

Polarity-alternating electrical pulses enable relay activation of CO₂ and dimethylamine on synergetic sites for efficient N,N-dimethylformamide synthesis

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ABSTRACT

The electrocatalytic synthesis of N,N-dimethylformamide (DMF) from CO₂ and dimethylamine (DMA) presents a sustainable alternative to traditional thermo-catalytic technique demanding high temperature and pressure. However, the essential C–N coupling process is severely hindered by the difficult activation of DMA in common CO₂-amine co-reduction systems. Herein, we propose a pulsed electrolysis strategy featuring reversed electric polarities that enables relay catalysis for efficient production of DMF from CO₂ and DMA using a self-supported nanowire array electrode rich in Cu–Ag interfaces. In-situ spectroscopy results indicate that DMA is oxidatively dehydrogenated into *N(CH₃)₂ on the oxidized Cu sites during the positive pulse, while CO₂ is reductively hydrogenated into *OCHO on the metallic Ag sites in the following negative pulse, thus boosting the C–N coupling efficiency. A record DMF Faradaic efficiency reaching 40.1% is achieved with a yield up to 278.4 μmol h^{−1} cm^{−2}. This study highlights the co-activation of reactants in electrocatalysis, and broadens the field of CO₂ utilization.

1. Introduction

Employing CO₂ as a building block in chemical production driven by renewable electricity presents an ideal model for future green chemical industry, of which the zero or even negative carbon footprint feature is essential to the global goal of carbon neutrality [1,2]. Albeit a series of hydrocarbons [3–5], carboxylic acids [6–8], and alcohols [9–12] with one or more carbon atoms can be directly produced by state-of-the-art catalysts in electrocatalytic CO₂ reduction, the categories of products are still far from satisfactory since the reactants CO₂ and H₂O only containing C, H, and O elements. Therefore, it is highly demanded to develop new electrocatalytic reactions that involves CO₂ and other compounds [13].

C–N bond formation is crucial in organic synthesis, and the obtained organonitrogen compounds are widely used in pharmacy, pesticides, fertilizer, and biological agents [14–17]. Among the various organonitrogen compounds, amides, especially N,N-dimethylformamide (DMF), plays a vital role in global chemical market that the annual scale

exceeds 2 billion with a compound annual growth rate of 3.2%. DMF not only serves as a widespread solvent by virtue of its relative chemical inertness and excellent miscibility, but also is an important feedstock in the synthesis of polymers and pharmaceuticals [18,19]. Nevertheless, the employment of fossil fuel-derived CO and dimethylamine (DMA) along with the high-temperature/high-pressure reaction conditions (323–473 K, 0.5–11 MPa) in traditional industrial DMF synthesis inevitably raise the concerns about fossil fuel consumption and carbon emission.

In comparison, employing CO₂ instead of CO as the building block in the electrosynthesis of DMF can proceed under moderate conditions, with the CO₂ hydrogenation accomplished via H₂O-mediated proton-coupled electron transfer process at cathode (HN(CH₃)₂ + CO₂ + H₂O + 2e[−] → HCON(CH₃)₂ + 2OH[−]). Up to now, electrosynthesis of amides has been achieved via co-reduction of CO₂ and reducible N-compounds such as NO_x, during which the two reactants both adsorb and get hydrogenated on the electrode for favorable C–N coupling [20–23]. However, when it comes to the co-electrolysis of CO₂ with irreducible

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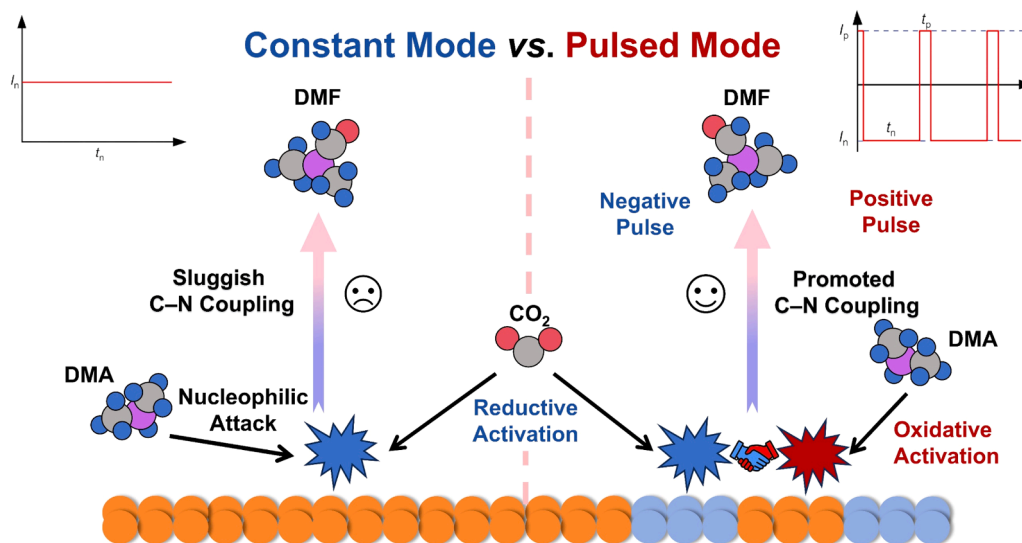


Fig. 1. Schematic illustration for the conventional constant mode electrolysis (left) and the pulsed mode electrolysis (right) in DMF synthesis from CO₂ and DMA. The blue, gray, purple, red, orange, and light blue spheres represent H, C, N, O, Cu, and Ag atoms, respectively.

ammonia/amines such as DMA, the C–N coupling becomes far more challenging. On these occasions, CO₂ adsorption and hydrogenation occur alone on the electrode under reductive current, followed by the nucleophilic attack of the N atom in DMA to the electron-deficient C atom in the CO₂-derived intermediates (left part in Fig. 1) [24]. The latter process is quite sluggish and thus retard the C–N coupling process [25]. For example, with ammonia and CO₂, a total amides Faradaic efficiency (FE) of merely ~1.2% was achieved by Cu nanoparticles even using a gas diffusion electrode [26]. Therefore, a crucial point to promote the C–N bond formation between CO₂ and DMA lies in the activation of both substrates, *i.e.*, reductive hydrogenation of CO₂ and oxidative dehydrogenation of the amine group in DMA, which however, seems like a dilemma in constant potential/current electrolysis.

