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Article

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Posted Date: April 22nd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-9274540/v1>

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Additional Declarations: There is **NO** Competing Interest.

Thermal sculpting of nanoconfined single-atom cavities enables urea electrosynthesis with near- unity selectivity

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Abstract

Electrocatalytic urea synthesis from CO_2 and NO_3^- offers a sustainable alternative to energy-intensive industrial methods, yet precise C–N coupling remains hindered by kinetic mismatches between the reduction reactions. Here, we report a strategy leveraging programmable Zn-node gasification to thermally sculpt 1.5–1.8 nm cavities within zeolitic imidazolate frameworks, hosting atomically dispersed Cu–N₄ sites. Thermal transformation retains macroscopic framework, creating size-matched nanoconfined environments for selective catalysis. An optimal confinement metric descriptor (9.64) is introduced as a predictive design parameter, correlating cavity geometry with local electric field and Cu d-band modulation. This design stabilizes *CO and *NO intermediates, effectively suppressing parasitic reactions and lowering C–N coupling barriers. Consequently, the catalyst delivers a record urea yield of 71.32 g g_{cat}^{−1} h^{−1} with 98.9% Faradaic efficiency in gas diffusion cells. Pilot-scale testing confirms its stability over 300 h, establishing nanoconfinement as a pivotal design principle for high-performance urea electrosynthesis.

Keywords: Electrosynthesis; Urea; Thermal sculpting; Nanoconfined cavities; Near-unity selectivity

Main

Since its inception 200 years ago¹, the global chemical industry has remained profoundly reliant on urea, which continues to be the cornerstone nitrogen fertilizer sustaining nearly half of the world's population²⁻⁵. However, current urea production integrating Haber-Bosch and Bosch-Meiser processes⁶ accounts for 2% of the global energy consumption and 1.5% of total carbon dioxide (CO₂) emissions^{7,8}. Electrosynthesis of urea with CO₂ and nitrate (NO₃⁻) offers a compelling, carbon-neutral alternative, potentially transforming environmental pollutants into high-value chemicals under ambient conditions⁹. By utilizing renewable electricity, this pathway can bypass the high energy barriers of traditional manufacturing and facilitate the decentralized production of urea directly from wastewater and flue gas⁹⁻¹².

Despite the feasibility of electrocatalytic urea synthesis, the process faces a fundamental bottleneck characterized by a severe kinetic mismatch between the CO₂ and NO₃⁻ reduction and hydrogen evolution reactions (CO₂RR, NO₃RR and HER)¹³. Conventional catalytic interfaces act as "infinite domains", where active site distribution and intermediate diffusion are unrestricted^{14,15}. In such scenarios, key intermediates including *CO, *NO and *H rapidly undergo side reactions such as ammonia, nitrogen and hydrogen evolution, resulting in insufficient concentration to facilitate bimolecular C–N coupling¹⁶. Besides, the coordination environment of metal active sites critically regulates the C–N coupling pathway by tuning *CO adsorption and reactant enrichment^{17,18}. The lack of a tailored nanoconfined environment with properly coordinated active sites is the primary reason that existing catalysts cannot simultaneously achieve high yield and near-unity selectivity^{19,20}.

Here, we developed a thermal sculpting strategy based on programmable Zn-node

gasification in zeolitic imidazolate frameworks (ZIFs) to create size-controlled nanoconfined cavities that host optimized Cu–N₄ single-atom sites. Unlike conventional carbonization that induces structural densification or collapse^{18,21}, the multi-stage programmable pyrolysis protocol guides the formation of 1.5–1.8 nm cavities which are proposed to provide a size-matched environment that minimizes the energy barrier of adsorbed molecules and suppresses the side reactions (Fig. 1a)²². More importantly, a confinement descriptor was established to quantitatively bridge cavity geometry, local electric field, and electronic structure, thereby defining a generalizable design principle for nanoconfined electrocatalysis. This strategy achieves an unprecedented urea yield of 71.32 g g_{cat}^{−1} h^{−1}, Faradaic efficiency (FE) of 98.9%, turnover frequency of 5277 h^{−1} at −0.7 V, and over 300 h continuous stability at the pilot scale, providing a generalizable engineering strategy for tailoring site-specific nanoconfinement in framework-derived materials for practical, high-throughput electrosynthesis.

Controlled sculpting via Zn vapor gasification

The Cu modified ZIF precursor (ZIF-Cu) was solvothermally synthesized by mixing zinc nitrate, copper nitrate trihydrate, and 2-methylimidazole in a methanol-deionized water mixed solvent (Supplementary Information, Section 2.1)²³. Fourier transform infrared (FT-IR) spectroscopy illustrates characteristic imidazole ring and Zn–N/Cu–N bond peaks (Supplementary Fig. 1), and powder X-ray diffraction (XRD) patterns validates its typical rhombic dodecahedral framework (Supplementary Fig. 2)¹¹. N₂ adsorption–desorption yields a Brunauer-Emmett-Teller specific surface area of 1748.5 m² g^{−1} with a 1.5 nm dominant pore size (Supplementary Fig. 3). Scanning electron microscopy (SEM, Supplementary Fig. 4) and transmission electron microscopy (TEM, Supplementary Fig. 5) reveal uniform rhombic

microcrystals, with all data collectively verifying successful ZIF-Cu construction.

The thermally sculpted ZIF-Cus (tZIF-Cus) were fabricated via a designed multi-stage pyrolysis protocol, optimized based on thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) of the ZIF-Cu precursor with tailored temperature ramps and isothermal holds for each target pyrolysis temperature (Supplementary Fig. 6, Supplementary Information, Section 2.2). Below 600 °C, the removal of occluded solvents and the condensation of organic linkers occur, transforming the flexible ZIF framework into a rigid, N-doped carbon scaffold. At 800 °C, the material retains the intrinsic 1.5 nm pore size of the ZIF precursor, with underdeveloped pore volume (Fig. 1b, c). As the temperature approaches the boiling point of Zn (905 °C, Supplementary Fig. 6b)²¹, framework Zn species undergo reduction and gasification, acting as both an internal sacrificial template and thermal chisel to etch sub-nanometer spaces in the hardening carbon matrix, while Cu and nitrogen species stabilize the surrounding architecture against collapse²⁴. For tZIF-Cu₉₀₀, the proportion of 1.8 nm micropores significantly increases, corresponding to the dissociation of intrinsic ZIF pores and formation of new cavities via ligand polycondensation and graphitization (Supplementary Fig. 7)^{25,26}. At 1000 °C, 2.6 nm pores develop and disperse while tZIF-Cu₁₁₀₀ exhibits excessive graphitization and framework collapse with loss of ordered porous structure (Fig. 1c).

Throughout the entire heating process, XRD patterns of tZIF-Cus exhibit only broad peaks of graphitic carbon, with no detectable signals of Cu, Zn or their oxides (Supplementary Fig. 2). The dodecahedron morphology is largely preserved below 1000 °C (Fig. 1b, d and Supplementary Figs. 8 and 9). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) provides direct visual confirmation,

with atomically dispersed Cu sites observed as uniform bright spots within the matrix (Fig. 1d and Supplementary Fig. 10). The mesoscopic pore structure can also be resolved (Supplementary Fig. 11). Energy-dispersive X-ray spectroscopy (EDS) elemental mapping confirms the uniform distribution of Cu, and that nearly all Zn had been evaporated (Supplementary Fig. 12). Inductively coupled plasma optical emission spectrometry results demonstrate that the residual Zn content was below 0.03 wt%. Comprehensive characterizations corroborate the absence of nanoclusters during thermal sculpting. By contrast, the imidazole framework of undoped ZIF completely collapsed (Supplementary Fig. 13) while Co and Fe doping preserved the morphology (Supplementary Figs. 14 and 15) under the same pyrolysis conditions.

