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# Defect-engineered N-doped carbon stabilizes Cu<sup>+</sup> active sites for bifunctional CO<sub>2</sub> electroreduction to CO and formate

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The development of bifunctional electrocatalysts capable of steering CO<sub>2</sub> reduction toward selective C<sub>1</sub> products under mild conditions remains central to advancing next-generation electrochemical technologies. Here, we demonstrate that stabilization of Cu<sup>+</sup> species by N-doped carbon derived from tea leaves (TL9) enables highly selective and durable CO<sub>2</sub> electroreduction to CO and formate. Uniformly dispersed Cu<sub>2</sub>O nanoparticles supported on TL9 exhibit strong metal–support interactions and form stable Cu–N<sub>x</sub> coordination that preserves the active Cu<sup>+</sup>/Cu<sup>0</sup> interface during operation. Structural, spectroscopic, and electrochemical analyses reveal that this tailored interface suppresses Cu agglomeration and hydrogen evolution, promoting efficient two-electron transfer pathways. The optimized TL9/Cu-40% catalyst achieves faradaic efficiencies approaching 90% for CO and formate at –0.6 V vs. RHE and maintains over 60% selectivity after 24 h of continuous operation. These findings highlight how defect-engineered carbon supports can precisely regulate Cu oxidation states to enhance efficiency, selectivity, and stability—offering a robust design principle for bifunctional catalysts that couple renewable electricity with CO<sub>2</sub> valorization.

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## 1. Introduction

The electrochemical reduction of carbon dioxide (CO<sub>2</sub>RR) has attracted increasing attention as a viable approach to closing the carbon cycle while generating value-added fuels and chemicals using renewable electricity. Significant progress has been achieved in developing copper-based electrocatalysts, which uniquely enable the formation of a wide spectrum of products ranging from CO and formate to multicarbon (C<sub>2</sub><sup>+</sup>) species such as ethylene and ethanol.<sup>1,2</sup> However, achieving high selectivity toward desired products remains a major challenge, as competing hydrogen evolution and complex multi-electron pathways often limit the overall reaction efficiency.<sup>3,4</sup>

Among the various CO<sub>2</sub>RR products, CO and formate stand out as particularly attractive due to their simple two-electron transfer pathways. In contrast to C<sub>2</sub><sup>+</sup> products that require high overpotentials, intricate C–C coupling steps, and often

suffer from poor durability, the generation of CO and formate is both kinetically and thermodynamically more favorable. Consequently, these reactions can deliver higher faradaic efficiencies (FE) under milder operating conditions, providing a practical route for sustainable CO<sub>2</sub> utilization.<sup>5</sup> Beyond efficiency, these C<sub>1</sub> products serve as versatile intermediates: CO is a cornerstone of syngas chemistry and an essential feedstock for downstream processes such as Fischer–Tropsch and methanol synthesis,<sup>6–8</sup> while formate is a stable liquid fuel that can be used directly in formate fuel cells or upgraded into formic acid and oxalate-derived polymer feedstocks.<sup>5</sup> Formate, in particular, should be regarded not merely as a terminal product but as a key gateway intermediate. Its coupling to oxalate unlocks pathways toward a spectrum of downstream chemicals—including glycolic acid, ethylene glycol, glyoxal, and metal oxalates—offering a more practical and scalable alternative to the direct but less selective C<sub>2</sub><sup>+</sup> formation route. Together, CO and formate represent a complementary product pair, balancing gaseous intermediates for large-scale synthesis with liquid fuels and chemical precursors that integrate seamlessly into existing infrastructures.

The ability of copper to toggle between Cu<sup>+</sup> and Cu<sup>0</sup> oxidation states is widely recognized as a crucial factor governing CO<sub>2</sub>RR selectivity. Cu<sup>+</sup> species stabilize key intermediates (*e.g.*, \*COOH for CO, \*OCHO for formate), whereas Cu<sup>0</sup> facilitates electron transfer and product desorption.<sup>9–11</sup> However, under strongly reducing potentials, Cu<sup>+</sup> tends to convert irreversibly to

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metallic Cu.<sup>12</sup> One promising strategy to overcome this limitation is the use of N-doped carbon supports, which can anchor Cu<sup>+</sup> species at defect sites and stabilize them *via* coordination with pyridinic or pyrrolic nitrogen functionalities.<sup>13</sup> By tuning the metal-support interaction and dispersion, such hybrid catalysts can maintain a favorable Cu<sup>+</sup>/Cu<sup>0</sup> balance during operation, thereby enhancing both selectivity and stability. Previous studies have demonstrated that N-doped carbon supports play a crucial role in stabilizing Cu-based active sites for selective CO<sub>2</sub> electroreduction. Porous N-doped carbon-supported Cu catalysts have achieved high efficiencies toward C<sub>1</sub> products such as CO and formate by promoting CO<sub>2</sub> adsorption and stabilizing Cu<sup>+</sup> species.<sup>9</sup> Similarly, Cu<sub>2</sub>O/Cu-based composites immobilized on N-doped graphene have shown enhanced formate selectivity at low overpotentials through synergistic metal-support interactions that suppress hydrogen evolution and facilitate charge transfer.<sup>14</sup> These reports collectively highlight the importance of nitrogen-containing carbon supports in regulating Cu oxidation states and reaction pathways.

In this study, we systematically investigate Cu<sub>2</sub>O nanoparticles supported on N-doped carbon derived from tea leaves and compare their CO<sub>2</sub>RR performance with those supported on commercial activated carbon. We demonstrate that nitrogen functionalities not only promote uniform dispersion of Cu<sub>2</sub>O but also suppress agglomeration and excessive reduction to metallic Cu, resulting in enhanced activity and long-term durability. The optimized catalyst achieves FE approaching 90% for CO and formate at −0.6 V vs. RHE and maintains over 60% selectivity after 24 h of continuous operation. These findings highlight the advantages of targeting CO and formate as practical C<sub>1</sub> products and provide mechanistic insights into how support chemistry governs Cu speciation and overall CO<sub>2</sub>RR performance.

## 2. Experimental

### 2.1 Synthesis of N-doped carbon support

N-Doped carbon derived from tea leaves was synthesized following a previously reported procedure.<sup>15</sup> Briefly, the precursor was prepared by carbonizing and activating tea leaves pretreated with potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) at a weight ratio of 1:1.5. Activation was conducted in a horizontal tubular furnace at 900 °C with a heating rate of 5 °C min<sup>−1</sup> and held for 1 hour under a continuous N<sub>2</sub> flow of 200 cm<sup>3</sup> min<sup>−1</sup>. The resulting material was thoroughly washed with RO water and dried at 105 °C overnight. The sample was denoted as TL9, where “9” refers to the activation temperature of 900 °C.

### 2.2 Preparation of copper/carbon composites

Solution A was prepared by dissolving 1.11 g of copper(II) acetate monohydrate (Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O) in 25 mL of distilled water and stirring at 70 °C for 10 min. Subsequently, 0.6 g of TL9 was introduced into the solution and sonicated for 10 min to ensure homogeneous dispersion. In parallel, solution B was prepared by dissolving 0.95 g of NaOH and 0.83 g of ascorbic acid in

20 mL of distilled water. Solution B was then added dropwise to solution A under continuous stirring, and the reaction was maintained for 30 min. The resulting product was collected by filtration, thoroughly washed with distilled water, and dried to obtain the TL9/Cu-*x*% composite, where *x* denotes the Cu<sub>2</sub>O content in wt%. For comparison, YEC/Cu-40% was synthesized by replacing TL9 with commercial activated carbon (YEC-8A) under otherwise identical conditions.

### 2.3 Material characterizations

X-ray diffraction (XRD) patterns were obtained using a PANalytical Empyrean diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) over a  $2\theta$  range of 10°–80° at a step size of 0.02°. The morphology and elemental composition were analyzed by scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM-EDS, HITACHI SU8020). Transmission electron microscopy (TEM, HITACHI HT7700) was employed to examine the particle size and lattice fringes of Cu<sub>2</sub>O nanoparticles. N<sub>2</sub> adsorption-desorption isotherms were recorded at −196 °C using a MicrotracBEL BELSORP mini-X analyzer to evaluate the textural properties. All samples were degassed under vacuum (10<sup>−3</sup> kPa) at 150 °C for 6 hours prior to measurement. The specific surface area ( $S_{\text{BET}}$ ) was calculated by the Brunauer–Emmett–Teller (BET) method. The total pore volume ( $V_{\text{total}}$ ) was estimated from adsorption data at  $P/P_0 = 0.99$ , while the micropore volume ( $V_{\text{micro}}$ ) was obtained using the Dubinin–Radushkevich (DR) equation. The mesopore volume ( $V_{\text{meso}}$ ) was determined by subtracting  $V_{\text{micro}}$  from  $V_{\text{total}}$ .

X-ray photoelectron spectroscopy (XPS) was performed on a JEOL JPS-9010 MC with a Mg K $\alpha$  source (12 kV, 25 mA) under a base pressure of 10<sup>−7</sup> Pa. Thermogravimetric analysis (TGA, Mettler Toledo TGA/DSC 1) was used to quantify the Cu<sub>2</sub>O loading in the composites. H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR, BELCAT-B, BEL Japan Inc.) was conducted to evaluate the reducibility and dispersion of Cu<sub>2</sub>O nanoparticles.<sup>16</sup> Approximately 20 mg of sample was reduced *in situ* under a flow of 5% H<sub>2</sub>/Ar from room temperature to 800 °C at a heating rate of 5 °C min<sup>−1</sup>. Raman spectra were acquired using a Horiba LabRAM HR Evolution spectrometer with a 532 nm excitation laser to assess graphitization and defect density. The ratio of disordered (D) to graphitic (G) band intensities ( $I_{\text{D}}/I_{\text{G}}$ ) was determined from deconvoluted peak intensities.