Herein, we propose a pulsed electrolysis strategy featuring electric field with periodically alternating polarity in DMF synthesis, which enables relay activation of DMA and CO₂ for improved C–N coupling efficiency (right part in Fig. 1). To further boost the efficacy, a self-supported 3D electrode with high density of Cu–Ag interfaces is designed. The Cu site promotes the oxidative hydrogenation of DMA into ^{*}N(CH₃)₂ during the positive pulse, while the adjacent Ag site facilitates the reductive activation of CO₂ to formate intermediate (^{*}OCHO) within the negative period, thus synergistically expediting the C–N formation. As a result, a high FE_{DMF} up to 40.1% is achieved by the CuAg composite electrode using pulsed electrolysis, about 4 times as high as that by single Cu electrode under constant mode at identical current density. Moreover, a DMF yield reaching 278.4 μmol h^{−1} cm^{−2} and long stability over 120 h are delivered. The performances rank top among those of reported state-of-the-art electrocatalysts. This work highlights the importance of pulsed electrolysis in boosting C–N coupling efficiency, and demonstrates the feasibility of expanding CO₂ conversion to complex electrosynthesis.

2. Results and discussion

2.1. Fabrication and characterization of CuAg electrode

The method for fabricating self-supported 3D CuAg bimetallic electrode was illustrated in Fig. 2a. Cu foam-supported CuO nanowire arrays, noted as CuO NWs, was first prepared via chemical etching and subsequent annealing treatment according to our previous work [7]. Scanning electron microscope (SEM) image for the CuO NWs reveals that numerous micrometer-long nanowires with diameters ranging from

200 to 300 nm cover the Cu foam, exhibiting its high surface area (Figure S1). CuAg electrode was then synthesized by electrodeposition of Ag on CuO NWs under reductive current. As the electrodeposition time increases, the surface of the nanowire becomes rougher, and a series of CuAg electrodes with different Ag proportion are obtained (Fig. 2b; Figure S2 and Table S1). Energy dispersive X-ray elemental mapping demonstrates the uniform dispersion of Ag nanoparticles (NPs) with sizes ranging from 2 to 20 nm on the surface of CuO NWs (Fig. 2c). To gain close observation on the surface structure of the CuAg nanowires, aberration-corrected scanning transmission electron microscope (AC-STEM) was employed. As shown in Fig. 2d, the lattice fringes with interplanar spacing of 0.232 nm belong to CuO (111) plane. Moreover, clear lattice fringes with interplanar spacing of 0.236 nm corresponding to Ag (111) plane were observed in a Ag NP, with the Cu–Ag interface marked using a blue dot line.

X-ray diffractograms of CuO NWs and CuAg both exhibit peaks belonging to CuO and Cu (Fig. 2e). In addition to the CuO (111) and (111) peaks, the peaks at 38.2°, 44.4°, and 64.6° for CuAg can be assigned to the Ag (111), Ag (200), and Ag (220), respectively, confirming the presence of Ag on CuAg. The valence states of Cu and Ag were investigated using X-ray photoelectron spectroscopy (XPS). The two evident satellite peaks at 942.9 and 962.5 eV in Cu 2p XPS spectrum indicate Cu²⁺ species in CuAg (Fig. 2f) [27]. The deconvoluted result of Cu 2p_{3/2} peak suggests a mixed Cu valence states. Therefore, we further recorded the Cu LMM Auger line, where a strong Cu²⁺ signal with a weak Cu⁺ peak was observed, confirming the majority of Cu²⁺ with a small amount of Cu⁺ in CuAg (Figure S3). In Ag 3d XPS spectrum, the two peaks at 368.5 and 374.5 eV suggest the metallic Ag NPs in CuAg, consistent with the X-ray diffraction result (Fig. 2g) [28].

2.2. Performance assessment on the electrocatalytic conversion of CO₂ and DMA to DMF

The electrocatalytic performances were first assessed in a two-compartment membrane electrode assembly (MEA) electrolyzer under constant mode (Fig. 3a; Figure S4). Prior to the electrocatalysis, CuO NWs and CuAg were electrochemically reduced by cathodic linear sweep voltammetry (LSV) until coincident curves were obtained, and employed as the cathodes (working electrodes). CO₂-saturated DMA and KOH aqueous solution were circulated in the cathodic and anodic sides via a peristaltic pump, respectively. The gaseous products were monitored using a gas chromatography, and only H₂ was detected as the

