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Potential-driven dynamic strain in chemical bonds for urea electrosynthesis

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Regulating the bond lengths of electrocatalysts to manipulate their surface-attached intermediates is crucial for orienting the parallel NO_3^- and CO_2 reduction pathways towards the target urea product. However, in potentiostatic systems, the fixed bond lengths cannot selectively control the competition among multiple thermodynamic processes. Herein, we successfully balanced the activities of NO_3^- and CO_2 reduction in urea electrosynthesis by constructing a potential-driven dynamic system, in which the Cu–O bond lengths in the Cu_5 -PPF electrocatalyst were precisely controlled between 2.12/2.24 Å and 2.37/2.34 Å. The dynamic elastic strain of Cu–O bond lengths optimized the N- and C-pathways separately, achieving the highest urea-selective performance at equilibrium. In the dynamic system, the FE_{urea} was up to 61.6%. *In situ* spectroscopy and theoretical analyses revealed that the shorter Cu–O bond lengths favored the N-pathway, promoting the generation of key *NO intermediates, while the elongated Cu–O bond lengths enhanced the adsorption of CO_2 and the formation of *COOH in the C-pathway. Moreover, controlled experiments revealed that the dynamic system did not enhance the FE_{urea} of Cu_3 -TPF and Cu_3 -clusters due to their structural rigidity, further highlighting the importance of dynamic bond strain in optimizing catalytic performance.

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Introduction

Electrosynthesis of urea offers a sustainable alternative to the conventional Bosch–Meiser process, helping to alleviate the energy crisis.^{1–3} However, the selectivity of urea is usually undesirable due to the competition among complex thermodynamic pathways.^{4–6} To overcome the thermodynamic energy barrier of the critical C–N coupling step, significant efforts have focused on developing novel catalysts, as outlined in Table S1.^{7–10} Despite these advancements, optimizing the C–N coupling step alone is insufficient to enhance the urea selectivity throughout the entire reaction sequence. The competition from parallel reduction reactions, specifically the NO_3^- reduction reaction (NO_3RR) and CO_2 reduction reaction (CO_2RR), severely impedes urea formation.^{11,12} In general, the rate determining step requires the selective progression of the

NO_3RR and CO_2RR to a certain stage, producing specific C-species and N-species to form C–N bonds. However, in most cases, undesired side reactions always outweigh urea formation due to the overwhelming reduction of one reactant over the other.^{13–15} For example, the C-pathway often generates by-products such as CO, CH_4 , HCOOH and C_2H_4 ,^{16–21} while the N-pathway produces unwanted species like NO_2^- , NO, N_2 , N_2H_4 , and NH_4^+ .^{22,23} Therefore, developing strategies to finely manipulate the competition among these reactions in urea electrosynthesis is essential but remains a significant challenge.

The selectivity and conversion rate of urea electrosynthesis benefit from precise control over the activities of parallel NO_3^- and CO_2 reductions.^{24,25} Regulating the bond lengths of electrocatalysts to manipulate their surface-attached intermediates is a promising strategy for orienting multiple thermodynamic pathways towards the target product.^{26,27} The length of the metal–ligand bond (M–L bond) is an intrinsic property of the electrocatalyst that affects electron distribution, polarity, and the energy gap.^{28–32} Numerous studies have shown that adjusting M–L bond lengths can influence the adsorption behavior and binding energy of active species.^{33–36} For example, Qin's team showed that incorporating Sb into CuS elongated the Cu–S bond from 2.24 Å to 2.30 Å, which shifted the CO_2RR product selectivity from HCOOH to CO by modulating the binding mode of intermediates.³⁷ Wang's team demonstrated that extending the Cu–O bond length in the $\text{Cu}_1\text{-CeO}_2$ catalyst induced the formation of hindered Lewis pairs, facilitating the

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effective activation of CO₂.⁵ In contrast, shorter bond lengths appear to be more favorable in the NO₃RR. Zhu *et al.* showed that hcp-Ru₁Co catalysts with shorter Ru–Co bond lengths exhibited enhanced NO₃[−] adsorption. Furthermore, the strengthened interatomic interactions between Ru and Co at shorter bond lengths effectively lowered the free energy barriers for the hydrogenation of key *NO intermediates.³⁸ Although significant achievements have been made in exploring the relationship between bond lengths and reaction mechanisms, optimizing multiple competing sequential steps simultaneously throughout the sequential reaction is still difficult in static systems.

In this work, we constructed a dynamic system to separately optimize the C- and N-pathways in urea synthesis by precisely controlling the bond lengths of the electrocatalyst. We used a Cu₅Cl₂(μ₃-OH)₂ pentacluster-based porous honeycomb-like 3D framework (Cu₅Cl₂(μ₃-OH)₂ PPF) as the initial structure, which was subsequently dechlorinated and deoxygenated under operating conditions to generate Cu₅-PPF as the catalyst. Experimental and theoretical evidence suggested when the pulse potential alternated between −0.5 V and −0.7 V (*vs.* RHE), the Cu–O bond lengths in Cu₅-PPF dynamically switched between 2.12/2.24 Å and 2.37/2.34 Å. The elastic strain of the Cu–O bonds kept the catalytic center in an ‘alternating activated’ state, dynamically regulating the surface-bonded N- and C-intermediates. The shorter Cu–O bond length at −0.5 V favored the formation of the critical *NO species in the N-pathway, whereas the elongated Cu–O bond length at −0.7 V promoted CO₂ adsorption and the formation of *COOH in the C-pathway. The periodic elastic strain of the bond lengths alternated between the dominance of the N- and C-pathways, directing the entire reaction sequence towards the desired urea product. Compared to potentiostatic conditions (FE_{urea} = 33.1%), the dynamic system achieved a remarkable increase in FE_{urea} to 61.6%. To further assess the role of strain effects on bond length, we selected Cu₃-TPF and Cu₃-clusters as comparative samples and evaluated their electrocatalytic performance. Unfortunately, these systems did not exhibit an improved FE_{urea} under pulse-driven dynamic conditions, likely due to the structural rigidity of the triangular Cu₃-coordinated pattern. This work deepens the understanding of the structure–activity relationship and offers a novel approach to control the competitive electrocatalytic pathways in dynamic systems.