### 2.4 Electrochemical measurements

Electrochemical measurements were performed in a two-compartment, gas-tight glass H-cell separated by an anion exchange membrane (AMVN). A Pt plate (1.0 × 1.0 cm<sup>2</sup>) and a Hg/HgOH electrode in 1 M NaOH served as the counter and reference electrodes, respectively. The working electrode consisted of the catalyst coated onto carbon paper (Toray, TGP-H-120, 1.0 × 1.0 cm<sup>2</sup>).

The catalyst ink was prepared by mixing the catalyst, carbon black, and polyvinylidene fluoride (PVDF) in a weight ratio of 8 : 1 : 1 in *N*-methyl-2-pyrrolidone (NMP) to form a homogeneous slurry. Carbon black was added to enhance electrical



conductivity and facilitate electron transport across the electrode.<sup>17</sup> The ink was applied to the carbon paper using a doctor blade (250  $\mu\text{m}$  thickness) and dried under vacuum at 80  $^{\circ}\text{C}$  overnight. The electrolyte (0.5 M  $\text{KHCO}_3$ ) was continuously saturated with  $\text{CO}_2$  at a flow rate of 20 sccm, and all experiments were conducted at room temperature.

Electrochemical impedance spectroscopy (EIS) was performed prior to  $\text{CO}_2\text{RR}$  testing to determine the solution resistance ( $R_s$ ) and charge-transfer resistance ( $R_{ct}$ ) from Nyquist plots.  $R_s$  was used to correct the  $iR$  drop, and all potentials were converted from the Hg/HgOH reference to the reversible hydrogen electrode (RHE) scale for accurate comparison of catalytic activity.

Gaseous products ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ ) were quantified using gas chromatography with a flame-ionization detector (GC-FID) equipped with a Porapak Q (60/80) column and He as the carrier gas.  $\text{H}_2$  and  $\text{CO}$  were analyzed using GC with a thermal-conductivity detector (GC-TCD) equipped with a molecular sieve 5A column and He as the carrier gas. Liquid products were analyzed by high-performance liquid chromatography (HPLC) equipped with a refractive-index detector (RID) using 5 mM  $\text{H}_2\text{SO}_4$  as the mobile phase and a Shodex SH1011 Sugar column

as the stationary phase. Moreover, the formation of formate was verified by  $^1\text{H}$  NMR spectroscopy of the post-reaction electrolyte using Bruker Avance III<sup>TM</sup> HD 600 MHz, and  $\text{D}_2\text{O}$  as the solvent. All electrochemical measurements and products quantifications were performed at least three times. The reported FE represent the average values, and the error bars correspond to the standard deviation.

### 3. Results and discussion

#### 3.1 Structural characteristics of the carbon samples and composites

The porous characteristics of all samples are summarized in Table S1. Both TL9 and YEC exhibit comparable BET surface areas ( $S_{\text{BET}}$ ) and total pore volumes. Their  $\text{N}_2$  adsorption-desorption isotherms (Fig. 1a) display combined type I and type IV profiles with H4-type hysteresis loops, indicative of predominantly microporous structures containing a small fraction of slit-like mesopores. The slightly more pronounced hysteresis in TL9 suggests a marginally higher mesopore content than in YEC, consistent with the  $V_{\text{meso}}$  values in Table S1. However, this difference is relatively minor and unlikely to

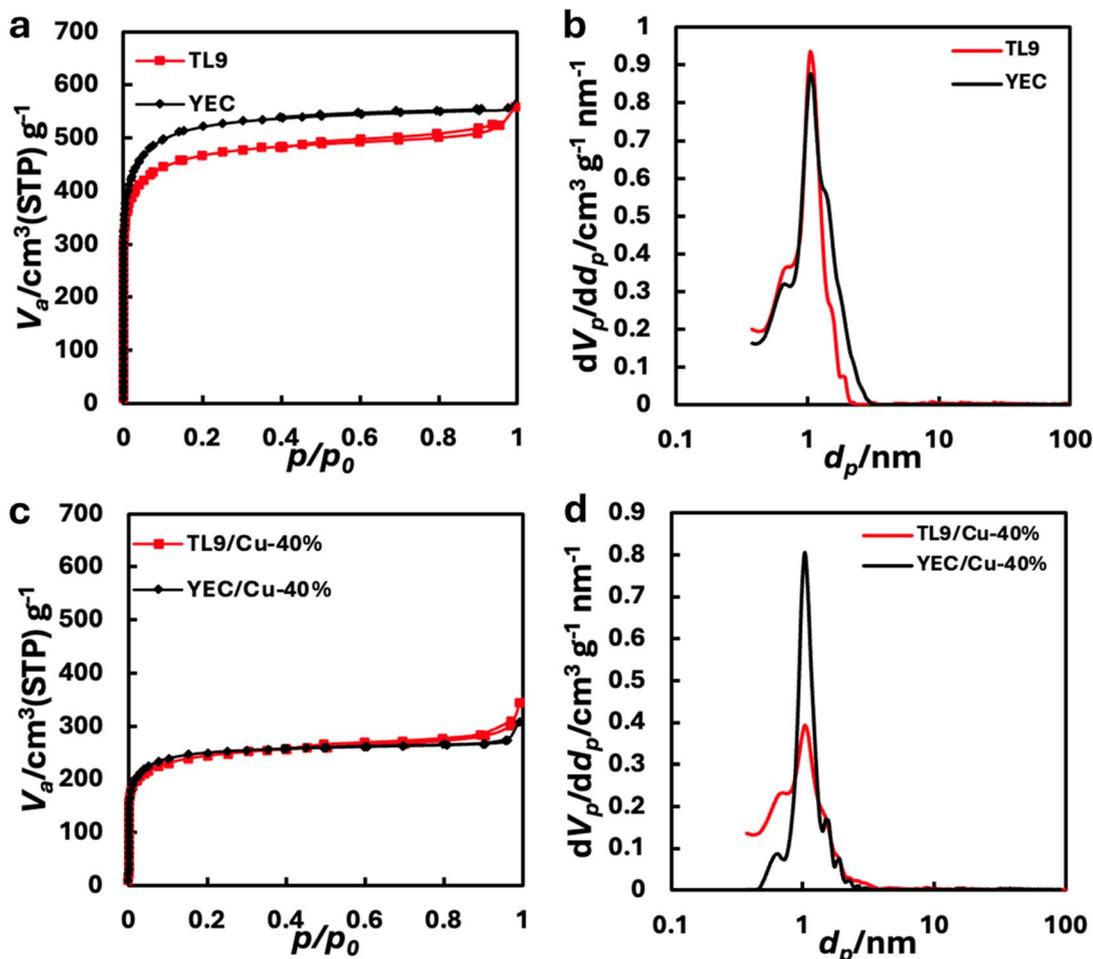


Fig. 1 (a)  $\text{N}_2$  adsorption-desorption isotherms and (b) NLDFT pore size distribution of TL9 and YEC samples. (c)  $\text{N}_2$  adsorption-desorption isotherms and (d) NLDFT pore size distribution of TL9/Cu-40% and YEC/Cu-40% composites.



significantly affect their comparative electrocatalytic performance. As shown in Fig. 1b, both samples possess similar pore size distributions dominated by micropores ( $\sim 1$  nm).

Upon  $\text{Cu}_2\text{O}$  incorporation, the adsorbed volume and corresponding surface area and pore volume decreased progressively with increasing  $\text{Cu}_2\text{O}$  loading (Fig. S1a). Notably, TL9/Cu-50% exhibits a type II isotherm (Fig. S1b), characteristic of macroporous adsorbents with strong adsorbate-adsorbent interactions,<sup>18</sup> accompanied by a substantial loss of  $S_{\text{BET}}$  and  $V_{\text{micro}}$ . This behavior indicates that excessive  $\text{Cu}_2\text{O}$  loading likely blocks or fills the available pores of the carbon support. Fig. 1c compares the isotherms of TL9/Cu-40% and YEC/Cu-40%, both showing combined type I/IV features with H4-type hysteresis loops. The depletion of micropores ( $\sim 1$  nm) observed for TL9/Cu-40% (Fig. 1d) suggests partial blockage of micropores during  $\text{Cu}_2\text{O}$  deposition, whereas the reduction in pore volume of YEC around 1.5 nm implies  $\text{Cu}_2\text{O}$  deposition within larger mesopores or interparticle voids.

