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Electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>RR) to synthesize multicarbon products is a critical route for sustainable CO<sub>2</sub> utilization, yet achieving high selectivity and current density simultaneously remains challenging. While enhancing \*CO coverage on catalysts is pivotal for promoting C–C coupling, the dynamic competition between intermediate enrichment and microenvironment regulation necessitates innovative strategies. Here, we employ surface ligand engineering to construct a tunable hydrophobic microenvironment on Cu<sub>2</sub>O catalysts, using imidazolium-based ionic liquids with alkyl side chains of varying lengths. The optimized OMIIm-Cu<sub>2</sub>O catalyst achieves a C<sub>2+</sub> selectivity of 63.3% in alkaline media and 30.7% in acidic media. Mechanistic studies reveal that hydrophobic long-chain ligands elevate local \*CO concentration, facilitating efficient C–C coupling. This work highlights microenvironment modulation as a viable pathway to bridge the gap between high efficiency and industrial-current-density performance in CO<sub>2</sub>RR.

**Keywords:** Electrochemical CO<sub>2</sub> reduction; C<sub>2+</sub> product selectivity; Copper-based catalysts; \*CO concentration.

## 1. Introduction

Electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) driven by renewable electricity to synthesize C<sub>2+</sub> products represents a pivotal pathway for CO<sub>2</sub> resource utilization. C–C coupling, the rate-determining step in generating C<sub>2+</sub> products, is directly constrained by the \*CO coverage on the catalyst surface.<sup>1–3</sup> Consequently, various strategies have been employed to enhance the local \*CO concentration and promote C<sub>2+</sub> product formation, including size and morphology control,<sup>4,5</sup> surface doping,<sup>6,7</sup> and oxidation modulation.<sup>8,9</sup> Nam *et al.* reported

# Imidazolium ligand-modified Cu<sub>2</sub>O catalysts for enhancing C<sub>2+</sub> selectivity in CO<sub>2</sub> electroreduction *via* local \*CO enrichment†

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that Cu electrodes with a mesoporous structure can enrich \*CO intermediates within the mesopores, thus enhancing the selectivity toward C<sub>2+</sub> products.<sup>10</sup> Likewise, Jung *et al.* demonstrated that porous Cu/Cu<sub>2</sub>O aerogel catalysts yield a higher \*CO concentration around the catalyst surface compared to nanoparticle or planar film catalysts.<sup>11</sup> Notably, current technological systems still face challenges in simultaneously achieving high faradaic efficiency (FE >70%) and ultra-high current densities (>600 mA cm<sup>−2</sup>), primarily due to the dynamic competition between mass transport limitations and the decay of electrochemically active sites.

Surface ligand engineering offers a precise means of controlling CO<sub>2</sub>RR selectivity by modulating the catalyst's electronic structure, steric hindrance, and local microenvironment. Ligands can alter the adsorption strength of intermediates (*e.g.*, \*COOH, \*CO) *via* electronic effects, thereby directing the product pathway.<sup>12,13</sup> In addition, steric hindrance can suppress the hydrogen evolution reaction or adjust product distribution,<sup>14–17</sup> while optimization of the local microenvironment enhances target product activity by increasing reactant concentration or suppressing side reactions.<sup>14,15,18</sup> Furthermore, ligands can stabilize intermediates through chemical interactions (such as hydrogen bonding to lock \*COOH) or enable dynamic restructuring (as observed in MOF-derived catalysts) to adapt to reaction conditions, facilitating efficient C–C coupling and selective product formation.

Herein, we constructed a tunable hydrophobic microenvironment *via* surface ligand engineering to enrich \*CO intermediates locally and promote C–C coupling, thereby enhancing the selectivity toward C<sub>2+</sub> products. Using ionic liquids as precursors, we synthesized a series of copper-based catalysts modified with imidazolium ligands bearing alkyl side chains of varying lengths. Characterization by ATR-FTIR, XPS, and EDS elemental mapping confirmed the successful surface modification of Cu<sub>2</sub>O by the ligands. In both acidic and alkaline media, the CO faradaic efficiency initially increased and then decreased with longer ligand side chains, whereas the C<sub>2+</sub> product selectivity exhibited a non-

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monotonic trend, first decreasing and then increasing as the side chain lengthened. Notably, the OMIm-Cu<sub>2</sub>O catalyst demonstrated the best performance in both media, achieving a C<sub>2+</sub> selectivity of 63.3% under alkaline conditions (19% improvement) and 30.7% under acidic conditions (2.8-fold increase). Mechanistic investigations revealed that the long-chain imidazolium ligands enhance the hydrophobicity of the local microenvironment, thereby increasing the local \*CO concentration and facilitating C<sub>2</sub> product formation.

