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Electrochemical CO₂ reduction (CO₂RR) to synthesize multicarbon products is a critical route for sustainable CO₂ 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 Cu₂O catalysts, using imidazolium-based ionic liquids with alkyl side chains of varying lengths. The optimized OMIIm-Cu₂O catalyst achieves a C₂₊ 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 CO₂RR.

Keywords: Electrochemical CO₂ reduction; C₂₊ product selectivity; Copper-based catalysts; *CO concentration.

1. Introduction

Electrochemical CO₂ reduction reaction (CO₂RR) driven by renewable electricity to synthesize C₂₊ products represents a pivotal pathway for CO₂ resource utilization. C–C coupling, the rate-determining step in generating C₂₊ products, is directly constrained by the *CO coverage on the catalyst surface.^{1–3} Consequently, various strategies have been employed to enhance the local *CO concentration and promote C₂₊ product formation, including size and morphology control,^{4,5} surface doping,^{6,7} and oxidation modulation.^{8,9} Nam *et al.* reported

Imidazolium ligand-modified Cu₂O catalysts for enhancing C₂₊ selectivity in CO₂ 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 C₂₊ products.¹⁰ Likewise, Jung *et al.* demonstrated that porous Cu/Cu₂O aerogel catalysts yield a higher *CO concentration around the catalyst surface compared to nanoparticle or planar film catalysts.¹¹ Notably, current technological systems still face challenges in simultaneously achieving high faradaic efficiency (FE >70%) and ultra-high current densities (>600 mA cm^{−2}), 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 CO₂RR 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.^{12,13} In addition, steric hindrance can suppress the hydrogen evolution reaction or adjust product distribution,^{14–17} while optimization of the local microenvironment enhances target product activity by increasing reactant concentration or suppressing side reactions.^{14,15,18} 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 C₂₊ 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 Cu₂O 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 C₂₊ product selectivity exhibited a non-

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monotonic trend, first decreasing and then increasing as the side chain lengthened. Notably, the OMIm-Cu₂O catalyst demonstrated the best performance in both media, achieving a C₂₊ 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 C₂ product formation.

2. Results and discussion

2.1 Characterization of Cu₂O@imidazole

We prepared the Cu₂O@imidazole sample *via* a ligand assisted wet chemistry method (details in ESI†). We first

performed structural characterization of Cu₂O and Cu₂O@imidazole *via* XRD. As shown in Fig. 1a, the diffraction peaks of Cu₂O and Cu₂O@imidazole align well with the standard cubic Cu₂O 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 Cu₂O, respectively. Notably, Cu₂O@imidazole retained identical diffraction patterns to Cu₂O, regardless of the alkyl chain length of the imidazolium ligands. This confirms that the surface modification preserves the crystalline structure of Cu₂O.

We conducted SEM and TEM to confirm the microstructure of Cu₂O@imidazole. The synthesized Cu₂O exhibited irregular nanoclusters with particle sizes ranging from 50 to 150 nm (Fig. S1†). Notably, Cu₂O@imidazole retained a similar