Raman spectra of TL9, YEC, TL9/Cu-40%, and YEC/Cu-40% (Fig. 2) exhibit two prominent peaks at  $\sim 1340$   $\text{cm}^{-1}$  (D band) and  $\sim 1580$   $\text{cm}^{-1}$  (G band), corresponding to disordered and graphitic carbon structures, respectively.<sup>19</sup> Deconvolution of the spectra reveals four components:  $\text{D}^*$  ( $\sim 1200$   $\text{cm}^{-1}$ ), D ( $\sim 1340$   $\text{cm}^{-1}$ ),  $\text{D}^{**}$  ( $\sim 1530$   $\text{cm}^{-1}$ ), and G ( $\sim 1590$   $\text{cm}^{-1}$ ),

representing various C=C stretching and C-H wagging modes associated with structural disorder.<sup>20</sup> The degree of disorder, evaluated from the  $I_{\text{D}}/I_{\text{G}}$  ratio using the four-peak model,<sup>21</sup> follows the order TL9 > YEC > TL9/Cu-40% > YEC/Cu-40% (Table S2). Specifically, TL9 (3.42) exhibits higher disorder and edge-plane exposure than YEC (2.94). After  $\text{Cu}_2\text{O}$  incorporation,  $I_{\text{D}}/I_{\text{G}}$  increases to 3.83 and 3.06 for TL9/Cu-40% and YEC/Cu-40%, respectively, indicating that  $\text{Cu}_2\text{O}$  disrupts the  $\text{sp}^2$  network and introduces additional defects.<sup>22</sup> On the other hand, N-doped defect sites—particularly pyridinic and pyrrolic N—are known to act as preferential anchoring centers for Cu-based species. During  $\text{Cu}_2\text{O}$  deposition, these pre-existing defects may be selectively occupied rather than newly generated. Hence the attachment of  $\text{Cu}_2\text{O}$  nanoparticles at these defect-rich regions perturbs the local  $\pi$ -conjugation and modifies the Raman scattering cross-section of neighboring bonds.<sup>23</sup> Because Raman spectroscopy provides a spatially averaged measure of disorder, the preferential consumption and electronic modification of defect sites can manifest as a higher apparent  $I_{\text{D}}/I_{\text{G}}$  ratio. Therefore, the observed increase likely reflects a combination of (i) perturbation of the  $\text{sp}^2$  lattice at metal-support interfaces and (ii) selective deposition of  $\text{Cu}_2\text{O}$  onto intrinsic defect sites. The smaller increase of  $I_{\text{D}}/I_{\text{G}}$  ratio in YEC/Cu-40% suggests weaker  $\text{Cu}_2\text{O}$  anchoring on YEC compared to TL9.

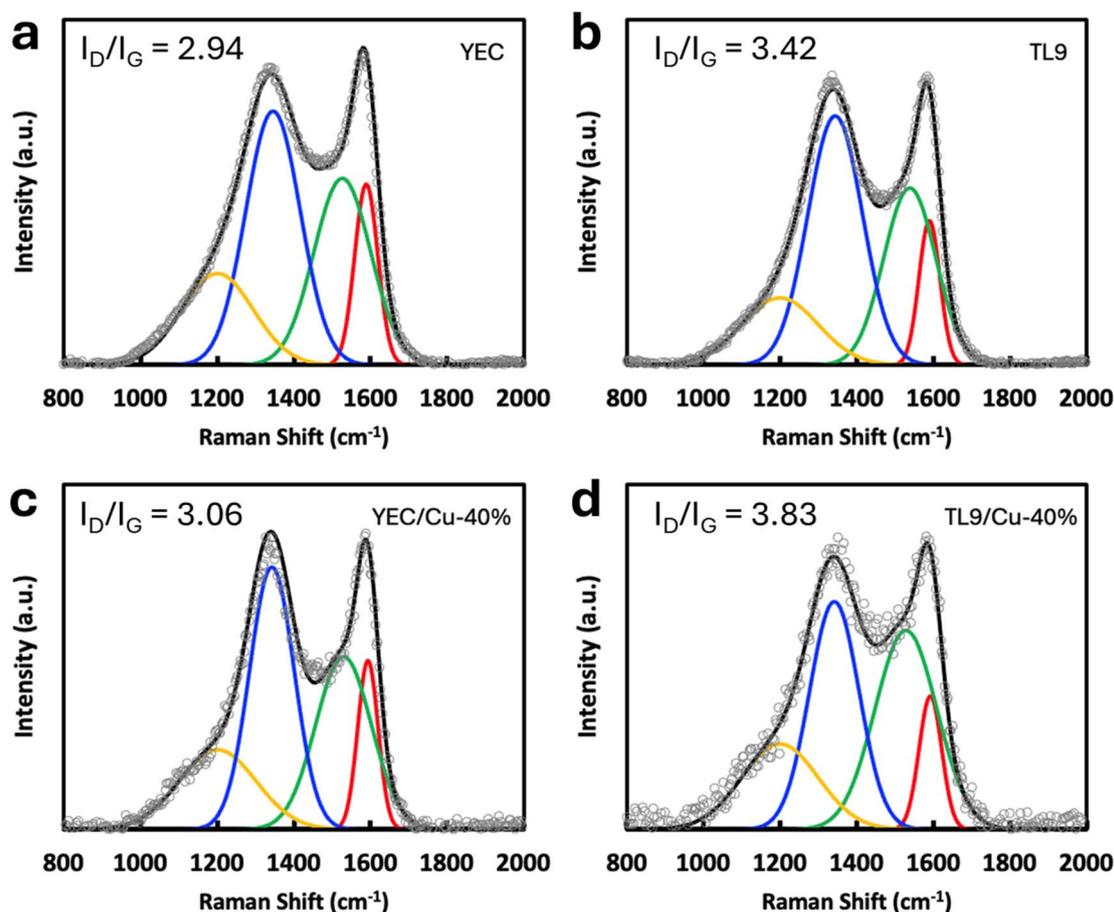


Fig. 2 Raman spectra of (a) YEC, (b) TL9 (c) YEC/Cu-40%, and (d) TL9/Cu-40%. Note that the circle and solid lines represent the raw data and curve fitting after peak deconvolution, respectively. The peak intensity ratio,  $I_{\text{D}}/I_{\text{G}}$ , is also shown in each figure.



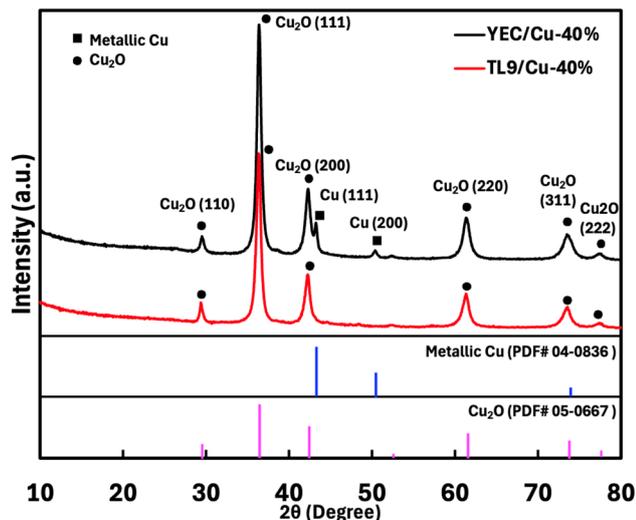


Fig. 3 XRD patterns corresponded to YEC/Cu-40% and TL9/Cu-40% together with the references, metallic Cu and  $\text{Cu}_2\text{O}$ .

Thermogravimetric analysis (TGA, Fig. S2) supports the Raman findings. TL9 exhibits an earlier onset of decomposition—approximately 50 °C lower than YEC—reflecting its more defect-rich and less thermally stable framework.<sup>24</sup> Although such defects decrease structural stability, they are often catalytically beneficial.<sup>25</sup> The residual weight ( $\sim 20\%$ ) of TL9 likely arises from inherent mineral components (K, Si, Ca, Mg, P, Na) in tea-leaf-derived carbon.<sup>26,27</sup> These residues are not catalytically active for  $\text{CO}_2$  reduction but can marginally lower the electrical conductivity of the carbon matrix.<sup>28</sup>

X-ray diffraction (XRD) analysis was conducted to determine the crystalline phases of copper species in the composites (Fig. 3). The diffraction peaks of YEC/Cu-40% at 36.4°, 42.3°, and 61.4° correspond to the (111), (200), and (220) planes of cubic  $\text{Cu}_2\text{O}$  (PDF# 05-0667). Additional peaks at 43.3° and 50.4° correspond to metallic Cu (PDF# 04-0836), indicating partial reduction of  $\text{Cu}^+$  to  $\text{Cu}^0$  during synthesis. Such reduction is typically observed when the Cu precursor lacks sufficient anchoring functionalities.<sup>29</sup> In contrast, TL9/Cu-40% displays