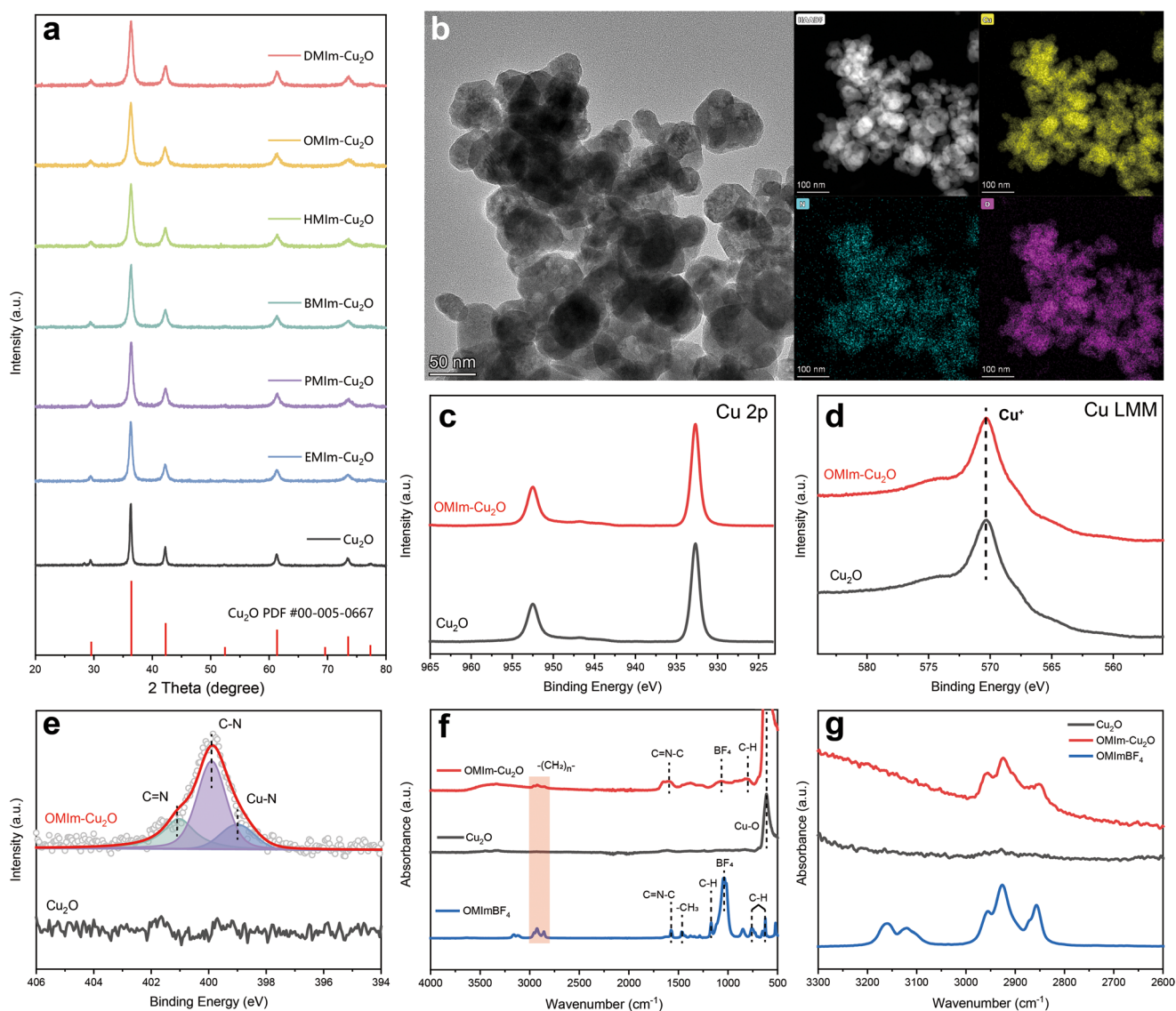
## 2. Results and discussion

### 2.1 Characterization of Cu<sub>2</sub>O@imidazole

We prepared the Cu<sub>2</sub>O@imidazole sample *via* a ligand assisted wet chemistry method (details in ESI†). We first

performed structural characterization of Cu<sub>2</sub>O and Cu<sub>2</sub>O@imidazole *via* XRD. As shown in Fig. 1a, the diffraction peaks of Cu<sub>2</sub>O and Cu<sub>2</sub>O@imidazole align well with the standard cubic Cu<sub>2</sub>O reference (PDF#00-005-0667), with no detectable impurity phases. Peaks observed at 29.5°, 36.4°, 42.3°, 61.3°, and 73.5° correspond to the (110), (111), (200), (220), and (311) planes of Cu<sub>2</sub>O, respectively. Notably, Cu<sub>2</sub>O@imidazole retained identical diffraction patterns to Cu<sub>2</sub>O, regardless of the alkyl chain length of the imidazolium ligands. This confirms that the surface modification preserves the crystalline structure of Cu<sub>2</sub>O.

We conducted SEM and TEM to confirm the microstructure of Cu<sub>2</sub>O@imidazole. The synthesized Cu<sub>2</sub>O exhibited irregular nanoclusters with particle sizes ranging from 50 to 150 nm (Fig. S1†). Notably, Cu<sub>2</sub>O@imidazole retained a similar



**Fig. 1** (a) XRD patterns of the synthesized Cu<sub>2</sub>O and Cu<sub>2</sub>O@imidazole catalysts; (b) high-resolution TEM image of OMIm-Cu<sub>2</sub>O, HAADF-STEM and EDS element mapping of OMIm-Cu<sub>2</sub>O; (c) Cu 2p spectra of Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O; (d) Cu LMM spectra of Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O; (e) N 1s spectra of Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O; (f) ATR-FTIR spectra of Cu<sub>2</sub>O, OMIm-Cu<sub>2</sub>O and OMIm-BF<sub>4</sub>; (g) ATR-FTIR spectra of Cu<sub>2</sub>O, OMIm-Cu<sub>2</sub>O and OMIm-BF<sub>4</sub> enlarged in the range of 2600–3300 cm<sup>−1</sup>.



morphology to Cu<sub>2</sub>O without significant structural alterations (Fig. 1b). HRTEM image revealed distinct lattice spacings of 0.24 nm in Cu<sub>2</sub>O, corresponding to the Cu<sub>2</sub>O(111) (PDF#00-005-0667). In contrast, the lattice spacing measured for OMIm-Cu<sub>2</sub>O was 0.21 nm, which aligns with the Cu<sub>2</sub>O(200) (Fig. S2†). These showed excellent consistency with XRD pattern. HAADF-STEM coupled with EDS mapping demonstrated uniform distribution of Cu, O, and N elements on the OMIm-Cu<sub>2</sub>O surface (Fig. 1b). The distinct presence of N provides direct evidence for the successful modification of imidazolium cations on the Cu<sub>2</sub>O surface.