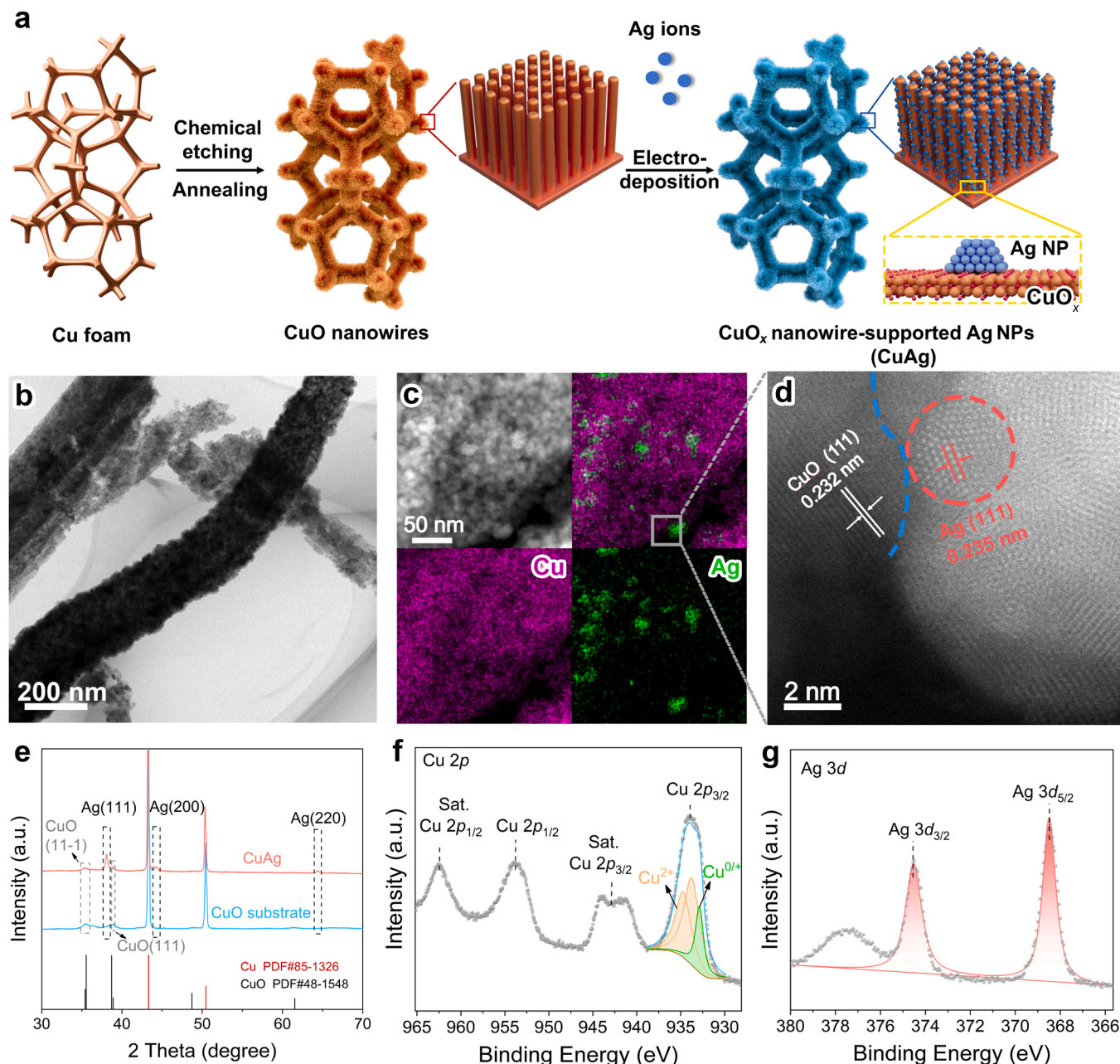


Fig. 2. Structural characterizations of CuAg bimetallic electrode. (a) Schematic illustration for the synthesis of self-supported CuAg electrode. (b) TEM, (c) elementary mapping, and (d) AC-STEM images for CuAg. (e) XRD patterns for CuO nanowire substrate and CuAg. (f) Cu 2p and (g) Ag 3d XPS spectra for CuAg.

byproduct (Figure S5). The liquid products were analyzed using nuclear magnetic resonance (NMR), and DMF and HCOOH were determined as the dominant products (Figure S6 & S7). Controlled experiments indicated that DMF and HCOOH could be only generated with current on, suggesting that the C–N coupling happened during electrolysis (Figure S8). Moreover, other possible N-containing byproducts such as *N*-methylformamide and formamide were not detected, indicative of the high selectivity of DMA conversion. CuAg electrodes with different electrodeposition time (Ag proportion) were evaluated. A volcano-type relationship between FE_{DMF} and electrodeposition time (Ag proportion) was obtained, where CuAg synthesized with an electrodeposition time of 240 s (with 9 wt% Ag) exhibited the highest FE_{DMF} with CO₂-saturated 1.0 M DMA solution (Figure S9 & S10). Unless special statement, the CuAg electrode in the following manuscript refers to the sample synthesized with an electrodeposition time of 240 s. As shown in Fig. 3b, the FE_{HCOOH} and FE_{DMF} both increase significantly in the presence of Ag at

various current densities (j), and an FE_{DMF} up to 15.4% is achieved at 20 mA cm⁻², 2.9 times as high as that in the absence of Ag. To evaluate the intrinsic activity of Cu and CuAg, electrochemically active surface area (ECSA) measurements were performed. Benefitting from the numerous Ag NPs, CuAg displays a high ECSA value of 2190 cm², 1.7 times higher than that of Cu (Figure S11). Nevertheless, the ECSA-corrected DMA partial current density by CuAg is still higher than that by Cu, signifying the promoted C–N coupling process on CuAg bimetallic sites (Figure S12).

Pulsed electrolysis strategy using current with periodically alternating polarity was then employed to boost the DMF formation on CuAg electrode (Fig. 3c). The durations of positive pulse (t_p) and negative pulse (t_n) were set as 2 and 10 s, respectively. As a result, the FEs for HCOOH and DMF are improved prominently (Fig. 3d). A maximum FE_{DMF} of 22.8% was delivered at $|j| = 20$ mA cm⁻², 48% higher than that under constant mode. Moreover, a DMF yield of 152.6 μmol h⁻¹ cm⁻²