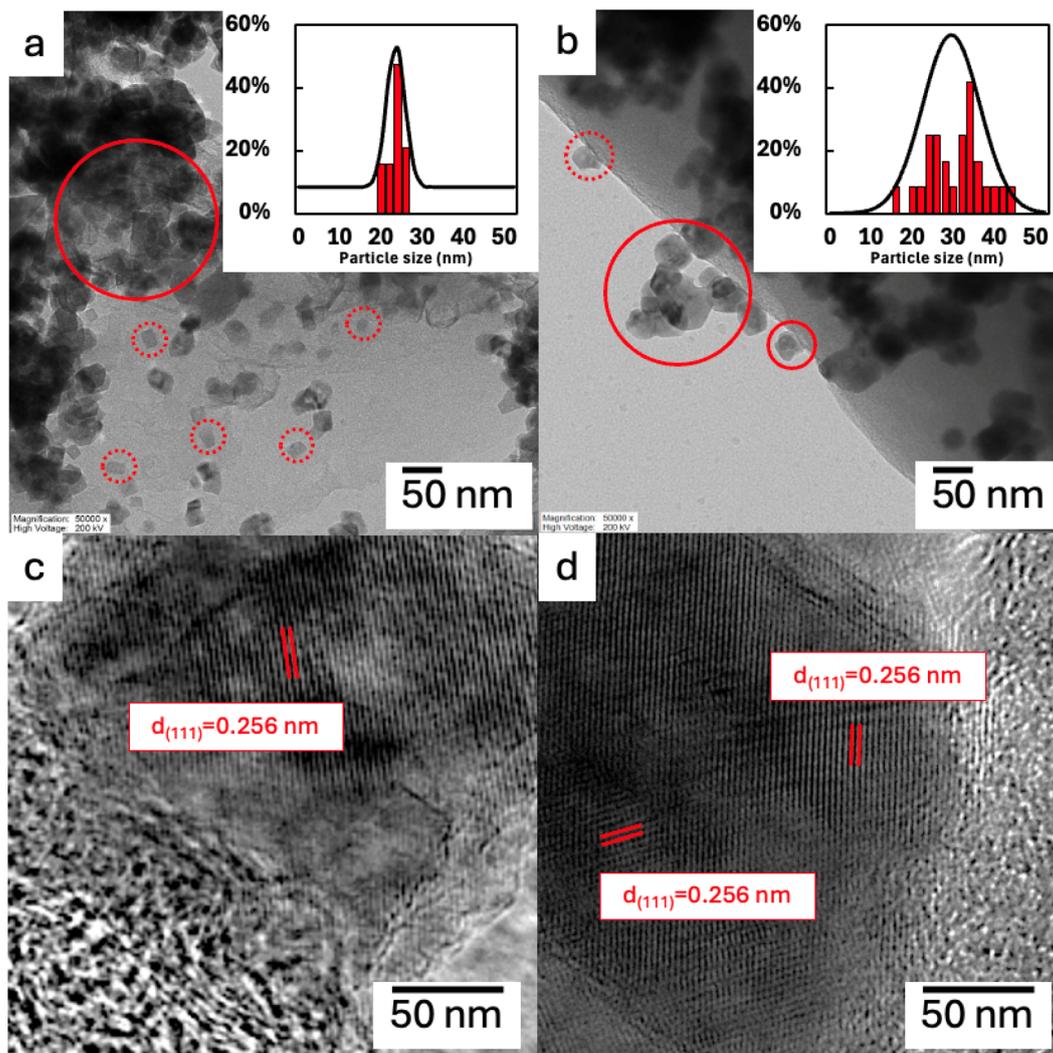


Fig. 4 TEM images of (a) TL9/Cu-40% and (b) YEC/Cu-40% composites. The inset shows particle size distribution of each sample. High-resolution TEM images (c) and (d) highlight lattice fringes corresponding to the (111) plane of  $\text{Cu}_2\text{O}$  ( $d = 0.256 \text{ nm}$ ) in both samples.



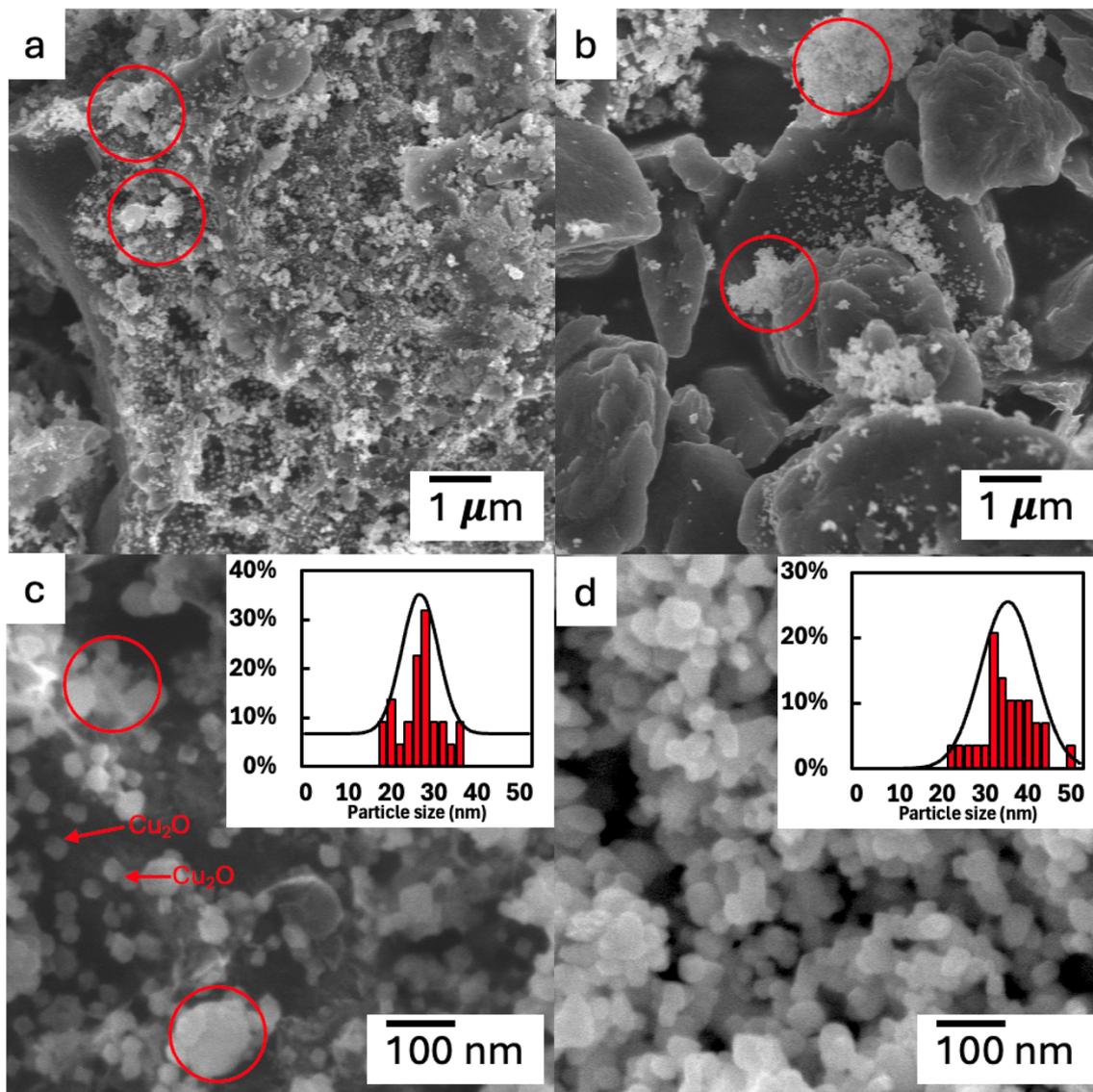


Fig. 5 SEM images of (a) TL9/Cu-40% and (b) YEC/Cu-40% composites along with their high-resolution images (c) and (d). The inset shows particle size distribution of each sample.

only Cu<sub>2</sub>O reflections, with no detectable Cu<sup>0</sup> peaks, suggesting that nitrogen functionalities in TL9 stabilize Cu<sup>+</sup> species.<sup>30</sup> The stabilization effect persists across all Cu<sub>2</sub>O loadings (10–50%), as confirmed by XRD (Fig. S3).

Based on the Scherrer equation, the average Cu<sub>2</sub>O crystallite size was ~16 nm for both TL9/Cu-40% and YEC/Cu-40%. However, transmission electron microscopy (TEM) reveals distinct nanoparticle morphologies (Fig. 4). In YEC/Cu-40%, Cu<sub>2</sub>O nanoparticles are agglomerated into polycrystalline structures (~30 nm; Fig. 4b). Conversely, TL9/Cu-40% shows uniformly dispersed Cu<sub>2</sub>O nanoparticles with an average diameter of ~20 nm (Fig. 4a). The evolution of Cu<sub>2</sub>O dispersion with increasing loading is shown in Fig. S4: at low loadings (10–20%), partial coalescence is observed; at 30%, secondary nucleation leads to uniform nanoparticle formation; and above 40%, agglomeration again dominates.<sup>31,32</sup> High-resolution TEM

(Fig. 4c and d) confirms lattice fringes with *d*-spacing of 0.256 nm, consistent with the (111) plane of Cu<sub>2</sub>O, with TL9/Cu-40% displaying single-crystal domains while YEC/Cu-40% forms multi-grained polycrystals.

Scanning electron microscopy (SEM, Fig. 5) further supports the TEM results. TL9/Cu-40% exhibits homogeneously distributed Cu<sub>2</sub>O nanoparticles across the carbon surface, with few large aggregates (Fig. 5a), whereas YEC/Cu-40% displays large Cu<sub>2</sub>O clusters localized in interparticle voids (Fig. 5b). Higher-magnification images reveal average particle sizes of ~27 nm for TL9/Cu-40% and ~35 nm for YEC/Cu-40% (Fig. 5c and d). Although SEM values are slightly larger due to imaging conditions, both analyses confirm superior dispersion and smaller particle size on TL9. The defect-rich surface of TL9 provides abundant anchoring sites, facilitating uniform nucleation and suppressing Cu<sub>2</sub>O agglomeration.