To investigate the chemical states of Cu<sub>2</sub>O and Cu<sub>2</sub>-O@imidazole, XPS measurements were performed. As shown in Fig. 1c, the Cu 2p spectra of both Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O exhibited two distinct peaks at binding energies of 932.7 eV and 952.5 eV, corresponding to the Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> orbitals of Cu(I) or Cu(0), respectively. To further differentiate between Cu(I) and Cu(0), Cu LMM Auger spectra was conducted (Fig. 1d). It revealed a prominent peak at 570.3 eV, assigned to Cu(I). Notably, no significant differences were observed in the Cu 2p or Cu LMM spectra between Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O, confirming the consistent presence of Cu(I) species, in agreement with XRD results. For the OMIm-Cu<sub>2</sub>O catalyst, the N 1s spectrum (Fig. 1e) displayed three characteristic peaks: a peak at 399.0 eV attributed to Cu–N bonding,<sup>19</sup> and two additional peaks centered at 399.9 eV and 401.0 eV, corresponding to the C–N and C=N bonds in the imidazolium ring of OMIm-BF<sub>4</sub>.<sup>20,21</sup> These confirm the successful anchoring of imidazolium on the Cu<sub>2</sub>O. In contrast, no N 1s signal was detected in the same energy range for the Cu<sub>2</sub>O sample.

To confirm the presence of imidazolium molecular modification, ATR-FTIR was employed. The spectra of Cu<sub>2</sub>O, OMIm-Cu<sub>2</sub>O, and OMIm-BF<sub>4</sub> are shown in Fig. 1f. For Cu<sub>2</sub>O, a single band at 610 cm<sup>-1</sup> was observed, attributed to the Cu–O bond.<sup>22,23</sup> In contrast, the OMIm-Cu<sub>2</sub>O spectrum retained the Cu–O stretching band at 610 cm<sup>-1</sup> but exhibited additional peaks at 810, 1080, 1600, 2900, and 3340 cm<sup>-1</sup>. The broad peak at 3340 cm<sup>-1</sup> corresponds to O–H stretching vibrations from adsorbed water, while the remaining bands are associated with the surface-bound imidazolium molecular layer. For comparison, OMIm-BF<sub>4</sub> exhibited characteristic vibrational bands: the strongest peak at 1080 cm<sup>-1</sup> was assigned to the BF<sub>4</sub><sup>-</sup> anion,<sup>24,25</sup> the C=C–N in-plane stretching vibration of the imidazolium ring appeared at 1570 cm<sup>-1</sup>,<sup>26</sup> the symmetric stretching vibration of –CH<sub>3</sub> on the imidazolium ring was observed at 1468 cm<sup>-1</sup>,<sup>27,28</sup> and peaks at 1167, 750, and 620 cm<sup>-1</sup> originated from C–H of the imidazolium ring.<sup>27,29</sup> These imidazolium-related peaks were also detected at analogous positions in the OMIm-Cu<sub>2</sub>O. Crucially, the methylene C–H stretching vibrations (2800–3000 cm<sup>-1</sup>) of the octyl chain in OMIm-BF<sub>4</sub> were prominently retained in OMIm-Cu<sub>2</sub>O (Fig. 1g).<sup>30</sup> These results provide conclusive evidence for the successful modification of the Cu<sub>2</sub>O surface with imidazolium.

