

# Promoting the Intermediates Hydrogenation for Urea Electrosynthesis Over an “Active Hydrogen Pump” Catalyst

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**Abstract:** Electrocatalytic coupling of CO<sub>2</sub> and NO<sub>3</sub><sup>−</sup> offers a sustainable approach for urea production. However, the limited supply of active hydrogen (\*H) hinders the formation of the key carbon- and nitrogen-containing intermediates, thus impeding the selective C–N coupling. Herein, we developed copper molybdate (Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub>) nanorods, which could serve as “active hydrogen pump” catalysts by regulating the water dissociation and hydrogen adsorption. Such electrocatalyst would guarantee a steady \*H supply for intermediates hydrogenation, hence boosting the generation of \*CO and \*NH<sub>2</sub> intermediates for selective C–N coupling and urea production. In a CO<sub>2</sub>-saturated 0.1 M KNO<sub>3</sub> solution, Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> achieved a maximum urea yield rate of 177 mmol h<sup>−1</sup> g<sup>−1</sup> with a urea-producing FE of 40% in a flow cell configuration, outperforming most reported electrocatalysts. This study underscores the crucial role of \*H, which may guide the exploration of advanced catalysts for expediting the sustainable synthesis of indispensable chemicals requiring rapid intermediates hydrogenation.

## Introduction

Urea (CO(NH<sub>2</sub>)<sub>2</sub>), a nitrogen fertilizer containing 46% nitrogen, is essential for promoting rapid crop growth and serves as a key feedstock for producing fine chemicals.<sup>[1–4]</sup> However, conventional industrial methods for urea production, such as the Haber–Bosch and Bosch–Meiser processes, are plagued by high energy consumption and massive carbon dioxide emissions.<sup>[5–9]</sup> Developing a clean and efficient technology for urea production under milder conditions is imperative.<sup>[10–12]</sup> Electrosynthesis of urea by coupling CO<sub>2</sub> with NO<sub>3</sub><sup>−</sup> has

recently emerged as a promising alternative under ambient conditions, which environmentally transforms the greenhouse gas and waste streams into value-added product.<sup>[13–16]</sup> Such route involves 16-electron transfer and two C–N coupling steps, accompanied with multiple intermediates that directly lead to complex transform mechanisms.<sup>[17–18]</sup> Substantial challenges remain in realizing selective C–N coupling.<sup>[19–21]</sup>

Given that the key C–N bond formation step is not a proton-coupled electron transfer process, an elegant electrocatalyst should facilitate the generation of intermediates that favor C–N coupling with low energy barrier. Derived from CO<sub>2</sub> and NO<sub>3</sub><sup>−</sup>, \*CO and \*NH<sub>2</sub> that feature the lowest unoccupied molecular orbital (LUMO) in low energy and lone pair of \*NH<sub>2</sub> in high energy, respectively, represent critical intermediates for selective C–N coupling to form \*CONH<sub>2</sub> as suggested by numerous studies. However, the sluggish hydrogenation issue in the electrocatalytic co-reduction of CO<sub>2</sub> and NO<sub>3</sub><sup>−</sup> processes is still remaining, which limits the \*CO and \*NH<sub>2</sub> formation kinetically and also leads to the production of undesired by-products.

Attributed to the moderate binding affinity for both C- and N-intermediates, copper (Cu)-based materials are emerging as active catalysts for electrochemical urea synthesis.<sup>[22–28]</sup> Hu’s group recently created a Cu<sub>AC</sub>–Cu<sub>SA</sub>@NC catalyst,<sup>[29]</sup> which could convert \*NO<sub>3</sub><sup>−</sup> to \*NH<sub>2</sub> through the synergistic effect of the “Cu<sub>AC</sub>” and “Cu<sub>SA</sub>” sites, revealing a relay catalysis process for the co-reduction of CO<sub>2</sub> and NO<sub>3</sub><sup>−</sup>. Zhao et al. constructed an innovative tandem catalyst (RP-AuCu),<sup>[30]</sup> featuring two compatible single-atom active sites of Au and Cu on red phosphorus. The Au sites regulated the CO<sub>2</sub> activation intermediates to generate electrophilic \*COOH, while the Cu active sites enhanced the electrophilic attack of \*COOH species on \*NH<sub>2</sub>, thereby promoting the selective formation of C–N bonds. Nevertheless, pristine

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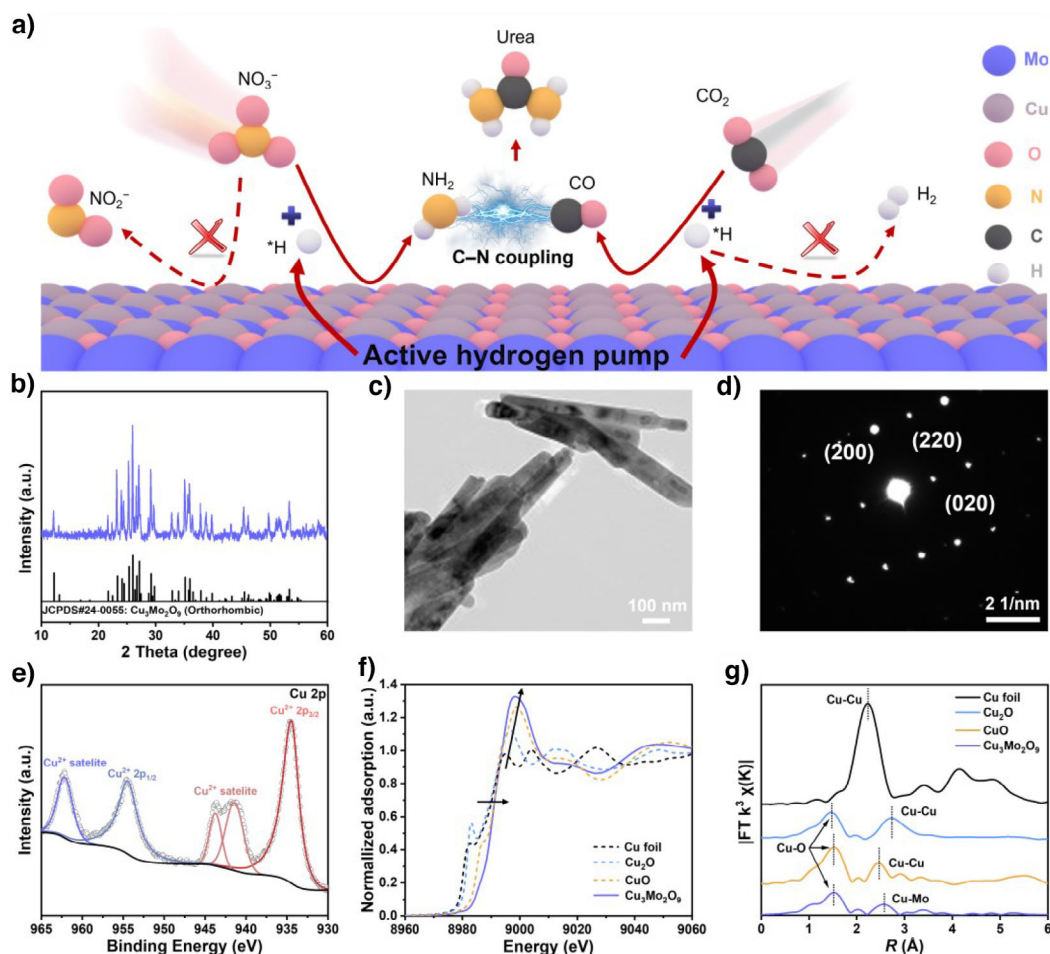
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Additional supporting information can be found online in the Supporting Information section



**Figure 1.** Structural and morphological characterization of  $\text{Cu}_3\text{Mo}_2\text{O}_9$ . a) Schematic illustration of urea electro-synthesis facilitated by an "active hydrogen pump" catalyst. b) XRD pattern. c) TEM image and d) corresponding SAED pattern. e) Cu 2p XPS spectrum. f) Cu K-edge XANES spectra. g) R-space EXAFS spectra.