Results and discussion

Preparation and characterization of the electrocatalyst

Cu₅Cl₂(μ₃-OH)₂ PPF was synthesized based on a report from Huang's group.³⁹ The structure of Cu₅Cl₂(μ₃-OH)₂ PPF is depicted in Fig. 1a. In Cu₅Cl₂(μ₃-OH)₂ PPF, two triangular clusters of [Cu₃(μ₃-OH)]⁴⁺ are linked together by a shared center Cu to form a square [Cu₅(μ₃-OH)₂(btca)₄][−] pentacene cluster. Each [Cu₅(μ₃-OH)₂(btca)₄][−] pentacluster was connected to ten identical pentacluster nodes *via* benzotriazole-5-carboxylic acid ligands (H₂btca) to generate a three-dimensional metal–organic framework with 1D channels. The scanning electron microscopy (SEM) and powder X-ray diffraction (PXRD) patterns of

Cu₅Cl₂(μ₃-OH)₂ PPF are displayed in Fig. 1b and c, respectively. All coordinated Cu atoms in Cu₅Cl₂(μ₃-OH)₂ PPF were in the Cu(II) oxidation state (Fig. 1d and e).

Potential-driven elastic strain of chemical bonds for electrocatalytic urea synthesis

According to previous reports, the coordination pattern of μ₃-O in tricopper can be disrupted under electrolysis conditions.⁴⁰ To determine the reliable structure of active sites, we calculated the energy changes for dechlorination (−0.08 eV) and dehydroxylation (−0.39 eV) of Cu₅Cl₂(μ₃-OH)₂ PPF, as illustrated in Fig. 2a. The results indicated that these processes were feasible under working conditions. Cyclic voltammetry of Cu₅Cl₂(μ₃-OH)₂ PPF further confirmed the removal of chlorine and hydroxyl groups. As shown in Fig. S1, a clear reduction peak was observed, indicating that the structural transformation was electrochemically irreversible. Consequently, Cu₅-PPF was identified as the active structure for urea electro-synthesis.

The electrochemical performance of Cu₅-PPF for the CO₂RR, NO₃RR and CO₂/NO₃[−] co-reduction was determined in neutral media. The corresponding linear sweep voltammetry (LSV) curves in Fig. 2b indicated that under CO₂/NO₃[−] co-reduction conditions, Cu₅-PPF exhibited higher activity than in the CO₂RR and NO₃RR at each potential, suggesting an additional current density generated by C–N coupling.⁴¹ Isotope labeling experiments confirmed the formation of ¹⁴NH₂CO¹⁴NH₂ and ¹⁵NH₂CO¹⁵NH₂ products (Fig. 2c). High performance liquid chromatography (HPLC) and colorimetric methods were utilized to quantify the urea product (Fig. 2d, S2 and S3). Additionally, the content of NH₄⁺ and NO₂[−] was determined by the indophenol blue method and naphthalenediamine hydrochloride method, respectively (Fig. S4 and S5).

Fig. 2e shows the trend of FE_{urea} with potential for Cu₅-PPF under potentiostatic conditions. Notably, we observed two optimal FE_{urea} at −0.5 V and −0.7 V, respectively, which were atypical compared to conventional volcano plots with only a single peak. Following this discovery, we assessed the CO₂RR and NO₃RR performance of Cu₅-PPF (Fig. S6). As the applied potential shifted negatively, the products of the CO₂RR transitioned from a predominance of H₂ to carbon-based products. In the case of the NO₃RR, the primary product NO₂[−] at lower potential was gradually supplanted by NH₄⁺ at higher potentials. NH₄⁺ is the final product of NO₃[−] reduction, and its formation severely competes with the C–N coupling pathway.^{6,8,25,42} For efficient urea generation, the incomplete reduction of the C- and N-pathways is superior because it enables the accumulation of specific intermediates that play crucial roles in urea production.^{43,44} Consequently, we speculated that there were two optimal potentials of −0.5 V and −0.7 V in our system, corresponding to the N- and C-pathways, respectively. Less NH₄⁺ was generated at −0.5 V, facilitating the production of massive incompletely reduced intermediates that were essential for the subsequent C–N coupling step. Additionally, significant conversion of CO₂ was observed as the applied potential shifted negatively from −0.7 V, initiating the sufficient activation of the C-pathway. This analysis provided