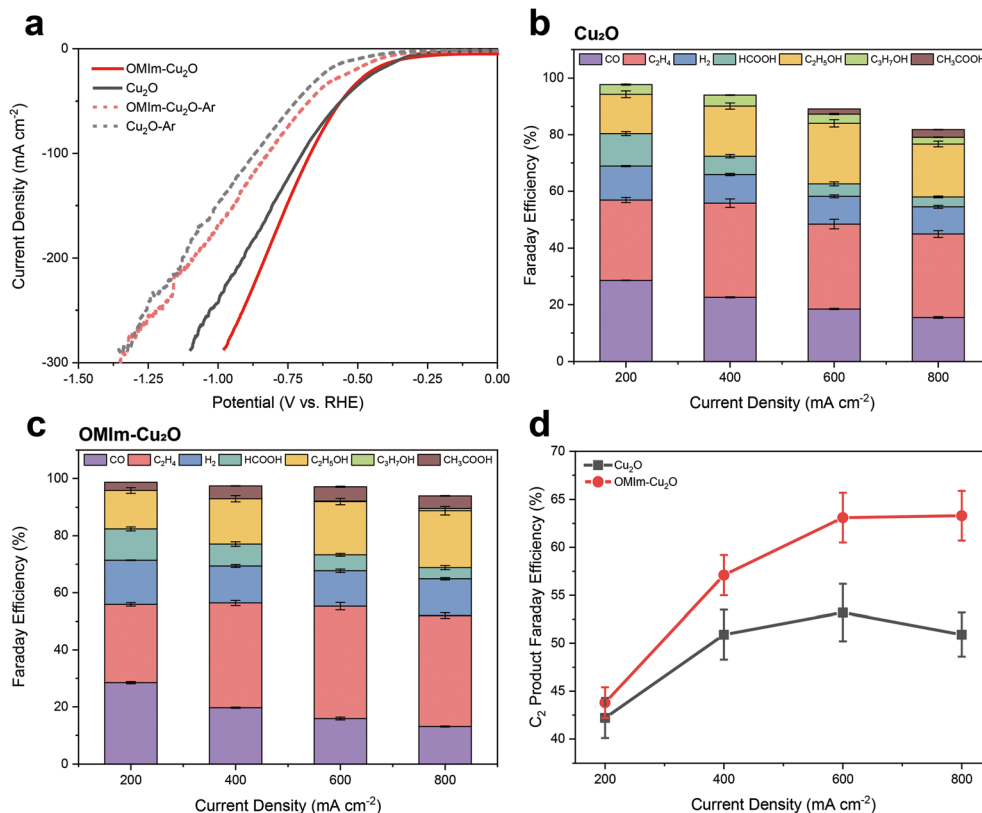
## 2.2 CO<sub>2</sub>RR performance

We firstly investigated the CO<sub>2</sub> reduction performance of Cu<sub>2</sub>-O@Imidazole in 1 M KOH electrolyte. We analyzed the gas products by an online gas chromatography (GC) and the liquid products by a nuclear magnetic resonance (NMR). The LSV curves in Fig. 2a demonstrate that both Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O exhibit significantly higher activity for CO<sub>2</sub>RR than HER. While the onset potentials for CO<sub>2</sub>RR were comparable between OMIm-Cu<sub>2</sub>O and Cu<sub>2</sub>O, the OMIm-Cu<sub>2</sub>O displayed a steeper slope, suggesting enhanced activity due to the imidazolium ligands. Product selectivity at varying current densities (200–800 mA cm<sup>-2</sup>) are presented in Fig. 2b and c. For Cu<sub>2</sub>O, CO and C<sub>2</sub>H<sub>4</sub> dominated the product distribution (Fig. 2b). The CO selectivity peaked at 28.6% at 200 mA cm<sup>-2</sup> but progressively decreased with higher current densities. Concurrently, C<sub>2+</sub> product selectivity for Cu<sub>2</sub>O measured 42.2%, 50.9%, 53.2%, and 50.9% at 200, 400, 600, and 800 mA cm<sup>-2</sup>, respectively. In contrast, the imidazolium-functionalized OMIm-Cu<sub>2</sub>O catalyst achieved substantially enhanced C<sub>2+</sub> product selectivity of 43.8%, 57.1%, 63.1%, and 63.3% under identical conditions (Fig. 2c and d). This systematic improvement across all tested current densities underscores the critical role of imidazolium modification in promoting multi-carbon product formation.

A series of Cu<sub>2</sub>O@imidazole catalysts with varying alkyl chain lengths were synthesized, including ethyl (EMIm-Cu<sub>2</sub>O), propyl (PMIm-Cu<sub>2</sub>O), butyl (BMIm-Cu<sub>2</sub>O), hexyl (HMIm-Cu<sub>2</sub>O), octyl (OMIm-Cu<sub>2</sub>O), and decyl (DMIm-Cu<sub>2</sub>O), with alkyl chains ranging from 2 to 10 carbons. Their CO<sub>2</sub>RR performance under alkaline conditions was systematically evaluated (Fig. 3a and b). The alkyl chain length exerted a pronounced influence on product selectivity, revealing distinct trends. As shown in Fig. 3a, CO selectivity exhibited a volcano-shaped dependence on chain length. BMIm-Cu<sub>2</sub>O (*n* = 4) achieved the highest CO selectivity of 64.6% at 200 mA cm<sup>-2</sup>, representing a 2.25-fold enhancement compared to Cu<sub>2</sub>O. In contrast, C<sub>2+</sub> product selectivity displayed an inverse trend, initially decreasing and then increasing with chain elongation. For shorter chains (*n* = 2, 3, 4), EMIm-Cu<sub>2</sub>O, PMIm-Cu<sub>2</sub>O, and BMIm-Cu<sub>2</sub>O showed lower C<sub>2+</sub> selectivity than Cu<sub>2</sub>O, with values diminishing as chain length increased. However, catalysts with longer alkyl chains (*n* = 6, 8, 10) reversed this trend, HMIm-Cu<sub>2</sub>O, OMIm-Cu<sub>2</sub>O, and DMIm-Cu<sub>2</sub>O demonstrating progressively higher C<sub>2+</sub> selectivity. Notably, OMIm-Cu<sub>2</sub>O (*n* = 8) achieved the highest C<sub>2+</sub> selectivity of 63.3% at 600 mA cm<sup>-2</sup>, underscoring the critical role of chain length in modulating multi-carbon product formation. A comparative analysis of key metrics (e.g., FE, partial current density) between OMIm-Cu<sub>2</sub>O and literature-reported imidazolium ligand-modified electrocatalysts (Table S1†) further confirms its state-of-the-art performance in C<sub>2+</sub> production. Furthermore, stability tests of the optimal OMIm-Cu<sub>2</sub>O catalyst at 600 mA cm<sup>-2</sup> revealed sustained performance over 6 hours, though gradual activity decay was observed (Fig. S3†). Post-stability







**Fig. 2** CO<sub>2</sub>RR performance of Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O under alkaline conditions. (a) LSV curves of Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O in CO<sub>2</sub> and Ar; (b) product faraday efficiency of Cu<sub>2</sub>O during CO<sub>2</sub>RR at different applied current densities; (c) product Faraday efficiency of OMIm-Cu<sub>2</sub>O during CO<sub>2</sub>RR at different applied current densities; (d) C<sub>2</sub>+ FE of OMIm-Cu<sub>2</sub>O and Cu<sub>2</sub>O at different current densities.

characterization indicated that morphological degradation and imidazolium ligand detachment may contribute to this decline (Fig. S4†).