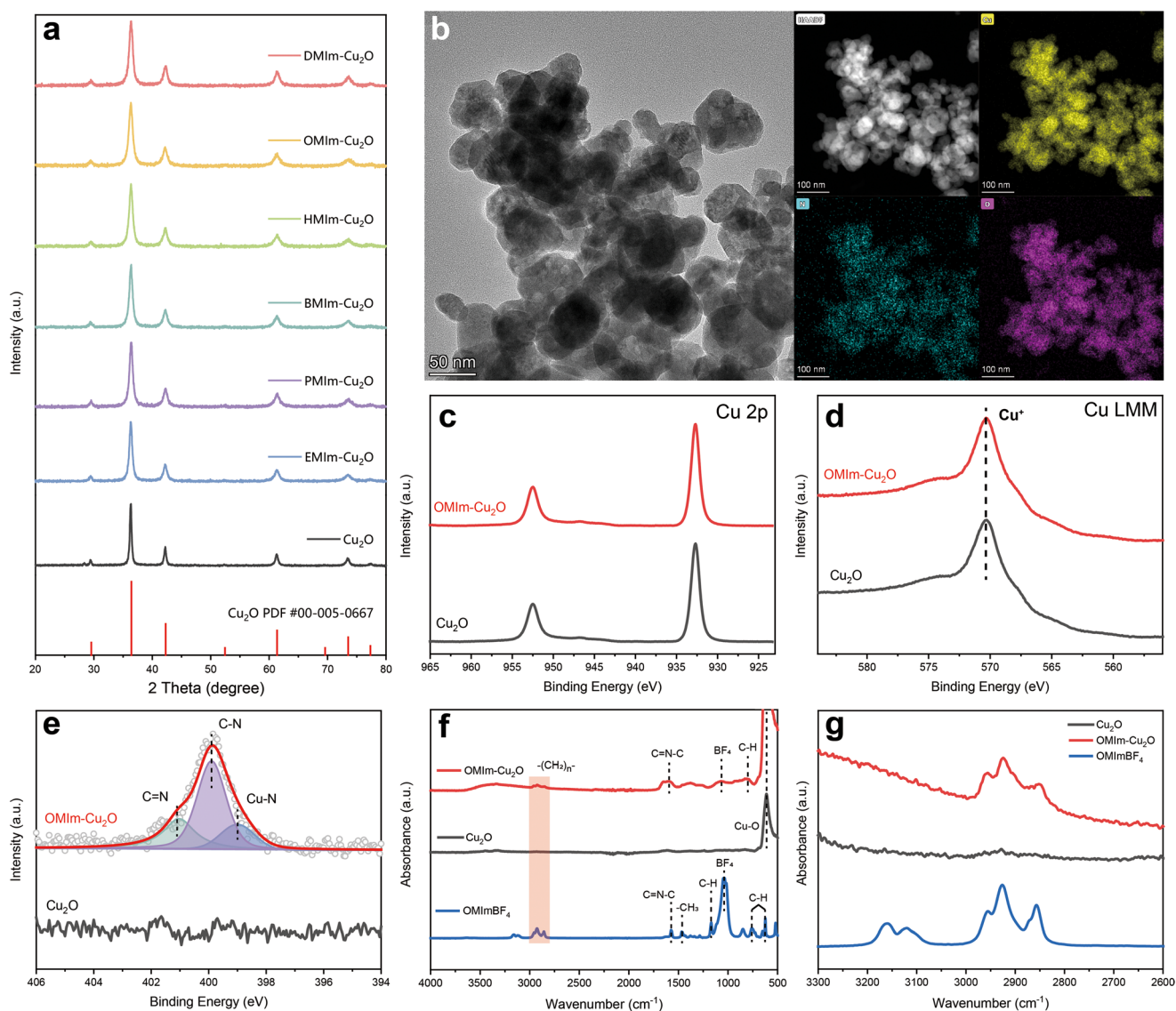


Fig. 1 (a) XRD patterns of the synthesized Cu₂O and Cu₂O@imidazole catalysts; (b) high-resolution TEM image of OMIm-Cu₂O, HAADF-STEM and EDS element mapping of OMIm-Cu₂O; (c) Cu 2p spectra of Cu₂O and OMIm-Cu₂O; (d) Cu LMM spectra of Cu₂O and OMIm-Cu₂O; (e) N 1s spectra of Cu₂O and OMIm-Cu₂O; (f) ATR-FTIR spectra of Cu₂O, OMIm-Cu₂O and OMIm-BF₄; (g) ATR-FTIR spectra of Cu₂O, OMIm-Cu₂O and OMIm-BF₄ enlarged in the range of 2600–3300 cm^{−1}.



morphology to Cu₂O without significant structural alterations (Fig. 1b). HRTEM image revealed distinct lattice spacings of 0.24 nm in Cu₂O, corresponding to the Cu₂O(111) (PDF#00-005-0667). In contrast, the lattice spacing measured for OMIm-Cu₂O was 0.21 nm, which aligns with the Cu₂O(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-Cu₂O surface (Fig. 1b). The distinct presence of N provides direct evidence for the successful modification of imidazolium cations on the Cu₂O surface.

To investigate the chemical states of Cu₂O and Cu₂-O@imidazole, XPS measurements were performed. As shown in Fig. 1c, the Cu 2p spectra of both Cu₂O and OMIm-Cu₂O exhibited two distinct peaks at binding energies of 932.7 eV and 952.5 eV, corresponding to the Cu 2p_{3/2} and Cu 2p_{1/2} 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 Cu₂O and OMIm-Cu₂O, confirming the consistent presence of Cu(I) species, in agreement with XRD results. For the OMIm-Cu₂O catalyst, the N 1s spectrum (Fig. 1e) displayed three characteristic peaks: a peak at 399.0 eV attributed to Cu-N bonding,¹⁹ 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-BF₄.^{20,21} These confirm the successful anchoring of imidazolium on the Cu₂O. In contrast, no N 1s signal was detected in the same energy range for the Cu₂O sample.

To confirm the presence of imidazolium molecular modification, ATR-FTIR was employed. The spectra of Cu₂O, OMIm-Cu₂O, and OMIm-BF₄ are shown in Fig. 1f. For Cu₂O, a single band at 610 cm⁻¹ was observed, attributed to the Cu-O bond.^{22,23} In contrast, the OMIm-Cu₂O spectrum retained the Cu-O stretching band at 610 cm⁻¹ but exhibited additional peaks at 810, 1080, 1600, 2900, and 3340 cm⁻¹. The broad peak at 3340 cm⁻¹ 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-BF₄ exhibited characteristic vibrational bands: the strongest peak at 1080 cm⁻¹ was assigned to the BF₄⁻ anion,^{24,25} the C=C-N in-plane stretching vibration of the imidazolium ring appeared at 1570 cm⁻¹,²⁶ the symmetric stretching vibration of -CH₃ on the imidazolium ring was observed at 1468 cm⁻¹,^{27,28} and peaks at 1167, 750, and 620 cm⁻¹ originated from C-H of the imidazolium ring.^{27,29} These imidazolium-related peaks were also detected at analogous positions in the OMIm-Cu₂O. Crucially, the methylene C-H stretching vibrations (2800–3000 cm⁻¹) of the octyl chain in OMIm-BF₄ were prominently retained in OMIm-Cu₂O (Fig. 1g).³⁰ These results provide conclusive evidence for the successful modification of the Cu₂O surface with imidazolium.