X-ray photoelectron spectroscopy (XPS) of tZIF-Cus reveals peaks at 932.4 eV and 952.2 eV in the Cu 2p region, while N 1s spectra substantiate the dominance of pyridinic nitrogen (8.7 at%)²⁷. These results, together with the C 1s and O 1s XPS spectra, confirms a favorable coordination environment for anchoring atomically dispersed Cu sites (Fig. 2a, b and Supplementary Figs. 16–18)²⁸. X-ray absorption near-edge structure (XANES) spectra illustrate a near-edge absorption peak at 8986 eV, indicating a near +1 valence state of Cu (Fig. 2c)^{29,30}. Extended X-ray absorption fine structure (EXAFS) fitting of the Cu K-edge reveals a dominant Cu–N scattering peak at ~ 1.5 Å (Fig. 2d, and Supplementary Fig. 19). The coordination number is determined to be 3.5 ± 0.43 with an average Cu–N bond length of 1.87 ± 0.01 Å, consistent with a Cu–N₄ environment (Fig. 2e)³¹. This coordination geometry remains relatively constant across the different pyrolysis temperatures.

Urea electrosynthesis

Electrochemical characterizations were used to investigate response activity of tZIF-Cus to different reactants. The tZIF-Cu₉₀₀ achieves the highest C–N co-reduction current density (Fig. 3a), the most positive NO₃RR onset potential, and moderate HER/CO₂RR activity (Supplementary Figs. 20–22, Supplementary Information, Section 3.1) which effectively suppresses the parasitic reactions, kinetically matching among NO₃RR, CO₂RR and HER. pH optimization tests validate its more favorable reaction kinetics in alkaline electrolyte (Supplementary Figs. 23 and 24). Meanwhile, tZIF-Cu₉₀₀ delivers the gentlest Tafel slope (47.6 mV dec^{−1}, Fig. 3b), the largest electrochemical surface area (128 cm² g^{−1}, Fig. 3c, Supplementary Fig. 25) and the lowest charge transfer impedance (Supplementary Fig. 26), indicating faster reaction kinetics and higher electrocatalytic potential response³². In contrast, tZIF-Cu₈₀₀ suffers from sluggish reaction kinetics, while tZIF-Cu₁₀₀₀ and tZIF-Cu₁₁₀₀ indicate severe loss of active area.

The urea electrosynthesis performance of tZIF-Cus was evaluated in a H-type cell and a gas diffusion electrode (GDE) cell (Supplementary Fig. 27), both of which were saturated with CO₂ and 0.1 M KNO₃/0.1 M KHCO₃. The H-type cell was used to evaluate the catalyst intrinsic activities for fundamental screening, while the GDE cell was employed to enhance mass transfer via a three-phase interface, enabling higher product yield under industrially relevant validation^{9,18}. During the reactions, urea, gas and liquid intermediates were quantified and qualified by chromatography and ¹⁵N NMR spectroscopy (Supplementary Figs. 28–32). In the H-type cell, tZIF-Cu₉₀₀ achieves a Faradaic efficiency (FE) for urea of 94.1% at −0.5 V vs. RHE, with a urea yield rate of 10.97 g g_{cat}^{−1} h^{−1} and a turnover frequency of 5277 h^{−1} at −0.7 V

vs. RHE (Fig. 3d). In the GDE cell, tZIF-Cu₉₀₀ delivers a urea yield of up to 71.32 g g_{cat}⁻¹ h⁻¹ with a FE of 98.9% at -0.7 V vs. RHE (Fig. 3e). The main by-products of this reaction are NH₄⁺ and NO₂⁻ (Fig. 3f). The NH₄⁺ production rate increases monotonically with increasing negative potential, confirming the potential dependence of the NO₃RR process (Supplementary Fig. 33). When CO₂ flow rate or NO₃⁻ concentration is raised, the yield of urea simultaneously promoted (Supplementary Fig. 34). After 20 cycles of reuse, only negligible loss of activity was observed (Supplementary Fig. 35). This activity and stability performance also outperform the tZIF-Fe and tZIF-Co (Supplementary Fig. 36) and counterpart catalysts in the previous studies (Fig. 3g, Supplementary Table 1)^{10,11,13,18,33-44}. The inferior urea electrosynthesis performance of Fe- and Co-based counterparts is mainly attributed to their upshifted d-band centers relative to Cu-N₄, which triggers competitive HER via excessively strong *H adsorption, and inhibits C-N coupling through over-stabilization of key *CO and *NO intermediates⁴⁵.

Descriptor-guided confined catalysis design

Excluding the interference from Cu-N₄ coordination environment (Fig. 2), single-atom loading density (Fig. 1d and Supplementary Fig. 8) and specific surface area (which shows a negative correlation with catalytic activity, Fig. 1c), the nanoconfinement effect is hypothesized as the primary factor governing the catalytic performance of tZIF-Cus, following a matching mechanism: Over-contracted cavities fail to enrich C- and N- reactants while over-sized cavities cause over-strong intermediate adsorption, favoring competitive adverse reactions.

This hypothesis on geometrical confined effect was first validated by molecular dynamics (MD) simulations. Guided by the N₂ adsorption-desorption pore size distribution (Fig. 1c), Cu-

N₄-embedded carbon cavity models were constructed with diameters of 1.0 nm, 1.5 nm, 1.8 nm, and 2.6 nm to simulate the diffusion behavior of reactants (CO₂, NO₃⁻, H₂O) and key intermediates (CO, NO). The 1.0 nm cavity is nearly inaccessible to all species. The predominant 1.5–1.8 nm cavity in optimal tZIF-Cu₉₀₀ balances reactant mass transport and intermediate confinement. Specifically, 1.8 nm cavities allow sufficient access of hydrated NO₃⁻ (0.63 nm diameter) and CO₂, while prolonging the retention of key CO and NO intermediates via moderate spatial confinement to accelerate C–N coupling kinetics (Fig. 4a, Supplementary Figs. 37–44, Supplementary Information, Section 4.1 and Supplementary Video 1–4).

Beyond geometric confinement, thermal sculpting induces unique electronic modulation of the active sites and electronic confined effect (Supplementary Information, Section 4.2). The pyridinic N-rich concave carbon cavity generates a strong localized electric field (3.05 Å⁻¹–4.09 V Å⁻¹, Supplementary Figs. 45 and 46) which exerts compressive strain on the central Cu atom, weakening the hybridization between Cu 3d and N 2p orbitals^{46,47}. Density functional theory (DFT) calculations verifies that this strain upshifted the Cu d-band center from –3.36 eV to –1.85 eV (Fig. 4b). This electronic modulation was further validated by XPS secondary electron cutoff edge upshift (Supplementary Fig. 47), positive shift of Cu 2p binding energy (Fig. 2b), and Cu K-edge XANES absorption edge shift (Fig. 2c). The upshifted d-band center and enhanced local electric field synergistically strengthen *CO/*NO adsorption, lower the rate-determining C–N coupling barrier⁴⁸, and thus promote urea electrosynthesis.

Based on the analyses on geometrical and electronic confined effects, a weighted-average confinement metric descriptor (CMD) system was established to bridge single-pore simulation

data and the multi-dispersed pore structure of catalysts. First, intrinsic CMD (CMD_i) for single-pore ideal models is defined as:

$$CMD_i = \frac{CEF_i}{CEF_{ref}} \times \left(1 + \frac{\Delta\varepsilon_{d,i}}{\Delta\varepsilon_{d,ref}} \right) \times \gamma_i \quad (1)$$

where CEF_i is simulated average confinement electric field; CEF_{ref} is reference CEF of unconfined planar Cu–N₄ sites; $\Delta\varepsilon_{d,i}$ is upshift amplitude of Cu d-band center relative to unconfined reference; $\Delta\varepsilon_{d,ref}$ is maximum d-band upshift for normalization; The steric hindrance correction factor γ_i is a continuous exponential function fitted by molecular dynamics simulation results, ranging from 0 to 1. It quantifies the reactant accessibility and intermediate retention efficiency of nanocavities, determined by the matching degree between pore size and the kinetic diameter of reaction species. Weighted average CMD (CMD_a) for actual multi-pore catalysts was defined as:

$$CMD_a = \sum CMD_i \times f_i \quad (2)$$

where f_i is the active pore volume fraction of the i-th pore size interval obtained from N₂ sorption measurements. This calculation links ideal simulation models to real catalysts by weighting the intrinsic confinement strength of each pore interval to quantify the overall confinement effect.

