Membrane electrode assembly (MEA) electrolyzers offer a means to scale up CO$_2$-to-ethylene electroconversion using renewable electricity and close the anthropogenic carbon cycle. To date, excessive CO$_2$ coverage at the catalyst surface with limited active sites in MEA systems interferes with the carbon-carbon coupling reaction, diminishing ethylene production. With the aid of density functional theory calculations and spectroscopic analysis, here we report an oxide modulation strategy in which we introduce silica on Cu to create active Cu-SiO$_x$ interface sites, decreasing the formation energies of OCOH$^*$ and OCCOH$^*$—key intermediates along the pathway to ethylene formation. We then synthesize the Cu-SiO$_x$ catalysts using one-pot coprecipitation and integrate the catalyst in a MEA electrolyzer. By tuning the CO$_2$ concentration, the Cu-SiO$_x$ catalyst based MEA electrolyzer shows high ethylene Faradaic efficiencies of up to 65% at high ethylene current densities of up to 215 mA cm$^{-2}$; and features sustained operation over 50 h.
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electroreduction (CO2RR), powered by renewable electricity, represents a carbon-neutral pathway for the production of value-added hydrocarbons and alcohols1–3. Ethylene, a precursor in the chemical industry, has been prioritized as a target in CO2RR owing to its annual global production of 140 million metric tons and a market value of 182 billion USD4. However, the present-day performance of CO2-to-ethylene electrocatalysis—in terms of efficiency, production rate, and stability—is insufficient to compete with ethylene production from fossil sources4,5.

Gas diffusion electrodes (GDEs) embedded in alkaline flow cell electrolyzers have enabled selective CO2-to-ethylene conversion at industrial-level production rates6,7. However, CO2 utilization remains low due to the rapid reaction of CO2 molecules and hydroxide ions in these systems5. In addition, direct contact between GDE and aqueous electrolyte leads to electrode flooding and catalyst deactivation8,9.

The membrane electrode assembly (MEA) electrolyzer, with a direct cathode/membrane/anode contact, offers a platform that is more stable than alkaline flow cell electrolyzers10–12. A low cell resistance of zero-gap MEA electrolyzers also enables the use of bicarbonate or carbonate electrolyte without sacrificing the CO2RR efficiency13,14. Copper (Cu) has an adequate activation energy of CO2 and shows near-optimal CO binding, a key to producing ethylene15,16. However, the Faradaic efficiency (FE) toward ethylene reported on bare Cu catalysts in MEA systems is limited to <50%10.

Excessive local CO2 at the Cu catalysts surface, a result of fast mass transport of CO2 in flowing gas systems, and a lack of active sites diminishes ethylene formation due to the strong lateral interaction between adsorbed CO2 and CO2RR intermediates17. Introducing an element through doping18,19, alloying20,21, or molecule-modification22,23, offers a means to modify the structure of metallic Cu catalysts and has improved the FEethylene to an impressive 64% in an MEA electrolyzer22, but with ethylene productivity <100 mA cm−2.

A recent techno-economic analysis indicates that practical and economic ethylene production requires productivities greater than 200 mA cm−2 (ref. 2). This indicates the need for catalysts that achieve both high selectivity (>60%) and high activity (>300 mA cm−2), likely through designing a catalyst capable of accelerating CO2 activation and enabling efficient and continuous electron/proton transfer steps with strict control over the key reaction step—the carbon–carbon (C–C) coupling3,24.

The formation of OCCOH* intermediate from C–C coupling has been identified as a key step toward ethylene production25. Low-index and stepped Cu facets reduce the formation energy of the OCCOH* intermediate, due to efficient charge transfer between surface step sites and CO2RR intermediates15. However, under-coordinated step sites are rare in bulk Cu and less stable compared to Cu(111).

Herein, we report an oxide modulation strategy based on silica—a modifier oxide that has strong affinities to Cu and O—to create abundant Cu-SiOx interface stepped sites, assisting CO2 activation and the formation of the OCCOH* intermediate. We first assess the role of silica in affecting CO2RR on Cu using density functional theory (DFT) calculations. We find that a silica addition on a Cu surface significantly lowers the formation energies of the key intermediates OCCOH* and OCCOH** at the Cu-SiOx interface sites via forming strong Si–O or Si–C bonds, and leads to a cascade of coupled electron/proton transfer reactions that enhance CO2-to-ethylene conversion. We then synthesize a Cu-SiOx catalyst using one-pot coprecipitation. Through microscopy and spectroscopy, we find that Si species uniformly distribute at the Cu surface, forming abundant Cu-SiOx interfaces to catalyze CO2. We integrate the Cu-SiOx catalyst in a MEA electrolyzer and achieve a FE of 65% at a current density of 215 mA cm−2 for CO2-to-ethylene conversion, two-fold greater ethylene productivity in MEA compared to literature benchmarks. We further assess the performance of the Cu-SiOx catalyst in dilute CO2 streams, with the aim of directly converting flue gases. We demonstrate stable CO2-to-ethylene conversion with FEs of >60% at current densities in the range of 120–300 mA cm−2 across a wide window of CO2 concentrations (10–100%) and for a run time over 50 h.