2.2 CO₂RR performance

We firstly investigated the CO₂ reduction performance of Cu₂-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 Cu₂O and OMIm-Cu₂O exhibit significantly higher activity for CO₂RR than HER. While the onset potentials for CO₂RR were comparable between OMIm-Cu₂O and Cu₂O, the OMIm-Cu₂O displayed a steeper slope, suggesting enhanced activity due to the imidazolium ligands. Product selectivity at varying current densities (200–800 mA cm⁻²) are presented in Fig. 2b and c. For Cu₂O, CO and C₂H₄ dominated the product distribution (Fig. 2b). The CO selectivity peaked at 28.6% at 200 mA cm⁻² but progressively decreased with higher current densities. Concurrently, C₂⁺ product selectivity for Cu₂O measured 42.2%, 50.9%, 53.2%, and 50.9% at 200, 400, 600, and 800 mA cm⁻², respectively. In contrast, the imidazolium-functionalized OMIm-Cu₂O catalyst achieved substantially enhanced C₂⁺ 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 Cu₂O@imidazole catalysts with varying alkyl chain lengths were synthesized, including ethyl (EMIm-Cu₂O), propyl (PMIm-Cu₂O), butyl (BMIm-Cu₂O), hexyl (HMIm-Cu₂O), octyl (OMIm-Cu₂O), and decyl (DMIm-Cu₂O), with alkyl chains ranging from 2 to 10 carbons. Their CO₂RR 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-Cu₂O (*n* = 4) achieved the highest CO selectivity of 64.6% at 200 mA cm⁻², representing a 2.25-fold enhancement compared to Cu₂O. In contrast, C₂⁺ product selectivity displayed an inverse trend, initially decreasing and then increasing with chain elongation. For shorter chains (*n* = 2, 3, 4), EMIm-Cu₂O, PMIm-Cu₂O, and BMIm-Cu₂O showed lower C₂⁺ selectivity than Cu₂O, with values diminishing as chain length increased. However, catalysts with longer alkyl chains (*n* = 6, 8, 10) reversed this trend, HMIm-Cu₂O, OMIm-Cu₂O, and DMIm-Cu₂O demonstrating progressively higher C₂⁺ selectivity. Notably, OMIm-Cu₂O (*n* = 8) achieved the highest C₂⁺ selectivity of 63.3% at 600 mA cm⁻², 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-Cu₂O and literature-reported imidazolium ligand-modified electrocatalysts (Table S1†) further confirms its state-of-the-art performance in C₂⁺ production. Furthermore, stability tests of the optimal OMIm-Cu₂O catalyst at 600 mA cm⁻² revealed sustained performance over 6 hours, though gradual activity decay was observed (Fig. S3†). Post-stability



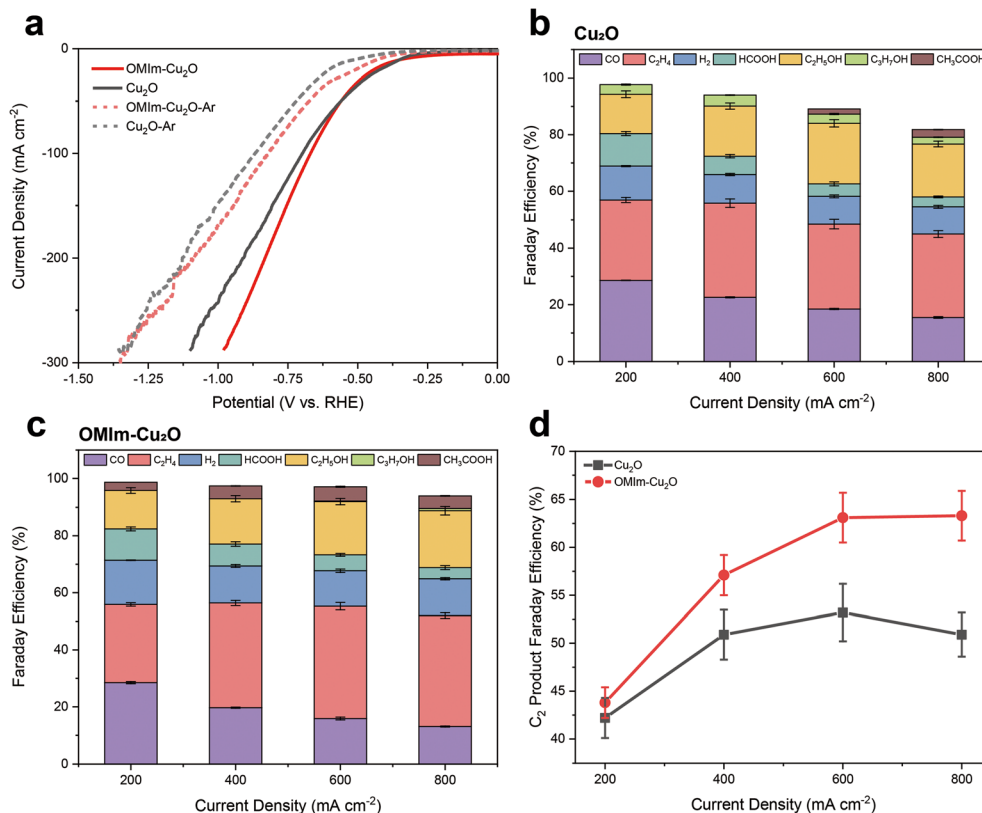


Fig. 2 CO₂RR performance of Cu₂O and OMIm-Cu₂O under alkaline conditions. (a) LSV curves of Cu₂O and OMIm-Cu₂O in CO₂ and Ar; (b) product faraday efficiency of Cu₂O during CO₂RR at different applied current densities; (c) product Faraday efficiency of OMIm-Cu₂O during CO₂RR at different applied current densities; (d) C₂+ FE of OMIm-Cu₂O and Cu₂O 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 Cu₂O and OMIm-Cu₂O under acidic electrolyte are shown in Fig. S5†. For Cu₂O, H₂ dominated as the primary product, with a selectivity of 51% at 200 mA cm⁻². Remarkably, for OMIm-Cu₂O, imidazolium modification significantly suppressed HER, reducing H₂ selectivity to 19.3% and 16.9% at 100 and 200 mA cm⁻², respectively. Additionally, the imidazolium modification completely inhibited CH₄ formation, in stark contrast to Cu₂O.

