Highlight

Solar Fuels

Molecular cages synchronise *CO retention and Cu^+ stabilisation for acidic ethylene electrosynthesis

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Abstract

Selective CO_2-to-ethylene conversion in acidic electrolytes requires catalysts that can sustain reactive carbon intermediates and maintain active copper states under demanding operating conditions. A surfactant-based molecular cage addresses these coupled challenges by confining CO intermediates near the copper surface while stabilising Cu^+ species that promote carbon–carbon coupling. This coordinated interfacial control delivers ethylene Faradaic efficiencies above 60% at current densities of 300–1100 mA cm^{-2}, alongside stable operation exceeding 195 h at an ethylene selectivity of approximately 50%. Beyond these performance gains, this study advances a broader catalyst design principle: controlling residence time of intermediates remain near active sites is as consequential as preserving the active sites themselves. Integrating intermediate confinement with oxidation-state stabilisation offers a promising route toward selective and durable acidic CO_2 electrolysis.

Electrochemical carbon dioxide reduction offers a compelling route for coupling renewable electricity with the production of carbon-based fuels and chemicals. [1] Ethylene is an attractive product because it is a major feedstock for polymer and chemical manufacturing. Cu is the only elemental catalyst that produces ethylene at appreciable rates; however, practical CO_2-to-ethylene conversion requires high carbon efficiency, selectivity, energy efficiency and durability. Meeting these requirements becomes more difficult at industrially relevant current densities, where concentration gradients and catalyst restructuring continually change the electrode surface.

Strongly acidic electrolysis can improve carbon utilisation by limiting the conversion of CO_2 into carbonate, thereby supporting high single-pass utilisation. [2,3] However, abundant protons favour hydrogen evolution, and the potential required for high-rate reduction can convert catalytically important Cu^+ into metallic Cu. Meanwhile, *CO intermediates may leave the surface before dimerization. Therefore, efficient ethylene formation requires sustained local *CO coverage and Cu^+ sites that favour *CO adsorption and C–C coupling. [4,5]

Several strategies have been proposed to address these challenges. Confinement structures slow *CO diffusion, dynamic Cu^0/Cu^+ interfaces promote C–C bond formation, and cationic groups reshape the acidic electrode-electrolyte interface. [5–7] Passivation layers can also improve copper stability. [8] However, each strategy may address only part of the problem: retaining *CO does not necessarily preserve Cu^+, and stabilising copper does not ensure sufficient *CO residence time. The challenge is to coordinate the catalyst state with the location and lifetime of carbon intermediates.

Chen et al. combined these concepts in a thin layer of cetyltrimethylammonium bromide (CTAB) assembled around Cu_2O. [9] They described the resulting coating as a molecular cage; its carbon chains created a confined space around the catalyst, while its charged head groups and water-repellent character reshaped the surrounding environment. The advantage of this design lies in the coordination of several interfacial effects within a single molecular layer (Figure 1a).

Theoretical calculations suggested that the CTAB molecular cage facilitates C–C coupling by maintaining *CO near the copper surface. The calculated *CO–*CO coupling barrier decreased after CTAB modification and decreased further as the local *CO coverage increased. Molecular dynamics simulations also indicated slower *CO diffusion from the coated surface (Figure 1b). Together, these results suggest that confinement provides neighbouring *CO intermediates with more opportunities to meet and react. The CTAB molecular cage also created a more positively charged and hydrophobic interface, as indicated by zeta potential and contact angle measurements. These properties may help limit proton access and competing hydrogen evolution while maintaining carbon intermediates near the catalyst. Thus, the proposed benefits of the cage arise from the combined effects of *CO confinement and interfacial regulation.

A major strength of this study is that Cu^+ stabilisation was observed under operating conditions rather than inferred solely from ex situ characterisation. Operando Cu K-edge X-ray absorption near-edge structure measurements placed the