Cu-based catalysts fail in supplying sufficient active hydrogen ( $^*\text{H}$ ) due to its weak hydrogen adsorption ( $\Delta G_{^*\text{H}} > 0$ ),<sup>[31–33]</sup> leading to the preferable production of  $\text{NO}_2^-$  by-product over  $^*\text{NH}_2$  intermediate and low urea yield.<sup>[34]</sup> With the purpose of facilitating the hydrogenation of both  $\text{NO}_3^-$  and  $\text{CO}_2$  on Cu-based catalysts to generate the abovementioned key intermediates, achievable strategy should be proposed to supply sufficient  $^*\text{H}$  for urea electro-synthesis through C–N coupling.

In this work, we proposed a proof-of-concept demonstration by developing a copper molybdate ( $\text{Cu}_3\text{Mo}_2\text{O}_9$ ) nanorod electrocatalyst for urea synthesis through the co-electrolysis of  $\text{NO}_3^-$  and  $\text{CO}_2$  under ambient conditions. Owing molybdenum (Mo), a conventional transitional metal for hydrogen evolution, the  $\text{Cu}_3\text{Mo}_2\text{O}_9$  electrocatalyst could serve as "active hydrogen pump" to guarantee the  $^*\text{H}$  supply (Figure 1a). The hydrogenation of  $\text{NO}_3^-$  and  $\text{CO}_2$  was accordingly boosted over the as-designed  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst, which was elucidated by density functional theory (DFT) calculations in combination with in situ electron paramagnetic resonance (EPR) experiments. A series of in situ analysis, including operando synchrotron-radiation Fourier transform infrared spectroscopy (SR-FTIR), isotope-labelled differen-

tial electrochemical mass spectrometry (DEMS), and in situ Raman analysis, strongly affirmed that  $^*\text{CO}$  and  $^*\text{NH}_2$  were indeed the determinant intermediates for selective C–N coupling. In a  $\text{CO}_2$ -saturated 0.1 M  $\text{KNO}_3$  solution,  $\text{Cu}_3\text{Mo}_2\text{O}_9$  achieved an average urea yield of  $177 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$  with a high Faraday efficiency (FE) of 40% at  $-0.8 \text{ V}$  versus reversible hydrogen electrode (RHE) in a flow cell, outperforming most reported electrocatalysts. This work offers a feasible strategy to overcome limitations in urea electro-synthesis in terms of both yield and selectivity, which may pave the way for developing electrocatalyst toward the synthesis of more value-added chemicals relying on active hydrogen.

## Results and Discussion

### Structural Characterization

The  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst was synthesized from molybdate and cupric acetate via a facile solvothermal process (for details, please Experimental section in the Supporting Information) Analysis using X-ray diffraction (XRD), Raman

spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and inductively coupled plasma atomic emission spectroscopy (ICP-OES) confirmed that the synthesized material was assigned to the  $\text{Cu}_3\text{Mo}_2\text{O}_9$  phase with an orthorhombic structure (Figure 1b and Figure S1, Table S1).<sup>[35,36]</sup> Scanning electron microscopy (SEM) (Figure S2) and transmission electron microscopy (TEM) images revealed that  $\text{Cu}_3\text{Mo}_2\text{O}_9$  exhibited a uniform nanorod morphology (Figure 1c and Figure S3a). High-resolution TEM (HRTEM) image showed interplanar spacings of 3.83 and 7.31 Å, corresponding to the (200) and (020) planes of  $\text{Cu}_3\text{Mo}_2\text{O}_9$ , respectively (Figure S3b). Selected-area electron diffraction (SAED) patterns were utilized to further examine the exposed facets of  $\text{Cu}_3\text{Mo}_2\text{O}_9$ . The rectangular and symmetrical SAED pattern displayed clear diffraction spots corresponding to the (200), (220) and (020) facets of  $\text{Cu}_3\text{Mo}_2\text{O}_9$  (Figure 1d), which could be attributed to the (002) zone-axis diffraction of the orthorhombic phase.

X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge structure (XANES) were employed to investigate the chemical state of  $\text{Cu}_3\text{Mo}_2\text{O}_9$ . The Cu 2p spectrum (Figure 1e) displayed two distinct split spin–orbit peaks at 934.5 eV ( $\text{Cu}^{2+} 2p_{3/2}$ ) and 954.6 eV ( $\text{Cu}^{2+} 2p_{1/2}$ ).<sup>[37]</sup> In addition, the peak of Cu Auger LMM spectrum was located at 917.5 eV (Figure S4a). These results indicated the +2 oxidation state of Cu in the  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst.<sup>[38–42]</sup> The XANES analysis further confirmed the Cu valence state as +2, as it almost closely matched the absorption edge of the standard CuO reference (Figure 1f).<sup>[43]</sup> Additionally, Fourier transform extended X-ray absorption fine structure (FT-EXAFS) spectra in R space revealed the prominent peaks at 1.5 and 2.6 Å assignable to Cu–O and Cu–Mo peak in the catalyst, respectively (Figure 1g).<sup>[44]</sup> The Mo 3d XPS spectrum revealed Mo in  $\text{Cu}_3\text{Mo}_2\text{O}_9$  was in the +6 oxidation state with distinct split spin–orbit peaks at 235.5 ( $\text{Mo}^{6+} 3d_{3/2}$ ) and 232.4 eV ( $\text{Mo}^{6+} 3d_{5/2}$ ) (Figure S4b).<sup>[45]</sup> Energy-dispersive X-ray spectroscopy (EDX) elemental mappings showed a uniform distribution of Cu, Mo, and O in  $\text{Cu}_3\text{Mo}_2\text{O}_9$  (Figure S5). To highlight the critical role of as-engineered “active hydrogen pump”  $\text{Cu}_3\text{Mo}_2\text{O}_9$  electrocatalyst, CuO, and  $\text{MoO}_3$  counterparts were also obtained, of which the synthesis details and structural information were presented in supplementary information (Figures S6 and S7).