Similar to alkaline conditions, variations in alkyl chain length induced systematic trends in acidic CO₂RR FE. As depicted in Fig. 3c, CO FE also followed a volcano-shaped dependence on chain length, peaking at 51.3% for HMIm-Cu₂O (*n* = 6) at 200 mA cm⁻². HMIm-Cu₂O obtained a 2.3-fold enhancement over unmodified Cu₂O. For C₂+ products, selectivity mirrored the alkaline trend, initially decreasing and then increasing with chain elongation. OMIm-Cu₂O (*n* = 8) achieved the highest C₂+ selectivity of 30.7% at 200 mA cm⁻² under acidic conditions,

representing a 2.8-fold improvement compared to Cu₂O (Fig. 3d). These results highlight the dual role of imidazolium ligands in acidic media: suppressing parasitic HER/CH₄ while promoting CO and C₂ 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 CO₂RR 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 Cu₂O, BMIm-Cu₂O and OMIm-Cu₂O during CO₂RR. 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⁻¹, purple peaks), asymmetric H-bonded water (~3400 cm⁻¹, yellow peaks), and ice-like water (~3220 cm⁻¹, red peaks). The proportional distribution of these three water configurations on the catalyst surface was quantified through relative peak area analysis (Fig. 4c).



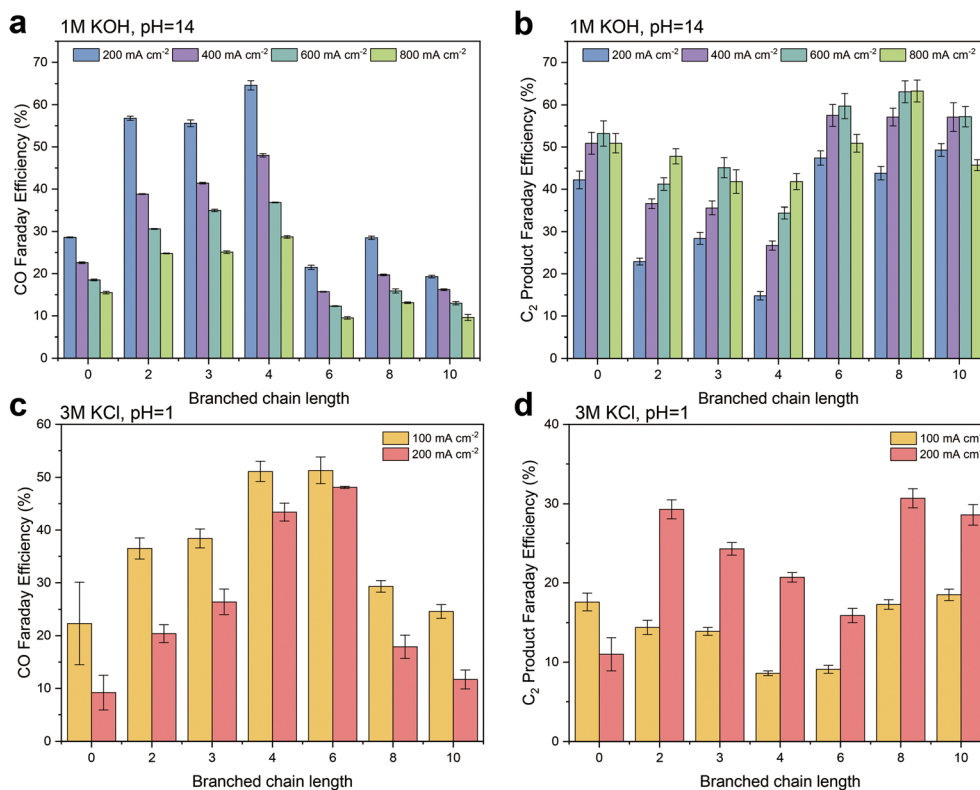


Fig. 3 Effects of imidazolium ligands with different branch lengths on product selectivity. (a) Relationship between imidazolium ligand branch length and CO selectivity under alkaline conditions; (b) relationship between imidazolium ligand branch length and C_{2+} product selectivity under alkaline conditions;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