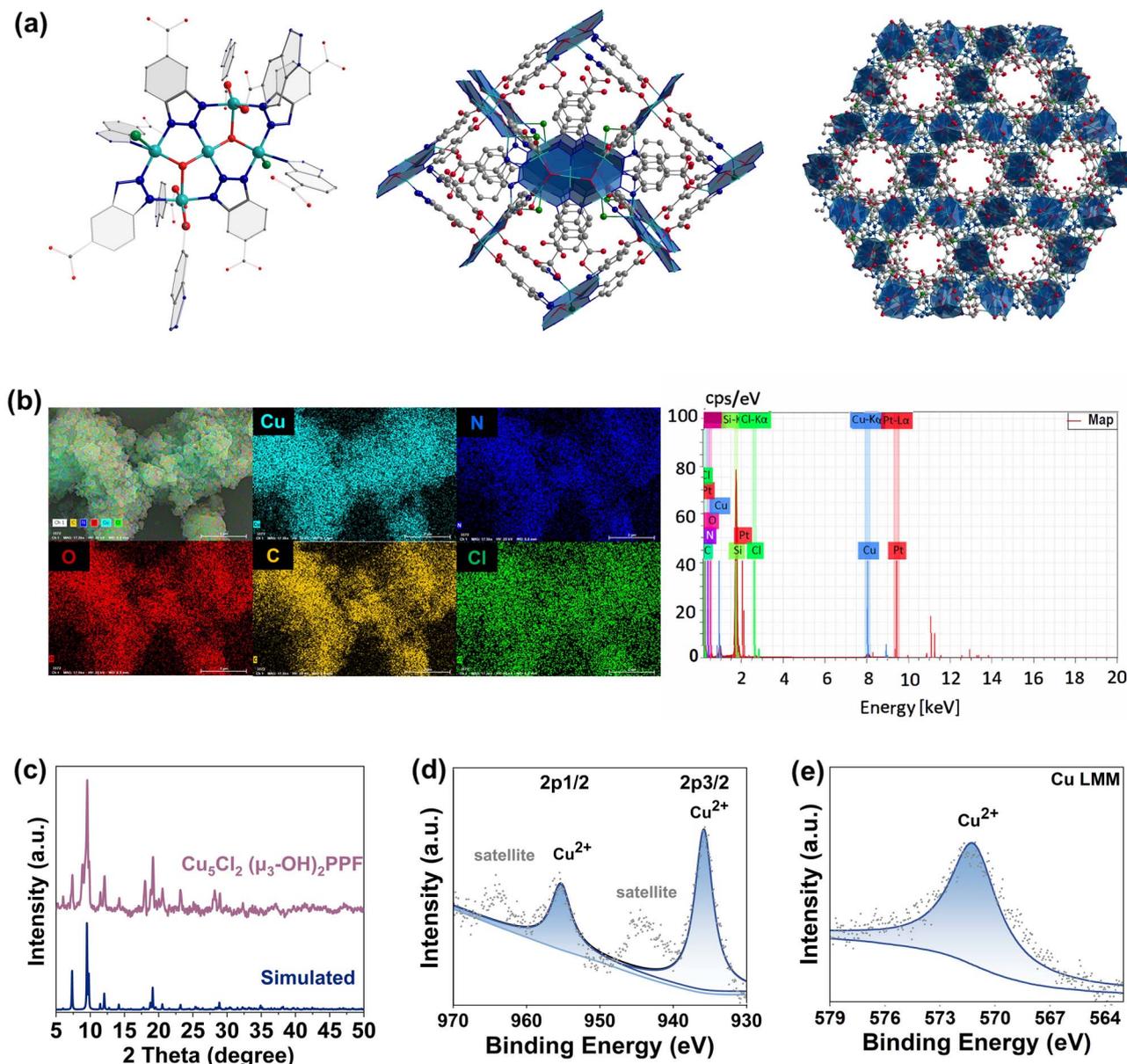


Fig. 1 (a) From left to right, the secondary building unit, ligand linking mode and 1-dimensional cavity channel of $\text{Cu}_5\text{Cl}_2(\mu_3\text{-OH})_2$ PPF. Among them, cyan, blue, gray, red, and green represent Cu, N, C, O, and Cl atoms, respectively. (b) SEM morphology and SEM-EDS mapping images of $\text{Cu}_5\text{Cl}_2(\mu_3\text{-OH})_2$ PPF. (c) PXRD and (d) XPS patterns and (e) Cu LMM Auger spectrum of $\text{Cu}_5\text{Cl}_2(\mu_3\text{-OH})_2$ PPF.

insights into the two FE_{urea} peaks observed at -0.5 V and -0.7 V.

We delve into the intrinsic mechanism of modulation driven by -0.5 V and -0.7 V from the unique structure of Cu_5 -PPF. As shown in Fig. 2a, although Cu_5 -PPF retained a similar framework to that of $\text{Cu}_5\text{Cl}_2(\mu_3\text{-OH})_2$ PPF, the removal of coordinated Cl and $\mu_3\text{-OH}$ groups introduces flexibility into the tetragonal $[\text{Cu}_5]^-$ pentacluster backbone. Studies have shown that increased applied voltage can lead to the elongation of bond lengths.^{45,46} To investigate this, we calculated the bond lengths of Cu_5 -PPF under applied potentials of -0.5 V and -0.7 V employing constant-potential DFT, in which the electrode potential was simulated by tuning the system's work function

through adjusting the total number of electrons. This approach, which has been widely used for modeling electrochemical interfaces,^{43,47,48} enables the assessment of how applied potential modulates electron transfer between Cu and N/O atoms, thereby influencing bond orders and resulting in bond length variations. As depicted in Fig. 2h, the Cu–O bond lengths in Cu_5 -PPF extended from 2.12/2.24 Å at -0.5 V to 2.37/2.34 Å at -0.7 V. The average bond length of the chemical bonds coordinated to Cu sites extended from 1.94 Å at -0.5 V to 1.96 Å at -0.7 V. According to previous studies, the length of the M–L coordination bond significantly affects the selectivity of electrocatalytic reactions.^{5,49,50} In particular, two distinct bond lengths can direct completely different CO_2RR pathways in the same



