

Dynamic Reconstitution Between Copper Single Atoms and Clusters for Electrocatalytic Urea Synthesis

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Electrocatalytic C–N coupling between carbon dioxide and nitrate has emerged to meet the comprehensive demands of carbon footprint closing, valorization of waste, and sustainable manufacture of urea. However, the identification of catalytic active sites and the design of efficient electrocatalysts remain a challenge. Herein, the synthesis of urea catalyzed by copper single atoms decorated on a CeO₂ support (denoted as Cu₁–CeO₂) is reported. The catalyst exhibits an average urea yield rate of 52.84 mmol h^{−1} g_{cat.}^{−1} at −1.6 V versus reversible hydrogen electrode. Operando X-ray absorption spectra demonstrate the reconstitution of copper single atoms (Cu₁) to clusters (Cu₄) during electrolysis. These electrochemically reconstituted Cu₄ clusters are real active sites for electrocatalytic urea synthesis. Favorable C–N coupling reactions and urea formation on Cu₄ are validated using operando synchrotron-radiation Fourier transform infrared spectroscopy and theoretical calculations. Dynamic and reversible transformations of clusters to single-atom configurations occur when the applied potential is switched to an open-circuit potential, endowing the catalyst with superior structural and electrochemical stabilities.

synthesis accounts for ≈2% of the global energy demands and results in 1.44% of global CO₂ emissions.^[2] Approximately 80% of the as-synthesized ammonia is subjected to a subsequent energy-intensive Bosch–Meiser process to produce urea, which is an important nitrogen fertilizer and chemical feedstock, as illustrated in Figure S1 (Supporting Information).^[3] Meanwhile, fertilizer-intensive agriculture and industrial emissions lead to the emission of nitrate pollutants, which pose a severe risk to human health and environment.^[4] Although the conversion of nitrate to ammonia can be achieved through catalytic reduction reactions driven by renewable electricity, further conversion to urea is still required by industrial processes.^[5] Electrocatalytic C–N coupling between carbon dioxide and nitrate provides a promising pathway to reduce the environmental impacts of urea production and to valorize waste from various industrial processes.^[6]

1. Introduction

The increase in population and the industrial synthesis of chemical feedstocks have led to significant consumption of non-renewable fossil resources, resulting in the emission of large amounts of carbon dioxide (CO₂) into the atmosphere.^[1] For example, the Haber–Bosch process for ammonia (NH₃)

processes.^[6] However, electrocatalytic urea synthesis is a multistep process involving diverse reactants and reactions, and therefore, the realization of favorable C–N coupling and urea formation remains a challenge.^[7]

Single-atom materials have received significant interest in the field of catalysis because of their high atomic utilization and activity.^[8] The reconstitution of single-atom catalysts may

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occur during electrolysis, resulting in inconsistencies between the real active site and the original catalytic configuration, particularly for catalysts with copper atoms as the metal center.^[9] Investigating the dynamic reconstitution of catalysts to identify the real active sites of catalytic reactions allows for the design of highly active catalysts.^[10] Significantly, the dynamic evolution of single-atom copper electrocatalysts in electrocatalytic urea synthesis has not been reported thus far.

Here, we fabricated copper single atoms decorated on a CeO₂ support (Cu₁-CeO₂). The as-prepared catalyst exhibits an average urea yield rate of 52.84 mmol h⁻¹ g_{cat}⁻¹ at -1.6 V versus reversible hydrogen electrode (RHE), which is the highest value that has ever been reported for coupling of carbon dioxide and nitrate. Operando X-ray absorption spectroscopy (XAS) demonstrates the reconstitution of single atoms (Cu₁) to clusters (Cu₄) during electrolysis. These electrochemically reconstituted Cu₄ clusters are genuine active sites for electrocatalytic urea synthesis. Favorable C-N coupling and urea formation on Cu₄ are validated via operando synchrotron-radiation Fourier transform infrared (SR-FTIR) spectroscopy and density functional theory (DFT) calculation. The dynamic and reversible transformation of clusters to single-atom configurations occurs when the applied potential was switched to an open-circuit potential, yielding a catalyst with high structural and electrochemical stabilities.

2. Results and Discussion

2.1. Preparation and Characterization of Electrocatalysts

Cu-CeO₂ samples were synthesized through wet impregnation and calcination and were labeled as L-Cu₁-CeO₂ or H-Cu-CeO₂ based on the low or high concentration of impregnated copper, respectively (unless stated otherwise, Cu₁-CeO₂ represents L-Cu₁-CeO₂). The detailed synthetic methods are summarized in Supporting Information. The Cu concentration in L-Cu₁-CeO₂ and H-Cu-CeO₂ was determined to be 3.99 and 10.13 wt% respectively using inductively coupled-plasma optical emission spectroscopy (ICP-OES, Table S2, Supporting Information). Scanning electron microscopy (SEM) in Figure S2 (Supporting Information) and transmission electron microscopy (TEM) images in Figure S3 (Supporting Information) show that the majority of L-Cu₁-CeO₂ and H-Cu-CeO₂ samples exhibit a nanorod morphology. However, numerous particles are distributed around the nanorods of H-Cu-CeO₂, which can be copper clusters or nanoparticles. The atomically dispersed copper in L-Cu₁-CeO₂ is shown in the aberration-corrected transmission electron microscopy (AC-TEM) image in Figure 1a. The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) image of L-Cu₁-CeO₂ in Figure 1b