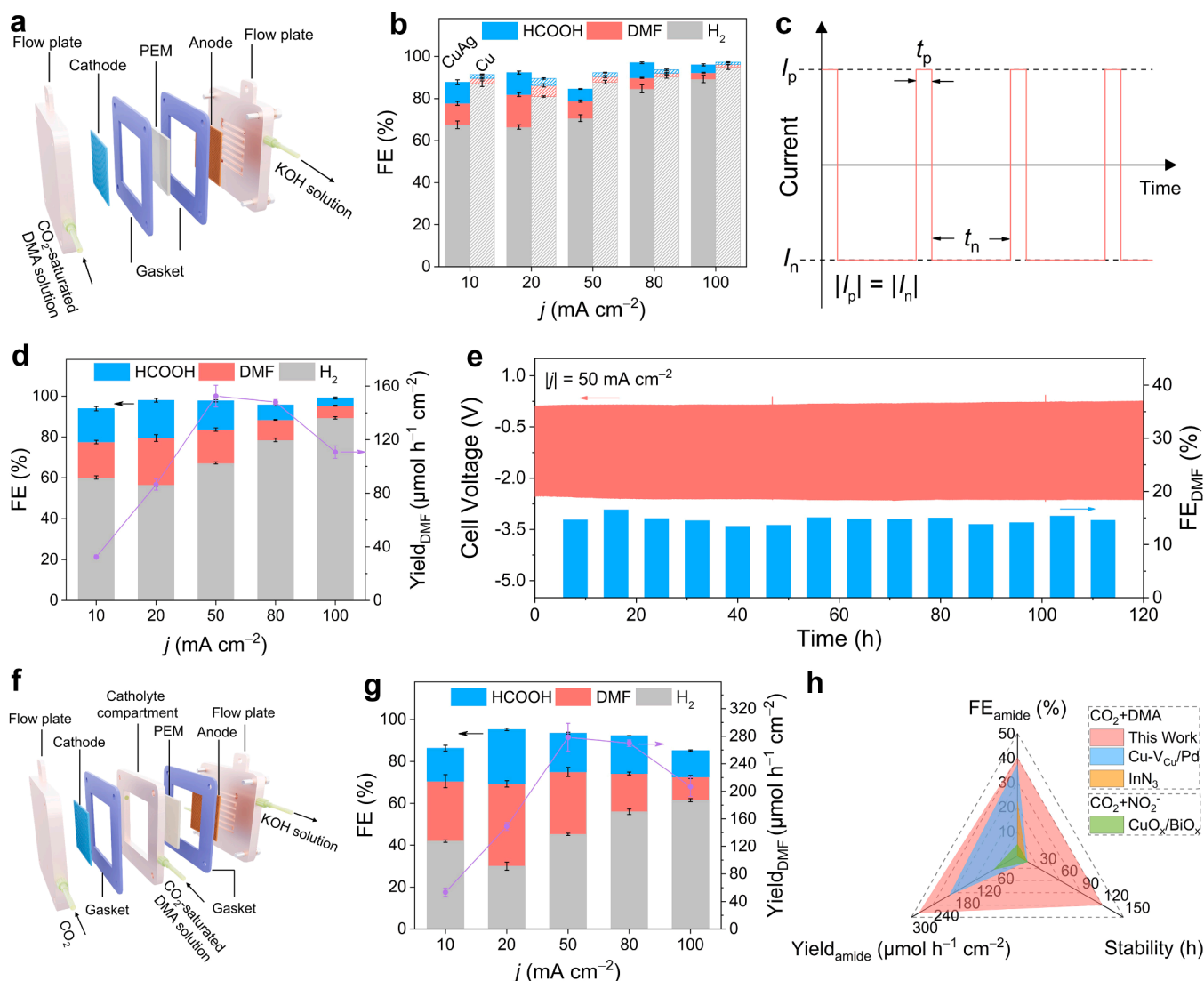


Fig. 3. Performance assessments on DMF electrosynthesis. (a) Schematic of the two-compartment MEA electrolyzer. (b) Product FEs for CuAg and Cu at different j using constant electrolysis in the MEA electrolyzer. (c) Input current-time signals of pulsed electrolysis. (d) FEs and yields of DMF for CuAg at different current densities using pulsed electrolysis in the MEA electrolyzer. (e) Long-term pulsed electrolysis test for CuAg at 50 mA cm⁻² in the MEA electrolyzer. (f) Schematic of the three-compartment flow cell. (g) FEs and yields of DMF for CuAg at different j using pulsed electrolysis in the flow cell. (h) Performance comparison of amide electrosynthesis from CO₂ and N-containing compounds (DMA or NO₂) between reported values and the results in this work. The error bars were obtained with at least three duplicates.

was achieved at $|j| = 50 \text{ mA cm}^{-2}$. The pulsed electrolysis with enhanced FE_{DMF} substantially reduced the energy consumption from 0.52 (for constant mode) to 0.29 kWh/mol_{DMF} ($|j| = 20 \text{ mA cm}^{-2}$). Besides, we also compare the performance between CuAg and Cu under pulsed mode (Figure S13). Resultingly, CuAg delivered significantly higher FE_{DMF} at each current density, evidencing the synergy of Cu–Ag sites in enhancing C–N coupling during pulsed electrolysis. Of note, the FE_{DMF}/FE_{HCOOH} value dropped drastically as $|j|$ increased for constant mode, whereas the value continued rising for pulsed mode at higher j , further suggesting the favored C–N coupling by virtue of the efficient DMA activation during positive pulse (Figure S14).

The influence of the t_p and t_n on the efficacy of pulsed electrolysis was further investigated at $|j| = 50 \text{ mA cm}^{-2}$. The t_p was first fixed at 2 s. As shown in Figure S15, the FE_{DMF} keeps rising as the t_n increases from 4 to 10 s. The markedly longer t_n than t_p required for improved FE_{DMF} indicates that the activation of amines during t_p is thermodynamically more favorable compared with the activation of CO₂ during t_n . Further prolonging t_n to 12 s, the FE_{DMF} drops slightly from 16.4% to 14.2%, which can be attributed to the reduced coverage of DMA-derived

intermediate due to consumption. With the ratio of t_p to t_n fixed at 1:5, pulsed electrolysis with various pulse periods ($t_p + t_n$) were performed (Figure S16). Interestingly, an FE_{DMF} of 9.5% is achieved when $t_p + t_n = 0.5 + 2.5 \text{ s}$, very close to that under constant mode (8.1%). The cell voltage-time profiles reveal that though j switched from -50 to $+50 \text{ mA cm}^{-2}$, the cell voltage (U) remained negative (Figure S17a). This result is attributed to the pronounced capacitance charging/discharging and electrochemical polarization over the electrode/solution interface under the electric field with quickly reversing polarity [29–31]. With the $t_p + t_n$ prolonged gradually to $2 + 10 \text{ s}$, the cell voltages of positive pulses (U_p) turn from -0.13 to $+0.04 \text{ V}$, and further to $+0.19 \text{ V}$, implying the efficient oxidative activation of DMA (Figure S17). Meanwhile, the cell voltages of negative pulses (U_n) decrease. In particular, a U_n of -2.81 V is obtained when $t_p + t_n = 2 + 10 \text{ s}$, smaller than that of constant mode ($U_{\text{constant}} = -2.98 \text{ V}$), manifesting that the enhanced oxidative activation of DMA lowers the overpotential of DMF generation. Further increasing $t_p + t_n$ to $5 + 25 \text{ s}$, an increased U_n (-2.99 V) close to U_{constant} is delivered even with a higher U_p of $+0.88 \text{ V}$, accompanied with a reduced FE_{DMF}, which is