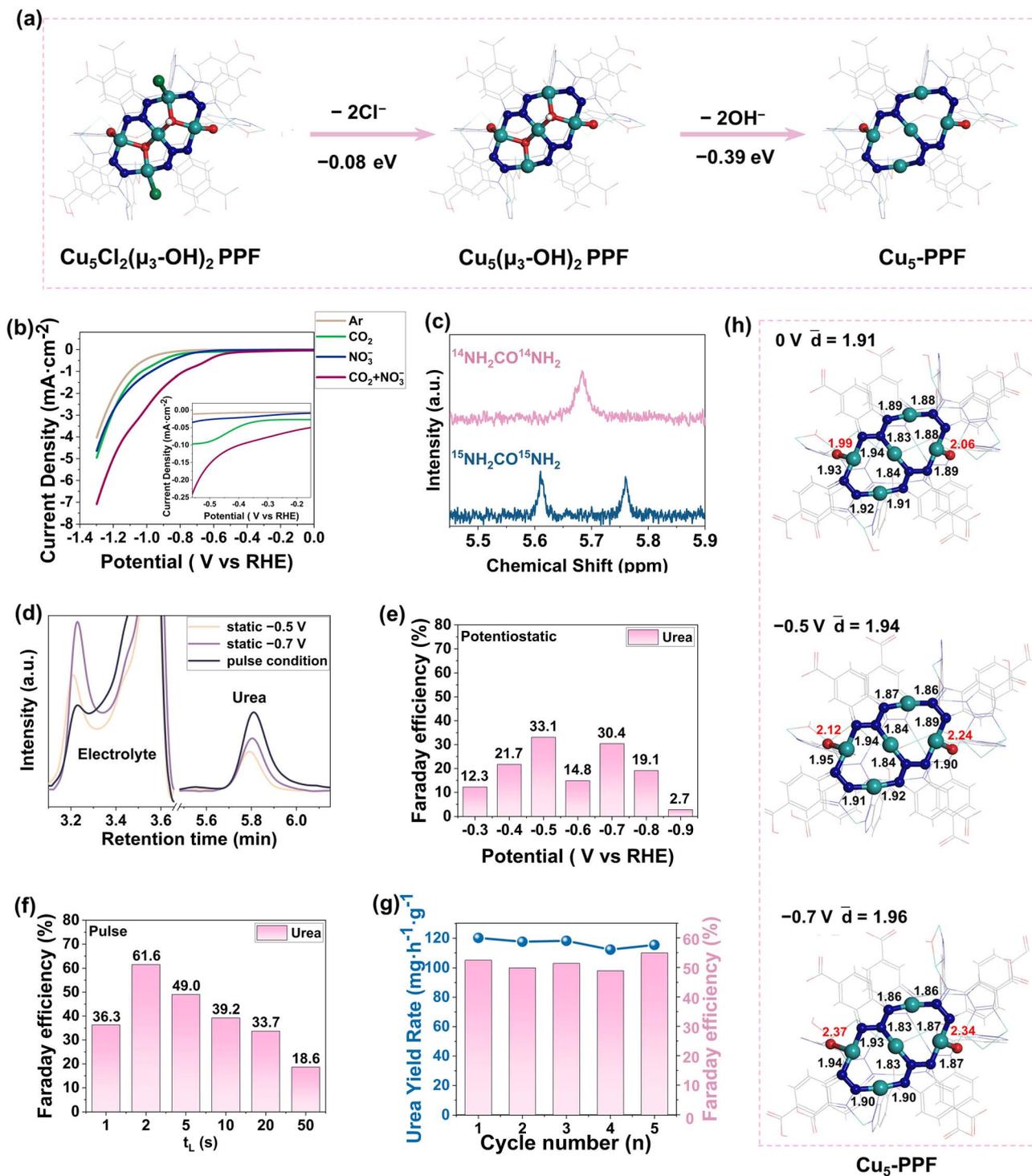


Fig. 2 (a) Energy changes of dechlorination and dehydroxylation for $\text{Cu}_5\text{Cl}_2(\mu_3\text{-OH})_2$ PPF. (b) LSV curve for $\text{Cu}_5\text{-PPF}$ under different conditions. (c) $^1\text{H-NMR}$ spectrum of $^{14}\text{NH}_2\text{CO}^{14}\text{NH}_2$ and $^{15}\text{NH}_2\text{CO}^{15}\text{NH}_2$. (d) HPLC spectra of urea generated from potentiostatic conditions and pulsed conditions. (e) FE_{urea} on $\text{Cu}_5\text{-PPF}$ under potentiostatic conditions. (f) Variation of FE_{urea} with t_L under pulsed conditions. Here, the t_U and t_L were set to 10 s, and the E_U and E_L were set to -0.5 V (vs. RHE) and -0.7 V (vs. RHE), respectively. All the C–N coupling reactions were carried out in 8 mM KNO_3 + 0.2 M K_2SO_4 solution saturated with CO_2 . (g) Yield $_{\text{urea}}$ and FE_{urea} for 5 cycles on $\text{Cu}_5\text{-PPF}$. (h) Calculated bond lengths near the Cu sites of $\text{Cu}_5\text{-PPF}$ at applied potentials of 0 V, -0.5 V, and -0.7 V, respectively.

reaction system.³⁷ For $\text{Cu}_5\text{-PPF}$, the bond length states induced by -0.5 V and -0.7 V likely manipulate two reaction pathways, specifically the corresponding N- and C-pathways.

By applying the pulse procedure with -0.5 V as the upper limit cathode potential (E_U) and -0.7 V as the lower limit cathode potential (E_L), dynamic elastic strain of the bond



lengths was induced by the alternating potentials. The impact of this dynamic system on urea performance is shown in Fig. 2f and S7, where the durations of upper limit cathode potential (t_U) and lower limit cathode potential (t_L) were optimized. Under optimal conditions of $t_U = 10$ s and $t_L = 2$ s, the FE_{urea} reached up to 61.6%. We further investigated the effect of the pulse potential direction by fixing the onset potential at -0.5 V. As shown in Fig. S8, applying more negative pulse potentials favored the urea formation pathway compared to less negative pulses. Notably, even when the less negative potential in the cycle is above the onset potential, urea is produced during the -0.5 V interval and contributes to the cycle-averaged FE. Under

pulsed conditions, the overall product distribution is determined by the full time-dependent sequence rather than by any instantaneous potential alone. Compared to the highest urea formation rate ($\text{Yield}_{\text{urea}}$) under potentiostatic conditions ($65.06 \text{ mg h}^{-1} \text{ g}^{-1}$), the dynamic system enhanced the $\text{Yield}_{\text{urea}}$ to $110.41 \text{ mg h}^{-1} \text{ g}^{-1}$ (Fig. S9). The dynamic bond length strain facilitated the sequential dominance of the C- and N-pathways within the same system, ultimately achieving the highest urea performance at optimal equilibrium. As depicted in Fig. 2g, the catalytic ability of $\text{Cu}_5\text{-PPF}$ was maintained after 5 catalytic cycles. Moreover, $\text{Cu}_5\text{-PPF}$ was able to operate for 3300 pulse cycles (shown in Fig. S10). The CO_2RR and NO_3RR performance

