) the first C–N to "NOCO" and (b) the second C–N to form NOCONO* on Cu₄/Mo₂C.
Fig. S4. (a) The Gibbs free energy profiles and (b) the maximum Gibbs free energy changes in the PDS for urea electrosynthesis on different Cuₓ/Mo₂C catalysts.
Fig. S5. All intermediates involved in the synthesis of urea on Cu₁/Mo₂C.
**Fig. S6.** Reaction energy landscape on the left for the subsequent reactions of co-adsorbed \( \text{NH}_2^* - \text{NH}_2^* \) and \( \text{CO}^* \) on Cu\(_n\)/Mo\(_2\)C (\( n = 1, 2, 3, 5, 6, 7 \)). On the right is the corresponding HER plot and a comparison of the hydrogen adsorption free energy (\( \Delta G_{H^+} \)) with the adsorption free energy of \((\text{NO}^* + \text{NO}^*)\) and \((\text{NO}^* + \text{NO}^* + \text{CO}^*)\).
Fig. S7. The dissolution potential value of Cu\textsubscript{n}/Mo\textsubscript{2}C (n = 1 ~ 7).
Fig. S8. Variations of temperature and energy as a function of the time for AIMD simulations of Cu₄/Mo₂C; insert are top and side views of the snapshot of atomic configuration. The simulation is run under 300 K for 10 ps with a time step of 2 fs.