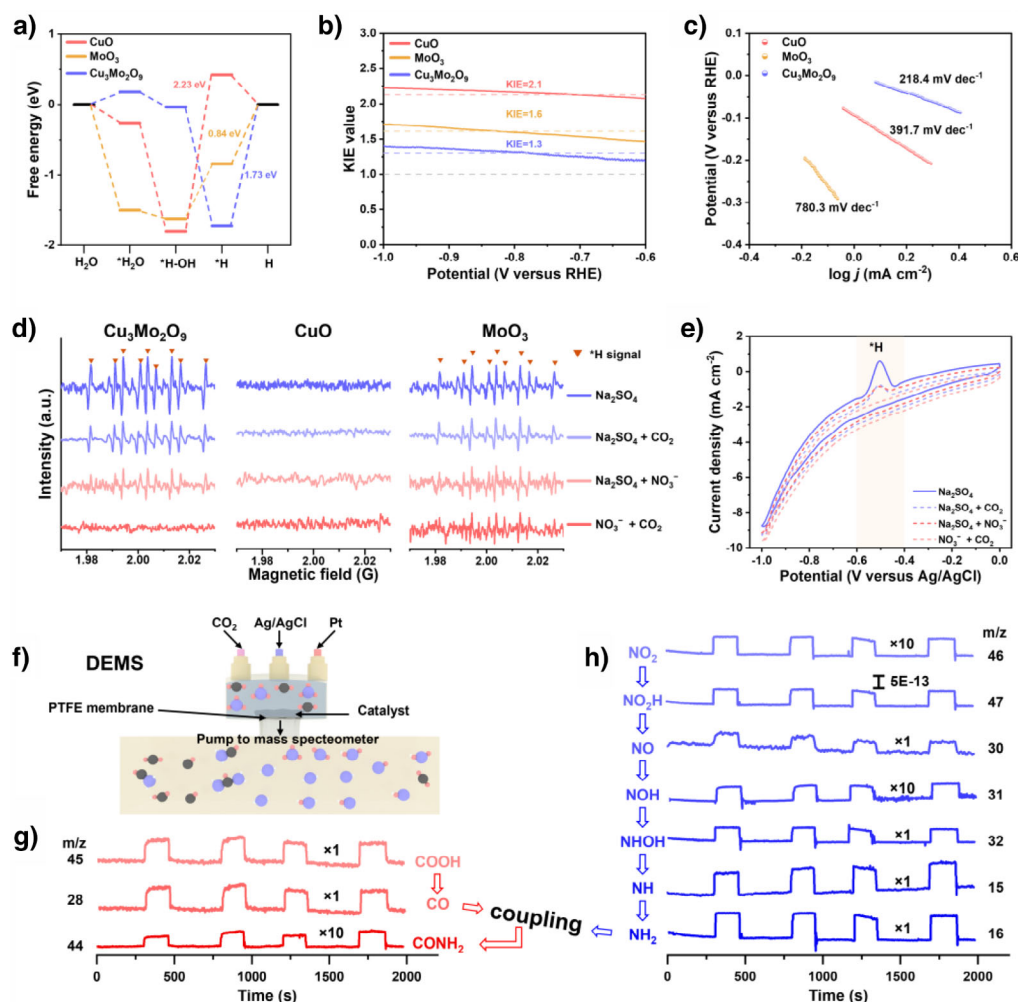
### Active Hydrogen Mediation Behavior

First, density functional theory (DFT) calculations were performed to determine the availability of active hydrogen. As shown in Figure 2a and Figures S8, the water dissociation ( $\text{*H-OH} \rightarrow \text{*H}$ ) is the rate-determining step (RDS) for CuO with a Gibbs free energy increase ( $\Delta G$ ) of 2.23 eV, implying its weak  $\text{*H}$  generation ability. Although the energy increase for the  $\text{*H}$  generation is much lower on  $\text{MoO}_3$  (0.78 eV), the  $\text{*H} \rightarrow 1/2\text{H}_2$  step only requires a low  $\Delta G$  of 0.84 eV. This suggests the preferable hydrogen evolution reaction on  $\text{MoO}_3$ ,<sup>[46]</sup> which may consume the surface  $\text{*H}$  and provide insufficient active hydrogen.<sup>[47,48]</sup> In sharp contrast, the formation of  $\text{*H}$  is much easier on  $\text{Cu}_3\text{Mo}_2\text{O}_9$  as reflected

in the  $\Delta G$  of  $-1.73$  eV for water dissociation, indicating that  $\text{Cu}_3\text{Mo}_2\text{O}_9$  is equipped with an “active hydrogen pump” for sufficient  $\text{*H}$  supply. In addition, the energy increase of  $\text{*H}$  desorption on  $\text{Cu}_3\text{Mo}_2\text{O}_9$  (1.73 eV) is much higher in contrast with that for  $\text{MoO}_3$  (+0.84 eV). Elucidated by the above theoretical prediction, the  $\text{*H}$  supplied by the “active hydrogen pump”  $\text{Cu}_3\text{Mo}_2\text{O}_9$  electrocatalyst is not favorable for HER, which might be utilized in the hydrogenation processes. To further explore the  $\text{*H}$  generation ability of  $\text{Cu}_3\text{Mo}_2\text{O}_9$ , kinetic isotopic effect (KIE) tests were conducted by replacing  $\text{H}_2\text{O}$  with  $\text{D}_2\text{O}$  to reveal the proton transfer kinetics during the  $\text{H}_2\text{O}$  splitting process.<sup>[48]</sup> The KIE values are determined by comparing the current densities observed in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  (Figure S9). As displayed in Figure 2b,  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst shows an average KIE value of 1.3, which is much lower than those of CuO (2.1) and  $\text{MoO}_3$  (1.6). This verifies that the hydrolysis process is boosted on  $\text{Cu}_3\text{Mo}_2\text{O}_9$  to facilitate  $\text{*H}$  delivery.

The quasi-in situ electron paramagnetic resonance (EPR) experiments were carried out to investigate the  $\text{*H}$  generation and the subsequent  $\text{*H}$ -mediated process, during which dimethyl-1-pyrrolidine-N-oxide (DMPO) served as the hydrogen radical trapping agent.<sup>[49]</sup> As evidenced by the intense nine-line EPR signals assignable to DMPO-H with a ratio of 1:1:2:1:2:1:2:1:1 in 0.1 M  $\text{Na}_2\text{SO}_4$  electrolyte (Figure 2d),  $\text{Cu}_3\text{Mo}_2\text{O}_9$  enables the production of massive  $\text{*H}$ . Notably, the DMPO-H signals of  $\text{Cu}_3\text{Mo}_2\text{O}_9$  are markedly attenuated upon the addition of  $\text{NO}_3^-$  (0.1 M  $\text{Na}_2\text{SO}_4$  + 0.1 M  $\text{KNO}_3$ ) or  $\text{CO}_2$  (0.1 M  $\text{Na}_2\text{SO}_4$  +  $\text{CO}_2$ ), and completely vanished in the electrolyte containing  $\text{NO}_3^-$  and  $\text{CO}_2$  simultaneously (0.1 M  $\text{KNO}_3$  +  $\text{CO}_2$ ). This suggests the accumulated  $\text{*H}$  will be rapidly consumed by the hydrogenation steps during the co-reduction of  $\text{CO}_2$  and  $\text{NO}_3^-$  process, which might conduce to the generation of key C- and N-containing intermediates for C–N coupling.<sup>[50]</sup> In sharp contrast, CuO fails in the producing  $\text{*H}$  as reflected in the barely detectable DMPO-H signals, in accordance with the theoretical prediction. Unlike  $\text{Cu}_3\text{Mo}_2\text{O}_9$  and CuO,  $\text{MoO}_3$  displays consistently weak signals regardless of the change in electrolyte. This demonstrates that the generated  $\text{*H}$  is more prone to the HER to hamper the hydrogenation of  $\text{NO}_3^-$  and  $\text{CO}_2$ .<sup>[51]</sup> The abovementioned  $\text{*H}$  production and corresponding hydrogenation processes can be further validated by the cyclic voltammetry (CV) tests, in which the characteristic active hydrogen peak is strongly correlated with the surface  $\text{*H}$  content.<sup>[52]</sup> As displayed in Figure 2e,  $\text{Cu}_3\text{Mo}_2\text{O}_9$  displays a significant  $\text{*H}$  signal, of which the intensity decreases drastically in the presence of  $\text{NO}_3^-$  or/and  $\text{CO}_2$ . Under the above conditions, no  $\text{*H}$  signal can be observed for CuO (Figure S10a), which is in agreement with the EPR results. Albeit  $\text{*H}$  emerges for  $\text{MoO}_3$  in 0.1 M  $\text{Na}_2\text{SO}_4$ , the introduction of  $\text{NO}_3^-$  and  $\text{CO}_2$  will not change the  $\text{*H}$  intensity (Figure S10b). This manifests that the  $\text{*H}$  generated on  $\text{MoO}_3$  favors the  $\text{H}_2$  evolution rather than hydrogenation of  $\text{NO}_3^-$  and  $\text{CO}_2$ . Additionally, based on the current densities observed by linear sweep voltammetry (LSV), the  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst exhibits a much lower Tafel slope (218.4  $\text{mV dec}^{-1}$ ) compared to CuO (391.7  $\text{mV dec}^{-1}$ ) and  $\text{MoO}_3$  (780.3  $\text{mV dec}^{-1}$ ) in 0.1 M  $\text{KNO}_3$  with  $\text{CO}_2$