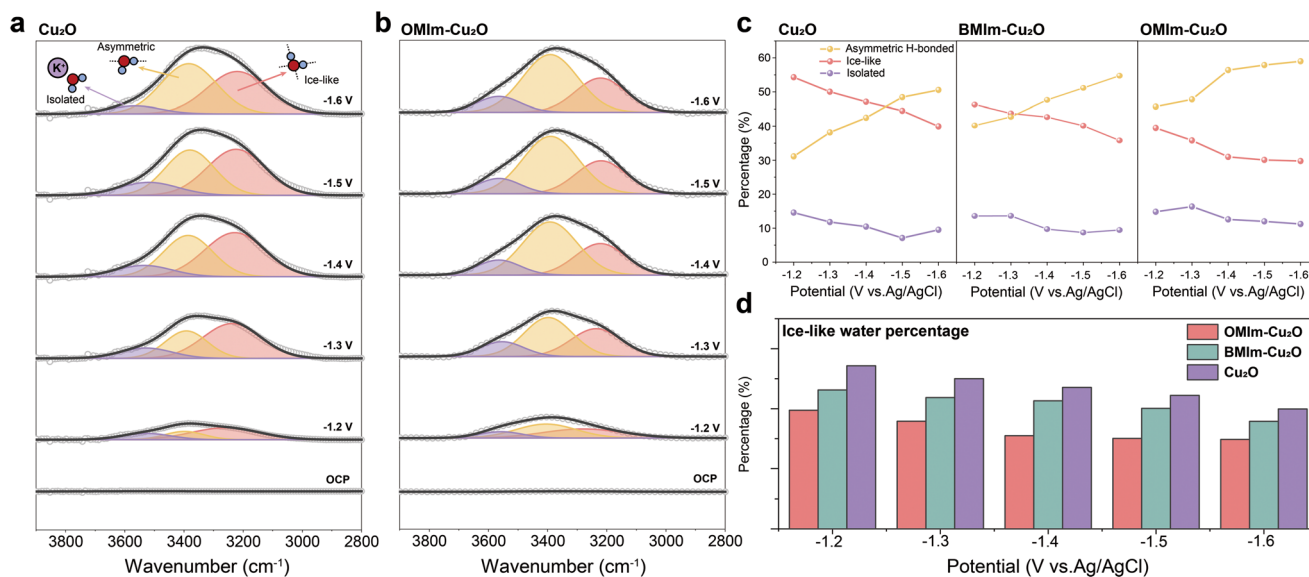


Fig. 4 Regulation of the H_2O hydrogen-bonding network after imidazolium ligands modification. (a) *In situ* ATR-SEIRAS spectra of interfacial H_2O during CO_2RR on a Cu_2O electrode in 1 M $KHCO_3$; (b) *in situ* ATR-SEIRAS spectra of interfacial H_2O during CO_2RR on an OMIm- Cu_2O electrode in 1 M $KHCO_3$. 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-Cu₂O and OMIm-Cu₂O exhibits further enhancement in asymmetric H-bonded water and greater suppression of ice-like water compared to unmodified Cu₂O 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.^{31–35} The observed decrease in ice-like water and concurrent increase in asymmetric H-bonded water confirm similar ordering processes on BMIm-Cu₂O and OMIm-Cu₂O surfaces.³¹ 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 Cu₂O and OMIm-Cu₂O. The calculated *C_{dl}* for Cu₂O and OMIm-Cu₂O were 1.57 and 1.60 mF cm⁻², 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 Cu₂O and OMIm-Cu₂O (Fig. S7†). At lower potentials, OMIm-Cu₂O exhibited a similar *R_{ct}* to that of Cu₂O. However, with increasing potential, the *R_{ct}* of OMIm-Cu₂O became significantly reduced compared to Cu₂O, 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 CO₂RR. As shown in Fig. 5a, b and S8†, the peak at ~1500 cm⁻¹ observed on Cu₂O, BMIm-Cu₂O and OMIm-Cu₂O corresponds to the symmetric O–C–O stretching vibration of adsorbed *COO⁻,³⁶ indicating CO₂ 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⁻¹ range at intermediate potentials suggests hydrogenation of *COO⁻ to *CO, a critical branching point for product selectivity.^{36,37} Notably, at higher potentials, OMIm-Cu₂O exhibits significantly weaker signals at ~1450 cm⁻¹ and ~1350 cm⁻¹ compared to Cu₂O and BMIm-Cu₂O (Fig. 5d), which are assigned to *OCCHO species formed through C–C coupling.³⁶ This observation aligns with the enhanced C₂₊ selectivity of OMIm-Cu₂O.

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

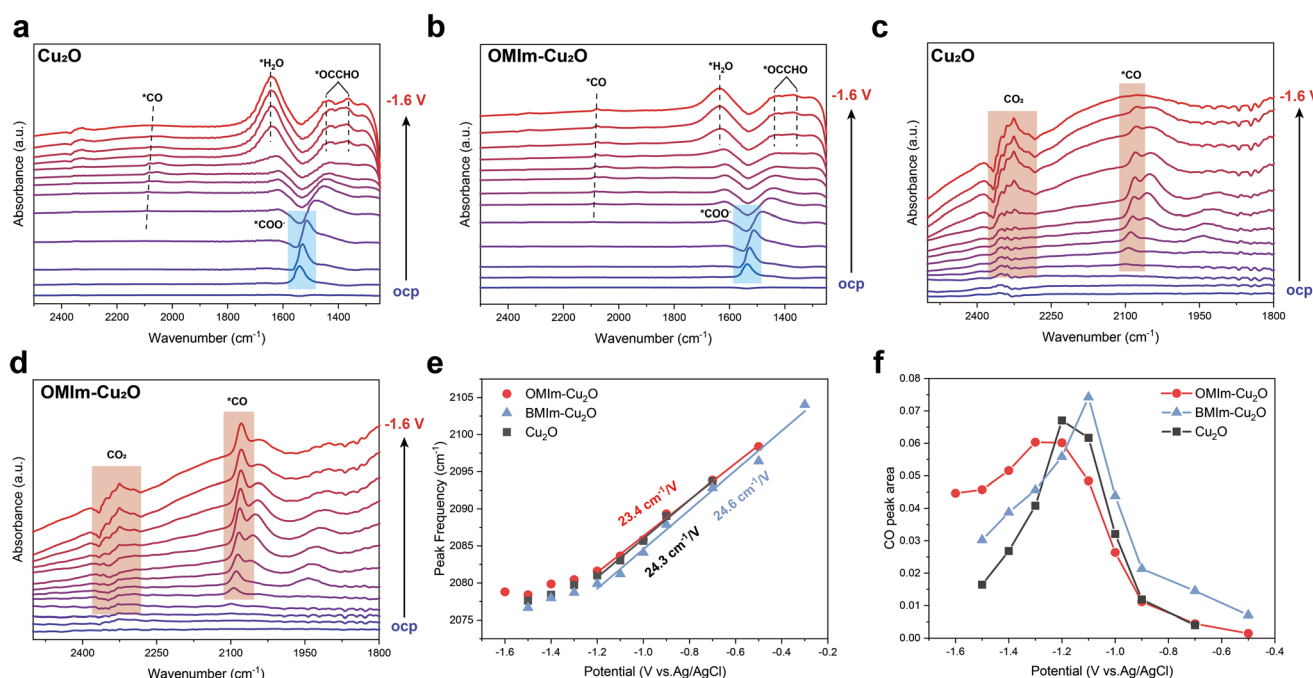


Fig. 5 Mechanistic study on the enhanced CO₂RR performance by imidazolium surface modification. *In situ* ATR-SEIRAS spectra of (a) Cu₂O and (b) OMIm-Cu₂O in CO₂-saturated 1 M KHCO₃ electrolyte; (c) magnified *in situ* ATR-SEIRAS spectra of Cu₂O and (d) OMIm-Cu₂O in the range of 2500–1800 cm⁻¹; (e) variation of *CO peak position with potential for Cu₂O, BMIm-Cu₂O and OMIm-Cu₂O. The Stark shift frequency was determined by linear fitting; (f) relationship between *CO peak area on the surface of Cu₂O, BMIm-Cu₂O and OMIm-Cu₂O and applied potential.