Under acidic conditions, the imidazolium ligand modification similarly influenced product selectivity. To effectively suppress the HER in acidic media, a high-concentration potassium ion environment was employed using 3 M KCl electrolyte acidified to pH = 1 with HCl. The product FE for Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O under acidic electrolyte are shown in Fig. S5†. For Cu<sub>2</sub>O, H<sub>2</sub> dominated as the primary product, with a selectivity of 51% at 200 mA cm<sup>-2</sup>. Remarkably, for OMIm-Cu<sub>2</sub>O, imidazolium modification significantly suppressed HER, reducing H<sub>2</sub> selectivity to 19.3% and 16.9% at 100 and 200 mA cm<sup>-2</sup>, respectively. Additionally, the imidazolium modification completely inhibited CH<sub>4</sub> formation, in stark contrast to Cu<sub>2</sub>O.

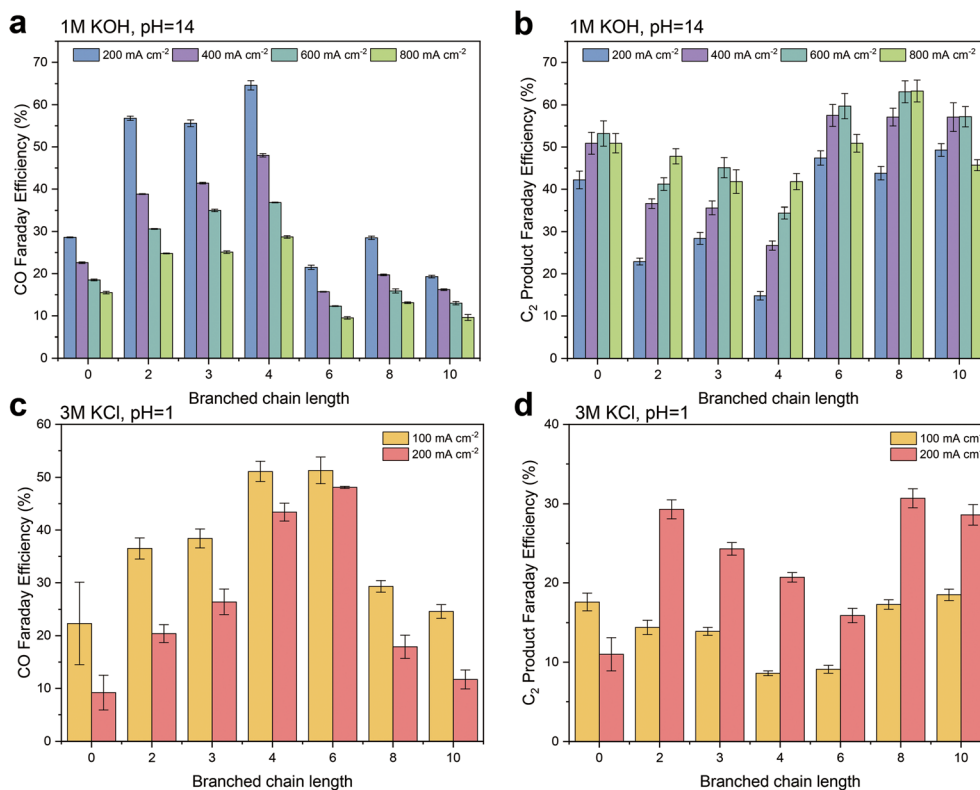
Similar to alkaline conditions, variations in alkyl chain length induced systematic trends in acidic CO<sub>2</sub>RR FE. As depicted in Fig. 3c, CO FE also followed a volcano-shaped dependence on chain length, peaking at 51.3% for HMIm-Cu<sub>2</sub>O (*n* = 6) at 200 mA cm<sup>-2</sup>. HMIm-Cu<sub>2</sub>O obtained a 2.3-fold enhancement over unmodified Cu<sub>2</sub>O. For C<sub>2</sub>+ products, selectivity mirrored the alkaline trend, initially decreasing and then increasing with chain elongation. OMIm-Cu<sub>2</sub>O (*n* = 8) achieved the highest C<sub>2</sub>+ selectivity of 30.7% at 200 mA cm<sup>-2</sup> under acidic conditions,

representing a 2.8-fold improvement compared to Cu<sub>2</sub>O (Fig. 3d). These results highlight the dual role of imidazolium ligands in acidic media: suppressing parasitic HER/CH<sub>4</sub> while promoting CO and C<sub>2</sub> pathways, with alkyl chain length serving as a critical modulator of interfacial reactivity.