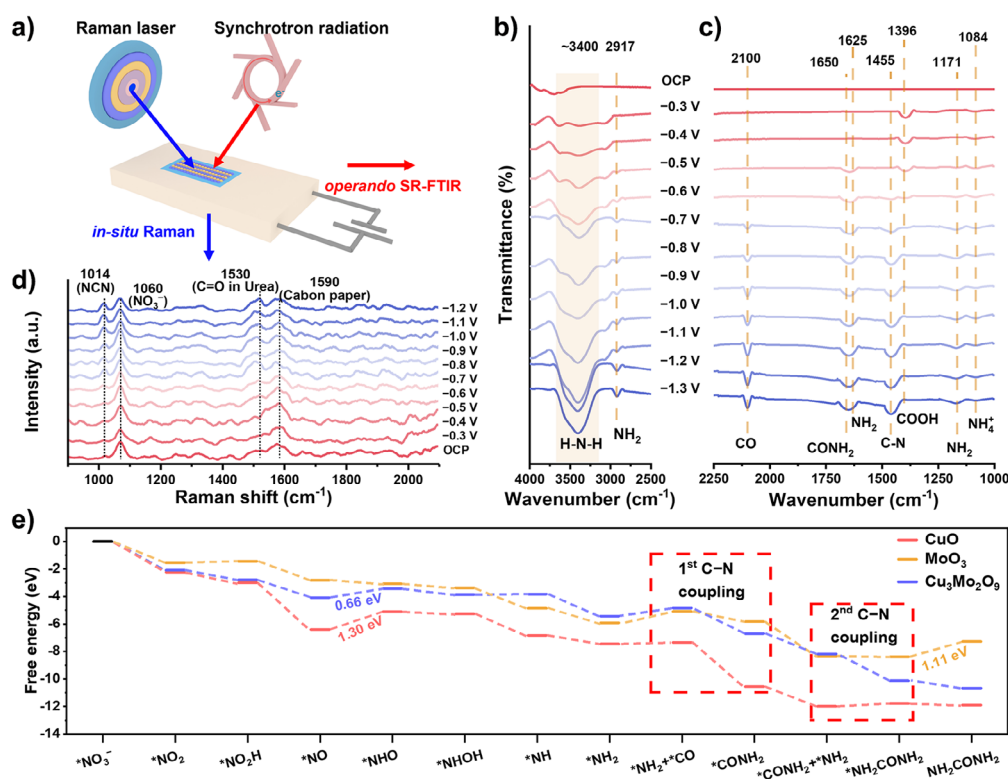
**Figure 2.** Analysis of active hydrogen generation and mediation behaviors. a) Calculated free energy diagrams of HER on  $\text{Cu}_3\text{Mo}_2\text{O}_9$ ,  $\text{CuO}$ , and  $\text{MoO}_3$ . b) KIE tests and c) Tafel plots of  $\text{Cu}_3\text{Mo}_2\text{O}_9$ ,  $\text{CuO}$  and  $\text{MoO}_3$  electrocatalysts. d) Quasi in situ EPR spectra of the solutions obtained after 10 min of electrolytic by  $\text{Cu}_3\text{Mo}_2\text{O}_9$ ,  $\text{CuO}$ , and  $\text{MoO}_3$  at  $-0.8$  V versus RHE using DMPO as the  $\cdot\text{H}$ -trapping reagent. e) Cyclic voltammograms of  $\text{Cu}_3\text{Mo}_2\text{O}_9$  electrocatalyst. f) Schematic diagram of online DEMS technique. Online DEMS signals of g) C- and h) N- intermediates in  $0.1$  M  $\text{KNO}_3$  with  $\text{CO}_2$  bubbling at  $-0.8$  V versus RHE for  $\text{Cu}_3\text{Mo}_2\text{O}_9$ .

bubbling (Figure 2c). This suggests that  $\text{Cu}_3\text{Mo}_2\text{O}_9$  favors both the  $\text{NO}_3\text{RR}$  and  $\text{CO}_2\text{RR}$  processes.<sup>[53]</sup> Indicated by the above comprehensive theoretical analysis and experiment results, the integration of Cu with Mo to synthesize  $\text{Cu}_3\text{Mo}_2\text{O}_9$  can endow the electrocatalyst with “active hydrogen pump”, which not only enables the generation of sufficient  $\cdot\text{H}$ , but also can promote the  $\cdot\text{H}$ -mediated hydrogenation of  $\text{CO}_2$  and  $\text{NO}_3^-$ . Attributed to the sufficient  $\cdot\text{H}$  supply for the hydrogenation of both the  $\text{NO}_3^-$  and  $\text{CO}_2$ , as-developed electrocatalyst may accelerate the generation of key C- and N-containing intermediates for selective urea electrosynthesis.<sup>[54]</sup>

### Mechanism Investigations in C–N Coupling

To monitor the C- and N-containing intermediates and determine the possible C–N coupling pathway on the  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst, online DEMS was implemented (for details, please

refer to the experimental section in Supplementary Information) (Figure 2f). As proved by the signals of  $\text{COOH}^+$  ( $m/z = 45$ ) and  $\text{CO}^+$  ( $m/z = 28$ ), the electrocatalytic  $\text{CO}_2\text{RR}$  process follows the “ $\text{CO}_2 \rightarrow \cdot\text{COOH} \rightarrow \cdot\text{CO}$ ” pathway (Figure 2g). Meanwhile, various N-containing intermediates signals are also observed (Figure 2h), which confirms the pathway of “ $\text{NO}_3^- \rightarrow \cdot\text{NO}_2\text{H} \rightarrow \cdot\text{NO} \rightarrow \cdot\text{NOH} \rightarrow \cdot\text{NHOH} \rightarrow \cdot\text{NH} \rightarrow \cdot\text{NH}_2$ ” toward electrocatalytic  $\text{NO}_3\text{RR}$  process. Apart from the above intermediates derived from individual  $\text{CO}_2\text{RR}$  and  $\text{NO}_3\text{RR}$  processes, the  $m/z = 44$  signal assignable to the  $\text{CONH}_2^+$  can also be detected. It demonstrates that the formation of C–N bond is realized by coupling  $\cdot\text{CO}$  with  $\cdot\text{NH}_2$  intermediates. No detectable  $\text{CONH}^+$  ( $m/z = 43$ ) signal excludes the possible C–N coupling pathway with  $\cdot\text{CO}$  and  $\cdot\text{NH}$  intermediates (Figure S11). As reflected in the DEMS results for  $\text{CuO}$  and  $\text{MoO}_3$ , nevertheless, the  $\text{CONH}_2^+$  signal is not detected, which might be attributed to the insufficient supply of key C- and N-containing intermediates for C–N coupling (Figures S12 and S13). When performing