The calculated CMD_a values for tZIF-Cu₈₀₀, tZIF-Cu₉₀₀, tZIF-Cu₁₀₀₀ and tZIF-Cu₁₁₀₀ are 8.18, 9.64, 6.82 and 4.57, respectively, indicating a strict positive correlation with urea electrosynthesis performance (Supplementary Information, Section 4.2). The maximum CMD_a of tZIF-Cu₉₀₀ arises from its full coverage of the 1.5–1.8 nm optimal confinement interval, which balances intermediate enrichment, electronic structure optimization and mass transport. tZIF-Cu₈₀₀ suffers from severe steric hindrance in 1.0–1.5 nm narrow pores, while

tZIF-Cu₁₀₀₀ and tZIF-Cu₁₁₀₀ have insufficient effective confinement pores, resulting in markedly degraded catalytic performance.

The control experiments were performed over tZIF-Cu₉₀₀ to identify key C–N coupling intermediates (Fig. 4c). CO was identified as the dominant carbon intermediate, with *NO, *NH₂OH and *CONH₂ as critical nitrogen intermediates. No urea was detected with N₂ or NH₄⁺ as the sole nitrogen source, verifying the core *CO/*NO coupling pathway. Temperature-programmed desorption further shows that tZIF-Cu₉₀₀ enables weak physical adsorption of CO and NO below 200 °C (Fig. 4d), retaining intermediates in an activated, mobile state ideal for coupling, in contrast to tZIF-Cu₁₀₀₀, which exhibits no physical adsorption, but over-strong chemical adsorption (200–400 °C) that inhibits the sequential reaction.

In situ Raman spectroscopy dynamically tracked active site and intermediate evolution during electrolysis (Fig. 4e)⁴⁹⁻⁵¹. With increasingly negative potential, the Cu₃(CO₃)₂(OH)₂ signal decreases while Cu–OH peaks intensify^{52,53}, indicating active site reconstruction. Peak intensities of key intermediates (*COOH, *NH₂, *NO, *CO) maximize at –0.7 V vs. RHE, consistent with optimal catalytic performance. A new peak at 1404.2 cm^{–1} suggests the C–N bond formation and urea synthesis^{50,51,54,55}. Operando attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) further monitored surface-adsorbed species (Fig. 4f)⁵⁶. Peaks at 1652 cm^{–1} (*CO), 1510 cm^{–1} (*NH₂CO) and 1730 cm^{–1} (N–C–N) emerge with increasing potential. Notably, the characteristic peak of the critical C–N coupling intermediate *CONO was detected at 1998 cm^{–1}, directly demonstrating that the size-matched cavity enriched reactive species and facilitated C–N bond formation. Electron paramagnetic resonance (EPR) detected a 2.3-fold stronger hydrogen radical (H·) signal on

tZIF-Cu₉₀₀ than on collapsed tZIF-Cu₁₁₀₀ (Supplementary Fig. 48). The nanoconfined cavity concentrates H $\cdot$ while imposing a steric penalty on H $\cdot$ dimerization to H₂, kinetically directing H $\cdot$ toward *NO hydrogenation rather than parasitic HER⁵⁷. Tert-butyl alcohol quenching experiments further confirms H $\cdot$ as a key reactive species for urea synthesis (Supplementary Fig. 49).

DFT calculations were performed to elucidate the thermodynamic and kinetic origins of the enhanced C–N coupling performance on the Cu–N₄ sites modulated by the nanoconfinement effect. For NO₃RR, NO₃[–] undergoes sequential deoxygenation via *NO₃[–] $\rightarrow$ *NO₃H $\rightarrow$ *NO₂ $\rightarrow$ *NO₂H $\rightarrow$ *NO, with the *NO $\rightarrow$ *NHO pathway identified as the most thermodynamically favorable with a negligible energy barrier of 0.12 eV (Supplementary Figs. 50–53), verifying *NO as the key nitrogen intermediate for C–N coupling. For CO₂RR, the first proton-coupled electron transfer step (*CO₂ $\rightarrow$ *COOH) is the rate-limiting step with an energy barrier of 1.35 eV (Supplementary Fig. 54a), while the HER shows a higher barrier of 1.49 eV (Supplementary Fig. 54b), indicating that HER is kinetically less favorable than CO₂ activation under operating conditions.

After the synchronous generation of *CO and *NO intermediates at the confined active sites (Fig. 5a, b and Supplementary Fig. 55), the first C–N bond forms via *CO + *NO $\rightarrow$ *CONO with an ultra-low activation barrier of 0.031 eV (Supplementary Fig. 56a), confirming that the initial C–N coupling is thermodynamically and kinetically facile. The *CONO intermediate then undergoes sequential hydrogenation to form *CONH₂ via *CONHO $\rightarrow$ *CONHOH $\rightarrow$ *CONH $\rightarrow$ *CONH₂. The second C–N coupling occurs between *CONH₂ and *NO₂ with an activation barrier of 0.26 eV (Supplementary Fig. 56b), which is identified as

the rate-determining step (RDS) of the overall urea synthesis pathway. Notably, all competing side reactions, including N–O bond dissociation, deep reduction to NH₃, and HER exhibit much higher energy barriers than the main C–N coupling pathway.

The nanoconfined cavity further modulates the reaction pathway: the enhanced local electric field and upshifted Cu d-band center optimize the adsorption strength of *CO and *NO intermediates, lowering the RDS energy barrier while suppressing the dissociation of key intermediates²⁸. This synergy of geometric and electronic confinement thermodynamically and kinetically steers the reaction toward selective urea formation, rather than competing side reactions.

Pilot-scale testing and economic viability

For pilot implementation, tZIF-Cu₉₀₀ was integrated into a modular zero-gap proton-exchange membrane electrolyzer stack paired with GDEs (Fig. 5c), with a controlled catalyst loading of 0.02–0.05 mg cm⁻². Operated continuously for 300 h using industrial waste flue gas and nitrate-rich wastewater as feedstocks, the catalyst delivered a stable urea production rate exceeding 2.4 g g_{cat}⁻¹ h⁻¹ with a FE of 90%, demonstrating reliable scale-up stability (Fig. 5d, Supplementary Information, Section 5). Post-operation characterizations corroborate the pristine rhombic morphology and atomic Cu dispersion were largely preserved, with no obvious Cu leaching or active site agglomeration (Fig. 5e, f).

Techno-economic analysis was performed to quantify the industrial viability of the technology, with the net levelized cost (C_{net}) defined as:

$$C_{net} = (C_e + C_m + C_l + C_d) - (R_c + R_{NO_3} + R_W + R_{raw}) \quad (3)$$

where C_e is energy consumption cost (14920 kWh t⁻¹ urea, 0.032 USD kWh⁻¹); $C_m + C_l +$

C_d are feed pretreatment, labor and equipment costs, minimized via shared infrastructure (38.56, 26.00, and 20.00 USD t⁻¹, respectively); R_c is carbon trading revenue from 1.87 t CO₂eq t_{urea}⁻¹ (20.76 USD t⁻¹); R_{NO_3} is saved nitrate wastewater treatment fees (96.00 USD t⁻¹); R_W is reclaimed water recycling income (2.45 USD t⁻¹); R_{raw} is raw material savings from waste valorization (132.79 USD t⁻¹). All parameters are based on 2026 industrial actual values^{58,59}.

The gross production cost was calculated at 562 USD t⁻¹, with comprehensive carbon compliance offsets, environmental and resource benefit deductions pushing the net levelized cost down to 113 USD t⁻¹ under European and American carbon compliance frameworks. Systematic sensitivity analysis (Supplementary Fig. 57 and Supplementary Section 5) verifies the broad commercialization feasibility of this technology, with competitiveness further consolidated by growing renewable energy penetration. This cost performance delivers a decisive edge over conventional Haber-Bosch urea production in Europe and North America (460–700 USD t⁻¹), which incurs an extra 150–170 USD t⁻¹ in carbon compliance costs. It also eliminates the safety premium of hazardous liquid ammonia logistics via decentralized production. Further optimization is projected to reduce the net cost below 90 USD t⁻¹, positioning this pathway as a competitive solution for sustainable fertilizer manufacturing.