adsorption capacity.^{38–40} Notably, Cu₂O, BMIm-Cu₂O and OMIm-Cu₂O display comparable Stark tuning rates (24.3, 24.6, and 23.4 cm⁻¹ V⁻¹), demonstrating that imidazolium modification does not alter the intrinsic *CO adsorption capability of Cu₂O. Both catalysts show an initial increase followed by a decrease in *CO peak area with increasing potential. However, BMIm-Cu₂O retains higher *CO concentrations than unmodified Cu₂O at higher potentials (>1.3 V vs. Ag/AgCl), though slightly lower than OMIm-Cu₂O (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-Cu₂O under high potentials reveals that imidazolium modification enhances local *CO coverage. These findings elucidate the optimization mechanism of imidazolium ligands for CO₂RR: 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 C₂+ product selectivity.

3. Conclusions

This study demonstrates that tailoring the alkyl chain length of imidazolium ligands enables microenvironment modulation for optimizing CO₂RR selectivity on Cu₂O catalysts. Structural analysis confirms the stable anchoring of imidazolium molecules *via* Cu–N coordination without altering the Cu₂O structure. A volcano-shaped dependence of CO selectivity on alkyl chain length is observed, with BMIm-Cu₂O (C₄) and HMIm-Cu₂O (C₆) 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 CH₄ 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 C₂+ selectivity. These findings underscore the critical role of ligand-engineered microenvironments in steering CO₂RR pathways.

4. Experimental section

4.1 Synthesis of Cu₂O

First, 2.0 g of anhydrous sodium tetraborate (Na₂B₄O₇) 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 CuCl₂. Upon incorporation of CuCl₂, 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 Cu₂O@imidazole

Catalysts modified with imidazolium of varying alkyl chain lengths (C₂–C₁₀) were designated as EMIm-Cu₂O, PMIm-Cu₂O, BMIm-Cu₂O, HMIm-Cu₂O, OMIm-Cu₂O, and DMIm-Cu₂O, respectively. Take the synthesis of EMIm-Cu₂O as an example: first, 2.0 g of anhydrous sodium tetraborate (Na₂B₄O₇) 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 (EMImBF₄) 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 CuCl₂. Upon introducing CuCl₂, 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-Cu₂O, BMIm-Cu₂O, HMIm-Cu₂O, OMIm-Cu₂O, and DMIm-Cu₂O were identical to that of EMIm-Cu₂O, except that EMImBF₄ was replaced with the corresponding imidazolium salts: PMImBF₄ (1-propyl-3-methylimidazolium tetrafluoroborate), BMImBF₄ (1-butyl-3-methylimidazolium tetrafluoroborate), HMImBF₄ (1-hexyl-3-methylimidazolium tetrafluoroborate), OMImBF₄ (1-octyl-3-methylimidazolium tetrafluoroborate), DMImBF₄ (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.