**Figure 3.** Mechanistic study. a) Schematic diagram of Operando SR-FTIR and in situ Raman techniques. Operando SR-FTIR spectra of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> collected under various applied potentials in the range of b) 4000–2500 cm<sup>-1</sup> and c) 2250–1000 cm<sup>-1</sup>. d) In situ Raman spectra of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> during urea electrosynthesis test. e) Free-energy diagram for urea production on the Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub>, CuO, and MoO<sub>3</sub>.

DEMS measurements on Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> for individual NO<sub>3</sub>RR and CO<sub>2</sub>RR processes, the higher NH<sub>2</sub><sup>+</sup> and CO<sup>+</sup> signals can be detected, respectively, in contrast with those obtained from the co-electrolysis of NO<sub>3</sub><sup>-</sup> and CO<sub>2</sub> (Figures S14–S17). In combination with the emergence of CONH<sub>2</sub><sup>+</sup> signal, the abovementioned difference confirms that \*CO and \*NH<sub>2</sub> are the determinant intermediates for C–N coupling. The isotope-labelled DEMS measurements by replacing <sup>14</sup>NO<sub>3</sub><sup>-</sup> with <sup>15</sup>NO<sub>3</sub><sup>-</sup> presents the CO<sup>15</sup>NH<sub>2</sub><sup>+</sup> signal (*m/z* = 45), which further verify the formation of C–N bond by coupling \*CO with \*NH<sub>2</sub> on Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> catalyst (for details, please see corresponding discussion and Figures S18–S19 in Supporting Information). On the basis of the above results, it infers that the “active hydrogen pump” supplies sufficient \*H for NO<sub>3</sub>RR and CO<sub>2</sub>RR during the co-electrolysis of NO<sub>3</sub><sup>-</sup> and CO<sub>2</sub> on Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub>, which can promote the production of key intermediates for C–N coupling.

To further uncover the C–N coupling mechanism of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub>, operando synchrotron-radiation Fourier transform infrared spectroscopy (SR-FTIR) and in situ Raman were employed to monitor the real-time reaction intermediates during the urea electrosynthesis (Figure 3a). Infrared signals in the range of 1000 to 4000 cm<sup>-1</sup> were recorded with the applied potential from -0.3 V to -1.3 V versus RHE (Figure S20). The H–N–H stretching mode and N–H stretching mode at ~3400 and 2917 cm<sup>-1</sup> gradually increase with the negative shift of the applied potential (Figure 3b), which signifies the formation of \*NH<sub>2</sub> intermediates.<sup>[55]</sup> For

the range from 2250 to 1000 cm<sup>-1</sup>, the infrared bands at 1625 and 1170 cm<sup>-1</sup> correspond to the bending mode and rocking mode of –NH<sub>2</sub> in urea (Figure 3c).<sup>[56,57]</sup> Additionally, the disappearance of the stretching vibrational modes for –COOH at 1396 cm<sup>-1</sup> and the subsequent appearance of CO at 2100 cm<sup>-1</sup> suggest the \*CO<sub>2</sub> → \*COOH → \*CO pathway to produce C-containing intermediate.<sup>[20,58]</sup> These findings showcase the activation and reduction of CO<sub>2</sub>/NO<sub>3</sub><sup>-</sup> in the electrochemical process.<sup>[59]</sup> Notably, the infrared bands at 1455 and 1650 cm<sup>-1</sup> are identified as the C–N bond and CO–NH<sub>2</sub> bond, respectively,<sup>[60,61]</sup> which verifies that C–N bond formation originates from the coupling of \*CO and \*NH<sub>2</sub> intermediates. Similarly, in situ Raman spectra show the gradually increased intensities of the versus (C–N) (1014 cm<sup>-1</sup>) and –NH<sub>2</sub> (1510 cm<sup>-1</sup>) bending vibration when shifting to more negative potentials (Figure 3d).<sup>[65]</sup> Accordingly, the comprehensive understanding based on online DEMS, operando SR-FTIR and in situ Raman elucidates that \*CO and \*NH<sub>2</sub> are the key intermediates for C–N coupling on Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> during the co-electrolysis of NO<sub>3</sub><sup>-</sup> and CO<sub>2</sub> process.

DFT calculations were employed to further examine the lowest energy pathway for the urea production process on the Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub>, CuO and MoO<sub>3</sub> catalysts. Initially, NO<sub>3</sub><sup>-</sup> will be reduced to produce \*NH<sub>2</sub> following the completion of the deoxidation and hydrogenation process (Figure 3e). Subsequently, the \*NH<sub>2</sub> intermediate can couple with \*CO to form \*CONH<sub>2</sub> intermediate, which is consistent with the experimental findings. In the urea electrosynthesis pathways,

the protonation of  $^*\text{NO}$  ( $^*\text{NO} \rightarrow ^*\text{NOH}$ ) is identified as the RDS for  $\text{Cu}_3\text{Mo}_2\text{O}_9$  and  $\text{CuO}$  catalysts. In contrast with  $\text{CuO}$  (1.30 eV),  $\text{Cu}_3\text{Mo}_2\text{O}_9$  requires a lower energy increase (0.66 eV) for  $^*\text{NOH}$  generation. This demonstrates that  $\text{Cu}_3\text{Mo}_2\text{O}_9$  enhances the  $\text{NO}_3\text{RR}$  activity to produce  $^*\text{NH}_2$  intermediates and thus increase the possibility of the C–N coupling between  $^*\text{CO}$  and  $^*\text{NH}_2$ . Although  $\text{MoO}_3$  had a lower  $\Delta G$  for  $^*\text{NH}_2$  generation, the  $^*\text{H}$  itself favors the HER process (Figure 2a). As elucidated by above DFT calculations and in situ spectroscopic analysis, as-engineered “active hydrogen pump”  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst can provide sufficient  $^*\text{H}$  for the formation of vital  $^*\text{CO}$  and  $^*\text{NH}_2$  intermediates. This boosts the C–N bond generation by coupling  $^*\text{CO}$  with  $^*\text{NH}_2$ , which may lead to exceptional urea electrosynthesis performance.

