

## RESEARCH ARTICLE

Reaction Engineering, Kinetics, and Catalysis

# Nitrogen-doped carbon-armored copper–nickel alloy electrocatalytic C–N coupling for urea synthesis

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## Abstract

Excessive CO<sub>2</sub> and NO<sub>x</sub> emissions surpass Earth's capacity, driving environmental degradation. Electrocatalytic CO<sub>2</sub> and NO<sub>3</sub><sup>−</sup> co-reduction offers a sustainable route to value-added chemicals like urea, addressing emissions and advancing green synthesis. However, copper-based catalysts, while efficient in CO<sub>2</sub>-to-hydrocarbon and nitrate-to-ammonia conversion, show limited activity for C–N coupling reactions. To address this, we developed a nitrogen-doped carbon nanotube-coated CuNi alloy catalyst (CuNi@C) leveraging bimetallic synergy to achieve a Faradaic efficiency (FE) of 32.8% for urea synthesis from CO<sub>2</sub> and NO<sub>3</sub><sup>−</sup> at −0.6 V (vs. RHE), with stable performance over 26 h. *In situ* ATR-SEIRAS and DFT calculations revealed that bridge adsorption of \*CO induced a Stark effect, promoting C–N bond formation, while a unique hydrogen-bonding network suppressed HER. \*NHO and \*CO were identified as key intermediates in the C–N coupling process.

## KEYWORDS

C–N coupling, copper–nickel alloy, electrocatalysis, nitrogen doping, urea

## 1 | INTRODUCTION

Urea holds a pivotal position across a wide spectrum of disciplines, including chemistry, agriculture, environmental science, and medicine.<sup>1–4</sup> In the realm of agriculture, as a nitrogen-rich fertilizer, it plays a crucial role in enhancing both the yield and quality of crops.<sup>5,6</sup> However, the traditional synthesis methodologies, exemplified by the well-known Waller and Haber–Bosch processes, are plagued with substantial drawbacks.<sup>7–9</sup> These methods are characterized by exorbitant energy consumption, the necessity for high-pressure and high-temperature conditions, and elevated production costs. Consequently, there is an urgent and growing impetus to explore and develop green alternatives. Technologies such as electrocatalysis, biocatalysis, and photocatalysis have emerged as promising candidates, offering the potential to revolutionize urea production by making it more efficient and environmentally friendly.<sup>10–13</sup> Among these innovative approaches, electrochemical synthesis stands out. It can be executed

under ambient temperature and pressure conditions. This not only leads to a remarkable reduction in energy consumption in comparison to the traditional high-temperature and high-pressure procedures,<sup>10</sup> but also enables the utilization of abundant and renewable raw materials like NO<sub>x</sub>, H<sub>2</sub>O, and CO<sub>2</sub>.

In the electrocatalytic co-reduction process for C–N coupling, CO<sub>2</sub> acts as the primary carbon source, while nitrogen sources include N<sub>2</sub>, nitrite (NO<sub>2</sub><sup>−</sup>), and nitrate (NO<sub>3</sub><sup>−</sup>).<sup>14</sup> The N ≡ N triple bond in non-polar N<sub>2</sub> exhibits high dissociation energy, making its activation and dissolution in the electrolyte challenging. This results in weak nitrogen adsorption on electrocatalyst surfaces, impeding the reaction's progress. Additionally, the strong binding energies of C–O and N ≡ N bonds necessitate higher potentials for dissociation, which often triggers competing side reactions, such as the hydrogen evolution reaction, thereby reducing the efficiency of electrochemical urea synthesis using CO<sub>2</sub> and N<sub>2</sub> as feedstocks.<sup>15,16</sup> In contrast, NO<sub>2</sub><sup>−</sup> and NO<sub>3</sub><sup>−</sup> have lower dissociation energies, requiring less electrical energy to