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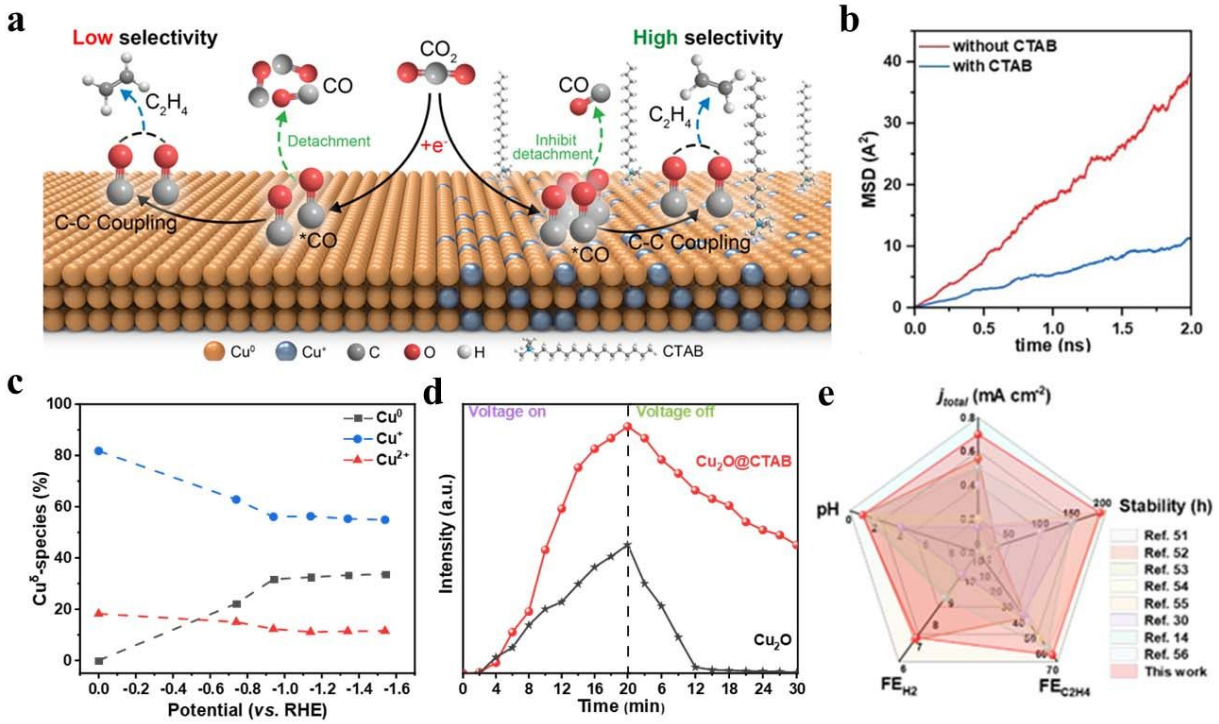


Figure 1 (a) Schematic diagram illustrating the effects of the CTAB molecular cage on *CO transport and the Cu oxidation state. (b) *CO diffusion on Cu_2O with and without CTAB. (c) Cu species in different oxidation states during the CO_2 reduction reaction (CO_2RR). (d) Time–intensity profiles of Fourier-transform infrared (FTIR) signals corresponding to *CO during voltage-on and voltage-off periods, reflecting the accumulation and decay kinetics of *CO on Cu_2O and Cu_2O@CTAB. (e) Comparison with other acidic CO_2RR systems. Reproduced with permission from Ref. [9]. Copyright 2026 American Chemical Society.

Cu_2O@CTAB absorption edge between those of Cu foil and Cu_2O throughout the investigated potential range (Figure 1c). Quantitative fitting showed that the Cu^+ fraction decreased from 81.8% in the initial state to 62.8% at −0.70 V *versus* the reversible hydrogen electrode and then approached a stable value of approximately 55% at more negative potentials. Complementary extended X-ray absorption fine structure and post-reaction X-ray photoelectron spectroscopy results supported the persistence of a Cu^+/Cu^0 interfacial population, whereas unmodified Cu_2O predominantly evolved towards metallic copper. Thus, the cage acts as a molecular guardrail, allowing partial reconstruction while preventing the complete loss of the catalytically active oxidation state. In situ attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy revealed that the Cu_2O@CTAB electrode maintained a stronger *CO signal under reducing conditions than unmodified Cu_2O. When the applied potential was removed, the signal persisted for up to 60 min with the cage, compared with approximately 12 min for bare Cu_2O. The molecular cage therefore converts *CO from a transient intermediate into a longer-lived interfacial reactant, linking prolonged interfacial residence time with enhanced C–C coupling (Figure 1d).

This combined effect was reflected in the reported device tests. In an acidic flow cell, Cu_2O@CTAB maintained an ethylene Faradaic efficiency above 60% at current densities ranging from 300 to 1100 mA cm^{-2}. At 500 mA cm^{-2}, the single-pass CO_2 utilisation for multicarbon products reached 64.7% at a flow rate of 1 sccm. In the long-term stability test, the Cu_2O@CTAB electrode operated for more than 195 h while maintaining an ethylene selectivity of approximately 50%. At the same current density, the ethylene and hydrogen Faradaic efficiencies (FE_C_2H_4 and FE_H_2, respectively), as well as the stability of Cu_2O@CTAB, compared favourably with those reported for most acidic CO_2RR systems (Figure 1e). These results are important because, for practical electrolysis, sustained performance across varying feed rates, current densities and operating times is more informative than selectivity at a single operating point. [9]

Several observations help distinguish the molecular cage effect from simpler explanations based on catalyst area or carbon contamination. Electrochemical surface area measurements showed only a modest increase after CTAB modification, which was insufficient to account for the large changes in selectivity and durability. Instead, the performance followed an optimised CTAB loading, consistent with the need to balance molecular coverage against reactant access. Isotopic electrolysis with $^{13}CO_2$ produced the expected signals for ^{13}CO and $^{13}C_2H_4$, confirming that the detected carbon products originated from the feed gas. Together with the operando measurements, these controls support a mechanistic interpretation in which the organic layer actively regulates the reaction microenvironment rather than serving as an inert hydrophobic coating.