Acknowledgements

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References

- 1 Z. Sun, Y. Hu, D. Zhou, M. Sun, S. Wang and W. Chen, Factors influencing the performance of copper-bearing catalysts in the CO₂ reduction system, *ACS Energy Lett.*, 2021, **6**, 3992–4022.
- 2 X. Zhi, Y. Jiao, Y. Zheng, K. Davey and S.-Z. Qiao, Directing the selectivity of CO₂ electroreduction to target C₂ products via non-metal doping on Cu surfaces, *J. Mater. Chem. A*, 2021, **9**, 6345–6351.
- 3 Z. Gu, H. Shen, Z. Chen, Y. Yang, C. Yang, Y. Ji, Y. Wang, C. Zhu, J. Liu, J. Li, T.-K. Sham, X. Xu and G. Zheng, Efficient electrocatalytic CO₂ reduction to C₂₊ alcohols at defect-site-rich Cu surface, *Joule*, 2021, **5**, 429–440.
- 4 Z.-Z. Niu, F.-Y. Gao, X.-L. Zhang, P.-P. Yang, R. Liu, L.-P. Chi, Z.-Z. Wu, S. Qin, X. Yu and M.-R. Gao, Hierarchical copper with Inherent hydrophobicity mitigates electrode flooding for high-rate CO₂ electroreduction to multicarbon products, *J. Am. Chem. Soc.*, 2021, **143**, 8011–8021.
- 5 H. Huo, J. Wang, Q. Fan, Y. Hu and J. Yang, Cu-MOFs derived porous Cu nanoribbons with strengthened electric field for selective CO₂ electroreduction to C₂₊ fuels, *Adv. Energy Mater.*, 2021, **11**, 2102447.
- 6 C. Peng, G. Luo, Z. Xu, S. Yan, J. Zhang, M. Chen, L. Qian, W. Wei, Q. Han and G. Zheng, Lithiation-enabled high-density nitrogen vacancies electrocatalyze CO₂ to C₂ products, *Adv. Mater.*, 2021, **33**, 2103150.
- 7 M. Li, Y. Ma, J. Chen, R. Lawrence, W. Luo, M. Sacchi, W. Jiang and J. Yang, Residual chlorine induced cationic active species on a porous copper electrocatalyst for highly stable electrochemical CO₂ reduction to C₂₊, *Angew. Chem.*, 2021, **60**, 11487–11493.
- 8 Z. Lyu, S. Zhu, M. Xie, Y. Zhang, Z. Chen, R. Chen, M. Tian, M. Chi, M. Shao and Y. Xia, Controlling the surface oxidation of Cu nanowires improves their catalytic selectivity and stability toward C₂₊ products in CO₂ reduction, *Angew. Chem., Int. Ed.*, 2021, **60**, 1909–1915.
- 9 C. Liu, J. Gong, J. Li, J. Yin, W. Li, Z. Gao, L. Xiao, G. Wang, J. Lu and L. Zhuang, Preatodized Cu surface for selective CO₂ electroreduction to C₁ or C₂₊ products, *ACS Appl. Mater. Interfaces*, 2022, **14**, 20953–20961.
- 10 K. D. Yang, W. R. Ko, J. H. Lee, S. J. Kim, H. Lee, M. H. Lee and K. T. Nam, Morphology-directed selective production of ethylene or ethane from CO₂ on a Cu mesopore electrode, *Angew. Chem., Int. Ed.*, 2017, **56**, 796–800.
- 11 C. Kim, K. M. Cho, K. Park, J. Y. Kim, G.-T. Yun, F. M. Toma, I. Gereige and H.-T. Jung, Cu/Cu₂O interconnected porous aerogel catalyst for highly productive electrosynthesis of ethanol from CO₂, *Adv. Funct. Mater.*, 2021, **31**, 2102142.
- 12 Z. Cao, S. B. Zacate, X. Sun, J. Liu, E. M. Hale, W. P. Carson, S. B. Tyndall, J. Xu, X. Liu, X. Liu, C. Song, J.-h. Luo, M.-J. Cheng, X. Wen and W. Liu, Tuning gold nanoparticles with chelating ligands for highly efficient electrocatalytic CO₂ reduction, *Angew. Chem., Int. Ed.*, 2018, **57**, 12675–12679.
- 13 Y. Yang, C. Zhang, C. Zhang, Y. Shi, J. Li, B. Johannessen, Y. Liang, S. Zhang, Q. Song, H. Zhang, J. Huang, J. Ke, L. Zhang, Q. Song, J. Zeng, Y. Zhang, Z. Geng, P.-S. Wang, Z. Wang, J. Zeng and F. Li, Ligand-tuning copper in coordination polymers for efficient electrochemical C–C coupling, *Nat. Commun.*, 2024, **15**, 6316.
- 14 D. Qin, S. Song, Y. Liu, K. Wang, B. Yang and S. Zhang, Enhanced electrochemical nitrate-to-ammonia performance of cobalt oxide by protic ionic liquid modification, *Angew. Chem., Int. Ed.*, 2023, **62**, e202304935.
- 15 Y. Chen, X. Zhou, X. Liu, Z. Tang, L. Wang and Q. Tang, Understanding the role of potential and cation effect on electrocatalytic CO₂ reduction in all-alkynyl-protected Ag₁₅ nanoclusters, *J. Am. Chem. Soc.*, 2025, **147**, 2699–2713.
- 16 H. Zhang, C. Xu, X. Zhan, Y. Yu, K. Zhang, Q. Luo, S. Gao, J. Yang and Y. Xie, Mechanistic insights into CO₂ conversion chemistry of copper bis-(terpyridine) molecular electrocatalyst using accessible operando spectrochemistry, *Nat. Commun.*, 2022, **13**, 6029.
- 17 J. J. Clerix, A. Sanz-Matias, S. Armini, J. N. Harvey and A. Delabie, Structural phases of alkanethiolate self-assembled monolayers (C1–12) on Cu[100] by density functional theory, *J. Phys. Chem. C*, 2020, **124**, 3802–3811.
- 18 J. Fu, W. Zhu, Y. Chen, Z. Yin, Y. Li, J. Liu, H. Zhang, J.-J. Zhu and S. Sun, Bipyridine-assisted assembly of Au nanoparticles on Cu nanowires to enhance the electrochemical reduction of CO₂, *Angew. Chem., Int. Ed.*, 2019, **58**, 14100–14103.
- 19 H. Cheng, X. Wu, X. Li, X. Nie, S. Fan, M. Feng, Z. Fan, M. Tan, Y. Chen and G. He, Construction of atomically dispersed Cu-N₄ sites via engineered coordination environment for high-efficient CO₂ electroreduction, *Chem. Eng. J.*, 2021, **407**, 126842.
- 20 Z. Li, W. Wang, Y. Chen, C. Xiong, G. He, Y. Cao, H. Wu, M. D. Guiver and Z. Jiang, Constructing efficient ion nanochannels in alkaline anion exchange membranes by the in situ assembly of a poly(ionic liquid) in metal-organic frameworks, *J. Mater. Chem. A*, 2016, **4**, 2340–2348.
- 21 Y. Sha, J. Zhang, X. Cheng, M. Xu, Z. Su, Y. Wang, J. Hu, B. Han and L. Zheng, Anchoring ionic liquid in copper electrocatalyst for improving CO₂ conversion to ethylene, *Angew. Chem., Int. Ed.*, 2022, **61**, e202200039.
- 22 V. Sudha, G. Murugadoss and R. Thangamuthu, Structural and morphological tuning of Cu-based metal oxide nanoparticles by a facile chemical method and highly electrochemical sensing of sulphite, *Sci. Rep.*, 2021, **11**, 3413.
- 23 N. Zayyoun, L. Bahmad, L. Laânab and B. Jaber, The effect of pH on the synthesis of stable Cu₂O/CuO nanoparticles by sol-gel method in a glycolic medium, *Appl. Phys. A: Mater. Sci. Process.*, 2016, **122**, 488.
- 24 A. Dong, X. Ye, J. Chen, Y. Kang, T. Gordon, J. M. Kikkawa and C. B. Murray, A generalized ligand-exchange strategy enabling sequential surface functionalization of colloidal nanocrystals, *J. Am. Chem. Soc.*, 2011, **133**, 998–1006.
- 25 S. Y. Kottsov, G. P. Kopitsa, A. E. Baranchikov, A. A. Pavlova, T. V. Khamova, A. O. Badulina, Y. E. Gorshkova, N. A. Selivanov, N. P. Simonenko, M. E. Nikiforova and V. K. Ivanov, Structural insight into ionogels: A case study of