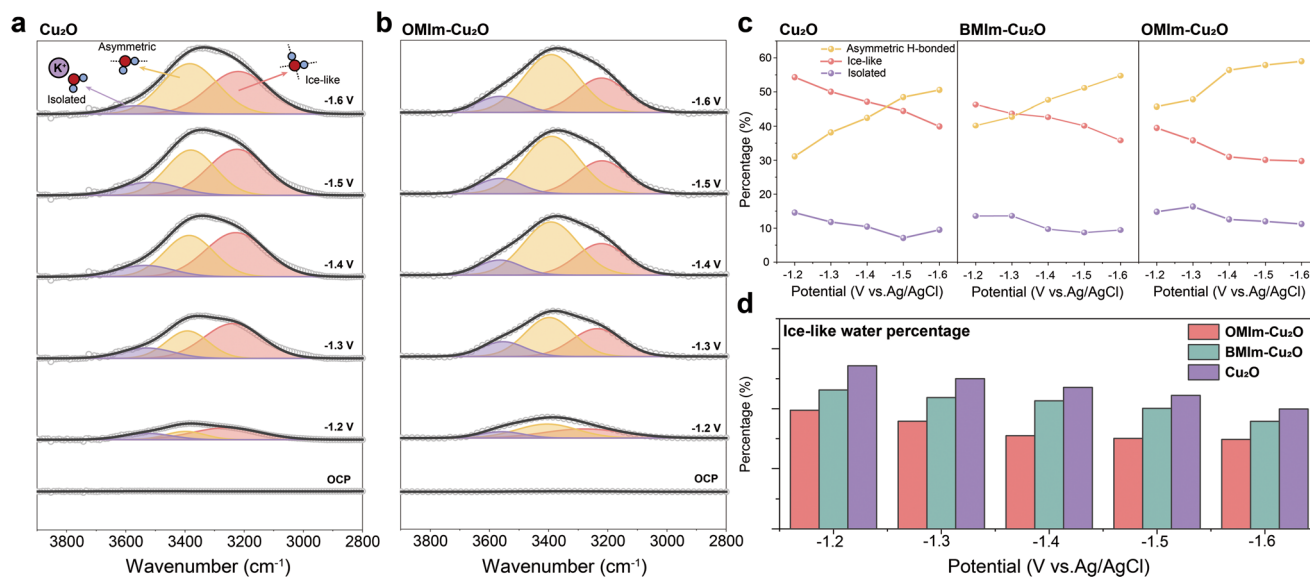
### 2.3 Mechanism study

The experimental data conclusively demonstrate the critical role of imidazolium ligand side-chain length in regulating CO<sub>2</sub>RR product selectivity. To elucidate the mechanistic origins of this enhancement, we investigated the interfacial microenvironment and dynamic structural effects through *in situ* ATR-SEIRAS. Fig. 4 and S6† displays the spectra of interfacial water for Cu<sub>2</sub>O, BMIm-Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O during CO<sub>2</sub>RR. Gaussian fitting of the spectra reveals that the O–H stretching vibration peaks of interfacial water (Fig. 4a, b and S6) can be deconvoluted into three distinct components, corresponding to three types of O–H stretching vibrations: isolated water molecules (~3570 cm<sup>-1</sup>, purple peaks), asymmetric H-bonded water (~3400 cm<sup>-1</sup>, yellow peaks), and ice-like water (~3220 cm<sup>-1</sup>, red peaks). The proportional distribution of these three water configurations on the catalyst surface was quantified through relative peak area analysis (Fig. 4c).





**Fig. 3** Effects of imidazolium ligands with different branch lengths on product selectivity. (a) Relationship between imidazolium ligand branch length and CO selectivity under alkaline conditions; (b) relationship between imidazolium ligand branch length and  $C_{2+}$  product selectivity under alkaline conditions; (c) relationship between imidazolium ligand branch length and CO selectivity under acidic conditions; (d) relationship between imidazolium ligand branch length and  $C_{2+}$  product selectivity under acidic conditions.



**Fig. 4** Regulation of the  $H_2O$  hydrogen-bonding network after imidazolium ligands modification. (a) *In situ* ATR-SEIRAS spectra of interfacial  $H_2O$  during  $CO_2RR$  on a  $Cu_2O$  electrode in 1 M  $KHCO_3$ ; (b) *in situ* ATR-SEIRAS spectra of interfacial  $H_2O$  during  $CO_2RR$  on an OMIm- $Cu_2O$  electrode in 1 M  $KHCO_3$ . Gaussian fits of the three O-H stretching modes are shown in purple, orange, and red, respectively; (c) the ratio of the three water peaks at the interface between  $Cu_2O$ , BMIm- $Cu_2O$  and OMIm- $Cu_2O$  during  $CO_2RR$ , obtained from the peak area ratio after Gaussian fitting; (d) the ratio of ice-like water at different potentials at the interface between  $Cu_2O$ , BMIm- $Cu_2O$  and OMIm- $Cu_2O$ .

Notably, the hydrogen-bonding structure of interfacial water undergoes significant changes with increasing applied

potential: the proportion of asymmetric H-bonded water increases markedly while ice-like water decreases. The