### Urea Electrosynthesis Performance

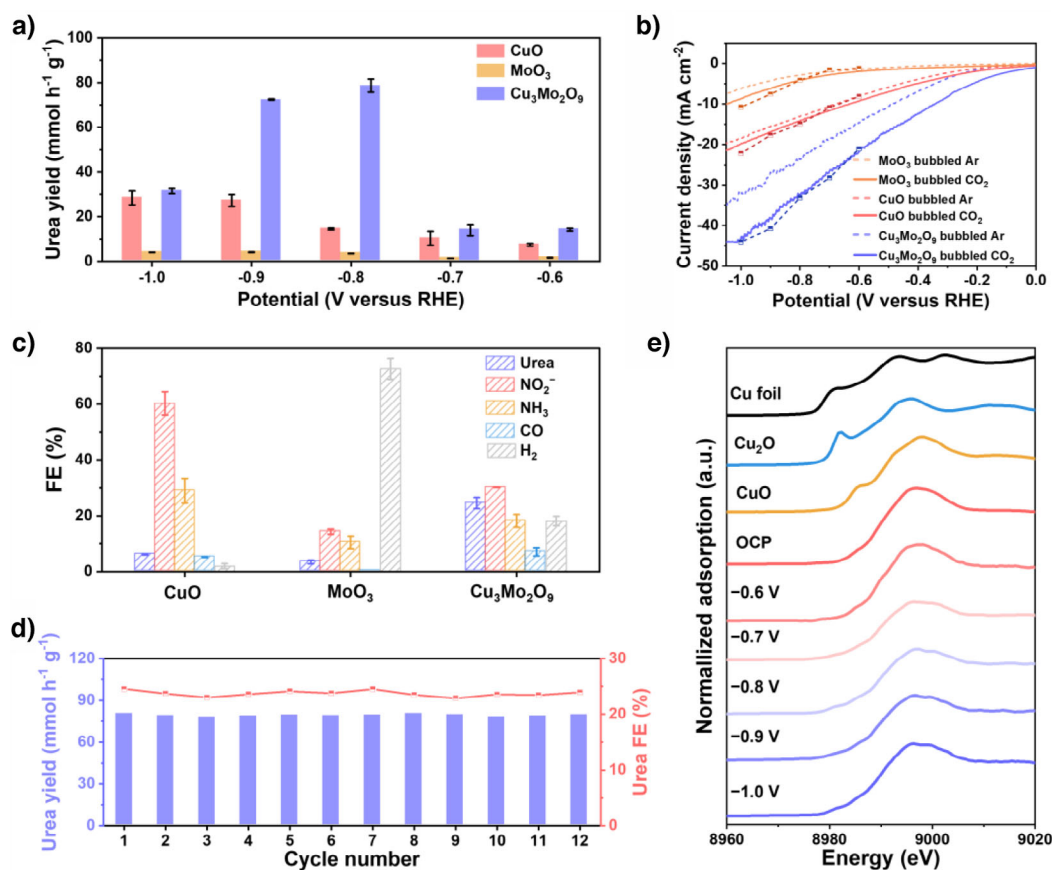
The urea electrosynthesis performance was first evaluated in an H-cell with a standard three-electrode system. As recorded by LSV, a higher current density is observed for the catalysts in the  $\text{CO}_2$ -saturated 0.1 M  $\text{KNO}_3$  compared to those in either the Ar-saturated or  $\text{CO}_2$ -saturated 0.1 M  $\text{Na}_2\text{SO}_4$  electrolytes, suggesting the co-reduction of  $\text{CO}_2$  and  $\text{NO}_3^-$  within the system (Figure 4b and Figure S21).<sup>[59]</sup> Furthermore,  $\text{Cu}_3\text{Mo}_2\text{O}_9$  exhibits a higher current density than  $\text{CuO}$  and  $\text{MoO}_3$  within the applied potential range, suggesting its higher activity toward urea electrosynthesis.<sup>[61]</sup>

Subsequently, the urea electrosynthesis performance was assessed using chronoamperometry across a potential range of  $-0.6$  to  $-1.0$  V versus RHE in a 0.1 M  $\text{KNO}_3$  electrolyte with  $20 \text{ mL min}^{-1}$   $\text{CO}_2$  bubbling into the catholyte (The optimization experiments of the  $\text{KNO}_3$  concentration and  $\text{CO}_2$  flow rate were described in the Supporting Information, Figures S22 and S23). Gas chromatography was employed to analyze the gaseous products, while ultraviolet-visible (UV–vis) spectroscopy was utilized to quantify products dissolved in the liquid (Figures S24–S26). The  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst delivers a volcano-shaped dependence of urea yield under the applied potentials (Figure 4a), achieving a peak urea yield rate of  $78.68 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$  at  $-0.8$  V versus RHE. It significantly exceeds the urea yield rates for  $\text{CuO}$  ( $14.41 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ ) and  $\text{MoO}_3$  ( $3.59 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ ) (Figures S27–S29). The urea yield rates calculated based on the  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy align with those obtained using the urease method (Figures S30 and S31). Additionally, qualitative confirmation of urea formation is achieved through  $^1\text{H}$  NMR analysis using  $\text{K}^{14}\text{NO}_3$  or  $\text{K}^{15}\text{NO}_3$  as the nitrogen source. Distinct peaks indicative of urea formation are observed, including a single broad peak at 5.65 ppm for  $\text{CO}^{(14)}\text{NH}_2)_2$  as well as the doublet peaks at 5.62 and 5.72 ppm for  $\text{CO}^{(15)}\text{NH}_2)_2$  (Figure S32), which verifies the origin of nitrogen in as-produced urea. Control experiments exclude the detection of urea in the absence of  $\text{CO}_2$ ,  $\text{NO}_3^-$ , catalyst, or applied potential (Figures S33–S35). The potential by-product  $\text{N}_2\text{H}_4$  is evaluated using the Watt and Chrisp method, and the UV–vis spectrum reveals no distinct  $\text{N}_2\text{H}_4$  peak (Figures S36 and S37). These validate that

the detected urea indeed stems from the urea electrosynthesis process by coupling  $\text{CO}_2$  and  $\text{NO}_3^-$  on  $\text{Cu}_3\text{Mo}_2\text{O}_9$ , rather than from external sources such as carbon paper, feed gas, or surface contamination.

Apart from urea, by-products including ammonia ( $\text{NH}_3$ ), nitrite ( $\text{NO}_2^-$ ),  $\text{H}_2$ , and trace amounts of  $\text{CO}$  are detected for  $\text{Cu}_3\text{Mo}_2\text{O}_9$ ,  $\text{CuO}$ , and  $\text{MoO}_3$  (Figures S38–S40). Thereinto,  $\text{Cu}_3\text{Mo}_2\text{O}_9$  achieved a maximum urea FE of 26% at  $-0.8$  V versus RHE (Figure 4c), which indicates its higher C–N coupling selectivity during the urea electrosynthesis process compared to  $\text{CuO}$  and  $\text{MoO}_3$  catalysts (Figure S41). This result is in accordance with the above DFT calculations. Electrochemically active surface area (ECSA) was normalized using electrochemical double-layer capacitance ( $C_{\text{dl}}$ ) measurements. Similar ECSA results for  $\text{Cu}_3\text{Mo}_2\text{O}_9$ ,  $\text{CuO}$ , and  $\text{MoO}_3$  suggest that the outstanding urea electrosynthesis performance of  $\text{Cu}_3\text{Mo}_2\text{O}_9$  should be originated from its inherent activity (Figure S42). Product distributions reveal that  $\text{CuO}$  primarily produces  $\text{NO}_2^-$  and  $\text{NH}_3$  by-products, while  $\text{MoO}_3$  catalyst predominantly proceeds the HER process (Figure 4c and Figures S38 and S39). Attributed to the promoted hydrogenation,  $\text{Cu}_3\text{Mo}_2\text{O}_9$  can produce more  $^*\text{NH}_2$  intermediates for selective C–N coupling as reflected in less  $\text{NO}_2^-$  and  $\text{NH}_3$ . Other than facilitating the urea production, the supply of sufficient  $^*\text{H}$  also improves the amounts of  $\text{H}_2$  and  $\text{CO}$  (Figure 4c and Figure S40). The  $^*\text{H}$  quenching test with the addition of tertiary butanol (TBA) shows the decrease in the yields of  $\text{NO}_2^-$ ,  $\text{NH}_3$ ,  $\text{CO}$ , and urea for  $\text{Cu}_3\text{Mo}_2\text{O}_9$  when increasing the TBA concentration (Figure S43). The Tafel slopes are approximately or exceed  $120 \text{ mV dec}^{-1}$  (Figure 2c), indicating that the first electron transfer in nitrate activation might be the RDS at low overpotentials.<sup>[46,62]</sup> According to the quasi-equilibrium Langmuir adsorption model, the RDS mainly involves the consumption of one proton. Based on the above results, the  $\text{NO}_3\text{RR}$  and  $\text{CO}_2\text{RR}$  pathways involve hydrogen-mediated reduction processes rather than electron transfer-mediated reduction,<sup>[46,63]</sup> which will accelerate the hydrogenation of N- and C-intermediates into  $^*\text{NH}_2$  and  $^*\text{CO}$ , respectively. Thereby, the likelihood of C–N coupling will be increased for realizing selective urea electrosynthesis.