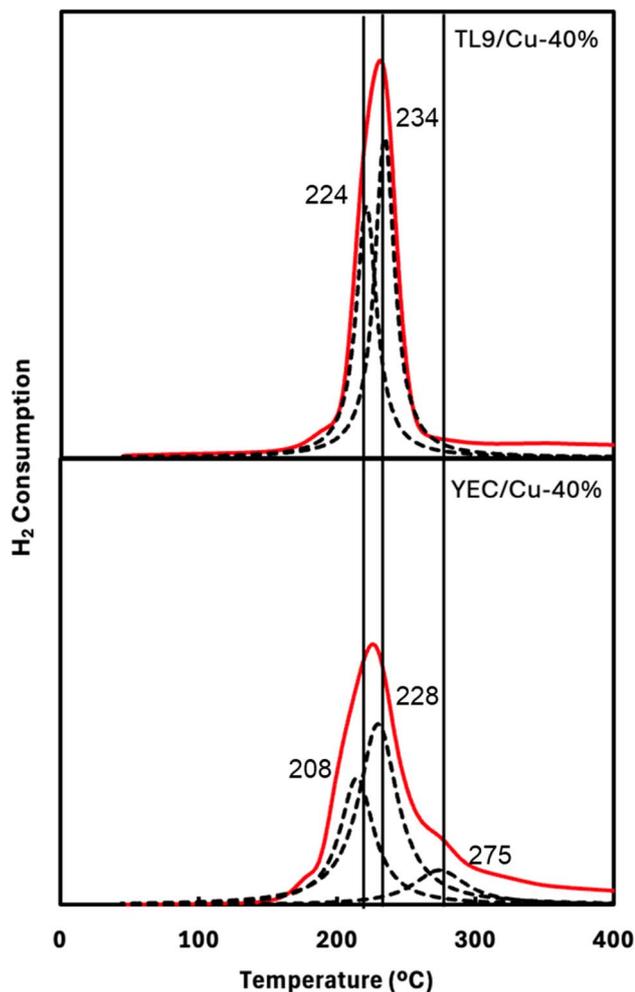


Fig. 6 H<sub>2</sub>-TPR profiles corresponded to TL9/Cu-40% and YEC/Cu-40%.

The evolution of Cu<sub>2</sub>O morphology with increasing loading on TL9 is illustrated in Fig. S5. At 10%, Cu<sub>2</sub>O nanoparticles are well dispersed, nucleating preferentially at defect sites (Fig. S5a). As the loading increases to 20%, these sites become saturated, leading to partial coalescence (Fig. S5b). At 30%, a bimodal microstructure appears, combining agglomerated and newly nucleated nanoparticles (Fig. S5c). At 40%, both coarsened clusters and secondary dispersion coexist (Fig. S5d), whereas at 50% loading, agglomeration becomes dominant (Fig. S5e). This loading-dependent morphological evolution is consistent with nucleation-coalescence dynamics commonly observed in heterogeneous catalytic systems.<sup>31,32</sup>

### 3.2 Reducibility and surface functionality

The H<sub>2</sub>-TPR profiles of the composites exhibit three main peaks at low, moderate, and high temperatures (Fig. 6), corresponding to the stepwise reduction of Cu<sub>2</sub>O to metallic Cu. These peaks are associated with the reduction of highly dispersed nanoparticles, loosely bound nanoparticles, and agglomerated Cu<sub>2</sub>O particles, respectively.<sup>16,33</sup> For YEC/Cu-40%, the first reduction

peak appears at 208 °C. In contrast, TL9/Cu-40% displays two sharp reduction peaks at 221 °C and 234 °C, which can be ascribed to uniformly distributed reducible Cu species of various particle sizes, consistent with the SEM and TEM observations. The upward shift of the first peak for TL9/Cu-40% signifies stronger metal-support interactions.<sup>34</sup> Moreover, YEC/Cu-40% exhibits an additional high-temperature peak at 275 °C, arising from the reduction of highly agglomerated Cu<sub>2</sub>O nanoparticles, as evident in the SEM images. The broader and lower-temperature second peak at 228 °C for YEC/Cu-40% further suggests weaker Cu<sub>2</sub>O-support interactions compared with TL9/Cu-40%. Together, the H<sub>2</sub>-TPR profiles corroborate the microscopic evidence that TL9 effectively promotes uniform Cu<sub>2</sub>O dispersion with stronger interfacial bonding.

The reduction behavior of the TL9/Cu series (10–50%) shows a clear loading-dependent trend (Fig. S6). At 10% loading (Fig. S6a), two reduction peaks are observed at 231 °C and 280 °C. The lower-temperature peak reflects strong interactions between Cu<sub>2</sub>O and defect sites on TL9,<sup>34</sup> while the higher-temperature peak likely arises from a small fraction of larger nanoparticles.<sup>35,36</sup> As the loading increases to 20% (Fig. S6b), both peaks intensify, indicating a greater number of reducible species. The reduction at 240 °C corresponds to loosely bound Cu<sub>2</sub>O clusters, in agreement with TEM (Fig. S4b) and SEM (Fig. S5b) results showing partial coalescence.<sup>32</sup> At 30–40% loadings (Fig. S6c and d), sharper and more intense reduction peaks appear, reflecting the secondary nucleation of Cu<sub>2</sub>O nanoparticles and the predominance of uniformly dispersed species. The strong reduction signal at 224 °C for TL9/Cu-40% indicates a higher fraction of these well-dispersed particles relative to TL9/Cu-30%. Partial coalescence remains evident, as seen from the secondary peaks at 237 °C (TL9/Cu-30%) and 234 °C (TL9/Cu-40%). This behavior is consistent with previous reports for supported copper catalysts, where intermediate metal loadings favor homogeneous dispersion and narrow distributions of reducible sites.<sup>16</sup> At 50% loading (Fig. S6e), a new peak emerges at 248 °C, indicating the formation of larger, weakly bound aggregates similar to those in YEC/Cu-40% (Fig. S6f). Overall, the 30–40% loading range yields the most uniform and reducible Cu species, whereas excessive loading promotes heterogeneity and particle agglomeration.

The XPS survey spectrum of TL9 (Fig. S7a) confirms the presence of C, N, and O as the main surface elements, with nitrogen comprising 0.43 at%. Upon Cu<sub>2</sub>O deposition, distinct Cu 2p signals appear in TL9/Cu-40% (Fig. S7b), confirming successful Cu incorporation. The N 1s spectrum of TL9 (Fig. 7a) exhibits three main peaks at 398.0, 400.0, and 401.0 eV, attributed to pyridinic-, pyrrolic-, and graphitic-N, respectively.<sup>37–40</sup> After Cu<sub>2</sub>O loading, a new peak emerges at 396.0 eV, concurrent with a marked decrease in pyrrolic-N intensity (Fig. 7b). The new feature is assigned to nitridic-like Cu–N<sub>x</sub> species,<sup>41–44</sup> formed *via* coordination of Cu with deprotonated pyrrolic-N.<sup>45</sup> This coordination facilitates electron donation from N to Cu, stabilizing Cu<sup>+</sup> sites and preventing over-reduction to Cu<sup>0</sup>. The resulting Cu–N<sub>x</sub> bonding rationalizes the preservation of catalytically active Cu<sup>+</sup>/Cu<sup>0</sup> species during CO<sub>2</sub>RR.<sup>45,46</sup>

The C 1s spectra (Fig. S8) display typical peaks corresponding to C–C (284.8 eV), C–O (286.0 eV), C=O (288.0 eV), and



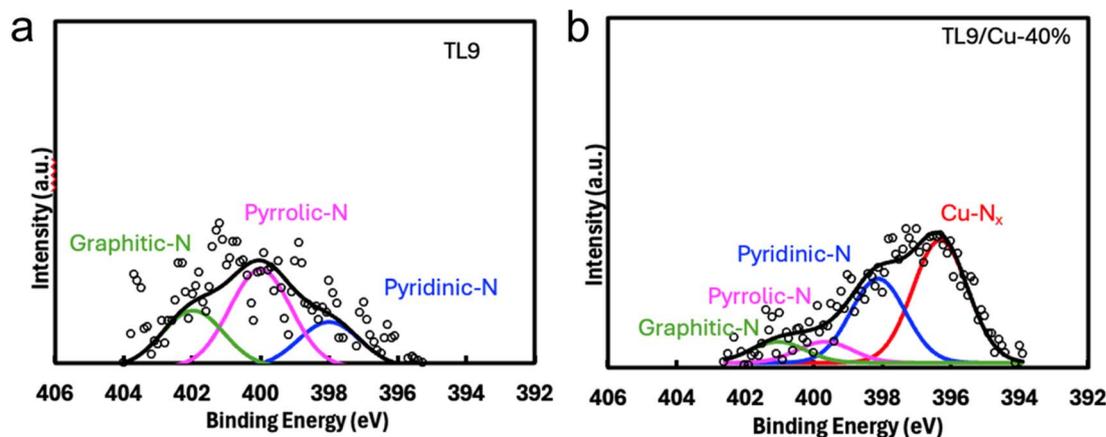


Fig. 7 N 1s spectrum of (a) TL9 and (b) TL9/Cu-40%.

O–C=O (289.6 eV). The O 1s spectra (Fig. S9) reveal components at 531.0 eV (O–C=O), 532.0 eV (C=O), 533.4 eV (C–O), and 535.0 eV (–OH).<sup>47–49</sup> A new feature at 530.5 eV appears in the composites, corresponding to Cu–O bonds in Cu<sub>2</sub>O/CuO species, further confirming the presence of Cu<sub>2</sub>O.