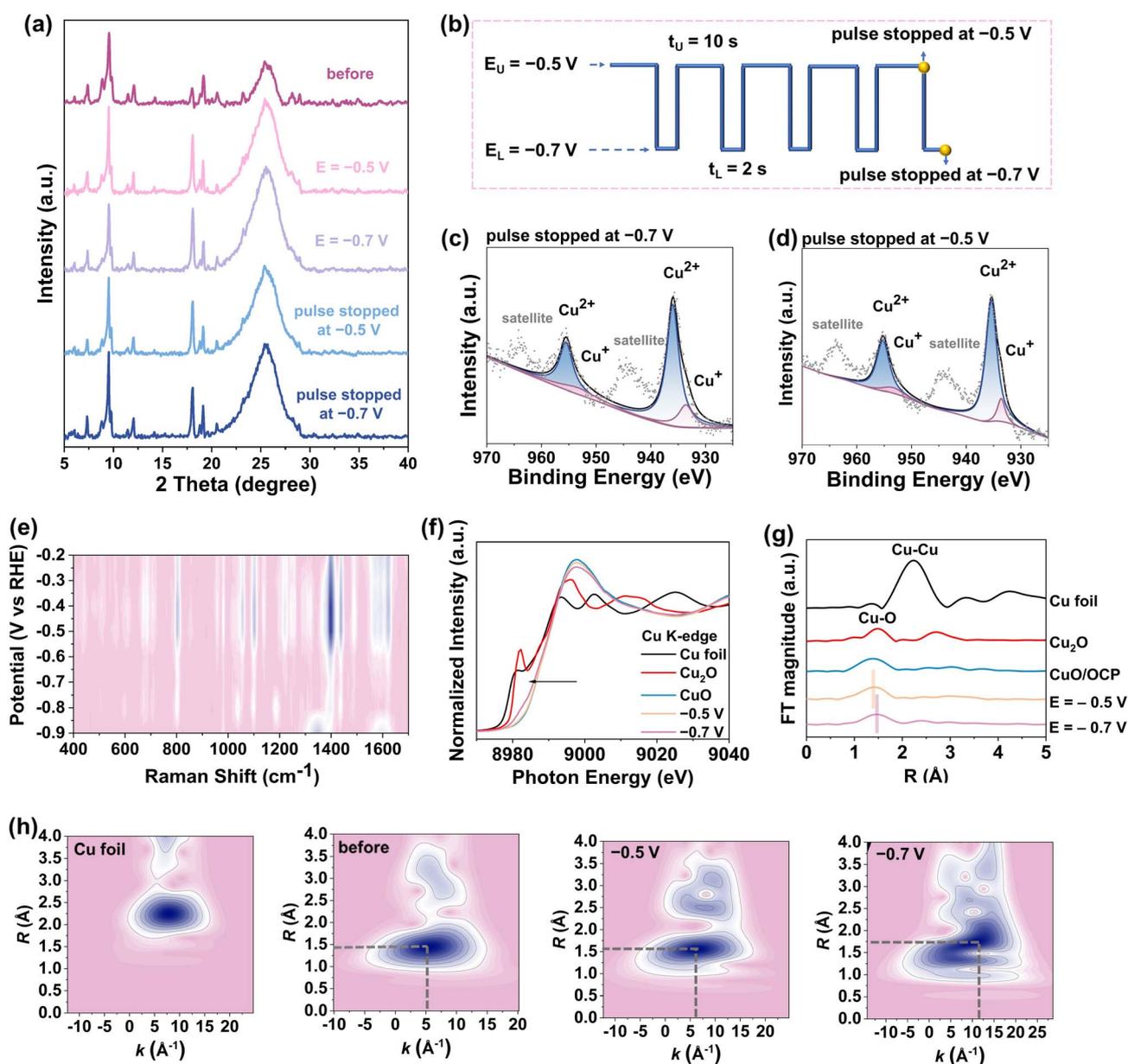


Fig. 3 (a) PXRD comparison of $\text{Cu}_5\text{-PPF}$ before and after 2 h of electrolysis. (b) Schematic diagram for the pulse sequence stopped at -0.5 V and -0.7 V. XPS spectra of $\text{Cu}_5\text{-PPF}$ after 2 h of electrolysis under pulsed conditions with the potential sequence stopped at (c) -0.7 V and (d) -0.5 V. (e) *In situ* Raman spectra of $\text{Cu}_5\text{-PPF}$. (f) Cu K-edge XANES and (g) FT-EXAFS spectra of $\text{Cu}_5\text{-PPF}$. (h) Wavelet-transform plots of Cu foil, $\text{Cu}_5\text{Cl}_2(\mu_3\text{-OH})_2$ PPF, and $\text{Cu}_5\text{-PPF}$ at -0.5 V and -0.7 V, respectively.



of Cu₅-PPF under pulsed conditions is presented in Fig. S11, emphasizing the incomplete reduction of C- and N-pathways that favored C–N coupling.

Fig. S12 and S13 illustrate the morphology and elemental distribution of Cu₅-PPF after the electrolysis reaction, demonstrating a uniform distribution of Cu, N, O, and C elements. In contrast, the Cl element showed a significant dissociation compared to the initial Cu₅Cl₂(μ₃-OH)₂ PPF, which aligned with the theoretical analysis. Fig. 3b presents a schematic representation indicating the termination position of the pulse sequence after 2 hours of electrolysis. As shown in Fig. 3a, the crystalline phase of Cu₅-PPF essentially preserved the original characteristics under both static and pulsed electrolysis. X-ray photoelectron spectroscopy (XPS) analysis revealed that the valence of Cu remained unchanged with varying pulse potentials, suggesting that the Cu oxidation states did not serve as an intrinsic character contributing to the dynamic modulation (Fig. 3c, d and S14). The Cu K-edge XANES spectra indicated that the Cu valence in Cu₅-PPF ranged between +1 and +2 under working conditions, attributed to the removal of Cl and μ₃-OH groups (Fig. 3f). *In situ* Raman spectroscopy was conducted to evaluate the electrochemical stability of Cu₅-PPF under varying applied potentials. As illustrated in Fig. 3e, Cu₅-PPF maintained its structural integrity at low potentials up to −0.7 V. Beyond this threshold, the intensity of characteristic vibrational signals declined markedly, and new peaks emerged at 1035 and 1188 cm^{−1}, indicating the formation of new chemical bonds. At −0.9 V, the original Cu₅-PPF framework was fully disrupted. Accordingly, −0.7 V was identified as the critical potential for structural preservation. At more negative potentials, excessive bond elongation led to bond cleavage and the formation of new bonding configurations. Fourier transform extended X-ray absorption fine structure (FT-EXAFS) and wavelet transform (WT)-EXAFS analysis of the Cu K-edge corroborated the significant elongation of the Cu–O/N bond at −0.7 V in comparison to both −0.5 V and the standard sample (Fig. 3g and h). Cu K-edge EXAFS fitting curves and the parameters for the Cu–N/O bonds in *R* space are displayed in Fig. S15 and Table S2. Compared to the original structure, the average Cu–N/O bond lengths extended to 1.93 Å and 1.95 Å at −0.5 V and −0.7 V, respectively. These experimental results validated the potential-induced elastic strain in the chemical bonds of Cu₅-PPF, thereby enabling the catalyst to flexibly adjust and adapt to the adsorption of various intermediates under pulse sequences.

Dynamic strain effect of bond lengths on reaction pathways

Advanced *in situ* attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was employed to monitor the evolution of reaction intermediates on Cu₅-PPF during urea generation. As shown in Fig. 4a, the peak at 1456 cm^{−1} was assigned to the formation of the C–N bond, indicating successful urea synthesis. A distinct band at 1215 cm^{−1} was attributed to the *COOH intermediate. Additionally, signals corresponding to *NO₂, *NO and *NH₂ species were detected, confirming the stepwise reduction of NO₃[−]. Notably, the *OCNO intermediate was identified by a characteristic peak at 2066 cm^{−1}, providing key mechanistic insight into the urea formation pathway.