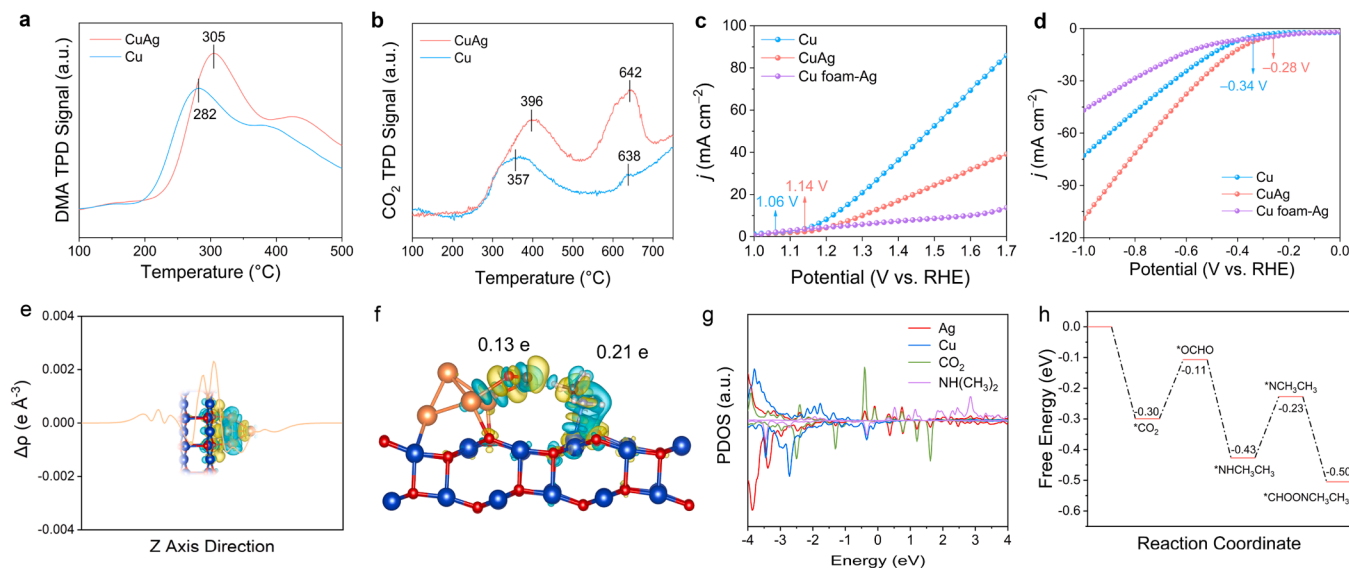


Fig. 4. Synergy of Cu–Ag sites in DMF synthesis. (a) DMA and (b) CO₂ TPD curves for CuAg and Cu. (c) Anodic LSV curves for Cu, CuAg and Cu foam-Ag in Ar-saturated 0.5 M K₂SO₄ + 1.0 M DMA solution. (d) Cathodic LSV curves for Cu, CuAg and Cu foam-Ag in CO₂-saturated 0.5 M K₂SO₄ + 1.0 M DMA solution. (e) Planar-averaged differential charge density profile and three-dimensional differential charge density plot of Ag/CuO along the Z-axis direction; yellow and cyan isosurfaces represent charge accumulation and depletion regions, respectively (isosurface value: 0.0025 e Å⁻³). (f) Side-view three-dimensional differential charge density plots of the co-adsorption configuration with CO₂ adsorbed at the Ag site and DMA adsorbed at the Cu site (isosurface value: 0.0025 e Å⁻³); Bader charge transfer values are labeled. (g) Projected density of states (PDOS) of the co-adsorption system of CO₂ and DMA on Ag/CuO. (h) Free energy diagram for the cooperative conversion of CO₂ and DMA to DMF over Ag/CuO.

ascribed to the reduced coverages of DMA- and CO₂-derived intermediates after long period of C–N coupling without timely replenishment.

We further studied the stability of CuAg electrode under pulsed electrolysis. Steady cell voltage-time signals were obtained with the FE_{DMF} kept around 15% during the 120-h electrolysis at $|j| = 50 \text{ mA cm}^{-2}$, accounting for the excellent durability of CuAg electrode (Fig. 3e). Meantime, the DMF concentration (c_{DMF}) increased linearly as the electrolysis time was prolonged, and finally a product solution containing ~11 mM DMF was obtained (Figure S18). We have characterized the CuAg electrode after stability test. The nanowire arrays were maintained after electrolysis (Figure S19). The EDX mappings show a uniform distribution of Ag over the nanowire (Figure S20a,b). To further study the dispersion of Ag NPs, high-magnification EDX mapping and AC-STEM images were taken (Figure S20c,d). The sizes of Ag NPs were kept around 10–20 nm, indicating no large aggregation of Ag occurred. No peak shift was observed in the Ag 3d XPS spectrum, indicative of the well remained metallic state (Figure S21). It has been reported that oxidized Cu can easily turn into metallic state under reductive conditions [32,33]. By virtue of the pulsed electrolysis, mixed copper states composed of mono- and zero-valence in similar proportions were obtained after test.

To enhance the supply of CO₂ over the CuAg electrode for improved C–N coupling, CO₂ and CO₂-saturated DMA solution were simultaneously fed using a three-compartment flow cell (Fig. 3f). Impressively, the Faradaic efficiencies of DMF were significantly boosted for both pulsed and constant electrolysis (Fig. 3g; Figure S22). An unprecedentedly high FE_{DMF} up to 40.1% was achieved at $|j| = 20 \text{ mA cm}^{-2}$, almost twice as much as that in MEA electrolyzer. With the FE_{DMF} remained above 30%, a DMF yield approaching 278.4 $\mu\text{mol h}^{-1} \text{ cm}^{-2}$ was delivered at $|j| = 50 \text{ mA cm}^{-2}$. Performance comparison about electrosynthesis of amides from CO₂ and N sources was conducted based on Faradaic efficiency, yield, and stability. As a result, CuAg electrode delivers excellent overall performances (Fig. 3h; Table S2) [20,21,24,26,34].

2.3. Synergetic effect of Cu and Ag in C–N coupling

To verify the roles of Cu and Ag sites in C–N coupling, temperature programmed desorption (TPD) for DMA and CO₂ were conducted on Cu and CuAg. Evident peaks at around 300 °C corresponding to DMA chemisorption were observed in the DMA-TPD spectra for both two catalysts (Fig. 4a). The peak shifts to higher temperature and grows stronger on CuAg, suggesting its promoted DMA adsorption capacity. In the CO₂-TPD spectrum of CuAg, two strong peaks centered at 396 and 642 °C emerge, corresponding to adsorbed HCO₃⁻/HCO₂⁻ and adsorbed CO₃²⁻, respectively (Fig. 4b) [35]. On the contrary, these two peaks become much weaker in the absence of Ag, indicating the enhanced adsorption of CO₂ on Ag.

Anodic LSV curves were recorded in an Ar-saturated electrolyte containing 0.5 M K₂SO₄ + 1.0 M DMA (Fig. 4c). The onset potential of DMA oxidation increased from 1.06 to 1.14 V vs. RHE with the introduction of Ag. The enlarged overpotential is attributed to the partially covered Cu surface by Ag NPs, indicating Cu as the preferred active site. Cathodic LSV curves in CO₂-saturated 0.5 M K₂SO₄ + 1.0 M DMA display that the onset potential for CO₂ reduction is lowered by 0.06 V on CuAg, evidencing the reduced energy requirement for CO₂ activation on Ag. This deduction was also verified by the in-situ Raman spectroscopic result (setup shown in Figure S23). The signal intensity of *CO₂, which is widely recognized as the initial intermediate in CO₂ reduction, is much higher for CuAg (Figure S24). The above results demonstrate that the DMA activation is more favorable on Cu, while Ag promotes the adsorption and activation of CO₂. Besides, electrodes synthesized via directly electrodepositing Ag on Cu foam (denoted as Cu foam-Ag) delivered markedly lower current densities for both anodic and cathodic LSV curves compared with CuAg and Cu, indicating the crucial role of nanowire structure in boosting the C–N coupling activity. Besides, an electrode was prepared through physically spraying Ag NPs onto CuO nanowire substrate, which exhibited lower FE_{DMF} in comparison with CuAg, demonstrating the synergy of CuAg interface in promoting C–N coupling (Figure S25).