High-resolution Cu 2p spectra (Fig. 8a) show signals at ~932–933 eV (Cu<sup>+</sup>/Cu<sup>0</sup>) and ~934–935 eV (Cu<sup>2+</sup>), with shake-up satellites at 940–945 eV. Because Cu 2p cannot unambiguously distinguish Cu<sup>0</sup> from Cu<sup>+</sup>,<sup>13</sup> Cu LMM Auger analysis was performed (Fig. 8b).<sup>50</sup> The Auger spectra reveal that TL9/Cu-40%

consists mainly of Cu<sup>+</sup> (~70%), with minor fractions of Cu<sup>0</sup> (~14%) and Cu<sup>2+</sup> (~16%). By contrast, YEC/Cu-40% contains a larger proportion of Cu<sup>0</sup> (~34%) alongside Cu<sup>+</sup> (~52%) and Cu<sup>2+</sup> (~14%), as summarized in Table S3. These findings agree well with the XRD results, where metallic Cu reflections appear only in the YEC/Cu composite. Overall, the XPS and TPR analyses confirm that the nitrogen functionalities in TL9 effectively stabilize Cu<sup>+</sup> species, suppressing their reduction to Cu<sup>0</sup> during synthesis.<sup>29</sup> To clarify the origin of Cu–N<sub>x</sub> coordination despite the low overall nitrogen content, the evolution of Cu–N<sub>x</sub> species

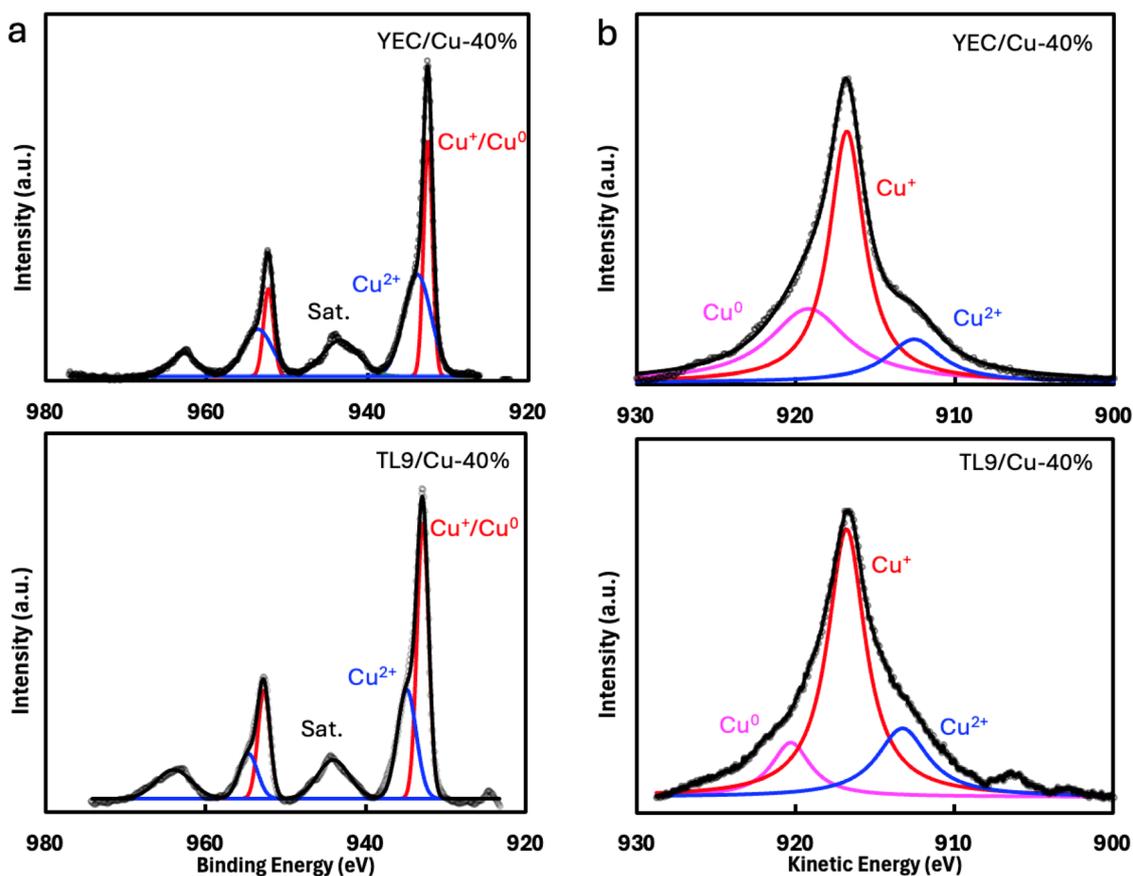


Fig. 8 Cu 2p (left) and Cu LMM (right) spectra of (a) YEC/Cu-40% and (b) TL9/Cu-40%.



with increasing Cu loading was quantified by XPS and is summarized in Fig. S10 and Table S4. Notably, the relationship between Cu at% and Cu-N<sub>x</sub> content reveals a distinct saturation trend. The Cu-N<sub>x</sub> concentration increases in proportion to Cu loading up to approximately 4.4 at% Cu (corresponding to a nominal loading of 40 wt%), beyond which it reaches a plateau despite further increases in total Cu content. This behavior indicates that nitrogen defect sites offer a finite yet sufficient number of strong anchoring sites that become fully occupied at intermediate Cu loadings. Additional Cu introduced beyond this threshold is therefore deposited predominantly as non-coordinated Cu<sub>2</sub>O. These results highlight that effective stabilization of Cu does not require a stoichiometric N-Cu ratio; rather, a small fraction of strategically located nitrogen defects can anchor a large Cu population through localized Cu-N<sub>x</sub> coordination.

In summary, the structural, reducibility, and surface analyses collectively demonstrate that TL9 supports the uniform dispersion of Cu<sub>2</sub>O nanoparticles strongly anchored at nitrogen defect sites, whereas YEC promotes larger aggregates with weaker metal-support interactions. The stabilization of Cu<sup>+</sup> species in TL9—corroborated by XPS, Cu LMM, and H<sub>2</sub>-TPR results—underscores the critical role of nitrogen functionalities in maintaining active Cu<sup>+</sup>/Cu<sup>0</sup> interfaces essential for efficient CO<sub>2</sub> reduction catalysis.

### 3.3 Evaluation of the CO<sub>2</sub>RR performances

Electrochemical impedance spectroscopy (EIS) was conducted to elucidate the interfacial kinetics and transport characteristics of the Cu-loaded carbon catalysts. Fig. 9 shows the Nyquist plots and equivalent-circuit fitting for TL9/Cu-40% and YEC/Cu-40%. Both samples exhibit a small semicircle in the high-frequency region, followed by a depressed mid-frequency response and a low-frequency Warburg tail.

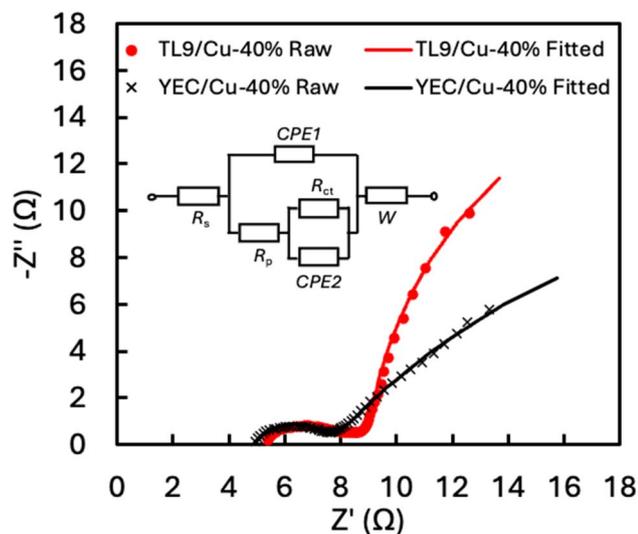


Fig. 9 Nyquist plots for the EIS analysis on the TL9/Cu-40% and the YEC/Cu-40% in 0.5 M KHCO<sub>3</sub> solutions after purged with CO<sub>2</sub> for 20 min at open circuit potential (inset: equivalent circuit).

The first high-frequency semicircle is assigned to ion transport within the porous carbon matrix. This interpretation follows the previous reports,<sup>51,52</sup> who demonstrated that porous electrodes inherently display a high-frequency arc originating from pore-channel ion transport. In our system, the high-frequency response is described by a CPE1 with  $n \sim 0.55$  for TL9/Cu-40%, which indicates strongly non-ideal capacitive behavior. Such CPE behavior arises when the electrode surface is heterogeneous—typically due to features such as pore networks, surface roughness, and defects—which create a distribution of local double-layer capacitances instead of a single uniform capacitor.<sup>53</sup> Therefore, the CPE in this region reflects the defect-rich and highly porous structure of the TL9 carbon support. The corresponding resistance shown in Table S5 ( $R_p = 3.43 \Omega$  for TL9/Cu-40% and  $2.80 \Omega$  for YEC/Cu-40%), hence reflects pore/film resistance.

The mid-frequency region represents the actual faradaic charge-transfer resistance ( $R_{ct}$ ) associated with the Cu active sites. Although the semicircle is depressed due to constant-phase behavior and partial overlap with diffusion, equivalent-circuit fitting allows reliable extraction of  $R_{ct}$ . TL9/Cu-40% shows a significantly lower charge-transfer resistance ( $R_{ct} = 26 \Omega$ ) compared to YEC/Cu-40% ( $R_{ct} = 40 \Omega$ ), indicating more favorable electron-transfer kinetics. The CPE2 exponent for this branch differs markedly between the two catalysts: TL9/Cu-40% exhibits almost ideal capacitive behavior ( $n \sim 1.05$ ), while YEC/Cu-40% shows strong interfacial heterogeneity ( $n \sim 0.60$ ). These features suggest that the Cu-electrolyte interface in TL9 is more uniform, likely due to better Cu dispersion.

At low frequencies, both catalysts display a Warburg diffusion tail, but the magnitude is substantially larger for YEC/Cu-40%, implying more severe mass-transport limitations within its carbon structure. In contrast, the lower diffusion impedance observed for TL9/Cu-40% indicates more efficient CO<sub>2</sub> and ion transport through its more open pore network.