Guided by these ATR-FTIR findings, Density Functional Theory (DFT) calculations were subsequently performed to elucidate the detailed reaction mechanisms. Although constant-potential DFT cannot capture the full dynamic evolution of metastable catalyst states during pulsed electrolysis, analyzing reaction pathways at representative static potentials (*e.g.*, −0.5 V and −0.7 V) has been widely adopted to gain qualitative insight into pulse-driven mechanisms and is considered a practical and informative approximation under current computational limitations.^{51–54} These two potentials are not intended to mimic real-time oscillation, but rather to approximate the anodic and cathodic conditions within the pulse cycle. Researchers have indicated that the length of M–L significantly affected the adsorption properties of active intermediates, further controlling the reaction pathways.^{55,56} To delve deeper into the impact of the elastic strain of bond lengths on the reaction, we calculated the Gibbs free energy profiles on Cu₅-PPF at −0.5 V and −0.7 V (Tables S3 and S4). In our system, the key N- and C-species for the first step of C–N coupling were *NO and *COOH, respectively. For the N-pathway shown in Fig. 4b, free energy changes (Δ*G*) for all *NO intermediate formation steps at −0.5 V were lower than the corresponding steps at −0.7 V, indicating a preference for shorter bond lengths in N-containing species generation. Electrostatic potential analysis revealed that the catalyst surface exhibited more positive potential regions at −0.5 V, facilitating preferential adsorption of negatively charged NO₃[−] (Fig. S16). For the initial step in the N-pathway (*NO₃ → *HNO₃), hydrogenation at −0.5 V was energetically more favorable than that at −0.7 V, which can be attributed to differences in the adsorption configurations of *NO₃. Several *NO₃ adsorption modes were considered, including single O-bonding to edge or central Cu–N sites, double O-bonding involving two edge Cu–N sites, and double O-bonding to edge Cu and central Cu–N/O sites. A potential-dependent trend was observed: at −0.5 V, double O-bonding configurations were preferred, promoting *NO₃ activation and subsequent hydrogenation, whereas at −0.7 V, single O-bonding became more stable (Fig. S17). Similar site-specific bonding behavior and Cu-site synergy were also observed for other key intermediates along the reaction pathway. The second rate-determining step of the N-pathway was governed by the elastic strain of the Cu–O bonds in Cu₅-PPF. Elongation of the Cu–O bond lengths at higher potentials enabled the Cu atoms to carry more positive charge, enhancing the binding with the oxygen atom in *NO₂ and making the subsequent ring-opening hydrogenation more difficult. Consequently, the shorter Cu–O bond lengths driven by −0.5 V resulted in a lower energy change for the *NO₂ → *HNO₂ step. Additionally, the shorter Cu–O bond length was more favorable for both the first and second C–N coupling steps (Fig. 4c and d). Calculations depicted in Fig. 4d revealed that for the C-pathway, a more negative potential (−0.7 V) favored the formation of C-containing intermediates. The extended Cu–O bond lengths driven by −0.7 V allowed the Cu atoms with more positive charge to stabilize the O-terminus of *CO₂, promoting adsorption of CO₂ and *COOH formation with thermodynamically supported Δ*G* values of −0.58 eV and −0.16 eV compared to 0.12 eV and −0.02 eV at −0.5 V.

In summary, the significant elastic strain of bond lengths in Cu₅-PPF regulated the adsorption strength and the binding