Density function theory (DFT) calculations were then employed to reveal the synergy of Cu and Ag. Differential charge density calculations

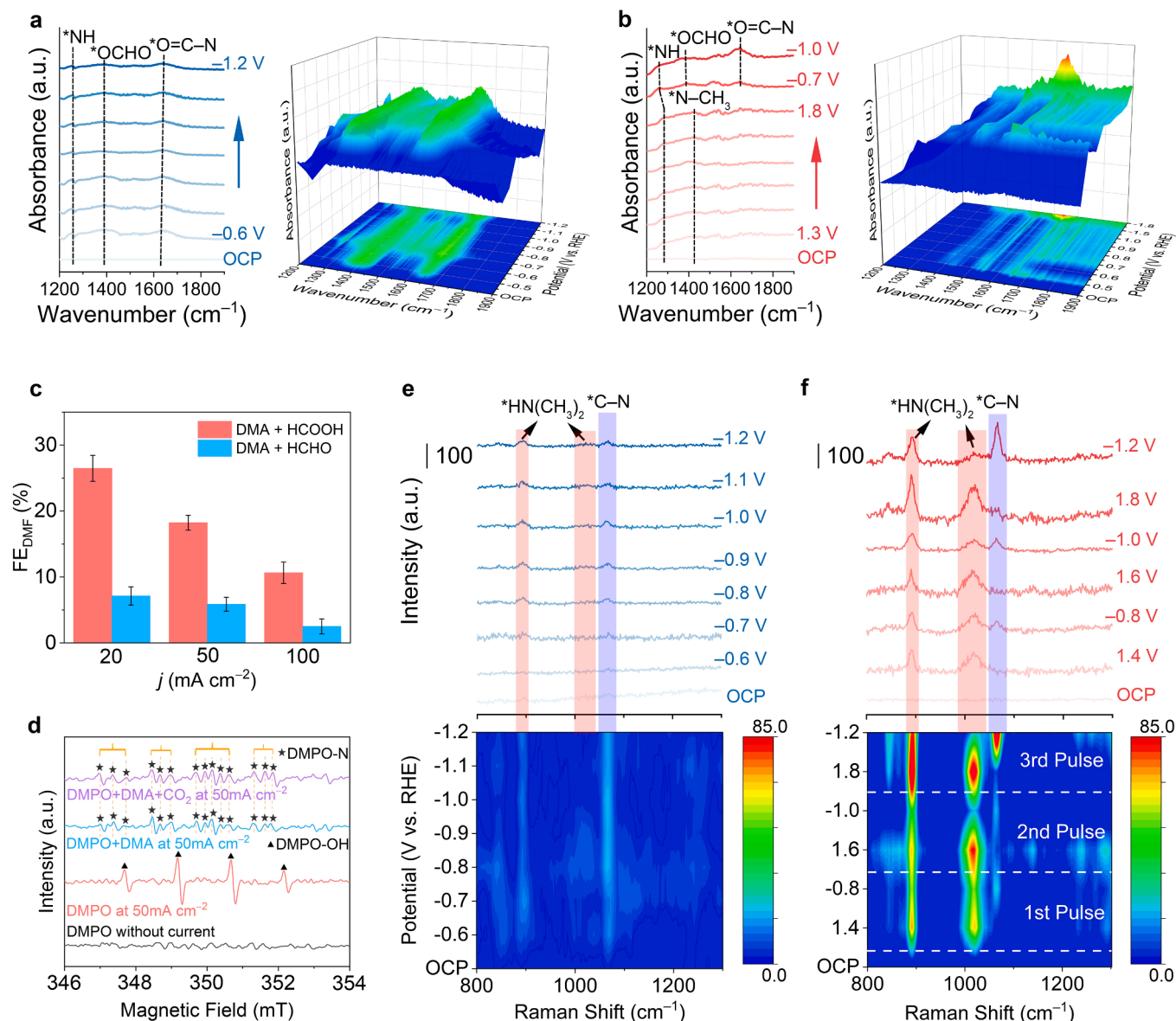


Fig. 5. Mechanism study of C–N coupling under pulsed electrolysis. In-situ ATR-SEIRAS spectra and corresponding 3D images for CuAg under (a) a series of cathodic potentials and (b) a series of anodic potentials followed by cathodic ones. (c) FE_{DMF} from DMA + HCOOH or DMA + HCHO by CuAg under pulsed mode. (d) Quasi-in-situ EPR tests for N-centered radicals trapping using DMPO under different conditions. In-situ Raman spectra and corresponding contour map for (e) constant mode and (f) pulsed mode by CuAg.

were performed to elucidate the interfacial electronic structure of the CuAg system. The results reveal pronounced charge redistribution at the Ag–CuO interface, with charge accumulation (yellow isosurfaces) predominantly distributed near the CuO surface and charge depletion (cyan isosurfaces) concentrated at the base of the Ag cluster (Fig. 4e), indicating electron deficiency at the Ag sites and a corresponding increase in electron density at the CuO surface. The planar-averaged differential charge density profile along the Z-axis further confirms that a positive peak appears on the CuO side and a negative region on the Ag side at the interface, quantitatively demonstrating directional charge transfer from the Ag sites to the CuO surface and the formation of a pronounced interfacial electronic interaction between the two components.

In addition, differential charge density analysis reveals evident interfacial charge transfer at both the Ag– CO_2 and Cu– $\text{NH}(\text{CH}_3)_2$ interfaces; Bader charge analysis quantifies transfers of 0.13 e from Ag to CO_2 and 0.21 e from Cu to $\text{NH}(\text{CH}_3)_2$ (Fig. 4f). Projected density of state (PDOS) analysis further elucidates the activation mechanism of CO_2 and $\text{NH}(\text{CH}_3)_2$ at the orbital level (Fig. 4g). Below the Fermi level, the CO_2 -

derived states exhibit significant energy-level overlap with the Ag projected density of states, indicative of σ -donation from the O lone pairs of CO_2 to the vacant s orbital of $\text{Ag}^{\delta+}$; near the Fermi level, a localized CO_2 state emerges, corresponding to back-donation from the filled Ag d orbitals into the $\text{CO}_2 \pi^*$ antibonding orbital, which weakens and polarizes the C=O bond, induces CO_2 bending and activation, and enhances the electrophilicity of the C atom, providing a favorable electronic structural basis for subsequent $^*\text{H}$ attack on the C center to form $^*\text{OCHO}$. The DMA-derived states exhibit energy-level overlap with the Cu 3d states near the Fermi level, indicating effective coordinative interaction between the N lone pair and the Cu 3d orbitals; the interfacial charge transfer from Ag to CuO strengthens the electronic interaction between Cu and the N–H bond, thereby weakening N–H bond and facilitating cooperative N–H proton extraction by the adjacent lattice O, which promotes the oxidative dehydrogenation process.

To quantitatively substantiate the above activation mechanisms, crystal orbital Hamilton population (COHP) analysis was performed on the C–O and N–H bonds (Figure S26). A larger absolute value of

integrated COHP (ICOHP) indicates stronger bonding interaction and higher bond strength. In the pristine CuO system, CO₂ exists in a physisorbed state with an ICOHP of -19.357 eV, indicating that CuO possesses negligible chemical activation capability toward CO₂; upon introduction of the Ag NPs, CO₂ transitions to a chemisorbed state with pronounced antibonding state occupation near the Fermi level and an ICOHP reduced to -16.638 eV, a decrease of approximately 2.72 eV in magnitude relative to the pristine CuO system, quantitatively confirming a significant reduction in C–O bond strength. For the N–H bond, the ICOHP at the Cu site (-7.537 eV) is smaller in magnitude than that at the Ag site (-7.832 eV), indicating more pronounced N–H bond weakening at the Cu site, which confirms Cu as the preferential active site for HN(CH₃)₂ dehydrogenation.