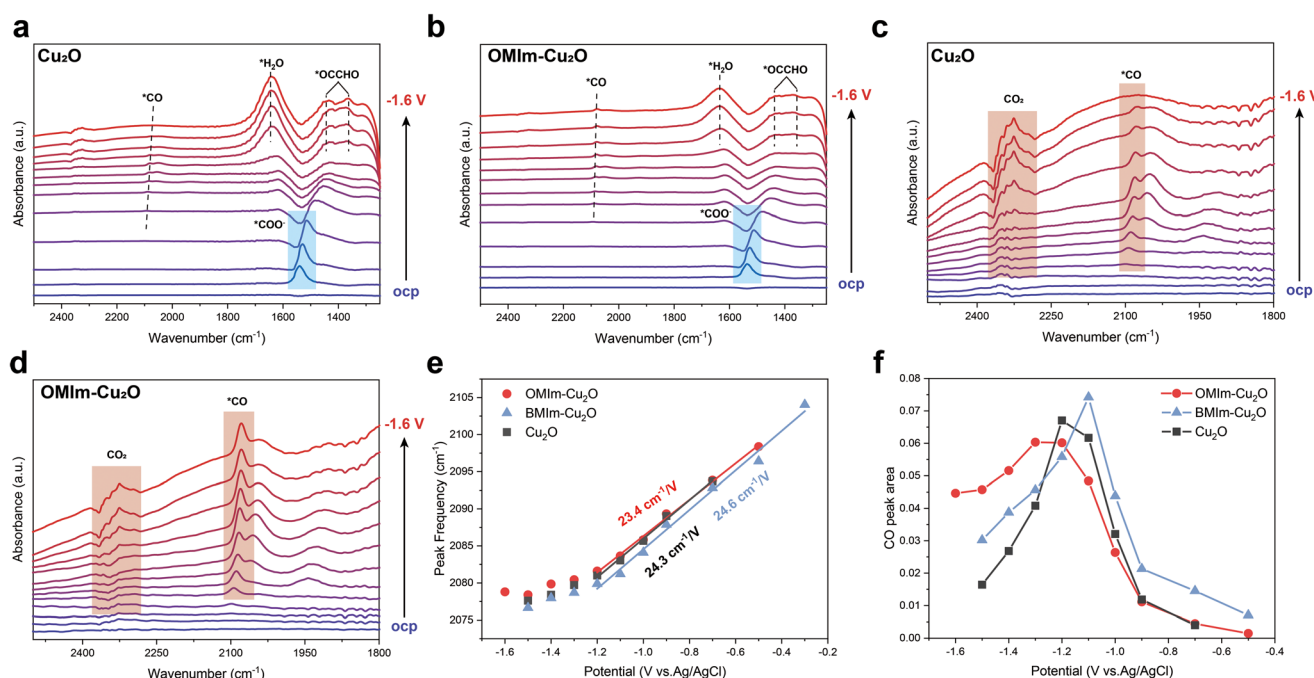
reduction in ice-like water (the predominant configuration in bulk solvent) suggests electric field-induced enrichment of metal cations at the catalyst surface and subsequent reorganization of interfacial water distribution. However, imidazolium-modified BMIm-Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O exhibits further enhancement in asymmetric H-bonded water and greater suppression of ice-like water compared to unmodified Cu<sub>2</sub>O across all potentials (Fig. 4c and d). This phenomenon aligns with previous reports demonstrating that flexible alkyl chains of organic ligands undergo electric field-regulated structural reorganization at solid-liquid interfaces.<sup>31–35</sup> The observed decrease in ice-like water and concurrent increase in asymmetric H-bonded water confirm similar ordering processes on BMIm-Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O surfaces.<sup>31</sup> The imidazolium ligand modification regulated the microenvironment. The long alkyl chains in the ligand layer undergo spontaneous self-organization, forming a structured molecular arrangement that effectively reduces water molecule density at the interfacial region. This ultimately constructs a gradient hydrophobic-aerophilic microenvironment at the electrochemical interface. Moreover, the percentage of ice-like water at the electrode-electrolyte interface decreases monotonically with increasing alkyl chain length, demonstrating the regulatory role of alkyl chain length in modulating the hydrophobicity balance within the local microenvironment.

Next, we estimated the ECSA of Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O. The calculated *C<sub>dl</sub>* for Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O were 1.57 and 1.60 mF cm<sup>-2</sup>, respectively, indicating comparable ECSA

values between the two catalysts (Fig. S7†). To investigate the influence of imidazolium modification on charge transfer properties, we conducted EIS measurements for Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O (Fig. S7†). At lower potentials, OMIm-Cu<sub>2</sub>O exhibited a similar *R<sub>ct</sub>* to that of Cu<sub>2</sub>O. However, with increasing potential, the *R<sub>ct</sub>* of OMIm-Cu<sub>2</sub>O became significantly reduced compared to Cu<sub>2</sub>O, demonstrating that the imidazolium ligand modification substantially enhances charge transfer capability at elevated working potentials.

Subsequently, we employed *in situ* ATR-SEIRAS to monitor the evolution of surface-active intermediates during CO<sub>2</sub>RR. As shown in Fig. 5a, b and S8†, the peak at ~1500 cm<sup>-1</sup> observed on Cu<sub>2</sub>O, BMIm-Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O corresponds to the symmetric O–C–O stretching vibration of adsorbed \*COO<sup>-</sup>,<sup>36</sup> indicating CO<sub>2</sub> adsorption and accumulation at low potentials. This intermediate diminishes progressively as the potential increases, consistent with its transformation into downstream species. Concurrently, the emergence of \*CO intermediates in the 2000–2100 cm<sup>-1</sup> range at intermediate potentials suggests hydrogenation of \*COO<sup>-</sup> to \*CO, a critical branching point for product selectivity.<sup>36,37</sup> Notably, at higher potentials, OMIm-Cu<sub>2</sub>O exhibits significantly weaker signals at ~1450 cm<sup>-1</sup> and ~1350 cm<sup>-1</sup> compared to Cu<sub>2</sub>O and BMIm-Cu<sub>2</sub>O (Fig. 5d), which are assigned to \*OCCHO species formed through C–C coupling.<sup>36</sup> This observation aligns with the enhanced C<sub>2+</sub> selectivity of OMIm-Cu<sub>2</sub>O.

The \*CO peaks at 2080–2100 cm<sup>-1</sup> exhibit Stark shifts (Fig. 5e), where the Stark tuning rate—primarily influenced by intermediate coverage—serves as an indicator of the \*CO



**Fig. 5** Mechanistic study on the enhanced CO<sub>2</sub>RR performance by imidazolium surface modification. *In situ* ATR-SEIRAS spectra of (a) Cu<sub>2</sub>O and (b) OMIm-Cu<sub>2</sub>O in CO<sub>2</sub>-saturated 1 M KHCO<sub>3</sub> electrolyte; (c) magnified *in situ* ATR-SEIRAS spectra of Cu<sub>2</sub>O and (d) OMIm-Cu<sub>2</sub>O in the range of 2500–1800 cm<sup>-1</sup>; (e) variation of \*CO peak position with potential for Cu<sub>2</sub>O, BMIm-Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O. The Stark shift frequency was determined by linear fitting; (f) relationship between \*CO peak area on the surface of Cu<sub>2</sub>O, BMIm-Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O and applied potential.