Conclusion

In summary, this study establishes a programmable thermal sculpting approach and a descriptor-based nanoconfinement strategy as general design principles for high-efficiency urea electrosynthesis. By precisely controlling the gasification of Zn nodes, we constructed size-matched cavities that synergistically modulate the geometric and electronic environments

of the active sites. The resultant catalyst achieves near-unity Faradaic efficiency and record-high 71.32 g_{cat}⁻¹ h⁻¹ urea yield, supported by 300-h pilot-scale stability. The introduction of the confinement metric descriptor provides a quantitative framework for understanding and designing confined catalytic systems. These findings not only advance the state-of-the-art in C–N coupling but also provide a scalable and economically viable synthetic route for the sustainable production of nitrogenous fertilizers from environmental pollutants. Future research may extend this "thermal sculpting" paradigm to other complex electrocatalytic transformations where intermediate confinement and kinetic matching are paramount.

Methods

Synthesis of tZIF-Cu

The tZIF-Cu precursor was synthesized via a solvothermal method. Briefly, 1.97 g 2-methylimidazole was dissolved in 75 mL methanol and 5 mL deionized water. A second solution of 1.695 g zinc nitrate hexahydrate, 80 mg copper nitrate trihydrate, and 50 mg polyvinylpyrrolidone K30 (dispersant) in 80 mL methanol was sonicated to homogeneity, then added dropwise into the 2-methylimidazole solution. The mixture was maintained at 60 °C for 12 h static, then 12 h with continuous stirring. The solid product was collected by centrifugation, washed with methanol, and vacuum-dried at 60 °C overnight. ZIF-Fe and ZIF-Co control precursors were prepared via the same protocol, with copper nitrate trihydrate replaced by equimolar nitrate enneahydrate and cobalt nitrate hexahydrate, respectively.

Dried ZIF-Cu powder was ground in an agate mortar and sieved through a 200-mesh screen to mitigate localized overheating and metal agglomeration during subsequent thermal

processing. A programmed pyrolysis under high-purity argon was rationally designed based on the precursor's TGA-DSC thermal behavior: the sample was first heated to 300 °C at 2 °C min⁻¹ and held for 2 h to remove residual solvents, then ramped to 600 °C at 1 °C min⁻¹ with a 3 h hold for gradual ligand decomposition and pre-carbonization without framework collapse. Tailored thermal protocols were applied for final pyrolysis temperatures of 800–1100 °C to balance Cu–N₄ active site formation, carbon graphitization, and structural integrity (Supplementary Information Section 2.2). Control catalysts were synthesized via the 900 °C protocol, with all samples stored in an argon-filled glovebox to prevent active site oxidation and passivation.

Electrosynthesis of urea

All measurements were performed on a CHI 660E workstation. H-cell tests used a gas-tight three-electrode cell separated by a pretreated Nafion 117 membrane (activated in 5 wt% H₂O₂ and H₂SO₄ at 80 °C, rinsed with DI water). The electrolyte was CO₂-saturated 0.1 M KHCO₃/0.1 M KNO₃ (pH 6.8), with a saturated calomel electrode and Pt foil counter electrode. The working electrode was fabricated by drop-casting catalyst ink (1.0 mg catalyst dispersed in 950 µL ethanol and 50 µL 5 wt% Nafion, sonicated 1 h) onto Toray TGP-H-060 carbon paper (1×1 cm², loadings 0.1 mg cm⁻²), air-dried at ambient conditions. All electrochemical measurements were conducted with 85% iR-drop compensation to correct for the ohmic resistance of the electrolyte. Prior to electrolysis, the catholyte was purged with CO₂ (100 mL min⁻¹, 30 min). Constant-potential electrolysis was conducted for 30 min at each potential, with continuous CO₂ flow (20 mL min⁻¹). Isotope labeling tests were performed under identical conditions, and urea concentration was quantified via diacetyl monoxime colorimetry, urease

assay, and ^1H NMR.

Flow cell tests used a custom circulating three-electrode GDE cell, with all shared parameters consistent with H-cell tests. Two precision machined graphite serpentine flow field plate were integrated on the both side of the GDE, with 1 mm-wide, 1 mm-deep flow channels at a 1 mm pitch to ensure uniform electrolyte and CO_2 distribution across the electrode active area. The anodic/cathodic chambers were connected to a 50 mL catholyte reservoir (circulated at 50 mL min^{-1}). The cathode was the similar ink-coated Toray carbon paper ($1\times 1\text{ cm}^2$, gradient loadings $0.005\text{--}0.1\text{ mg cm}^{-2}$), with an IrO_2/Ti mesh counter electrode. CO_2 was continuously fed to the cathode gas chamber (20 mL min^{-1}) to maintain the three-phase interface, and electrolysis was performed at -0.5 to -0.9 V vs. RHE.

Pilot test

A pilot-scale system was designed for industrial implementation, integrated with a steel plant for simultaneous valorization of CO_2 -containing flue gas and nitrate-rich wastewater. The core was a modular stack reactor equipped with IrO_2/Ti anodes and tZIF- Cu_{900} -loaded GDE cathodes ($0.02\text{--}0.05\text{ mg cm}^{-2}$ loading), separated by $125\text{ }\mu\text{m}$ Nepem-W membranes. CO_2 feed ($10\text{--}20\text{ vol}\%$) was pretreated via a bag filter and activated carbon; nitrate feed (raw wastewater $300\text{--}1800\text{ mg L}^{-1}$) was concentrated to 0.5 M via reverse osmosis, adjusted to pH $5\text{--}7$. The 14 parallel module stacks were operated at $2.2\text{--}2.5\text{ V}$ cell voltage, $5\text{--}12.5\text{ mA cm}^{-2}$ current density, $30\text{--}40\text{ }^\circ\text{C}$ cathode temperature. Humidified CO_2 was fed at $0.5\text{--}1.0\text{ L min}^{-1}$, electrolyte circulated at $2\text{--}5\text{ L h}^{-1}$. Solid urea ($\geq 99.5\%$ purity) was recovered from cathode effluent via vacuum evaporation, with system robustness validated via 300 h continuous operation (Supplementary Information Section 5).

Data availability

All relevant data that support the findings of this study are presented in the Manuscript and Supplementary Information. Source data are provided in this paper. The source data can also be accessed through the fig-share repository and are freely available for download.

Code availability

Quantum chemical calculations were performed via the open-source ORCA 5.0 package: initial structures were built in Avogadro 2, geometry optimization and frequency calculations were conducted at the B3LYP/def-SVP level, followed by single-point energy and electronic property calculations at the B3LYP/def2-TZVP level, with wavefunction analysis performed using Multiwfn 3.8. Periodic electronic structure calculations were carried out with Vienna Ab initio Simulation Package (VASP, PAW pseudopotentials, PBE functional with D3 dispersion correction). Molecular dynamics simulations were performed via Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).

Acknowledgements

We are grateful for financial support from National Key Research and Development Program of China (2024YFB4006500), National Natural Science Foundation of China (22576019, 52370052), Beijing Natural Science Foundation (F251038), The Joint Funds of the National Natural Science Foundation of China (U2340219), Beijing Changping Science and Technology Vice President Special Project (202507002061).

Author contributions

L.Y. and Y.D. conceived and designed the research project. L.Y. and B.Y designed, synthesized and characterized the materials. B.Y. and Y.Z. performed tests and characterizations

measurements. B.Y. conducted the catalytic experiments and performed the theoretical calculations. L.Y., Y.D., and Q.H. helped with discussion of the paper. B.Y., L.Y., Y.D., and Q.H. co-wrote and revised the paper. All authors contributed to this work and read the paper.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information. The online version contains Supplementary material available

Figure legends

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Fig. 4 | Geometry and electronic confinement reaction mechanism. **a**, Molecular dynamics simulations conducted on the small molecule entry and exit scenarios of the Cu–N₄ doped C–N hexagonal ring structure model with pore diameters of 1.0 nm, 1.5 nm, 1.8 nm and 2.6 nm. The trajectories clearly demonstrated that NO₃[−] were difficult to enter the 1.0 nm pores and could freely traverse in the 2.6 nm pores, while they were restricted in diffusion within the 1.5–1.8 nm pores. **b**, d-band of Cu shifts in Cu–N₄ doped C–N hexagonal ring structure model with pore diameters of 1.0 nm, 1.5 nm, 1.8 nm and 2.6 nm; **c**, Possible intermediate in the C–N coupling process at − 0.7 V vs. RHE. All the C and N sources with a concentration of 50 mM

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Fig. 5 | Reaction pathway identification and pilot-scale implementation. **a**, Comprehensive free-energy diagram for urea production and nitrate reduction on the Cu-N₄ active site. **b**, Optimized C-N coupling reaction pathway and key intermediate configurations derived from DFT calculations. **c**, Schematic and photograph of the integrated pilot urea synthesis electrolyzer stack. **d**, continuous stability plot showing urea yield rates over 300 h of operation at high current densities. Transition to modular membrane electrode assembly stacks demonstrates the stability and economic feasibility of nanoconfined urea synthesis for industrial application. **e**, Post-mortem SEM and AC HAADF-STEM image of the used tZIF-Cu₉₀₀ catalyst confirm the preservation of dodecahedral morphology and atomic Cu dispersion. **f**, Post-mortem XPS of the used tZIF-Cu₉₀₀ proves that its chemical environment remains stable.