On the basis of the above electronic structure analysis, free energy calculations were carried out for the cooperative conversion of CO₂ and NH(CH₃)₂ to DMF (Fig. 4h). On the CO₂ activation side, CO₂ spontaneously adsorbs at the Ag site to form *CO₂ ($\Delta G = -0.30$ eV), indicating effective CO₂ capture capability of the Ag^{δ+} site; subsequent hydrogenation of *CO₂ to *OCHO is endothermic by 0.19 eV. On the DMA activation side, NH(CH₃)₂ adsorbs at the Cu site to form *NHCH₃CH₃ ($\Delta G = -0.32$ eV), reflecting strong coordinative interaction between the Cu site and NH(CH₃)₂; subsequent N–H bond cleavage to yield *N(CH₃)₂ is endothermic by 0.20 eV. The near-identical thermodynamic demands of the two uphill steps indicate that CO₂ hydrogenation and DMA dehydrogenation are thermodynamically well-matched. Finally, C–N coupling between *OCHO and *N(CH₃)₂ ($\Delta G = -0.27$ eV) is a highly thermodynamically spontaneous step. The maximum uphill free energy change along the entire pathway being only 0.20 eV, demonstrating that the interfacial synergistic effect of Ag/CuO confers significant thermodynamic advantages for driving the coupling of CO₂ and DMA to DMF.

We then sought to disclose the valence states of Cu and Ag during the pulsed electrolysis. As shown in Figure S27, ex-situ XPS spectra were collected for CuAg catalyst at different electrolysis time (*t*): pristine CuAg (*t* = 0 s), CuAg after one positive pulse (*t* = *t_p*), and CuAg after one pulse cycle (*t* = *t_p* + *t_n*). The deconvoluted Cu 2p_{3/2} XPS spectra show that divalent copper is in the majority for both pristine CuAg and CuAg after one positive pulse. However, the peak corresponding to Cu^{0/+} rises after the subsequent negative pulse. The Cu LMM Auger lines reveal that Cu²⁺ is partially reduced to Cu⁺ by the negative current [36]. According to the Ag 3d XPS spectra, Ag NPs remained metallic state during the whole cycle, in agreement with the XPS result in stability test.

Furthermore, we pursue to gain insight into the changes of oxidation states and dynamic local bonding structure of Cu during DMA activation under real operating conditions using in-situ X-ray absorption spectroscopy (XAS) [37]. Figure S28 presents the in-situ XAS setup. The in-situ X-ray absorption near edge structure (XANES) spectra of Cu *K*-edge at different potentials were recorded (Figure S29a). The pre-edge peak ranging from 8975 to 8985 eV due to the 1 *s* → 4p_z transition and the white-line peak centered at 8996.3 eV due to the 1 *s* → 4p_{x,y} transition proves a mixture of Cu₂O and CuO species in CuAg at open-circuit potential (OCP). When an anodic potential of 1.6 V vs. RHE is applied, although the pre-edge lines almost coincide with that at OCP, the white-line peak right shifts to 8996.9 eV, indicative of a slight increase in Cu oxidation state by positive pulse. Notably, both the pre-edge and white-line peaks shift to lower energies with a subsequent cathodic potential of -1.0 V vs. RHE, suggesting the reduction in Cu oxidation state during negative pulse. The oxidation states of Cu were further quantitatively analyzed using linear combination fitting (LCF) of the in-situ XANES spectra (Figure S30). The result in Table S3 indicates a mixed Cu valence states of 30% Cu₂O + 70% CuO in CuAg at OCP and 1.6 V vs. RHE. Notably, when the cathodic potential of -1.0 V vs. RHE was on, the content of Cu₂O significantly increased, suggesting the formation of Cu⁺ sites during the negative pulse. The varied local coordination environment of the Cu sites was further demonstrated by the in-situ Cu *K*-edge Fourier-transform extended X-ray absorption fine

structure (FT-EXAFS) spectroscopy (Figure S29b). No metallic Cu–Cu coordination path was observed. The peak corresponding to Cu–O coordination path intensified with the anodic potential on, suggesting a higher Cu–O coordination number, which implies new bond generated on the coordinatively unsaturated Cu sites during the DMA activation. When the potential was reversed to -1.0 V vs. RHE, the reduction of oxidized Cu species contributed to the decreased Cu–O coordination number.

2.4. Enhancement mechanism of pulsed electrolysis on CuAg electrode

In-situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) was employed to disclose the intermediate evolution of C–N coupling during constant and pulsed electrolysis in CO₂-saturated 1.0 M DMA solution (setup shown in Figure S31) [38]. As shown in Fig. 5a, no characteristic peak was observed at OCP, indicating that C–N coupling reaction is an electrochemical process. As cathodic potentials on, three peaks at around 1255, 1386, and 1645 cm⁻¹ emerge, which are assigned to N–H bending vibration in *HN(CH₃)₂, O–C–O symmetric vibration of *OCHO, and C=O stretching of *O=C–N in DMF, respectively [7,34,39–41]. Accordingly, *OCHO was determined as the key CO₂-derived intermediate in C–N coupling, in line with the pronounced FE_{HCOOH} in performance evaluation. It was further evidenced by replacing CO₂ with HCOOH, the direct product from *OCHO, where higher FE_{DMF} values were achieved at different *j* compared with the result in Fig. 3d (Fig. 5c). Besides, HCHO was also chosen as a substitution for CO₂. The poor FE_{DMF} values delivered in the presence of HCHO and DMA imply that HCHO and its derived intermediates are unlikely favored in DMF formation [42,43]. We then applied a series of anodic potentials followed by cathodic potentials to simulate the polarity reversing near the electrode surface (Fig. 5b). It is noteworthy that within the anodic potential range, the peak positions for *N–H bending vibration in DMA shift to higher wavenumbers at ~ 1270 cm⁻¹. Meanwhile, a new peak at ~ 1430 cm⁻¹ corresponding to *N–CH₃ in *N(CH₃)₂ appears [36]. These results indicate that efficient adsorption and dehydrogenation of DMA occur during the positive pulse. When the potential was reversed to cathodic potentials, *OCHO and *O=C–N species appear while *N–CH₃ signal diminishes, demonstrating that the DMA-derived *N(CH₃)₂ is coupled with *OCHO for DMF formation.