Overall, the EIS analysis demonstrates that TL9/Cu-40% possesses (i) lower charge-transfer resistance, (ii) more ideal double-layer characteristics, and (iii) reduced diffusion impedance compared to YEC/Cu-40%. These features collectively explain the superior CO<sub>2</sub> reduction activity of the TL9-derived catalyst.

The cyclic voltammetry (CV) profiles (Fig. 10a) show that TL9/Cu-40% exhibits a slightly more negative onset potential ( $-0.8$  V vs. RHE) than YEC/Cu-40% ( $-0.6$  V vs. RHE), suggesting partial suppression of the hydrogen evolution reaction (HER). HER is primarily governed by surface electronic structure and the availability of metallic Cu<sup>0</sup> and uncoordinated sites. YEC/Cu-40%, which contains a higher fraction of metallic Cu and agglomerated nanoparticles, facilitates rapid H<sup>+</sup> adsorption and therefore exhibits higher HER currents at a given potential. In contrast, TL9/Cu-40% maintains a higher Cu<sup>+</sup>/Cu<sup>0</sup> ratio stabilized by Cu-N<sub>x</sub> coordination, which kinetically suppresses hydrogen evolution despite a slightly more negative onset potential.<sup>54,55</sup> This is further supported by electrochemical double-layer capacitance ( $C_{dl}$ ) measurements (Fig. 10b), where TL9/Cu-40% displays a higher capacitance ( $72.2 \text{ mF cm}^{-2}$ ) than YEC/Cu-40% ( $51.9 \text{ mF cm}^{-2}$ ), indicative of a larger



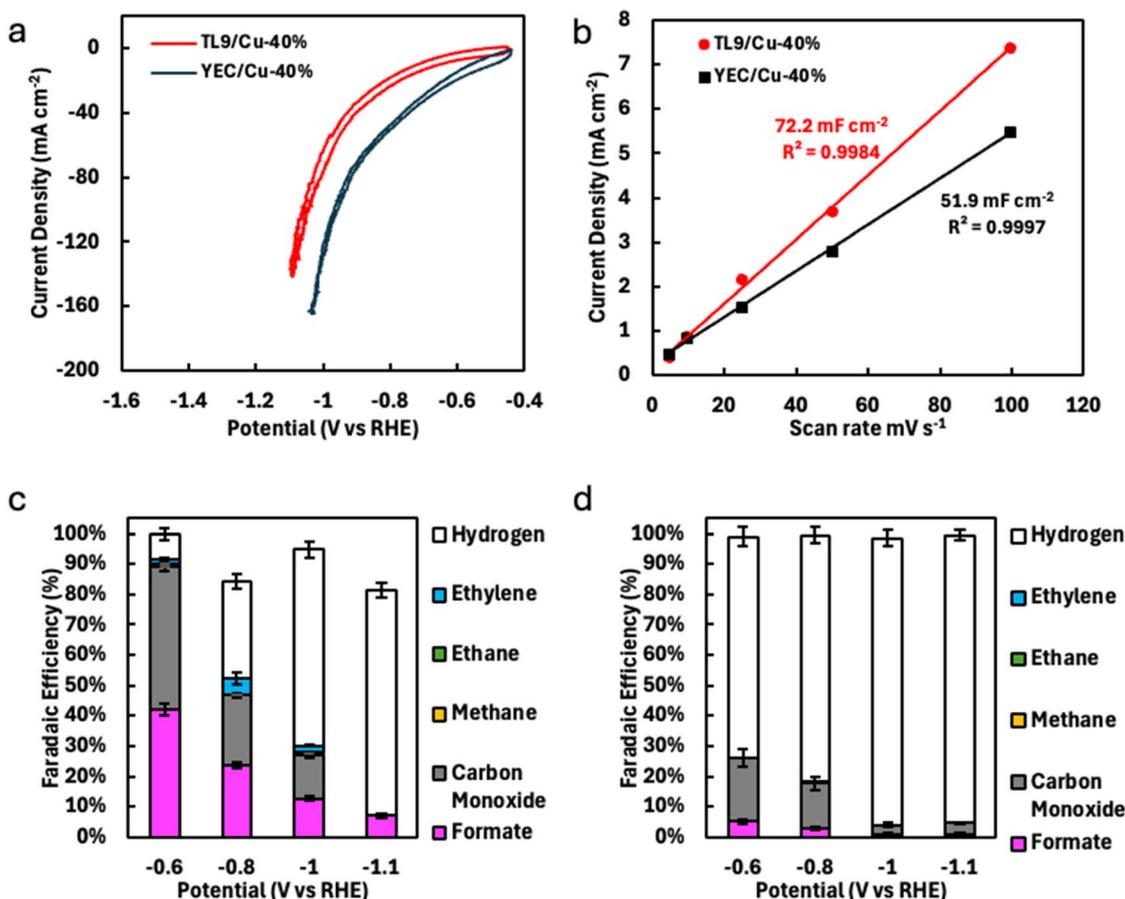


Fig. 10 (a) Cyclic voltammograms and (b) double-layer capacitance ( $C_{dl}$ ) of TL9/Cu-40% and YEC/Cu-40%. FE of (c) TL9/Cu-40% and (d) YEC/Cu-40% using H-type cell in 0.5 M KHCO<sub>3</sub> electrolyte saturated with CO<sub>2</sub> (pH = 7.4).

electrochemically active surface area (ECSA). Despite the slightly delayed onset, TL9/Cu-40% demonstrates markedly superior CO<sub>2</sub>RR activity, achieving ~90% FE toward C<sub>1</sub> products at -0.6 V vs. RHE, compared with only 28% for YEC/Cu-40% (Fig. 10c and d). Remarkably, even at -0.8 V—where HER typically dominates—the FE of TL9/Cu-40% remains above 50%, underscoring its strong CO<sub>2</sub>RR selectivity.

During CO<sub>2</sub> electroreduction, the Cu oxidation state dynamically evolves toward a mixed Cu<sup>+</sup>/Cu<sup>0</sup> interface.<sup>30,56</sup> Cu<sup>+</sup> sites stabilize key intermediates such as \*COOH (for CO) and \*OCHO (for formate), whereas neighboring Cu<sup>0</sup> domains promote electron transfer, product desorption, and C-C coupling toward C<sub>2</sub><sup>+</sup> products.<sup>13,56,57</sup> Unstabilized Cu<sup>+</sup> species tend to reduce to Cu<sup>0</sup>, forming so-called oxide-derived Cu (OD-Cu), which mainly produces CO through the \*COOH pathway.<sup>12</sup> Nitrogen species may also act as HER sites,<sup>58</sup> thus competing with CO<sub>2</sub>RR. XPS analysis confirmed that TL9/Cu-40% retains a larger Cu<sup>+</sup> fraction than YEC/Cu-40%, consistent with the stabilizing effect of N dopants that anchor Cu<sup>+</sup> and suppress its full reduction to metallic Cu. This stabilization preserves a favorable Cu<sup>+</sup>/Cu<sup>0</sup> balance during operation, optimizing C<sub>1</sub>-product formation.<sup>1</sup> The persistence of Cu<sup>+</sup> at N-anchored sites promotes selective CO and formate generation,<sup>57</sup> whereas the dominance of metallic Cu and exposed N sites in YEC/Cu-40%

results in lower CO<sub>2</sub>RR selectivity and CO as the major product. These results confirm that the Cu<sub>2</sub>O-N-carbon interaction critically governs the reaction pathway by sustaining catalytically active Cu<sup>+</sup>/Cu<sup>0</sup> interfaces.<sup>59</sup>

The superior CO<sub>2</sub>RR activity of TL9/Cu-40% arises from the uniform dispersion and strong anchoring of Cu<sub>2</sub>O nanoparticles at nitrogen defect sites. Homogeneously distributed Cu species offer a higher density of electronically consistent active centers, reflected by the larger C<sub>dl</sub> (72.2 mF cm<sup>-2</sup> vs. 51.9 mF cm<sup>-2</sup> for YEC/Cu-40%), and thus a greater ECSA.<sup>60,61</sup> These features facilitate the stabilization of \*COOH and \*OCHO intermediates and enhance electron transfer while suppressing HER. Consequently, TL9/Cu-40% sustains >50% FE for CO<sub>2</sub>RR even at -0.8 V, a potential at which HER typically dominates. In contrast, agglomerated Cu<sub>2</sub>O in YEC/Cu-40% lowers the effective ECSA and exposes non-Cu sites that favor hydrogen evolution. These findings underscore that nanoscale dispersion and interfacial uniformity are decisive factors translating directly into CO<sub>2</sub>RR activity and selectivity.

CV curves of TL9/Cu composites with varying Cu<sub>2</sub>O loadings (10–50%) are presented in Fig. S11a. All samples show similar onset potentials near -0.8 V vs. RHE, suggesting that CO<sub>2</sub> activation thermodynamics are relatively unaffected by loading. However, the catalytic current increases markedly from 10 to



40%, reflecting enhanced ECSA (Fig. S11b). At 50%, the current slightly declines, implying that excessive  $\text{Cu}_2\text{O}$  induces nanoparticle agglomeration, which impedes charge transfer and site accessibility.<sup>62</sup> The corresponding FEs (Fig. S11c–f) reveal that at 10% (Fig. S11c),  $\text{H}_2$  is the dominant product, with limited CO and formate formation due to the low ECSA and exposure of uncoordinated N sites that favor HER.<sup>58</sup> Increasing the loading to 20% (Fig. S11d) enhances CO production, but formate selectivity remains low because  $\text{Cu}_2\text{O}$  agglomeration reduces the stabilized  $\text{Cu}^+$  fraction, favoring the  $^*\text{COOH}$  pathway. At 30% (Fig. S11e),  $\text{CO}_2\text{RR}$  activity improves significantly, producing both CO and formate, attributed to a balanced  $\text{Cu}^+/\text{Cu}^0$  ratio from more uniform  $\text{Cu}_2\text{O}$  coverage. The highest performance occurs at 40% (Fig. 10c), where optimal  $\text{Cu}^+/\text{Cu}^0$  balance yields abundant active sites and an FE of  $\sim 90\%$  toward  $\text{CO}_2\text{RR}$  products. Further increasing the loading to 50% (Fig. S11f) lowers formate selectivity and increases  $\text{H}_2$  ( $\sim 20\%$ ), consistent with agglomeration observed by SEM and  $\text{H}_2\text{-TPR}$ . This aggregation diminishes the stabilized  $\text{Cu}^+$  fraction, similar to the 20% sample, leading again to CO-dominated products.