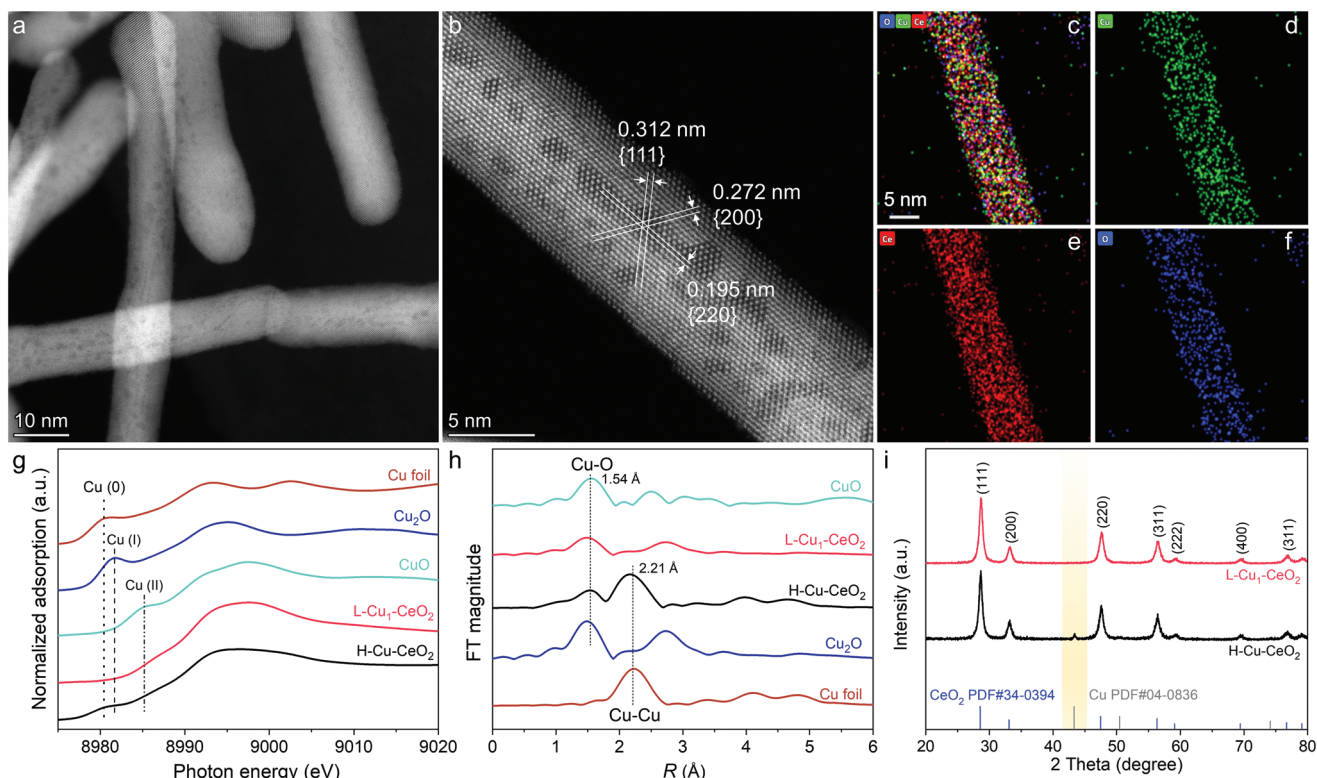


Figure 1. a) Aberration-corrected transmission electron microscopy (AC-TEM) image and b) aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) image of L-Cu₁-CeO₂. c–f) Elemental mappings of copper, cerium, and oxygen of L-Cu₁-CeO₂. g) Cu K-edge X-ray absorption near-edge structure (XANES) spectra and h) Cu R-space extended X-ray absorption fine structure (EXAFS) spectra of L-Cu₁-CeO₂, H-Cu-CeO₂ and reference samples including Cu foil, Cu₂O, and CuO. i) X-ray diffraction (XRD) patterns of L-Cu₁-CeO₂ and H-Cu-CeO₂.

reveals the lattice fringes with spacings of 0.312, 0.272, and 0.195 nm, corresponding to the (111), (200) and (220) lattice planes of cubic CeO_2 , respectively.^[11] The elemental mappings in Figures 1c–f and energy-dispersive spectroscopy (EDS) mapping in Figure S4 (Supporting Information) reveal the uniform distribution of Cu, Ce, and O in $\text{L-Cu}_1\text{-CeO}_2$.

Cu K-edge X-ray absorption near-edge structure (XANES) spectra (Figure 1g) show that copper species in $\text{L-Cu}_1\text{-CeO}_2$ and H-Cu-CeO_2 are cationic, with an oxidation state close to that of CuO . The absence of Cu–Cu scattering paths in the Cu *R*-space extended X-ray adsorption fine structure (EXAFS) spectrum of $\text{L-Cu}_1\text{-CeO}_2$ (Figure 1h) indicates that copper species are atomically dispersed, and the bonding distance of Cu–O is 1.54 Å.^[12] The presence of Cu–Cu bonds with a length of 2.21 Å is determined using the EXAFS spectrum of H-Cu-CeO_2 , suggesting the existence of Cu clusters or nanoparticles in H-Cu-CeO_2 . The X-ray photoelectron spectroscopy (XPS) profile of Cu $2p_{3/2}$ is deconvoluted into two peaks located at ≈ 933.6 eV, corresponding to Cu^{2+} , and 932.5 eV, which is attributed to Cu^0 or Cu^{1+} .^[13] A significant enhancement in the area of the peak at 932.5 eV is observed for H-Cu-CeO_2 compared to that of $\text{L-Cu}_1\text{-CeO}_2$ owing to Cu agglomeration (Figure S5, Supporting

Information). As depicted in Figure 1i, no characteristic diffraction peaks of Cu (PDF No.#04-0836) are observed in the X-ray diffraction (XRD) pattern of $\text{L-Cu}_1\text{-CeO}_2$, and all the diffraction peaks are indexed to the fluorite structure of CeO_2 (PDF No. 34-0394). However, characteristic peaks of Cu were observed in the H-Cu-CeO_2 spectrum. This demonstrates that Cu clusters or nanoparticles form in H-Cu-CeO_2 with an increase in the Cu content.

2.2. Electrochemical Performance of Catalysts for Application in Urea Synthesis

The electrocatalytic activity of catalysts toward C–N coupling was investigated in an H-type cell using a potentiostat (Figure S7, Supporting Information) by applying potentials ranging from -1.7 to -1.2 V vs RHE. CO_2 -saturated-0.1 M KHCO_3 containing 50 mM KNO_3 was chosen as the electrolyte with a continuous influx of CO_2 . The urea was quantified using the urease decomposition method based on the indophenol blue spectrophotometric method (Supporting Information).^[15,14] As illustrated in Figure 2a, the urea yield rate of $\text{Cu}_1\text{-CeO}_2$ is