To further validate our conjecture, quasi-in-situ electron paramagnetic resonance (EPR) experiments using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the trapping agent for capturing N-centered radical species in the electrolyte after electrolysis (Fig. 5d) [44–46]. Only •OH radical from water oxidation was detected at an anodic *j* of 50 mA cm⁻² in the absence of DMA. In comparison, new DMPO-trapped N-centered radical signals (DMPO–N) with four sets of multiplets arise in the presence of DMA or DMA + CO₂, indicative of the preferred oxidation of DMA to *N-intermediate compared with water oxidation [40,47].

After confirming the intermediates of CO₂ reduction and DMA oxidation in DMF synthesis, a question naturally arises: during which pulse does the C–N coupling occur? Although the in-situ ATR-SEIRAS results show that C–N bonds form during the negative pulse, the lack of CO₂ activation at the initial anodic potentials cannot exclude the positive pulse-driven C–N coupling in long-term pulsed electrolysis. To address this question, we further recorded the in-situ Raman spectra for CuAg at both constant and pulsed modes. The spectra for constant mode in Fig. 5e reveal that three peaks arise as the cathodic potentials on. The two weak peaks at 892 and 1022 cm⁻¹ are assigned to the A_{1g} and e_{2g} modes of adsorbed DMA, respectively [34,48]. Meanwhile, a *C–N peak at 1066 cm⁻¹ was observed, indicating the formation of DMF [49]. As the cathodic potential negatively shifts from -0.6 to -1.0 V vs. RHE, both of the two species signals increase. Further altering the potential to -1.2 V vs. RHE, the peaks drop due to the competing HER. Then, a series of potential couples with reversed polarities were applied consecutively (Fig. 5f). Significantly stronger *HN(CH₃)₂ peaks were observed at

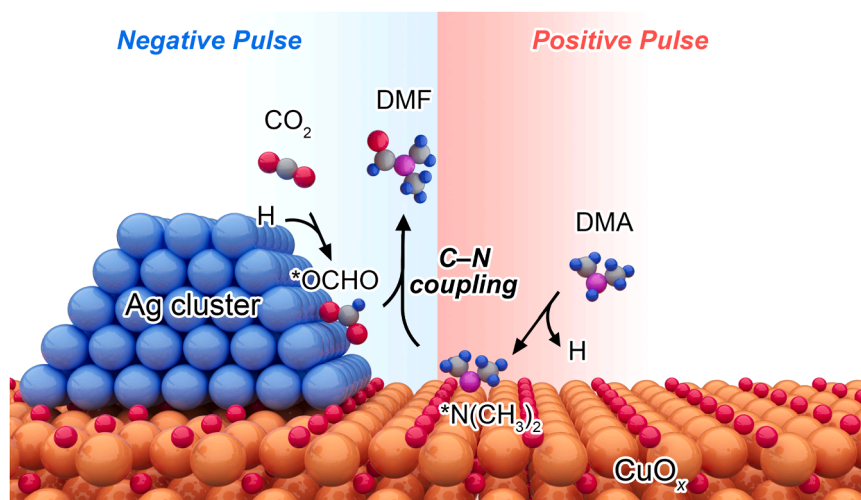


Fig. 6. Schematic illustration of the proposed C–N coupling mechanism for pulsed electrolysis.

anodic potentials compared to those at constant mode, and the signals intensified as the potential increased from 1.4 to 1.6 and further to 1.8 V vs. RHE, again validating the efficient DMA adsorption and activation during the positive pulse. Of note, barely no *C–N peak emerged at anodic potentials. On the contrary, as the potentials were reversed from anodic to cathodic values, for example, from 1.4 to -0.8 V vs. RHE, the *C–N peak appeared with markedly high intensity compared to that at -0.8 V vs. RHE in constant mode; meanwhile, the *HN(CH₃)₂ peaks decayed. These trends were observed in all the three pulse periods (1.4/ -0.8 , 1.6/ -1.0 , and 1.8/ -1.2 V vs. RHE), as clearly presented in the corresponding contour map below, demonstrating that the C–N coupling proceeds during the negative pulse. In-situ Raman spectra using isotope-labeling DMA (HN(CD₃)₂) were also recorded at different pulse potentials. As shown in Figure S32, the two peaks corresponding to adsorbed HN(CD₃)₂ redshifted compared to those in DMA solution [50, 51]. Meanwhile, the *C–N signal also shifted to a lower value of 1052 cm^{-1} in the isotope-labeling test, signifying the formation of deuterated DMF. Of note, the HN(CD₃)₂ peak intensity slightly reduced when the potential was reversed from anodic to cathodic value, and significant *C–N peak was only observed in the negative pulse. This result agrees with that in DMA solution in Fig. 5f. Therefore, we can confirm that the activated N intermediate survives in the following negative pulse and participates in the C–N coupling.

Therefore, we proposed a possible reaction pathway featuring relay activation of DMA and CO₂ over the Cu–Ag interface under pulsed electrolysis for the DMF formation (Fig. 6). During the positive pulse, DMA is adsorbed and dehydrogenated into *N(CH₃)₂ on the oxidized Cu sites. When negative pulse is applied, CO₂ is activated and hydrogenated into the *OCHO species at Ag NPs. Meanwhile, the electron-rich environment weakens the adsorption of nucleophilic N in *N(CH₃)₂, thereby promoting the C–N coupling for efficient DMF production.

3. Conclusion

By virtue of the innovative pulsed electrocatalytic strategy, efficient synthesis of DMF was achieved through C–N coupling from CO₂ and DMA on synergetic Ag–Cu interface. The record DMF FE was 40.1%, and the production rate was $278.4\text{ }\mu\text{mol h}^{-1}\text{ cm}^{-2}$. In-situ ATR-SEIRAS and Raman spectroscopy results revealed a relay activation mechanism in the DMF formation. In the positive pulse, DMA was oxidatively dehydrogenated into *N(CH₃)₂ over the oxidized Cu sites. When the polarity of the electric field was reversed, *OCHO formed through the reductive hydrogenation of CO₂ on the Ag sites, and coupled with *N(CH₃)₂ from adjacent Cu sites, thus accelerating the C–N bond formation. This work provides a sustainable approach for amide synthesis with CO₂

utilization.

CRediT authorship contribution statement

Ming-Yang Song: Methodology, Formal Analysis, Investigation. **Yu Li:** Conceptualization, Methodology, Formal Analysis, Writing – Original Draft, Writing – Review & Editing, Supervision, Funding Acquisition. **Cun-Biao Lin:** Methodology, Formal Analysis, Writing – Review & Editing. **Xing-Qi Tao:** Investigation, Validation. **Tong-Bu Lu:** Supervision, Funding Acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2026.127021.

Data availability

Data will be made available on request.

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