Long-term electrolysis (Fig. 11) further demonstrates the stability advantage of TL9/Cu-40%. All long-term electrolysis performed under identical conditions at an applied potential of  $-0.6$  V vs. RHE in  $\text{CO}_2$ -saturated 0.5 M  $\text{KHCO}_3$  with a  $\text{CO}_2$  flow rate of 20 sccm. The FE for TL9/Cu-40% remains above 60% after 24 h, with current density stabilizing at  $\sim 1.5$   $\text{mA cm}^{-2}$ . This modest decline suggests partial surface restructuring yet retention of a significant fraction of active  $\text{Cu}^+/\text{Cu}^0$  sites.<sup>63</sup> By contrast, YEC/Cu-40% exhibits rapid deactivation, with FE dropping from  $\sim 25\%$  to  $<15\%$  and current density declining substantially, consistent with weaker Cu-support interactions leading to  $\text{Cu}_2\text{O}$  agglomeration and irreversible reduction to  $\text{Cu}^0$ . Overall, these observations confirm that nitrogen defect anchoring in TL9 not only enhances  $\text{CO}_2\text{RR}$  activity and selectivity but also mitigates degradation, enabling sustained catalytic performance under prolonged operation.

To further confirm the identity of the liquid-phase product, the post-electrolysis electrolyte was analyzed by  $^1\text{H}$  NMR and

HPLC. As shown in Fig. S13, a distinct resonance at  $\sim 8.4$  ppm, characteristic of formate, was observed in the  $^1\text{H}$  NMR spectrum, with no detectable signals from other liquid products. Quantitative HPLC chromatogram of the post-electrolysis electrolyte (Fig. S14), together with the corresponding calibration curve (Fig. S15), further confirms formate as the dominant liquid product.

### 3.4 Post- $\text{CO}_2\text{RR}$ surface functionalities

To directly verify the stabilizing effect of TL9 on  $\text{Cu}^+$  species, post- $\text{CO}_2\text{RR}$  Cu LMM Auger XPS analysis was performed and compared with the pristine catalysts, as shown in Fig. S12. The relative fractions of  $\text{Cu}^+$ ,  $\text{Cu}^0$ , and  $\text{Cu}^{2+}$  were quantified by peak deconvolution and are summarized in Table S6.

As shown in Fig. S12a, TL9/Cu-40% before  $\text{CO}_2\text{RR}$  consists predominantly of  $\text{Cu}^+$  species ( $\sim 64\%$ ), with only a minor contribution from  $\text{Cu}^0$  ( $\sim 14\%$ ). After 24 h of  $\text{CO}_2$  electroreduction (Fig. S12a, bottom), the Cu LMM spectrum of TL9/Cu-40% shows that a substantial fraction of  $\text{Cu}^+$  is retained ( $\sim 36\%$ ), with only a moderate increase in the  $\text{Cu}^0$  component. Importantly, the  $\text{Cu}^+$  peak position and intensity remain clearly discernible, indicating that  $\text{Cu}^+$  is not fully reduced to metallic Cu during prolonged operation.

In contrast, YEC/Cu-40% (Fig. S12b) exhibits a markedly different behavior. Even before  $\text{CO}_2\text{RR}$ , YEC/Cu-40% contains a larger fraction of  $\text{Cu}^0$  ( $\sim 34\%$ ), consistent with weaker metal-support interactions. After  $\text{CO}_2\text{RR}$ , the Cu LMM spectrum shows a dominant  $\text{Cu}^0$  signal, with  $\text{Cu}^+$  becoming a minor component, evidencing extensive reduction of  $\text{Cu}^+$  to  $\text{Cu}^0$  during electrolysis.

Beyond demonstrating  $\text{Cu}^+$  stabilization, post-electrolysis Cu LMM Auger XPS analysis provides direct insight into the degradation mechanism. The observed decline in FE over extended electrolysis can be rationalized by several concurrent degradation processes. First, weakly stabilized  $\text{Cu}^+$  sites that are not strongly coordinated to nitrogen defects are preferentially reduced or lost during prolonged operation, whereas  $\text{Cu}^+$  species anchored through robust Cu- $\text{N}_x$  interactions remain

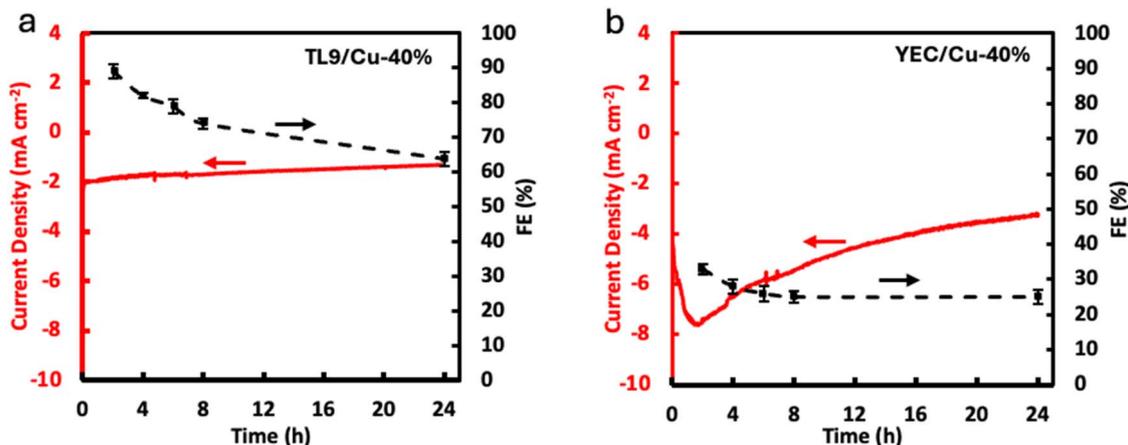


Fig. 11 Stability test of (a) TL9/Cu-40% and (b) YEC/Cu-40% at 0.6 V vs. RHE using H-type cell in 0.5 M  $\text{KHCO}_3$  electrolyte saturated with  $\text{CO}_2$  (pH = 7.4) for 24 hours.



catalytically active.<sup>10</sup> Second, sustained cathodic polarization induces electrochemical surface reconstruction, driven by local pH gradients, Cu atom migration, and dynamic restructuring of the catalyst surface.<sup>64,65</sup> Finally, these processes promote the gradual growth of metallic Cu domains, which tend to favor hydrogen evolution and CO formation over the formate pathway.<sup>66</sup> As a result, the relative contribution of C<sub>1</sub> products decreases with time, leading to the observed reduction in overall selectivity despite the persistence of strongly stabilized Cu–N<sub>x</sub> active sites.

Therefore, the performance decay reflects bias-induced Cu<sup>+</sup> evolution rather than failure of the Cu<sup>+</sup> stabilization mechanism, and the superior long-term selectivity of TL9/Cu-40% compared to YEC/Cu-40% directly supports the role of nitrogen defects in mitigating electrochemical degradation.

## 4. Conclusion

In summary, N-doped carbon derived from tea leaves provides a defect-rich scaffold that anchors Cu<sub>2</sub>O nanoparticles and stabilizes Cu<sup>+</sup> species through strong Cu–N<sub>x</sub> coordination. This interfacial stabilization enables a persistent Cu<sup>+</sup>/Cu<sup>0</sup> synergy that drives efficient CO<sub>2</sub> electroreduction to CO and formate while mitigating hydrogen evolution and catalyst deactivation. The optimized TL9/Cu-40% catalyst exhibits uniform Cu<sub>2</sub>O dispersion, high FE (~90%), and long-term operational stability exceeding 24 h. In contrast, Cu supported on commercial activated carbon suffers from particle agglomeration and loss of Cu<sup>+</sup> activity, underscoring the crucial role of metal–support interactions. By integrating surface defect engineering with sustainable biomass-derived carbons, this work redefines pathways toward scalable, selective, and stable CO<sub>2</sub> conversion. The demonstrated control over oxidation-state dynamics and dual product selectivity positions TL9/Cu as a model bifunctional system for the advanced electrocatalysts that merge material design with electrochemical functionality to unlock the next generation of CO<sub>2</sub>-to-chemicals technologies.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI): Tables S1–S6, additional N<sub>2</sub> adsorption-desorption isotherms, TGA plots, XRD patterns of the composites with various Cu<sub>2</sub>O loading on TL9, additional TEM and SEM images, H<sub>2</sub>-TPR profiles, XPS survey spectrum, C 1s spectra, and O 1s spectra, correlation between Cu atomic percentage and Cu–N□, additional catalytic performances, Cu LMM spectra before and after CO<sub>2</sub>RR electrolysis, <sup>1</sup>H NMR and HPLC data. See DOI: <https://doi.org/10.1039/d5ra08966b>.

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