439 References

- 440 1. Wöhler, F. Ueber künstliche Bildung des Harnstoffs. *Ann. Phys.* **88**, 253–256 (1828).
- 441 2. Li, J., Zhang, Y., Kuruvinashetti, K. & Kornienko, N. Construction of C–N bonds from
442 small-molecule precursors through heterogeneous electrocatalysis. *Nat. Rev. Chem.* **6**,
443 303–319 (2022).
- 444 3. Zhang, X. *et al.* Managing nitrogen for sustainable development. *Nature* **528**, 51–59
445 (2015).
- 446 4. Lan, R., Tao, S. & Irvine, J. T. S. A direct urea fuel cell – power from fertiliser and waste.
447 *Energy Environ. Sci.* **3**, 438–441 (2010).
- 448 5. Foster, S. L. *et al.* Catalysts for nitrogen reduction to ammonia. *Nat. Catal.* **1**, 490–500
449 (2018).
- 450 6. Mao, C., Byun, J., MacLeod, H. W., Maravelias, C. T. & Ozin, G. A. Green urea
451 production for sustainable agriculture. *Joule* **8**, 1224–1238 (2024).
- 452 7. Soloveichik, G. Electrochemical synthesis of ammonia as a potential alternative to the
453 Haber–Bosch process. *Nature Catalysis* **2**, 377–380 (2019).
- 454 8. MacFarlane, D. R. *et al.* A roadmap to the ammonia economy. *Joule* **4**, 1186–1205 (2020).
- 455 9. Zhou, Y. *et al.* Electrosynthesis of urea from carbon dioxide and waste nitrates: History,
456 recent progress, and future prospects. *Adv. Funct. Mater.* **36**, e15635 (2026).
- 457 10. Liu, S. *et al.* Selective electrosynthesis of urea from nitrate and carbon dioxide with low
458 overpotential. *Nat. Commun.* **17**, 1787 (2026).
- 459 11. Yuan, J., Liu, Z., Ma, L., Feng, Z. & Zhu K. Electrochemical reduction of CO₂ and N₂
460 into urea at ZIF-8 cathode. *J Electrochem. Soc.* **170**, 043503 (2023).
- 461 12. Xu, M. *et al.* Selective urea electrosynthesis from CO₂ and nitrate on spin-polarized
462 atomically ordered PdCuCo. *Adv. Mater.* **37**, 2505286 (2025).
- 463 13. Xu, M. *et al.* Kinetically matched C–N coupling toward efficient urea electrosynthesis
464 enabled on copper single-atom alloy. *Nat. Commun.* **14**, 6994 (2023).
- 465 14. Yuan, M. *et al.* Unveiling electrochemical urea synthesis by Co-activation of CO₂ and
466 N₂ with Mott–Schottky heterostructure catalysts. *Angew. Chem. Int. Ed.* **60**, 10910–
467 10918 (2021).
- 468 15. Lv, C. *et al.* Selective electrocatalytic synthesis of urea with nitrate and carbon dioxide.
469 *Nat. Sustain.* **4**, 868–876 (2021).
- 470 16. Yang, G. L. *et al.* Gaseous CO₂ coupling with N-containing intermediates for key C–N
471 bond formation during urea production from coelectrolysis over Cu. *ACS Catal.* **12**,
472 11494–11504 (2022).
- 473 17. Wei, X. *et al.* Lattice oxygen-driven Co-Adsorption of carbon dioxide and nitrate on
474 copper: A pathway to efficient urea electrosynthesis. *J. Am. Chem. Soc.* **147**, 6049–6057
475 (2025).
- 476 18. Gong, C. *et al.* Selective electrocatalytic synthesis of urea using entangled iron
477 porphyrins in covalent organic frameworks. *Nat. Synth.* **4**, 720–729 (2025).
- 478 19. Wang, J. *et al.* Confinement-induced indium oxide nanolayers formed on oxide support
479 for enhanced CO₂ hydrogenation reaction. *J. Am. Chem. Soc.* **146**, 5523–5531 (2024).
- 480 20. Xiao, L. *et al.* Pd-intercalated black phosphorus: An efficient electrocatalyst for CO₂
481 reduction. *Sci. Adv.* **10**, eadn2707 (2024).

21. Wang, Q. *et al.* Evolution of Zn(II) single atom catalyst sites during the pyrolysis-induced transformation of ZIF-8 to N-doped carbons. *Sci. Bull.* **65**, 1743–1751 (2020).
22. Lu, Y. *et al.* π - π Conjugated g-C₁₆N₁₉ skeleton-supported single-atom catalyst for nitrogen reduction reaction: A “lock and key” coevaluation of activity and selectivity involved in constant potential and pH effect. *Chem. Eur. J.* **31**, e02611 (2025).
23. Ren, W. *et al.* Isolated diatomic Ni-Fe metal-nitrogen sites for synergistic electroreduction of CO₂. *Angew. Chem. Int. Ed.* **58**, 6972–6976 (2019).
24. da Silva Montani, S., de Lima, J. F., Zanon Zotin, F. M. & Palacio, L. A. Thermal stability of copper-based MOF under different atmospheres. *J. Therm. Anal. Calorim.* **148**, 119–131 (2022).
25. Cheng, H. *et al.* Construction of atomically dispersed Cu-N₄ sites via engineered coordination environment for high-efficient CO₂ electroreduction. *Chem. Eng. J.* **407**, 126842 (2021).
26. Chen, X. *et al.* Metal-organic framework-derived mesoporous carbon nanoframes embedded with atomically dispersed Fe-N_x active sites for efficient bifunctional oxygen and carbon dioxide electroreduction. *Appl. Catal. B: Environ.* **267**, 118720 (2020).
27. Ma, S. *et al.* Ionic exchange of metal-organic frameworks for constructing unsaturated copper single-atom catalysts for boosting oxygen reduction reaction. *Small* **16** (2020).
28. Feng, G. *et al.* Engineered spatial confinement of Cu single-atoms with diagonal N-Cu-N motifs for high-rate CO₂ methanation. *Angew. Chem.* **137**, e202508497 (2025).
29. Wang, J., Wang, K., Wang, F. B. & Xia, X. H. Bioinspired copper catalyst effective for both reduction and evolution of oxygen. *Nat. Commun.* **5**, 5285 (2014).
30. Zhang, Z. *et al.* Self-established rapid magnesiation/De-magnesiation pathways in binary selenium-copper mixtures with significantly enhanced Mg-ion storage reversibility. *Adv. Funct. Mater.* **28**, 1701718 (2018).
31. Li, S. *et al.* Manipulating d-orbital of Cu single atom site by coordination engineering for selective oxidation of benzene. *Nat. Commun.* **16**, 5790 (2025).
32. Qiu, W. *et al.* Overcoming electrostatic interaction via pulsed electroreduction for boosting the electrocatalytic urea synthesis. *Angew. Chem. Int. Ed.* **63**, e202402684 (2024).
33. Cong, M. *et al.* Electrocatalytic urea synthesis from CO₂ and nitrate co-reduction on natural vitamin B12 coupled carbon nanotubes. *Appl. Catal. B: Environ.* **351**, 123941 (2024).
34. Leverett, J. *et al.* Tuning the coordination structure of Cu-N-C single atom catalysts for simultaneous electrochemical reduction of CO₂ and NO₃⁻ to urea. *Adv. Energy Mater.* **12**, 2201500 (2022).
35. Zhang, X. *et al.* Identifying and tailoring C-N coupling site for efficient urea synthesis over diatomic Fe-Ni catalyst. *Nat. Commun.* **13**, 5337 (2022).
36. Li, Z. *et al.* Synergistic electrocatalysis of crystal facet and O-vacancy for enhance urea synthesis from nitrate and CO₂. *Appl. Catal. B: Environ.* **338**, 122962 (2023).
37. Mao, Y. *et al.* Enhanced performance of oxygen vacancy-rich In-TiO₂ materials for electrocatalytic urea synthesis via a relay catalysis strategy. *Chem. Eng. J.* **485**, 150052 (2024).
38. Wei, X. *et al.* Dynamic reconstitution between copper single atoms and clusters for