To further highlight the role of  $^*\text{H}$  in enhancing urea synthesis performance for  $\text{Cu}_3\text{Mo}_2\text{O}_9$ , control experiments were conducted to assess their activity for  $\text{NO}_3\text{RR}$  and  $\text{CO}_2\text{RR}$  separately. In the individual  $\text{NO}_3\text{RR}$  tests, argon gas instead of  $\text{CO}_2$  was fed into the electrolyte. Over the  $\text{CuO}$  catalyst,  $\text{NO}_2^-$  is detected as the major product (Figure S44), while  $\text{H}_2$  formation predominates on  $\text{MoO}_3$  with a FE of nearing 100% at the applied potential range (Figure S45). Unlike  $\text{CuO}$  catalyst,  $\text{Cu}_3\text{Mo}_2\text{O}_9$  exhibits an increased  $\text{NH}_3$ -producing FE accompanied with less  $\text{NO}_2^-$  (Figure S46). Benefiting from the “active hydrogen pump”, the  $\text{NO}_2^-$  will be further hydrogenated by  $^*\text{H}$  to allow the supply of the key  $^*\text{NH}_2$  intermediate. When meeting  $^*\text{CO}$  derived from  $\text{CO}_2\text{RR}$  after introducing  $\text{CO}_2$  as a reactant, the  $^*\text{NH}_2$  will favor C–N coupling with the  $^*\text{CO}$  intermediate for selective urea electrosynthesis over  $\text{Cu}_3\text{Mo}_2\text{O}_9$ , which results in the decreased FEs and yields of both  $\text{NO}_2^-$  and  $\text{NH}_3$  (Figures S47 and S48). For individual  $\text{CO}_2\text{RR}$  experiments,



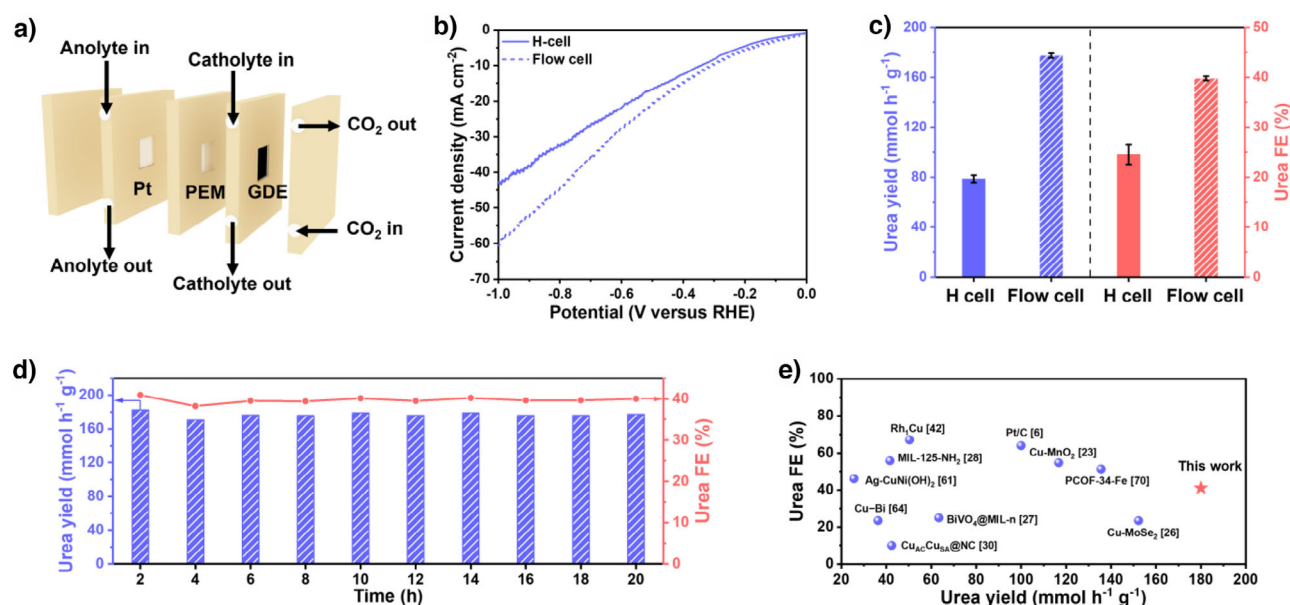
**Figure 4.** Urea electro-synthesis performance in H-cell. a) Urea yield rates at different potentials in 0.1 M  $\text{KNO}_3$  electrolyte with  $\text{CO}_2$  feeding gas. b) LSV curves in 0.1 M  $\text{KNO}_3$  with Ar or  $\text{CO}_2$  bubbling, and I–V plots in 0.1 M  $\text{KNO}_3$  with  $\text{CO}_2$  at different potentials. c) FEs of different products for CuO,  $\text{MoO}_3$  and  $\text{Cu}_3\text{Mo}_2\text{O}_9$  at  $-0.8$  V versus RHE in 0.1 M  $\text{KNO}_3$  electrolyte with  $\text{CO}_2$  feeding gas. d)  $\text{NH}_3$  yields and corresponding FEs for  $\text{Cu}_3\text{Mo}_2\text{O}_9$  during the long-term durability test. e) Cu K-edge in situ XANES spectra during the electrochemical urea electro-synthesis of  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst.