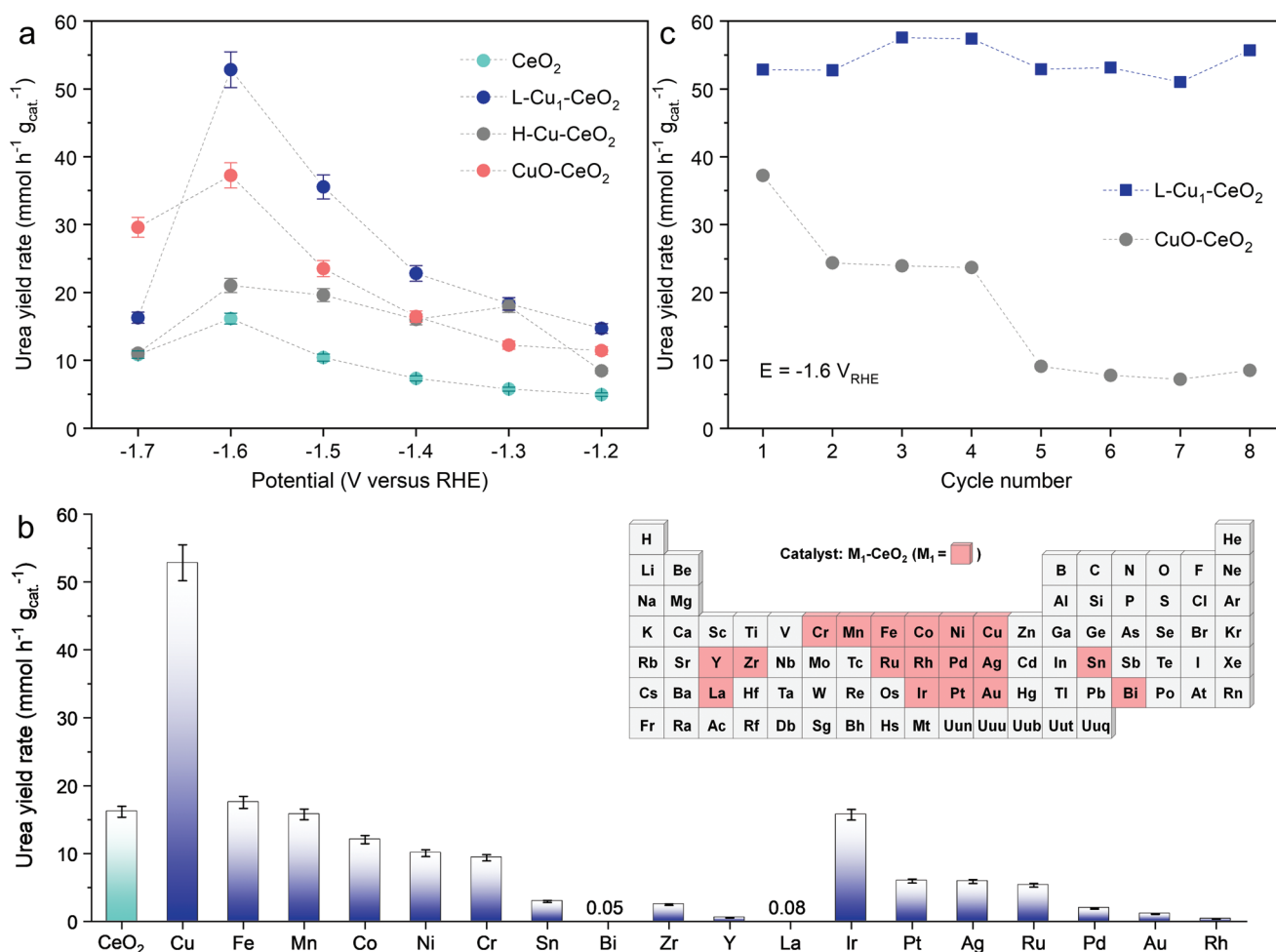


Figure 2. a) The urea yield rates of CeO_2 , $\text{L-Cu}_1\text{-CeO}_2$, H-Cu-CeO_2 , and CuO-CeO_2 catalysts at different applied potentials. b) The urea yield rates of $\text{M}_1\text{-CeO}_2$ (M represents different metals) at an applied potential of -1.6 V vs RHE. c) Stability test results of $\text{L-Cu}_1\text{-CeO}_2$ and CuO-CeO_2 catalysts.

significantly improved and reaches $52.84 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ at -1.6 V vs RHE, representing a more than three-fold increase compared with that of CeO_2 . The enhanced peaks of $\text{Cu}_1\text{-CeO}_2$ observed at higher temperatures in the CO_2 temperature-programmed desorption ($\text{CO}_2\text{-TPD}$) indicate the $\text{Cu}_1\text{-CeO}_2$ catalyst exhibits superior chemisorption capacity toward CO_2 than CeO_2 (Figure S9, Supporting Information). Additionally, CH_4 , CO , and C_2H_4 are detected during the CO_2 reduction process of $\text{Cu}_1\text{-CeO}_2$ (Figure S10, Supporting Information). Furthermore, the nitrate reduction ability of $\text{Cu}_1\text{-CeO}_2$ is considerably improved (Figure S13, Supporting Information). These results suggest that the introduction of copper species promotes the adsorption and activation of CO_2 and nitrate.