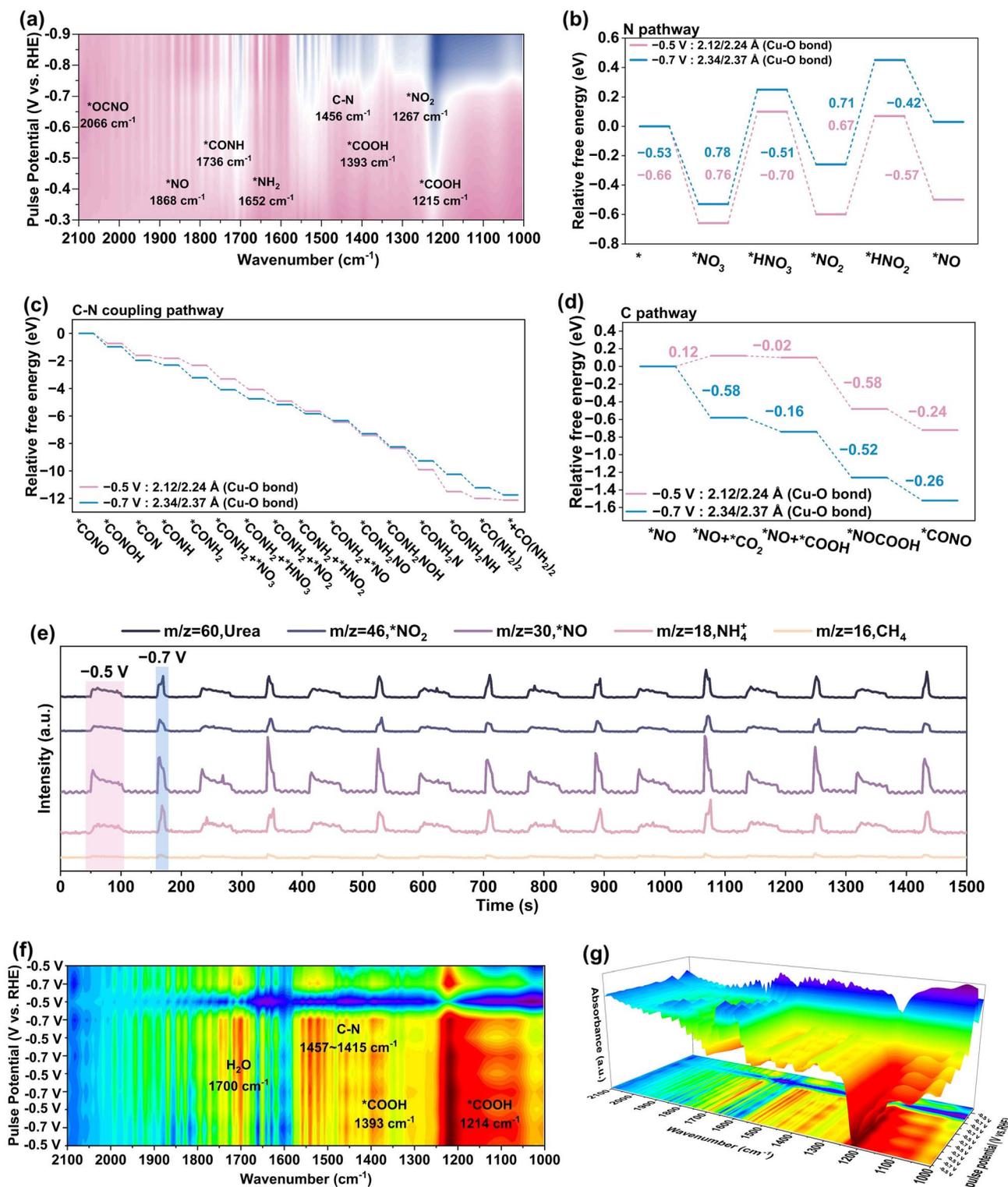


Fig. 4 (a) ATR-FTIR measurements under various potentials for Cu₅-PPF. Free energy profiles of (b) N-containing intermediates, (c) C–N coupling, and (d) C-containing intermediate pathways during urea electrosynthesis on Cu₅-PPF at –0.5 V and –0.7 V. (e) DEMS measurements of Cu₅-PPF during urea production. In CO₂ saturated 8 mM KNO₃ + 0.2 M K₂SO₄ solution, signals at $m/z = 60$ (urea), $m/z = 46$ (*NO₂), $m/z = 30$ (*NO), $m/z = 18$ (NH₄⁺) and $m/z = 16$ (CH₄) were recorded simultaneously. The tested potential pulse consists of a cathodic period at –0.5 V for 50 s and a period at –0.7 V for 10 s. Each individual electrolysis reaction was followed by a power-off period of 60 s to flush out air bubbles left in the chamber from the previous test. (f) ATR-FTIR and (g) the corresponding three-dimensional spectra of Cu₅-PPF under pulsed cycling.



behavior of intermediates. The elongated bond lengths induced by -0.7 V favored the adsorption of CO_2 and formation of $^*\text{COOH}$ intermediates, but tended to generate large amounts of NH_4^+ by-product. Conversely, shorter bond lengths driven by -0.5 V facilitated the production of essential $^*\text{NO}$ species but struggled to adsorb sufficient CO_2 for C-N coupling, in agreement with the experimental results depicted in Fig. S18. By precisely controlling the elastic strain of bond lengths through periodic alternating potentials, a dynamic switch between optimal N- and C-pathways within the same catalytic system was achieved.

Combined with theoretical calculations, we identified $^*\text{COOH}$ and $^*\text{NO}$ as the key intermediates in the C-N coupling pathway. *In situ* differential electrochemical mass spectroscopy (DEMS) was employed to monitor intermediates at -0.5 V and -0.7 V (Fig. 4e). Due to the continuous CO_2 flow during the experiment, direct detection of CO_2 signals was not feasible. Instead, CH_4 , a reduction product of $^*\text{COOH}$, was used as a marker of the C pathway.⁵⁷ No CH_4 signal was observed at -0.5 V, while a weak CH_4 signal emerged at -0.7 V, suggesting that the elongated Cu-O bonds at -0.7 V facilitated CO_2 adsorption and activation, in agreement with DFT results. For the N pathway, the $^*\text{NO}$ intermediate showed a strong signal relative to NO_2^- and NH_4^+ , confirming its key role in urea production. These *in situ* DEMS results validated the formation of $^*\text{COOH}$ and $^*\text{NO}$ intermediates, thereby supporting the proposed reaction mechanism. Moreover, DEMS

measurements under alternating potentials (-0.5 V and -0.7 V) further confirmed the dynamic evolution of active intermediates.

The ATR-FTIR spectra under dynamic conditions further demonstrated the response of the intermediates to the pulse potential, as shown in Fig. 4f and g. As the Cu-O bond lengths underwent dynamic strain, a clear periodic fluctuation in the strength of the C-N bonds and $^*\text{COOH}$ intermediates was observed. Notably, the formation of $^*\text{COOH}$ intermediates was preferentially favored in the extended bond length state, consistent with the free energy change and *in situ* DEMS analysis. As the pulse cycle progressed, the peak intensity at 1700 cm^{-1} decreased due to the constant consumption of H_2O . The consumption and dissociation of H_2O generated a large amount of $^*\text{H}$, which actively participated in the catalytic reaction to form intermediates.^{58,59}

Electrocatalytic performance of rigid structures under dynamic conditions

To further explore the dynamic elastic strain of bond lengths on urea electroynthesis, we selected a trinuclear cluster-based porous tubular 3D framework ($\text{Cu}_3\mu_3\text{-O TPF}$) and $\text{Cu}_3\mu_3\text{-OH}$ trinuclear clusters ($\text{Cu}_3\mu_3\text{-OH clusters}$) as comparison structures. The energy calculations for deoxidation of $\text{Cu}_3\mu_3\text{-O TPF}$ and dehydroxylation of $\text{Cu}_3\mu_3\text{-OH clusters}$ are shown in Fig. 5a and b, respectively. We identified $\text{Cu}_3\text{-TPF}$ and $\text{Cu}_3\text{-clusters}$ as the active structure under working conditions. The XRD pattern, XPS and