$\text{Cu}_3\text{Mo}_2\text{O}_9$  delivers higher CO yield and FE in contrast with CuO and  $\text{MoO}_3$  (Figures S49–S52). Additionally, CO-temperature-programmed gas desorption (CO-TPD) results indicate the strong signal intensity as well as high desorption temperature for  $\text{Cu}_3\text{Mo}_2\text{O}_9$  (Figure S53). As displayed in Figure S54,  $\text{Cu}_3\text{Mo}_2\text{O}_9$  does not show stronger  $\text{CO}_2$  adsorption in contrast with CuO and  $\text{MoO}_3$ , excluding the influence of  $\text{CO}_2$  adsorption and activation on the catalysis performance. In combination with the  $\text{CO}_2\text{RR}$  experiments, the above results infer that  $\text{Cu}_3\text{Mo}_2\text{O}_9$  can also provide sufficient and stabilized  $^*\text{CO}$  intermediate for C–N coupling. To further highlight the significant role of “active hydrogen pump” for  $\text{Cu}_3\text{Mo}_2\text{O}_9$ , we also synthesized the CuO/ $\text{MoO}_3$  catalyst (for details, please see corresponding discussion and Figures S55–S57 in Supporting Information). However, the maximum urea production rate ( $35.2 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ ) and the corresponding urea-producing FE (11.0%) of the CuO/ $\text{MoO}_3$  catalyst are much lower than those of  $\text{Cu}_3\text{Mo}_2\text{O}_9$ . The product distribution shows that the  $\text{NO}_2^-$  and  $\text{H}_2$  are the main byproducts, indicating the produced  $^*\text{H}$  by CuO/ $\text{MoO}_3$  is not supplied for  $\text{NO}_3\text{RR}$  and  $\text{CO}_2\text{RR}$  to promote the generation of  $^*\text{NH}_2$  and  $^*\text{CO}$ . Therefore, the “active hydrogen pump” behavior is crucial for the urea electro-synthesis process over  $\text{Cu}_3\text{Mo}_2\text{O}_9$ .

To evaluate the durability and reproducibility of the  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst in urea electro-synthesis, we conducted 12 continuous testing cycles (Figure 4d). The urea yield rates remain consistently high at approximately  $80 \text{ mmol h}^{-1} \text{ g}^{-1}$  with an average FE of 26%, demonstrating excellent electrochemical stability. During urea electro-synthesis, the Cu local structure was continuously monitored using in situ X-ray absorption spectroscopy (XAS). According to XANES spectra of the Cu K-edge (Figure 4e), the near-edge absorption energies of  $\text{Cu}_3\text{Mo}_2\text{O}_9$  remain consistent at the applied potential of  $-0.6$  to  $-1.0$  V versus RHE during the electrolysis, indicating no significant change in the valence state. The stability of  $\text{Cu}_3\text{Mo}_2\text{O}_9$  can also be explained by “active hydrogen pump” behavior, which accelerates the hydrogenation processes and electron transfer to avoid self-reconstruction and  $\text{NO}_2^-$  accumulation.<sup>[6]</sup> Characterization techniques, including XRD, SEM, TEM HRTEM, SAED, HAADF-STEM, and XPS confirm the exceptional stability of the  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst in its crystalline phase and nanostructure (Figures S58–S61).

Generally, a flow cell with gas diffusion electrode (GDE) (Figure 5a) is considered effective for catalytic reactions at the gas-solid interface, as the current density in a typical H-cell is limited due to the low solubility and slow dynamics of





**Figure 5.** Urea electrosynthesis performance in flow cell. a) Schematic diagram of the flow cell. b) LSV curves of  $\text{Cu}_3\text{Mo}_2\text{O}_9$  in H-cell and flow cell. c) Urea yields and urea FEs of  $\text{Cu}_3\text{Mo}_2\text{O}_9$  in H-cell and flow cell at  $-0.8$  V versus RHE. d) The durability and reproducibility of the  $\text{Cu}_3\text{Mo}_2\text{O}_9$  catalyst toward urea electrosynthesis in flow cell. e) Electrochemical performance comparison between  $\text{Cu}_3\text{Mo}_2\text{O}_9$  and reported catalysts.

gas-phase reaction molecules.<sup>[64]</sup> Equipped by the flow cell,  $\text{Cu}_3\text{Mo}_2\text{O}_9$  delivers an enhanced current density compared to the H-cell (Figure 5b), suggesting the possible promoted urea electrosynthesis activity. Quantitative measurements reveal that  $\text{Cu}_3\text{Mo}_2\text{O}_9$  achieves a maximum urea yield of  $177 \text{ mmol h}^{-1} \text{ g}^{-1}$  with an excellent urea FE of 40% at  $-0.8$  V versus RHE in the flow cell (Figure 5c and Figure S62), which surpasses that in the H-cell. Furthermore, the yields and FEs of  $\text{NO}_2^-$  in the flow cell significantly decrease compared to those in the H-cell. The results might be attributed to the efficient mass transfer at the electrolyte/catalyst interface during the urea electrosynthesis process. The sufficient  $^*\text{H}$  provided by the “active hydrogen pump” catalyst will accelerate the hydrogenation of C- and N-containing species to generate  $^*\text{CO}$  and  $^*\text{NH}_2$  intermediates, thereby expediting the C–N bond formation. During a 20 h continuous test, no significant current decay in current-time ( $I$ - $t$ ) curve further highlights the endurance of  $\text{Cu}_3\text{Mo}_2\text{O}_9$  (Figure S64a). Remarkably, both the urea yield rates and FEs remain stable within 20 h (Figure 5d and Figure S64b), proving  $\text{Cu}_3\text{Mo}_2\text{O}_9$  as an exceptional and stable catalyst for urea electrosynthesis. In sharp contrast, the urea electrosynthesis performance of as-designed “active hydrogen pump” catalyst outperforms most recently reported catalysts in the literatures (Figure 5e).<sup>[6,25,29,56,59,65]</sup>

## Conclusion

To summarize, we developed a  $\text{Cu}_3\text{Mo}_2\text{O}_9$  nanorod catalyst for urea synthesis through the co-electrolysis of  $\text{NO}_3^-$  and  $\text{CO}_2$  under ambient conditions. By regulating the water dissociation and hydrogen adsorption, as-developed  $\text{Cu}_3\text{Mo}_2\text{O}_9$  played a role as “active hydrogen pump” catalyst to supply sufficient  $^*\text{H}$  for promoting the hydrogenation of  $\text{NO}_3^-$  and

$\text{CO}_2$ , which was validated by DFT calculations in combination with quasi-in situ EPR experiments. As recorded by a series of in situ analysis, including operando SR-FTIR, isotope-labelled DEMS, and in situ Raman analysis,  $^*\text{CO}$  and  $^*\text{NH}_2$  were the vital intermediates derived from hydrogenation processes for selective C–N coupling. In a  $\text{CO}_2$ -saturated 0.1 M  $\text{KNO}_3$  solution,  $\text{Cu}_3\text{Mo}_2\text{O}_9$  delivered a maximum urea yield of  $177 \text{ mmol h}^{-1} \text{ g}^{-1}$  with a high urea FE of 40% at  $-0.8$  V versus RHE in the flow cell, which surpassed most reported literatures. This work not only emphasizes the crucial role of  $^*\text{H}$  for intermediates hydrogenation, but also provide a viable way to engineer achievable Cu-based catalysts for efficient urea electrosynthesis from  $\text{CO}_2$  and  $\text{NO}_3^-$ .

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### Conflict of Interests

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Active hydrogen • C–N coupling • Copper-based electrocatalysts • Intermediates hydrogenation • Urea electrosynthesis

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## Research Article

## Urea Electrosynthesis

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Promoting the Intermediates  
Hydrogenation for Urea Electrosynthesis  
Over an “Active Hydrogen Pump” Catalyst

The  $\text{Cu}_3\text{Mo}_2\text{O}_9$  nanorods was developed to serve as “active hydrogen pump” electrocatalyst, which could regulate the water dissociation and hydrogen adsorption. Such electrocatalyst would guarantee a steady  $^*\text{H}$  supply for intermediates hydrogenation, hence boosting the generation of  $^*\text{CO}$  and  $^*\text{NH}_2$  intermediates for selective C—N coupling and urea production.