- electrocatalytic urea synthesis. *Adv. Mater.* **35**, 2300020 (2023).
39. Geng, J. *et al.* Ambient electrosynthesis of urea with nitrate and carbon dioxide over iron-based dual-sites. *Angew. Chem. Int. Ed.* **62**, e202210958 (2023).
 40. Zhao, J. *et al.* Identifying the facet-dependent active sites of Cu₂O for selective C–N coupling toward electrocatalytic urea synthesis. *Appl. Catal. B: Environ.* **340**, 123265 (2024).
 41. Zhao, Y. *et al.* Efficient urea electrosynthesis from carbon dioxide and nitrate via alternating Cu–W bimetallic C–N coupling sites. *Nat. Commun.* **14**, 4491 (2023).
 42. Li, J. Y. *et al.* Remote carbon monoxide spillover improves tandem urea electrosynthesis. *Angew. Chem. Int. Ed.* **64**, e202421266 (2025).
 43. Chen, K. *et al.* Urea electrosynthesis from nitrate and CO₂ on diatomic alloys. *Adv. Mater.* **36**, 2402160 (2024).
 44. Yin, Y. *et al.* Efficient urea electrosynthesis from CO₂ and nitrate mediated by an ionic liquid bridge. *Nat. Sustain.* **9**, 108–116 (2026).
 45. Kang, H. *et al.* State-of-the-art structural regulation methods and quantum chemistry for carbon-based single-atom catalysts in advanced oxidation process: Critical perspectives into molecular level. *Adv. Mater.* **37**, 2505128 (2025).
 46. Yu, T. *et al.* Dynamic strain engineering for precise tuning of Fe d-band center in Fe–ZnO: enabling optimized *CO/*H adsorption and efficient *CHO formation. *Appl. Surf. Sci.* **732**, 166498 (2026).
 47. Wu, B. *et al.* Symmetry breaking of single-atom catalysts in heterogeneous electrocatalysis: reactivity and configuration. *Chem. Soc. Rev.* **55**, 114–143 (2026).
 48. Shang, Y., Chen, D., Chen, C. & Wang, S. Surface-functionalized two-dimensional materials towards electrocatalytic C–N coupling reaction for urea. *Catal.* **1**, 9 (2025).
 49. Zhao, Y. *et al.* Elucidating electrochemical CO₂ reduction reaction processes on Cu(hkl) single-crystal surfaces by in situ Raman spectroscopy. *Energy Environ. Sci.* **15**, 3968–3977 (2022).
 50. Khan, K. M., Krishna, H., Majumder, S. K. & Gupta, P. K. Detection of urea adulteration in milk using near-infrared raman spectroscopy. *Food Anal. Methods* **8**, 93–102 (2015).
 51. Barker, I. K., Fawcett, V. & Long, D. A. Solvent dependence of the resonance Raman spectra of azobenzene, 4-aminoazobenzene, 4-methylaminobenzene and 4-dimethylaminoazobenzene. *J. Raman Spectrosc.* **18**, 71–75 (1987).
 52. Chen, S. *et al.* MOF Encapsulating *n*-heterocyclic carbene-ligated copper single-atom site catalyst towards efficient methane electrosynthesis. *Angew. Chem. Int. Ed.* **61** (2022).
 53. Mu, S. *et al.* Hydroxyl radicals dominate reoxidation of oxide-derived Cu in electrochemical CO₂ reduction. *Nat. Commun.* **13**, 3694 (2022).
 54. Bae, S. E., Stewart, K. L. & Gewirth, A. A. Nitrate adsorption and reduction on Cu(100) in acidic solution. *J. Am. Chem. Soc.* **129**, 10171–10180 (2007).
 55. Chernyshova, I. V., Somasundaran, P. & Ponnurangam, S. On the origin of the elusive first intermediate of CO₂ electroreduction. *P. Natl. Acad. Sci. USA* **115**, E9261–E9270 (2018).
 56. Zhao, C. *et al.* Tailoring Activation intermediates of CO₂ initiates C–N coupling for highly selective urea electrosynthesis. *J. Am. Chem. Soc.* **147**, 8871–8880 (2025).
 57. Bie, C. *et al.* Nanoconfinement effects in electrocatalysis and photocatalysis. *Small* **21**,

- 570 2411184 (2025).
- 571 58. Feng, D. *et al.* Ni–Fe dual-site polymer catalyst for high performance and stable
572 electrochemical urea synthesis from CO₂ and NO₃[−]. *ChemSusChem* **19**, e202502676
573 (2026).
- 574 59. Guan, Y. *et al.* Enhancing the yield of electrocatalytic C–N coupling for urea synthesis:
575 challenges, strategies, and prospects. *Green Chem.* **28**, 783–812 (2026).