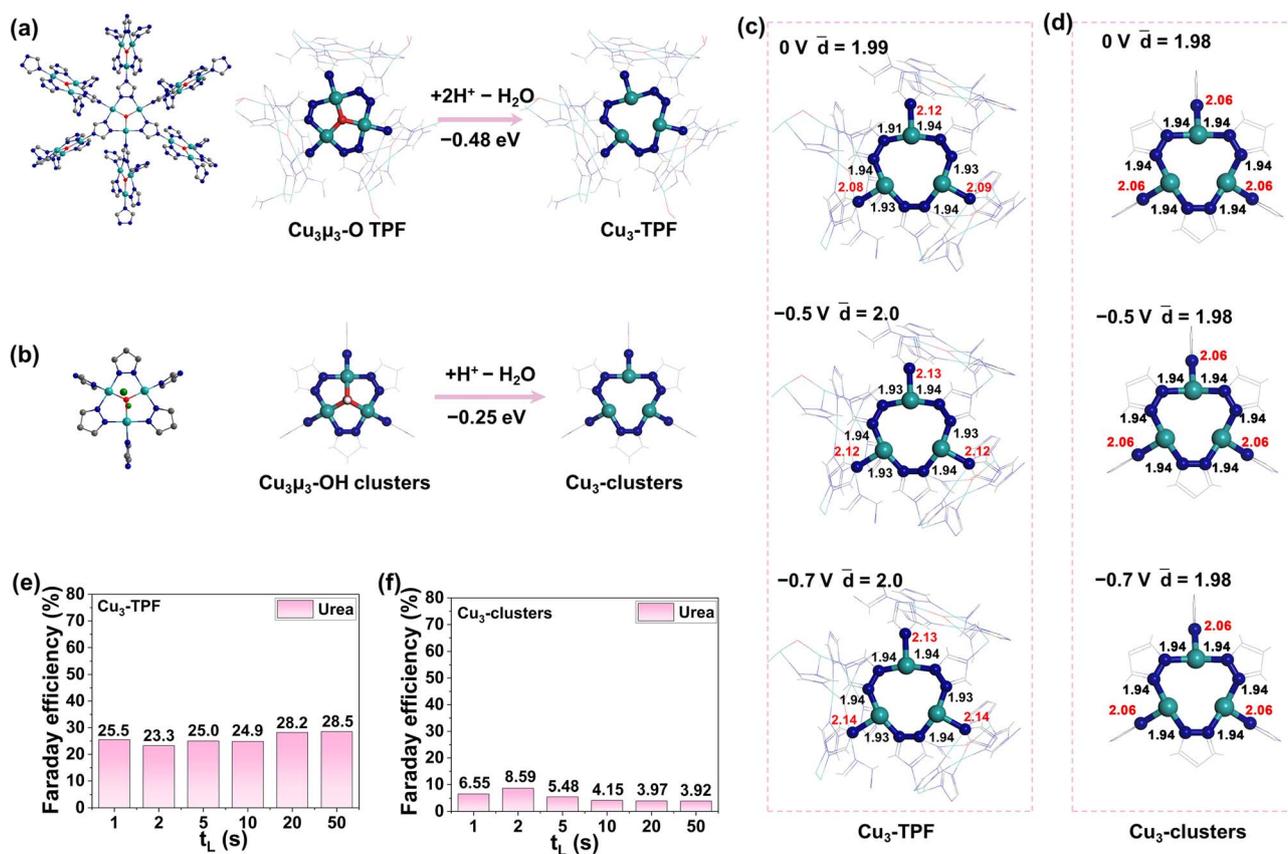


Fig. 5 Energy changes of (a) deoxidation for $\text{Cu}_3\mu_3\text{-O TPF}$ and (b) dihydroxylation for $\text{Cu}_3\mu_3\text{-OH}$. Bond lengths near the Cu sites of (c) $\text{Cu}_3\text{-TPF}$ and (d) $\text{Cu}_3\text{-clusters}$ at applied potentials of 0 V, -0.5 V, and -0.7 V, respectively. Variation of FE_{urea} with t_L under pulsed conditions for (e) $\text{Cu}_3\text{-TPF}$ and (f) $\text{Cu}_3\text{-clusters}$. The electrocatalytic conditions were consistent with those of $\text{Cu}_5\text{-PPF}$.



Cu LMM spectra of Cu₃-TPF and Cu₃-clusters are presented in Fig. S19–S22. The 3D structure and 1D channels of Cu₃μ₃-O TPF are depicted in Fig. S23. *In situ* Raman was employed to monitor the structural evolution of Cu₃-TPF at different potentials. As shown in Fig. S24, Cu₃-TPF exhibited pronounced stability. Though some new chemical bonds emerged within the 1100 to 2000 cm⁻¹ range at -0.9 V, the primary framework remained intact. We calculated the variations in bond lengths around the Cu sites of Cu₃-TPF at -0.5 V and -0.7 V. Compared to Cu₅-PPF, the average bond lengths of Cu₃-TPF exhibited minor changes (Fig. 5c), likely due to the more rigid planar triangular coordination mode of Cu₃ compared to the distorted square coordination of Cu₅-PPF. For Cu₃-TPF, the pulsed conditions did not enhance the urea selectivity, but instead resulted in a decrease compared to potentiostatic electrolysis (Fig. 5e and S25). This could be attributed to the inadequate strain of bond lengths in Cu₃-TPF to effectively modulate the C- and N-pathways. The situation for Cu₃-clusters was similar to that of Cu₃-TPF. Moreover, the urea synthesis activity of Cu₃-clusters was even less favorable due to their more rigid structure (Fig. 5d and f). The Yield_{urea} values of Cu₃-TPF and Cu₃-clusters are shown in Fig. S26 and S27, which were much lower than that of Cu₅-PPF under the same conditions. These results demonstrated the importance of dynamically evolving bond lengths in urea production.

Conclusion

In this work, we presented an effective strategy to control the parallel NO₃RR and CO₂RR pathways toward the desired urea product by dynamically regulating the elastic strain in the Cu–O bonds. The well-defined Cu₅Cl₂(μ₃-OH)₂ PPF served as the initial structure, which was subsequently dechlorinated and deoxygenated under working conditions to form Cu₅-PPF as the catalyst. Benefiting from the structural flexibility of Cu₅-PPF, dynamic elastic strain in the Cu–O bond lengths was induced by pulsed potentials. *In situ* spectroscopy combined with DFT results confirmed that the shorter Cu–O bond lengths driven by -0.5 V dominated the formation of key *NO species in the N-pathway. Furthermore, the elongation of Cu–O bonds promoted the adsorption of CO₂ and the formation of *COOH intermediates in the C-pathway. The dynamic strain effect on Cu–O bond lengths optimized the N- and C-pathways separately, ultimately reaching an equilibrium point of the highest urea selectivity. Under dynamic conditions, the FE_{urea} was up to 61.6%. To further validate the importance of the strain effect on bond lengths, we evaluated the rigidly structured Cu₃-TPF and Cu₃-clusters and assessed their urea synthesis performance. Since the bond lengths of Cu₃-TPF and Cu₃-clusters exhibited minimal strain, the pulse-driven dynamic system did not enhance their FE_{urea}. Our work provides valuable insights into the structure–activity relationship and inspires new directions for regulating multiple reaction pathways in dynamic systems.

Author contributions

Xin Zhang carried out the experimental studies: synthesis, characterization, catalysis and data analysis. Hao Sun carried

out the computational studies. Hai-Yan Zheng and Jian-Rong Zeng carried out the XAS experiments. Jing-Yao Liu, Chun-Yi Sun, Zhan Shi, and Zhong-Min Su supervised the whole project. All authors contributed to the writing of this manuscript and they have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as a part of the SI. See DOI: <https://doi.org/10.1039/d5sc04375a>.

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