To further explore whether the increase in the urea yield rate after the introduction of copper species is due to the electronic structure changes of CeO_2 or copper acting as the active site, various $\text{M}_1\text{-CeO}_2$ catalysts (M = different metals) were also investigated. Studies were conducted to determine whether other metals exhibit similar electronic regulatory advantages as those of copper. The urea yield rates of $\text{M}_1\text{-CeO}_2$ were tested at -1.6 V vs RHE (Figure S17, Supporting Information). As depicted in Figure 2b, the urea yield rate of $\text{Cu}_1\text{-CeO}_2$ is significantly higher than that of other $\text{M}_1\text{-CeO}_2$ catalysts. To validate the experimental results, DFT calculations were performed to investigate the activation capacity of four typical $\text{M}_1\text{-CeO}_2$ catalysts (M = Cu, Fe, Sn, and Ir) toward nitrate and CO_2 .^[15] The adsorption and activation of NO_3^- on the surfaces of $\text{Cu}_1\text{-CeO}_2$ and $\text{Fe}_1\text{-CeO}_2$ occur spontaneously without requiring external energy (Figure S18, Supporting Information). Moreover, N–O bonds in NO_3^- on the surfaces of $\text{Cu}_1\text{-CeO}_2$ ($1.502 \text{ \AA}$) and $\text{Fe}_1\text{-CeO}_2$ ($1.737 \text{ \AA}$) are significantly elongated (Figure S19, Supporting Information). This implies strong activation between NO_3^- and $\text{Cu}_1\text{-CeO}_2$ or $\text{Fe}_1\text{-CeO}_2$, which is consistent with the experimental results (Figure S20, Supporting Information). Among the four catalysts, $\text{Cu}_1\text{-CeO}_2$ exhibits the lowest adsorption energy toward CO_2 , and the O–C–O bond angle changes from 180° to 124.4° on the $\text{Cu}_1\text{-CeO}_2$ surface (Figure S21, Supporting Information). Such occurrences of bond bending represent the destabilization of the CO_2 electron cloud owing to strong interactions between O atoms in CO_2 and copper sites as well as C atoms in CO_2 and O atoms in CeO_2 .^[16] The high-coordinated Ce atoms are replaced by the low-coordinated Cu atoms. This leads to the transformation of the original tightly bound Ce–O configuration into a loosely bound Cu–O configuration with a longer bond length, further forming Cu–O frustrated Lewis Pairs and eventually resulting in the efficient activation of CO_2 .^[17] Moreover, the projected density of states (PDOS) of adsorbed NO_3^- and CO_2 on the four $\text{M}_1\text{-CeO}_2$ catalysts were analyzed. As plotted in Figure S22a,b (Supporting Information), new adsorption hybridization orbitals of $\text{Cu}_1\text{-CeO}_2$ with NO_3^- and CO_2 are observed between the conduction band and valence band edges.^[18] The generation of these orbitals facilitates electron migration in $\text{Cu}_1\text{-CeO}_2$ and provides new channels for electron exchange between NO_3^- or CO_2 and $\text{Cu}_1\text{-CeO}_2$. The PDOS results of other $\text{M}_1\text{-CeO}_2$ catalysts are discussed in the Supporting Information. In summary, we propose that only Cu–O bonds formed by Cu atoms that replace Ce atoms offer uniquely hindered Lewis acid-base active sites, probably because of the unique Cu–O–Ce moiety

in $\text{Cu}_1\text{-CeO}_2$.^[19] Additionally, copper species strengthen the adsorption and activation of CO_2 and NO_3^- , resulting in efficient urea synthesis on $\text{Cu}_1\text{-CeO}_2$.

2.3. Reversible Reconstitution between Copper Single-Atoms and Clusters

Stability is an important parameter that determines the performance of electrocatalysts. The stability of $\text{Cu}_1\text{-CeO}_2$ was evaluated by performing 8 continuous cycles at an applied potential of -1.6 V vs RHE. The urea yield rates remain at $\approx 52.84 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ for 8 cycles (Figure 2c), demonstrating the excellent electrocatalytic stability of $\text{Cu}_1\text{-CeO}_2$. However, the urea yield rate of the CuO-CeO_2 catalyst decreases rapidly from 37.23 to $24.40 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ at the second cycle, and further decreases to $7.23 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ in the subsequent cycles. The structures of $\text{Cu}_1\text{-CeO}_2$ and CuO-CeO_2 after electrolysis were analyzed by high-resolution transmission electron microscopy (HRTEM). In the HRTEM image of $\text{Cu}_1\text{-CeO}_2$ obtained after electrolysis, only the lattice fringes corresponding to CeO_2 are observed, which are similar to those observed in the initial $\text{Cu}_1\text{-CeO}_2$ image (Figure S26a,b, Supporting Information). However, the Cu (111) plane is detected in the HRTEM image of CuO-CeO_2 after electrolysis (Figures S26c,d, Supporting Information). Therefore, the reconfiguration of copper species to copper clusters or nanoparticles during electrochemical processes may be the reason for the significant decrease in CuO-CeO_2 stability. We speculate that a similar reconfiguration might have occurred during the electrolytic process with $\text{Cu}_1\text{-CeO}_2$. However, in contrast to that of CuO-CeO_2 , the reconfiguration of $\text{Cu}_1\text{-CeO}_2$ was reversible, and the electrocatalyst returned to its initial configuration when an open-circuit potential was applied, providing the catalyst with superior structural and electrochemical stabilities.

To monitor the structural evolution of $\text{Cu}_1\text{-CeO}_2$ with variations in the applied potential, operando XAS experiments were performed. As depicted in Figure 3a and Figure S30a (Supporting Information), the Cu K-edge XANES spectra of $\text{Cu}_1\text{-CeO}_2$ under reducing potentials exhibit normalized adsorption signals of Cu (0) and Cu (I) located at the lower edge energy than those of the $\text{Cu}_1\text{-CeO}_2$ catalyst under the open-circuit voltage (OCV) condition. Additionally, these normalized adsorption signals disappear when $\text{Cu}_1\text{-CeO}_2$ returns to OCV-2 condition. The Cu R-space EXAFS spectra in Figure 3b and Figure S30b (Supporting Information) show that the Cu first shell coordination evolves from Cu–O to mainly Cu–Cu bonding, and the Cu–Cu bond strengthens as the cathode potential increases to a coordination number of 7 at -1.6 V vs RHE, indicating the formation of copper clusters (Figure S31, detailed best-fit EXAFS parameters are listed in Table S3, Supporting Information).^[20] Meanwhile, the structural evolution of $\text{Cu}_1\text{-CeO}_2$ at -1.6 V vs RHE for different durations of electrolysis was monitored using operando XAS. Even when the duration is extended to 50 min, atomically dispersed copper can only aggregate to Cu_4 clusters but copper nanoparticles (Figures S30c,d, Supporting Information). The aforementioned results indicate the dynamic reconstitution of a copper single atom (Cu_1) to clusters (Cu_4) during C–N coupling.