adsorption capacity.<sup>38–40</sup> Notably, Cu<sub>2</sub>O, BMIm-Cu<sub>2</sub>O and OMIm-Cu<sub>2</sub>O display comparable Stark tuning rates (24.3, 24.6, and 23.4 cm<sup>-1</sup> V<sup>-1</sup>), demonstrating that imidazolium modification does not alter the intrinsic \*CO adsorption capability of Cu<sub>2</sub>O. Both catalysts show an initial increase followed by a decrease in \*CO peak area with increasing potential. However, BMIm-Cu<sub>2</sub>O retains higher \*CO concentrations than unmodified Cu<sub>2</sub>O at higher potentials (>1.3 V vs. Ag/AgCl), though slightly lower than OMIm-Cu<sub>2</sub>O (Fig. 5f). This trend aligns with the increasement of alkyl chain length, directly linking longer alkyl chains to enhanced CO retention. This potential-dependent behavior arises from competing processes: while \*CO accumulation dominates at lower potentials, its depletion at higher potentials results from C–C coupling of \*CO intermediates. The sustained high \*CO concentration on OMIm-Cu<sub>2</sub>O under high potentials reveals that imidazolium modification enhances local \*CO coverage. These findings elucidate the optimization mechanism of imidazolium ligands for CO<sub>2</sub>RR: The hydrophobic-aerophilic microenvironment constructed by long-chain imidazolium ligands elevates local \*CO concentrations at the catalyst interface, particularly under high-potential conditions. This enriched \*CO coverage facilitates C–C coupling kinetics, thereby improving C<sub>2</sub>+ product selectivity.

### 3. Conclusions

This study demonstrates that tailoring the alkyl chain length of imidazolium ligands enables microenvironment modulation for optimizing CO<sub>2</sub>RR selectivity on Cu<sub>2</sub>O catalysts. Structural analysis confirms the stable anchoring of imidazolium molecules *via* Cu–N coordination without altering the Cu<sub>2</sub>O structure. A volcano-shaped dependence of CO selectivity on alkyl chain length is observed, with BMIm-Cu<sub>2</sub>O (C<sub>4</sub>) and HMIm-Cu<sub>2</sub>O (C<sub>6</sub>) achieving 2.25- and 2.3-fold enhancements in CO FE under alkaline and acidic conditions. Remarkably, hydrophobic alkyl chains suppress hydrogen evolution and completely inhibit CH<sub>4</sub> formation. Mechanistically, the alkyl side chains form an electric field-induced hydrophobic layer, reducing interfacial ice-like water content by 10.1–14.8%, thereby enriching local \*CO intermediates. *In situ* ATR-SEIRAS evidence corroborates that this microenvironment facilitates \*CO retention and C–C coupling, rationalizing the enhanced C<sub>2</sub>+ selectivity. These findings underscore the critical role of ligand-engineered microenvironments in steering CO<sub>2</sub>RR pathways.

### 4. Experimental section

#### 4.1 Synthesis of Cu<sub>2</sub>O

First, 2.0 g of anhydrous sodium tetraborate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) was added to 70 mL of hot deionized water (90 °C) under continuous magnetic stirring for over 10 minutes to ensure complete dissolution, yielding a clear and homogeneous solution. After cooling the sodium tetraborate solution to

room temperature, 0.8 g of sodium ascorbate was introduced into the mixture under vigorous stirring. The stirring was maintained for an additional 10 minutes, followed by the addition of 0.4 g of CuCl<sub>2</sub>. Upon incorporation of CuCl<sub>2</sub>, the solution immediately transitioned to an orange-yellow coloration. After 7 minutes of reaction, the resulting product was isolated *via* centrifugation, thoroughly washed with deionized water, and subsequently vacuum-dried at 60 °C for 12 hours.

#### 4.2 Synthesis of Cu<sub>2</sub>O@imidazole

Catalysts modified with imidazolium of varying alkyl chain lengths (C<sub>2</sub>–C<sub>10</sub>) were designated as EMIm-Cu<sub>2</sub>O, PMIm-Cu<sub>2</sub>O, BMIm-Cu<sub>2</sub>O, HMIm-Cu<sub>2</sub>O, OMIm-Cu<sub>2</sub>O, and DMIm-Cu<sub>2</sub>O, respectively. Take the synthesis of EMIm-Cu<sub>2</sub>O as an example: first, 2.0 g of anhydrous sodium tetraborate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) was dissolved in 70 mL of hot deionized water (90 °C) under magnetic stirring for at least 10 minutes to form a clear solution. After cooling the solution to room temperature, 0.8 g of sodium ascorbate and 0.1 g of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF<sub>4</sub>) were added sequentially to the sodium tetraborate solution under vigorous stirring. The mixture was stirred continuously for 10 minutes, followed by the addition of 0.4 g of CuCl<sub>2</sub>. Upon introducing CuCl<sub>2</sub>, the solution rapidly turned orange-yellow. After 7 minutes, the product was collected *via* centrifugation, washed repeatedly with deionized water, and vacuum-dried at 60 °C for 12 hours. The synthesis procedures for PMIm-Cu<sub>2</sub>O, BMIm-Cu<sub>2</sub>O, HMIm-Cu<sub>2</sub>O, OMIm-Cu<sub>2</sub>O, and DMIm-Cu<sub>2</sub>O were identical to that of EMIm-Cu<sub>2</sub>O, except that EMImBF<sub>4</sub> was replaced with the corresponding imidazolium salts: PMImBF<sub>4</sub> (1-propyl-3-methylimidazolium tetrafluoroborate), BMImBF<sub>4</sub> (1-butyl-3-methylimidazolium tetrafluoroborate), HMImBF<sub>4</sub> (1-hexyl-3-methylimidazolium tetrafluoroborate), OMImBF<sub>4</sub> (1-octyl-3-methylimidazolium tetrafluoroborate), DMImBF<sub>4</sub> (1-decyl-3-methylimidazolium tetrafluoroborate).

### Data availability

The data supporting this article have been included as part of the ESI.†

### Conflicts of interest

The authors declare no conflict of interest.

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