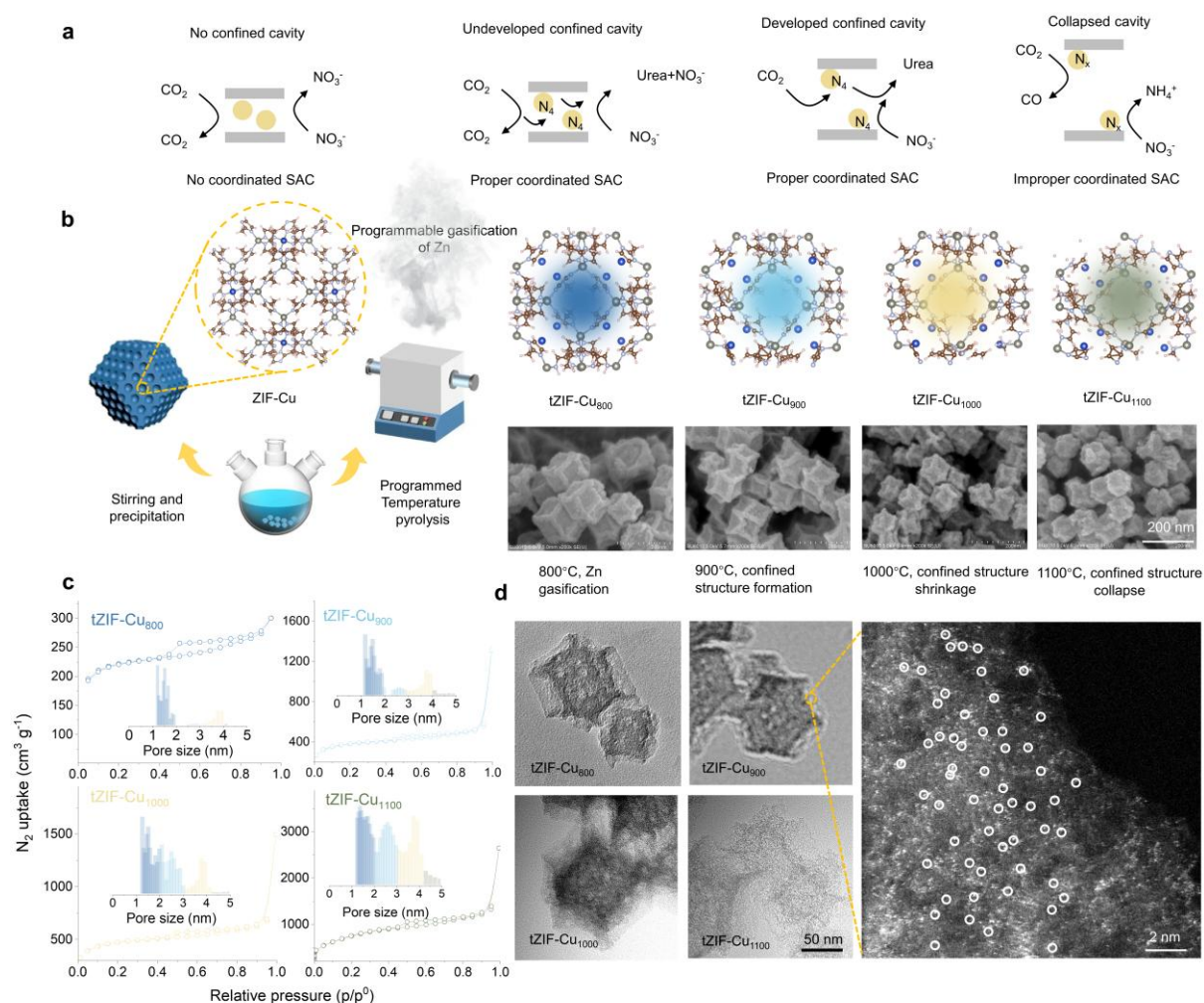


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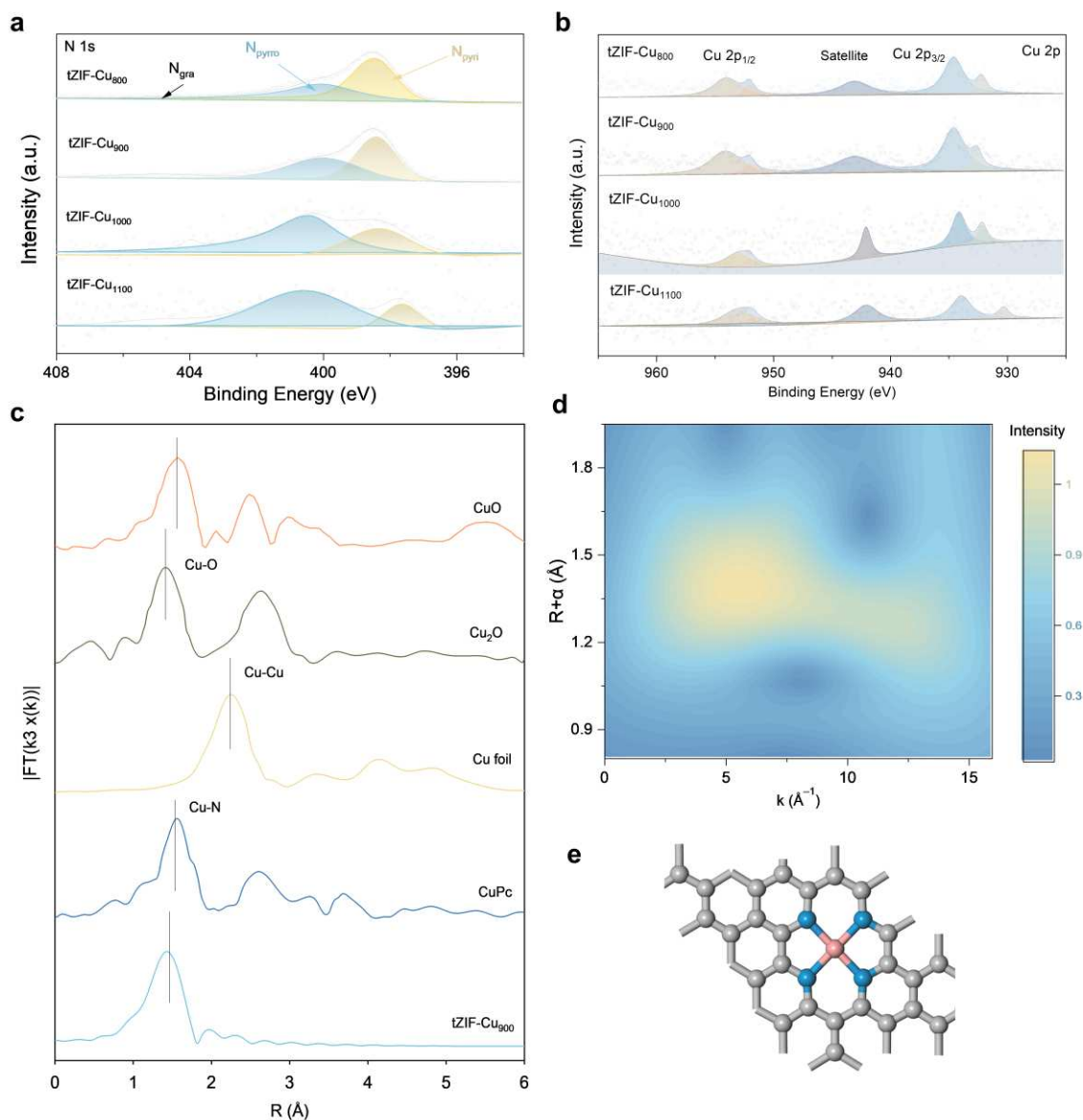


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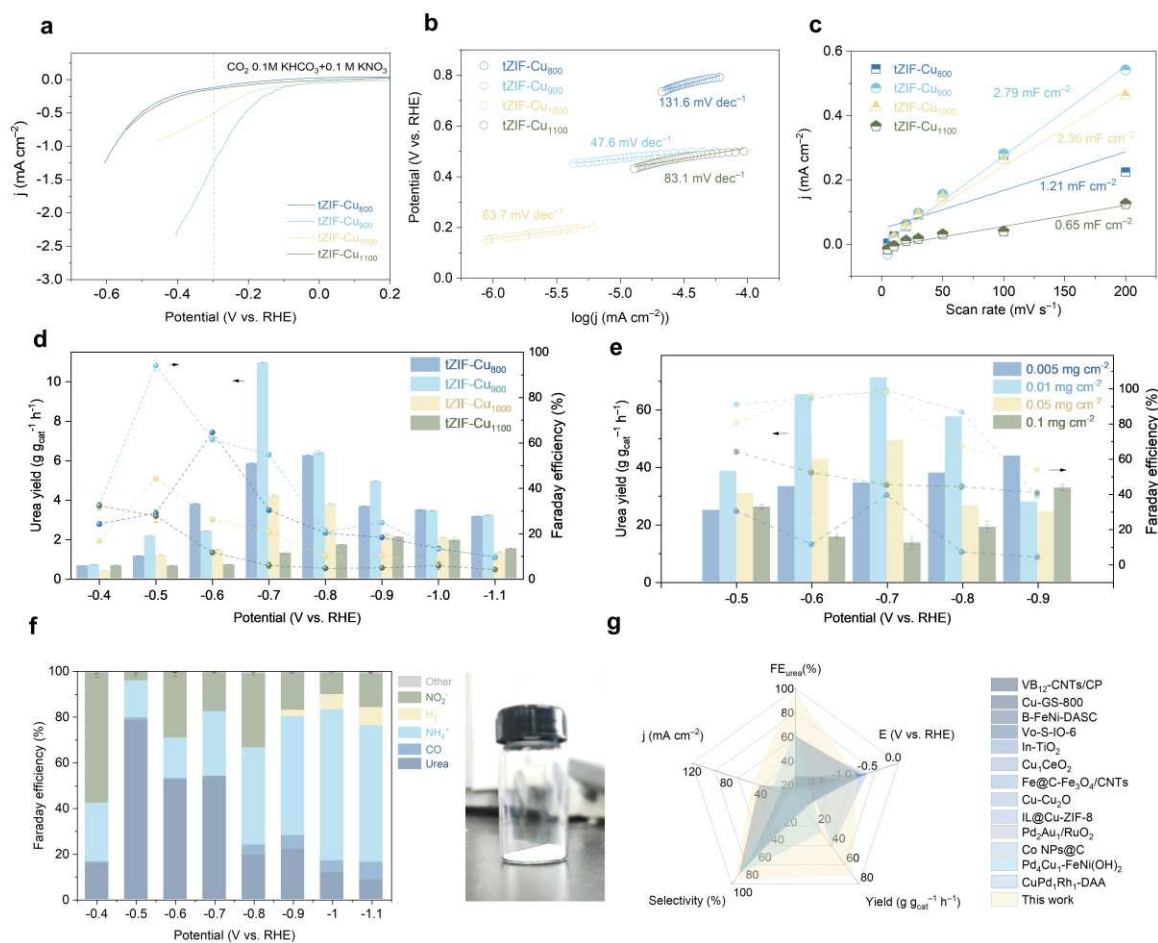