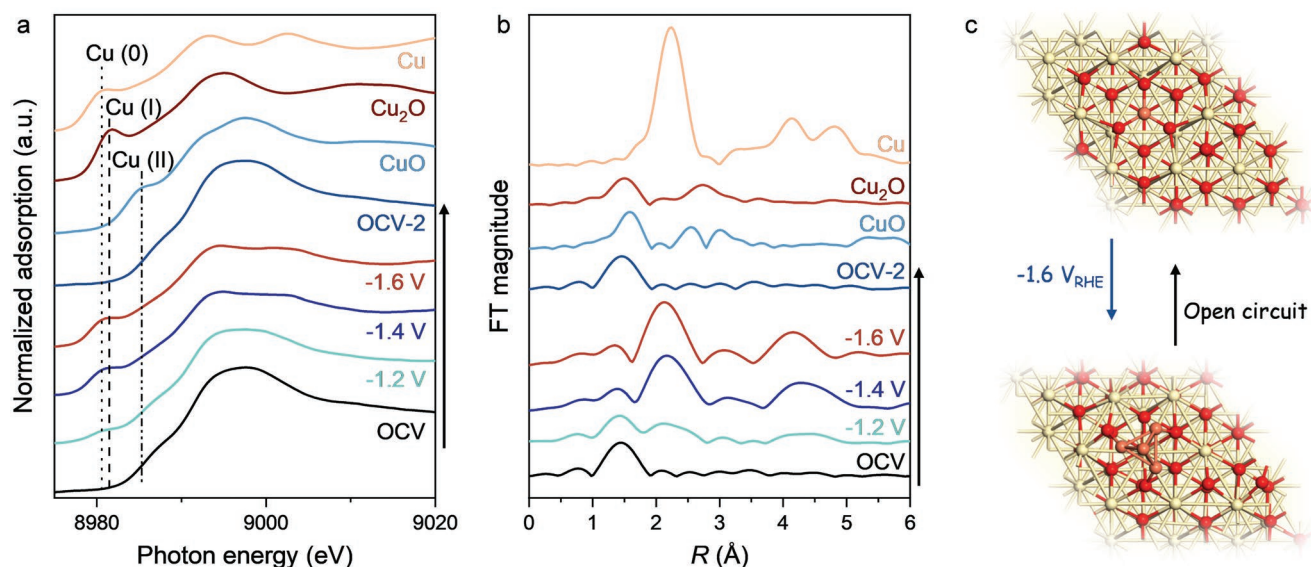


Figure 3. a) Cu K-edge XANES spectra of $\text{Cu}_1\text{-CeO}_2$ recorded at different cathodic potentials during C–N coupling. b) Cu R-space EXAFS spectra of $\text{Cu}_1\text{-CeO}_2$ recorded at different cathodic potentials during C–N coupling. c) Schematic diagram of reconstitution of copper single-atoms to clusters suggested by the operando XAS measurements.

Furthermore, the dynamic and reversible transformation of Cu_4 to Cu_1 configurations occurs when the applied potential is switched to the open-circuit potential, as depicted in Figure 3c. The copper concentrations in the electrolyte before and after electrolysis quantified using ICP-OES are listed in Table S4 (Supporting Information). The copper concentration in electrolytes after electrolysis does not increase significantly, which indicates that the transformation of Cu_4 to Cu_1 after the removal of voltage is not due to the dissolution of copper.^[21] The electrochemical C–N coupling performance of H-Cu-CeO_2 was also investigated to compare the difference between the copper clusters that exist during catalyst synthesis and those generated during electrolysis. H-Cu-CeO_2 exhibits poor C–N coupling activity when compared with $\text{Cu}_1\text{-CeO}_2$ (Figure 2a), indicating that the copper clusters existing during catalyst synthesis are not conducive to urea formation. However, they increase the yield of the by-product NH_3 (Figure S13, Supporting Information), which is consistent with the reports in the literature.^[9,22] In conclusion, electrochemically reconstituted Cu_4 clusters act as active sites for C–N coupling.

2.4. Mechanistic Studies

The evolution of the bond structure of reaction intermediate species during the electrocatalytic C–N coupling of the $\text{Cu}_1\text{-CeO}_2$ electrocatalyst was monitored via cutting-edge operando SR-FTIR measurements. The infrared signals were collected from 1000 to 4000 cm^{-1} during a scan from -1.2 to -1.7 V vs RHE. As presented in Figure 4a, $^*\text{OCNO}$ and C–N vibration bands are located at ≈ 2100 and ≈ 1449 cm^{-1} , and the peak intensities reach a maximum of -1.6 V vs RHE.^[23] The variation law of these characteristic peaks at different applied potentials is consistent with that of the urea yield rate with the applied potential, suggesting that urea formation is derived

from the crucial $^*\text{OCNO}$ intermediate species. Furthermore, high potentials promote the adsorption and activation of CO_2 and NO_3^- on $\text{Cu}_1\text{-CeO}_2$, which is beneficial to C–N coupling. Isotope-labeling operando SR-FTIR experiments were performed using $^{15}\text{NO}_3^-$ instead of NO_3^- to determine nitrogen source of urea. All nitrogen-related absorption peaks, including those of $^*\text{OC}^{15}\text{NO}$, C– ^{15}N , $^{15}\text{N-H}$, and $^{15}\text{NH}_2$ shift to lower wavelengths owing to isotopic effects,^[24] demonstrating that the produced urea originates from the co-electrolysis of $^{15}\text{NO}_3^-$ and CO_2 (Figure S32a, Supporting Information). Produced urea was also detected using nuclear magnetic resonance (NMR) spectroscopy. $\text{CO}(^{14}\text{NH}_2)_2$ produced by $^{14}\text{NO}_3^-$ and CO_2 appears as a triple coupling NMR peak, whereas that produced by $^{15}\text{NO}_3^-$ and CO_2 exhibits a double coupling NMR peak at different chemical shifts. (Figure S33, Supporting Information). Moreover, the increase in the integral area of the NH_4^+ peak after urease decomposition is due to the additional NH_4^+ derived by urea. The adsorption peaks of C–N and $^*\text{OCNO}$ are not observed in the operando SR-FTIR spectra obtained during controlled electrolysis experiments, including $\text{Ar} + \text{NO}_3^-$ and $\text{CO}_2 + \text{KHCO}_3$ (Figure S32b,c, Supporting Information). Urea is not detected in these control experiments (Figure S34, Supporting Information). The aforementioned results confirm that $^*\text{OCNO}$ is the pivotal intermediate in urea formation, and the carbon and nitrogen sources of urea are CO_2 and NO_3^- respectively.