The broader significance of this work lies in its treatment of an electrocatalytic interface as a coordinated reaction volume rather than as a collection of isolated binding sites. Conventional catalyst designs often focus on tuning adsorption energies

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at static active centres. The molecular cage concept adds two further coordinates: how long an intermediate remains within reach of the surface and whether the underlying catalyst retains the electronic state needed to use it. By synchronising intermediate confinement with valence-state stabilisation, this strategy alleviates the coupled kinetic-structural bottleneck that becomes acute in strongly acidic conditions. It also illustrates how an inexpensive surfactant layer can perform several functions that are usually assigned to separate catalyst components.

Several important questions remain. The Cu_2O scaffold undergoes substantial reconstruction during long-term electrolysis; even though CTAB remains associated with the electrode, the identity and spatial distribution of the steady-state Cu^+/Cu^0 sites warrant higher-resolution operando examination. The proposed electrostatic exclusion of protons should also be assessed through direct measurements of the local ion distribution and electric field under an applied potential. More broadly, confinement must be balanced: a cage that is too open cannot retain *CO, whereas a cage that is too dense may impede CO_2 delivery or product release. Systematic variation in molecular charge, chain length, anchoring group and packing density could transform this empirical coating approach into a quantitative design platform. Nevertheless, the message is compelling: efficient acidic CO_2 reduction depends not only on where carbon intermediates bind but also on how long they remain and what state the copper retains while they react.

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Reference

1. L. Zhang, Z. J. Zhao, J. Gong. Nanostructured materials for heterogeneous electrocatalytic CO_2 reduction and their related reaction mechanisms. *Angew. Chem. Int. Ed.* **2017**, 56, 11326–11353. DOI: 10.1002/anie.201612214
2. Y. Xie, P. Ou, X. Wang, Z. Xu, Y. C. Li, Z. Wang, J. E. Huang, J. Wicks, C. McCallum, N. Wang, Y. Wang, T. Chen, B. T. W. Lo, D. Sinton, J. C. Yu, Y. Wang, E. H. Sargent. High carbon utilization in CO_2 reduction to multi-carbon products in acidic media. *Nat. Catal.* **2022**, 5, 564–570. DOI: 10.1038/s41929-022-00788-1
3. Y. Chen, X. -Y. Li, Z. Chen, A. Ozden, J. E. Huang, P. Ou, J. Dong, J. Zhang, C. Tian, B. -H. Lee, X. Wang, S. Liu, Q. Qu, S. Wang, Y. Xu, R. K. Miao, Y. Zhao, Y. Liu, C. Qiu, J. Abed, H. Liu, H. Shin, D. Wang, Y. Li, D. Sinton, E. H. Sargent. Efficient multicarbon formation in acidic CO_2 reduction via tandem electrocatalysis. *Nat. Nanotechnol*. **2024**, 19, 311–318.
4. J. Li, Z. Wang, C. McCallum, Y. Xu, F. Li, Y. Wang, C. M. Gabardo, C. -T. Dinh, T. -T. Zhuang, L. Wang, J. Y. Howe, Y. Ren, E. H. Sargent, D. Sinton. Constraining CO coverage on copper promotes high-efficiency ethylene electroproduction. Nat. Catal. **2019**, 2, 1124-1131.
5. Y. Jiang, H. Li, C. Chen, Y. Zheng, S. -Z. Qiao. Dynamic Cu^0/Cu^+ interface promotes acidic CO_2 electroreduction. ACS Catal. **2024**, 14, 8310-8316.
6. Y. Kong, H. Yang, C. He, J. Sun, X. Jiang, X. Li, S. Feng, Y. Zhao, Q. Hu, C. He. Diffusion retardation induced by steric confinement to accelerate CO_2 electroreduction towards multicarbon products. *CCS Chem.* **2025**, 7, 1227–1239.
7. M. Fan, J. E. Huang, R. K. Miao, Y. Mao, P. Ou, F. Li, X. -Y. Li, Y. Cao, Z. Zhang, J. Zhang, Y. Yan, A. Ozden, W. Ni, Y. Wang, Y. Zhao, Z. Chen, B. Khatir, C. P. O'Brien, Y. Xu, Y. C. Xiao, G. I. N. Waterhouse, K. Golovin, Z. Wang, E. H. Sargent, D. Sinton. Cationic-group-functionalized electrocatalysts enable stable acidic CO_2 electrolysis. Nat. Catal. **2023**, 6, 763-772.
8. Q. Chen, Y. Tan, X. Wang, Q. Wang, H. Li, K. Liu, J. Fu, L. Chai, M. Liu, Z. Lin. Long-term stable acidic electroreduction of CO_2 to C_2 products at industrial current density using passivated copper. *Nat. Commun.* **2025**, 16, 8468. DOI: 10.1038/s41467-025-63318-0
9. Q. Chen, Y. Tan, H. Yu, Z. Mei, Y. Liu, Y. Xiao, Z. Wang, T. -S. Chan, H. Li, K. Liu, Z. Lin, L. Chai, M. Liu. Multifunctional molecular cages boost acidic CO_2 electroreduction to ethylene. J. Am. Chem. Soc. **2026**, 148, 19588-19597.