- 1-methyl-3-octyl-imidazolium tetrafluoroborate confined in aerosil, *Langmuir*, 2024, **40**, 23962–23972.
- 26 E. Navarrete-Astorga, J. Rodríguez-Moreno, E. A. Dalchiele, R. Schreiber, P. Leyton, J. R. Ramos-Barrado and F. Martín, A transparent solid-state ion gel for supercapacitor device applications, *J. Solid State Electrochem.*, 2017, **21**, 1431–1444.
 - 27 J. Jiang, D. Gao, Z. Li and G. Su, Gel polymer electrolytes prepared by in situ polymerization of vinyl monomers in room-temperature ionic liquids, *React. Funct. Polym.*, 2006, **66**, 1141–1148.
 - 28 J. A. Collado, I. Tuñón, E. Silla and F. J. Ramírez, Vibrational dynamics of histamine monocation in solution: an experimental (FT-IR, FT-Raman) and theoretical (SCRF-DFT) study, *J. Phys. Chem. A*, 2000, **104**, 2120–2131.
 - 29 N. Nanbu, Y. Sasaki and F. Kitamura, In situ FT-IR spectroscopic observation of a room-temperature molten salt|gold electrode interphase, *Electrochem. Commun.*, 2003, **5**, 383–387.
 - 30 J. Rodríguez, E. Navarrete, E. A. Dalchiele, L. Sánchez, J. R. Ramos-Barrado and F. Martín, Polyvinylpyrrolidone–LiClO₄ solid polymer electrolyte and its application in transparent thin film supercapacitors, *J. Power Sources*, 2013, **237**, 270–276.
 - 31 W. Ge, Y. Chen, Y. Fan, Y. Zhu, H. Liu, L. Song, Z. Liu, C. Lian, H. Jiang and C. Li, Dynamically formed surfactant assembly at the electrified electrode–electrolyte interface boosting CO₂ electroreduction, *J. Am. Chem. Soc.*, 2022, **144**, 6613–6622.
 - 32 E. Shirzadi, Q. Jin, A. S. Zeraati, R. Dorakhan, T. J. Goncalves, J. Abed, B.-H. Lee, A. S. Rasouli, J. Wicks, J. Zhang, P. Ou, V. Boureau, S. Park, W. Ni, G. Lee, C. Tian, D. M. Meira, D. Sinton, S. Siahrostami and E. H. Sargent, Ligand-modified nanoparticle surfaces influence CO electroreduction selectivity, *Nat. Commun.*, 2024, **15**, 2995.
 - 33 X. Kong, J. Zhu, Z. Xu and Z. Geng, Fundamentals and challenges of ligand modification in heterogeneous electrocatalysis, *Angew. Chem.*, 2025, **64**, e202417562.
 - 34 D. Kim, S. Yu, F. Zheng, I. Roh, Y. Li, S. Louisia, Z. Qi, G. A. Somorjai, H. Frei, L.-W. Wang and P. Yang, Selective CO₂ electrocatalysis at the pseudocapacitive nanoparticle/ordered-ligand interlayer, *Nat. Energy*, 2020, **5**, 1032–1042.
 - 35 L. Xiao, X. Zheng, J. Bai, J. Tan, D. Meng, Z. Zhang, H. Liu, L. Gong, S. Luo, S. Ye, Z. Jiang, L. Shan and S. Zhang, Ordered interfacial water generated at poly(ionic liquid) membrane surface imparts ultrafast water transport and superoleophobicity, *J. Am. Chem. Soc.*, 2025, **147**, 3507–3516.
 - 36 E. P. Delmo, Y. Wang, Y. Song, S. Zhu, H. Zhang, H. Xu, T. Li, J. Jang, Y. Kwon, Y. Wang and M. Shao, In situ infrared spectroscopic evidence of enhanced electrochemical CO₂ reduction and C–C coupling on oxide-derived copper, *J. Am. Chem. Soc.*, 2024, **146**, 1935–1945.
 - 37 N. J. Firet and W. A. Smith, Probing the reaction mechanism of CO₂ electroreduction over Ag films via operando infrared spectroscopy, *ACS Catal.*, 2017, **7**, 606–612.
 - 38 R. M. Hammaker, S. A. Francis and R. P. Eischens, Infrared study of intermolecular interactions for carbon monoxide chemisorbed on platinum, *Spectrochim. Acta*, 1965, **21**, 1295–1309.
 - 39 J. Uddin and A. B. Anderson, Trends with coverage and pH in Stark tuning rates for CO on Pt(111) electrodes, *Electrochim. Acta*, 2013, **108**, 398–403.
 - 40 P. Hollins and J. Pritchard, Infrared studies of chemisorbed layers on single crystals, *Prog. Surf. Sci.*, 1985, **19**, 275–349.