DFT calculations were performed to further explore the microscopic mechanism of enhancement in the urea synthesis performance on Cu_4 clusters. We constructed the $\text{Cu}_4\text{-CeO}_2$ with a Cu_4 cluster placed on a 2×3 CeO_2 (110) superlattice. The urea synthesis starts with $^*\text{NO}$ adsorption. In the case of pure CeO_2 , the interaction between Ce and $^*\text{NO}$ is weak ($\Delta E_{\text{ad}} = -0.04$ eV). The $^*\text{NO}$ can be chemically absorbed on coordinate unsaturated Cu_4 cluster with a stronger adsorption energy of -0.61 eV. After $^*\text{NO}$ adsorption, a fast and efficient C–N coupling between $^*\text{NO}$ and $^*\text{CO}$ is a prerequisite for the

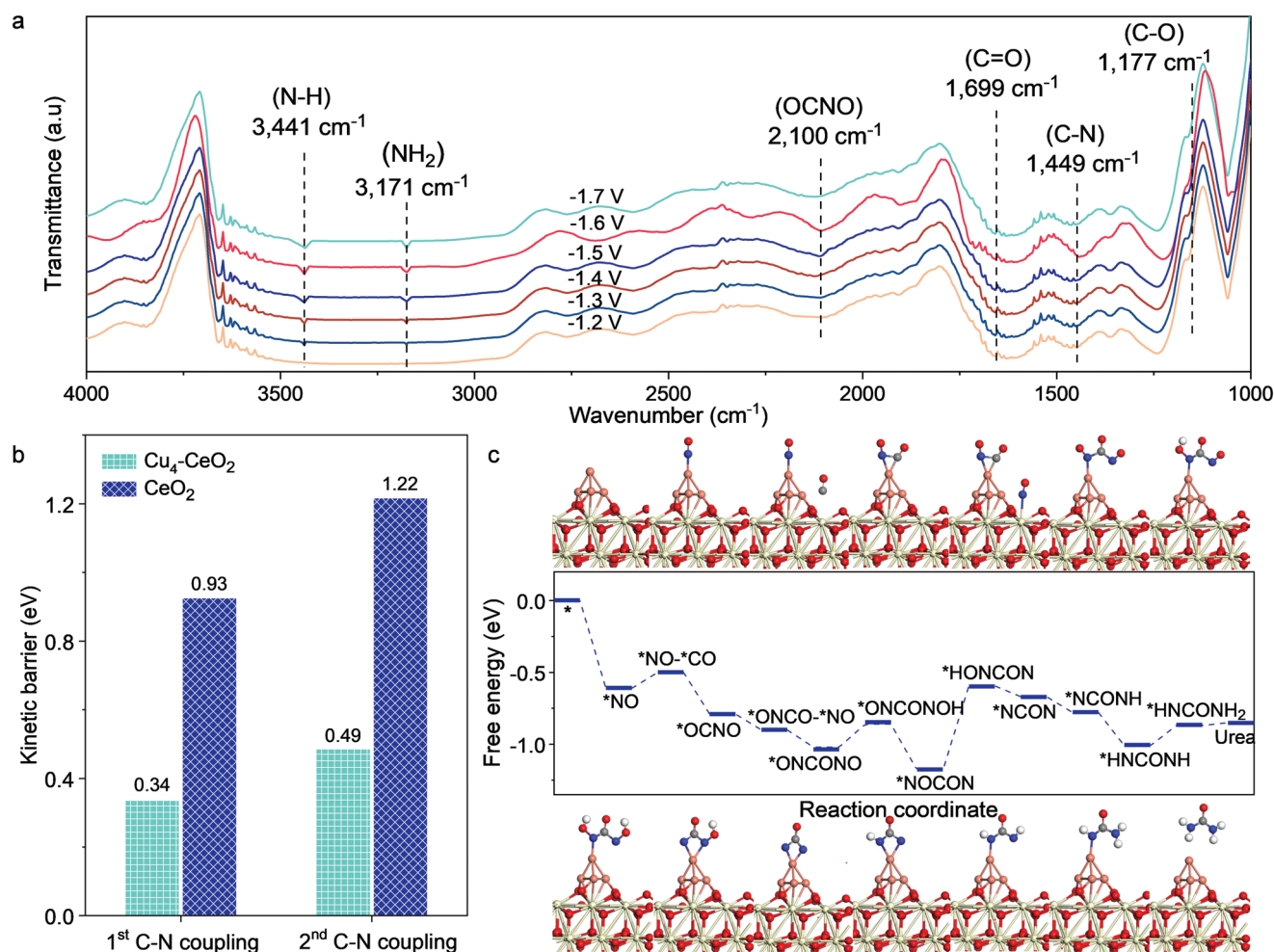


Figure 4. a) Operando SR-FTIR spectroscopy measurements under various applied potentials for Cu₄-CeO₂ during the electrocoupling of NO₃⁻ and CO₂. b) Comparison of kinetic barriers of *OCNO and *ONCONO on CeO₂ and Cu₄-CeO₂. c) Free-energy profiles and optimized geometric structure schematic of C–N coupling process on Cu₄-CeO₂ sample. Cu, Ce, O, N, C, and H atoms are labeled as pink, light yellow, red, blue, gray, and white spheres in the optimized geometric structure schematic, respectively.

smooth formation of urea. Notably, *OCNO intermediate species are formed through the Eley–Raideal (ER) mechanism, and *CO can attach to N atoms in *NO. The free energy of this process is calculated to be -0.29 and $+0.33$ eV for Cu₄-CeO₂ and CeO₂, respectively. The kinetic energy barriers of *CO and *NO coupling presented in Figure 4b indicate that the coupling barrier is moderate and surmountable in the case of Cu₄-CeO₂ ($+0.34$ eV) during the experiment. However, the energy barrier is $+0.93$ eV for CeO₂, prohibiting effective C–N coupling. Cu effectively alters the electronic state of CeO₂, enhances *NO adsorption and activation, and promotes C–N coupling. To synthesize urea, a second *NO species should be added to the *OCNO system. The formation of *ONCONO releases a free energy of -0.16 eV, and the energy barrier of this process is $+0.49$ eV for Cu₄-CeO₂, which are quite easy to overcome. The free energy diagram of each elementary reaction during the formation of urea on Cu₄-CeO₂ is presented in Figure 4c. The *ONCONO intermediate species are reduced to urea through eight electron-proton-transfer steps. The active Cu atom of Cu₄-CeO₂ is free-standing, consequently, *ONCONO

can be stabilized on Cu₄-CeO₂. Therefore, the formation of *HONCONO is the potential limiting step, and an energy input of $+0.58$ eV is required to drive this reaction. After the formation of the tower-like *NCON, the subsequent multiple electron-coupled-proton transfer processes are exothermic until the formation of *HNCONH₂ ($+0.13$ eV). The moderate limiting potential and C–N coupling energy barrier in this mechanism indicate a high catalytic performance of the free-standing Cu₄-CeO₂ system.