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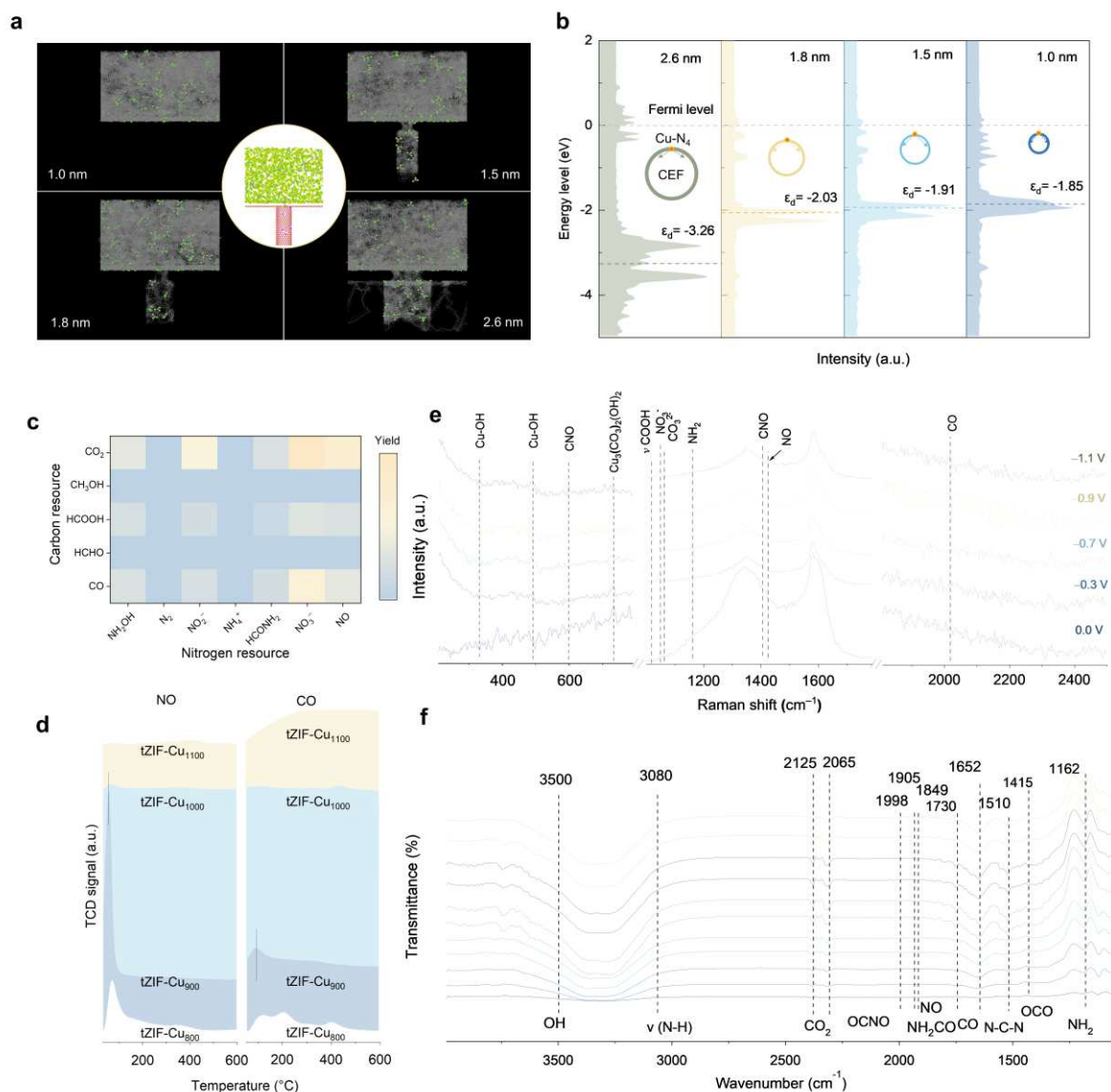
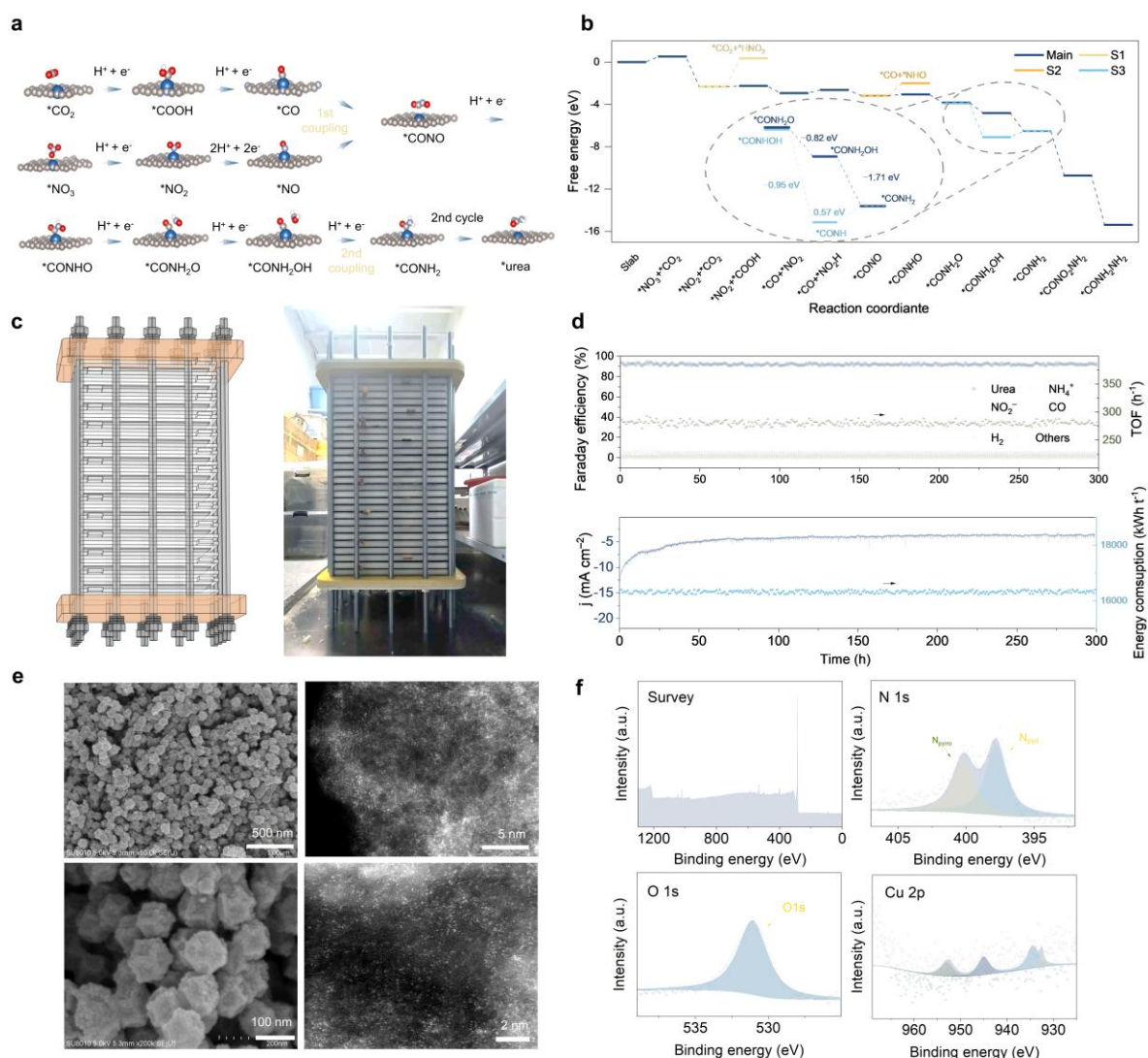


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