3. Conclusion

The direct co-electrolysis of nitrate and CO₂ is a sustainable strategy for industrial urea synthesis. Additionally, accurate identification of active sites under working conditions is a prerequisite for the development of an efficient electrocatalytic urea synthesis process. In this study, the operando XAS technique was applied to monitor the structural evolution of Cu₄-CeO₂ catalyst during C–N coupling. Cu²⁺ was gradually

reduced to Cu^+ and Cu^0 , then formed Cu_4 clusters under reducing potentials. When switching the applied potential to an open-circuit potential, Cu_4 clusters are reversibly deconstructed into single atoms. Considering the experimental and DFT calculation results, we propose that electrochemically reconstituted Cu_4 clusters are genuine active sites for C–N coupling and urea formation. The urea yield rate reaches a maximum of $52.84 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ at -1.6 V vs RHE, which is the highest value among those reported for the coupling of carbon dioxide and nitrate (Table S5, Supporting Information). This study provides significant insights into the reaction mechanism of urea synthesis, and the findings are expected to guide the rational design and development of C–N coupling systems in future.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

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 sites, clusters, copper single atoms, dynamic reconstitutions, urea synthesis

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- [1] a) Z. Liu, D. Guan, W. Wei, S. J. Davis, P. Ciais, J. Bai, S. Peng, Q. Zhang, K. Hubacek, G. Marland, R. J. Andres, D. C. Brown, J. Lin, H. Zhao, C. Hong, T. A. Boden, K. Feng, G. P. Peters, F. Xi, J. Liu, Y. Li, Y. Zhao, N. Zeng, K. He, *Nature* **2015**, 524, 335; b) M. D. Staples, R. Malina, S. R. H. Barrett, *Nat. Energy* **2017**, 2, 16202; c) B. R. Sutherland, *Joule* **2019**, 3, 2071.
- [2] a) C. Smith, A. K. Hill, L. Torrente-Murciano, *Energy Environ. Sci.* **2020**, 13, 331; b) G. Soloveichik, *Nat. Catal.* **2019**, 2, 377; c) S. L. Foster, S. I. P. Bakovic, R. D. Duda, S. Maheshwari,

- R. D. Milton, S. D. Minter, M. J. Janik, J. N. Renner, L. F. Greenlee, *Nat. Catal.* **2018**, 1, 490.
- [3] a) M. Wang, M. A. Khan, I. Mohsin, J. Wicks, A. H. Ip, K. Z. Sumon, C. T. Dinh, E. H. Sargent, I. D. Gates, M. G. Kibria, *Energy Environ. Sci.* **2021**, 14, 2535; b) W. Guo, K. Zhang, Z. Liang, R. Zou, Q. Xu, *Chem. Soc. Rev.* **2019**, 48, 5658; c) H. Shen, C. Choi, J. Masa, X. Li, J. Qiu, Y. Jung, Z. Sun, *Chem* **2021**, 7, 1708; d) S. K. Geng, Y. Zheng, S. Q. Li, H. Su, X. Zhao, J. Hu, H. B. Shu, M. Jaroniec, P. Chen, Q. H. Liu, S. Z. Qiao, *Nat. Energy* **2021**, 6, 904.
- [4] a) H. Xu, Y. Ma, J. Chen, W. X. Zhang, J. Yang, *Chem. Soc. Rev.* **2022**, 51, 2710; b) D. Wang, C. Chen, S. Wang, *Sci. China Chem.* **2022**, 65, <http://doi.org/10.1007/s11426-022-1419-y>; c) Y. Wang, C. Wang, M. Li, Y. Yu, B. Zhang, *Chem. Soc. Rev.* **2021**, 50, 6720.
- [5] a) Z. Song, Y. Liu, Y. Zhong, Q. Guo, J. Zeng, Z. Geng, *Adv. Mater.* **2022**, 34, 2204306; b) Y. Zeng, C. Priest, G. Wang, G. Wu, *Small Methods* **2020**, 4, 2000672; c) B. H. R. Suryanto, H. L. Du, D. Wang, J. Chen, A. N. Simonov, D. R. MacFarlane, *Nat. Catal.* **2019**, 2, 290.
- [6] a) C. Chen, N. He, S. Wang, *Small Sci.* **2021**, 1, 2100070; b) Y. Huang, R. Yang, C. Wang, N. Meng, Y. Shi, Y. Yu, B. Zhang, *ACS Energy Lett.* **2021**, 7, 284; c) C. Chen, X. Zhu, X. Wen, Y. Zhou, L. Zhou, H. Li, L. Tao, Q. Li, S. Du, T. Liu, D. Yan, C. Xie, Y. Zou, Y. Wang, R. Chen, J. Huo, Y. Li, J. Cheng, H. Su, X. Zhao, W. Cheng, Q. Liu, H. Lin, J. Luo, J. Chen, M. Dong, K. Cheng, C. Li, S. Wang, *Nat. Chem.* **2020**, 12, 717; d) C. Lv, L. Zhong, H. Liu, Z. Fang, C. Yan, M. Chen, Y. Kong, C. Lee, D. Liu, S. Li, J. Liu, L. Song, G. Chen, Q. Yan, G. Yu, *Nat. Sustainability* **2021**, 4, 868; e) Z. Tao, C. L. Rooney, Y. Liang, H. Wang, *J. Am. Chem. Soc.* **2021**, 143, 19630.
- [7] a) X. Wei, X. Wen, Y. Liu, C. Chen, C. Xie, D. Wang, M. Qiu, N. He, P. Zhou, W. Chen, J. Cheng, H. Lin, J. Jia, X. Z. Fu, S. Wang, *J. Am. Chem. Soc.* **2022**, 144, 11530; b) M. Jouny, J. J. Lv, T. Cheng, B. H. Ko, J. L. Zhu, F. Jiao, *Nat. Chem.* **2019**, 11, 846; c) X. Liu, Y. Jiao, Y. Zheng, M. J. , S. Z. Qiao, *Nat. Commun.* **2022**, 13, 5471.
- [8] a) Z. H. Xue, D. Luan, H. Zhang, X. Lou, *Joule* **2022**, 6, 92; b) M. F. Camellone, F. Dvořák, M. Vorokhta, A. Tovt, I. Khalakhan, V. Johánek, T. Skála, I. Matolínová, S. Fabris, J. Mysliveček, *ACS Catal.* **2022**, 12, 4859.
- [9] a) J. Yang, H. Qi, A. Li, X. Liu, X. Yang, S. Zhang, Q. Zhao, Q. Jiang, Y. Su, L. Zhang, J. F. Li, Z. Q. Tian, W. Liu, A. Wang, T. Zhang, *J. Am. Chem. Soc.* **2022**, 144, 12062; b) P. P. Yang, X. L. Zhang, F. Y. Gao, Y. R. Zheng, Z. Z. Niu, X. Yu, R. Liu, Z. Z. Wu, S. Qin, L. P. Chi, Y. Duan, T. Ma, X. S. Zheng, J. F. Zhu, H. J. Wang, M. R. Gao, S. H. Yu, *J. Am. Chem. Soc.* **2020**, 142, 6400.
- [10] a) A. Chen, X. Yu, Y. Zhou, S. Miao, Y. Li, S. Kuld, J. Sehested, J. Liu, T. Aoki, S. Hong, M. F. Camellone, S. Fabris, J. Ning, C. Jin, C. Yang, A. Nefedov, C. Wöll, Y. Wang, W. Shen, *Nat. Catal.* **2019**, 2, 334; b) X. Zhou, J. Shan, L. Chen, B. Xia, T. Ling, J. Duan, Y. Jiao, Y. Zheng, S. Z. Qiao, *J. Am. Chem. Soc.* **2022**, 144, 2079.
- [11] J. Li, S. Song, Y. Long, L. Wu, X. Wang, Y. Xing, R. Jin, X. Liu, H. Zhang, *Adv. Mater.* **2018**, 30, 1704416.
- [12] Y. Deng, A. D. Handoko, Y. Du, S. Xi, B. S. Yeo, *ACS Catal.* **2016**, 6, 2473.
- [13] Y. Wang, Z. Chen, P. Han, Y. Du, Z. Gu, X. Xu, G. Zheng, *ACS Catal.* **2018**, 8, 7113.
- [14] a) Y. Feng, H. Yang, Y. Zhang, X. Huang, L. Li, T. Cheng, Q. Shao, *Nano Lett.* **2020**, 20, 8282; b) M. Yuan, J. Chen, Y. Xu, R. Liu, T. Zhao, J. Zhang, Z. Ren, Z. Liu, C. Streb, H. He, C. Yang, S. Zhang, G. Zhang, *Energy Environ. Sci.* **2021**, 14, 6605.
- [15] G. F. Chen, Y. Yuan, H. Jiang, S. Y. Ren, L. X. Ding, L. Ma, T. Wu, J. Lu, H. Wang, *Nat. Energy* **2020**, 5, 605.
- [16] a) Y. B. Wang, Y. M. Wang, W. Z. Zhang, X. B. Lu, *J. Am. Chem. Soc.* **2013**, 135, 11996; b) S. Straub, P. Brünker, J. Lindner, P. Vöhringer, *Angew. Chem., Int. Ed.* **2018**, 130, 5094.

- [17] S. Zhou, Q. Wan, S. Lin, *Catalysts* **2022**, 12, 74.
- [18] a) R. Han, M. Qi, Z. Mao, X. Lin, P. Wu, *Phys. Lett. A* **2020**, 384, 126526; b) K. Wong, Q. Zeng, A. Yu, *Chem. Eng. J.* **2011**, 174, 408; c) A. Chutia, E. K. Gibson, M. R. Farrow, P. P. Wells, D. O. Scanlon, N. Dimitratos, D. J. Willock, C. R. A. Catlow, *Phys. Chem. Chem. Phys.* **2017**, 19, 27191; d) A. Chen, X. Yu, Y. Zhou, S. Miao, S. Li, S. Kuld, J. Sehested, J. Liu, T. Aoki, S. Hong, M. F. Camellone, S. Fabris, J. Ning, C. Jin, C. Yang, A. Nefedov, C. Wöll, Y. Wang, W. Shen, *Nat. Catal.* **2019**, 2, 334; e) J. Zhang, H. Wang, N. Wang, J. W. Sun, J. C. Yang, *Ranliao Huaxue Xuebao* **2022**, 50, 326.
- [19] L. Kang, B. Wang, Q. Bing, M. Zalibera, R. Büchel, R. Xu, Q. Wang, Y. Liu, D. Gianolio, C. C. Tang, E. K. Gibson, M. Danaie, C. Allen, K. Wu, S. Marlow, L. D. Sun, Q. He, S. Guan, A. Savitsky, J. J. Velasco-Vélez, J. Callison, C. W. M. Kay, S. E. Pratsinis, W. Lubitz, J. Y. Liu, F. R. Wang, *Nat. Commun.* **2020**, 11, 4008.
- [20] a) J. D. Grunwaldt, A. M. Molenbroek, N. Y. Topsøe, B. S. Clausen, *J. Catal.* **2000**, 194, 452; b) X. Zhao, F. Wang, X. Kong, R. Fang, Y. Li, *Nat. Commun.* **2022**, 13, 2591.
- [21] a) E. Boutin, A. Salamé, M. Robert, *Nat. Commun.* **2022**, 13, 4190; b) Z. Wang, Y. Wu, M. Wang, G. W. Brudvig, V. S. Batista, Y. Liang, Z. Feng, H. Wang, *Nat. Commun.* **2022**, 13, 4191; c) Z. Wang, Y. Wu, M. Wang, J. Jiang, K. Yang, S. Huo, X. F. Wang, Q. Ma, G. W. Brudvig, V. S. Batista, Y. Liang, Z. Feng, H. Wang, *Nat. Commun.* **2018**, 9, 418.
- [22] X. Zhang, C. Wang, Y. Guo, B. Zhang, Y. Wang, Y. Yu, *J. Mater. Chem. A* **2022**, 10, 6448.
- [23] a) C. Lv, C. Lee, L. Zhong, H. Liu, L. Yang, C. Yan, W. Yu, H. H. Hng, Z. Qi, L. Song, S. Li, K. P. Loh, Q. Yan, G. Yu, *ACS Nano* **2022**, 16, 8213; b) C. S. Jamieson, A. M. Mebel, R. I. Kaiser, *Phys. Chem. Chem. Phys.* **2005**, 7, 4089.
- [24] W. Cheng, X. Zhao, H. Su, F. Tang, W. Che, H. Zhang, Q. Liu, *Nat. Energy* **2019**, 4, 115.