Results

Density functional theory calculations. Excessive local CO2 at the Cu catalyst layer interferes with the adsorption of CO2RR intermediates, diminishing the C–C coupling at the Cu surface with limited active sites for ethylene production17. In light of this finding, we sought to identify, with the aid of DFT calculations, a catalyst candidate having abundant active sites to enable CO2 activation in MEA systems and facilitate the C–C coupling toward ethylene formation.

Si-based materials have been applied to facilitate CO2 hydrogenation; however, Si itself has been found to react irreversibly with CO2 by forming surface silanols (Si–OH) and siloxane (Si–O–Si) groups26,27. We instead considered silica, because it is more stable and is an efficient adsorbent material to capture CO228, besides it shows strong affinities to Cu29. We thus hypothesized that a Cu surface modified with silica could offer a new approach to CO2RR. Using DFT calculations we first introduced silica clusters at the Cu surface to establish a Cu-SiOx step surface configuration (Supplementary Fig. 1) and calculated the energetics of forming possible Cu-SiOx catalysts with various silica loadings (Supplementary Figs. 2–4 and Supplementary Table 1). We found a slight increase of the Si oxidation state from +1.9 to +2.4, as the silica concentration increases from 1/16 to 3/16 monolayer (ML) (i.e., 1.6–4.7%) (Fig. 1a).

We then investigated the first proton/electron transfer to CO2 (CO2(1gas) + H+ + e− ⇄ OCCOH−) with and without silica, a key step for CO2 activation (Supplementary Figs. 5–7). DFT results show that the Cu-SiOx catalyst significantly decreases the formation energy of OCCOH* up to ~0.7 eV compared to the bare Cu catalyst, due to the strong electronic interaction between Si and O/C in the OCCOH* intermediate (vide infra), indicating that a silica addition promises efficient CO2 activation.

We further calculated the formation energy of OCCOH* through the coupling of CO* and COH* (Fig. 1b), a key descriptor to enhance C2 production from CO2RR15,25. We examined the co-adsorption of CO* and COH* over the energetically favorable and metastable Cu-SiOx models (Supplementary Figs. 2–4) and found that all Cu catalysts, with and without silica, exhibit similar values (Supplementary Figs. 8–12), suggesting that the silica addition does not change the adsorption properties of CO* or COH*. However, various Cu-SiOx catalysts show a much higher adsorption energy of up to ~1.2 eV for the as-formed OCCOH* intermediate than the bare Cu catalyst (Supplementary Figs. 13–15). As a result, for the Cu-SiOx catalysts with equilibrium geometries, we found that increasing the silica loading up to 3.1% decreases the formation energy of OCCOH* by ~1.1 eV (Fig. 1b). A further increase of the silica concentration to 4.7% disfavors OCCOH* formation, showing reaction energy similar to that of bare Cu. This volcano-shaped dependence of the OCCOH* formation energy based on the silica loading suggests that a proper loading of silica on Cu could provide a means to construct active interface sites for improving C2.

To determine the role of silica in enhancing the OCCOH* adsorption at the Cu-SiOx step surface, we generated a differential charge density between OCCOH* and Cu-SiOx (at a silica
loading of 3.1%, Fig. 1c) in which silica loses electrons (blue) and the adsorbed OCCOH* gains electrons (yellow). For Si–C bond formation, the C¹ atom of the O=C²–C²–OH* intermediate has one electron in a \(sp^3\) orbital that bonds to Cu, while the C² atom makes more of a carbene and tends to bond more strongly to Si than Cu, increasing the adsorption energy of OCCOH* and thus decreasing the formation energy of OCCOH* up to 0.6 eV (Supplementary Figs. 16 and 17). A much stronger adsorption of OCCOH* over the Cu-SiOₓ catalyst is due to the formation of the Si–O bond between O²⁻ of the OCCOH* intermediate and silica at the Cu-SiOₓ step site, leading to an enhancement in the adsorption energy of OCCOH* and thus lowering the formation energy of OCCOH* up to ~1.2 eV (Supplementary Figs. 18 and 19).

When the silica loading is increased to 4.7%, the silica component energetically favors the formation a Si–O–Si layer, which fails to form Si–C or Si–O bond with the OCOH* and OCCOH* intermediates, due to the lack of unpaired electrons in Si. As a result, the Cu-SiOₓ catalyst shares similar adsorption energies of both the OCOH* and OCCOH* intermediates to the bare Cu catalyst (Supplementary Figs. 7 and 15). Collectively, the DFT calculations predict that introducing a silica addition at a loading of 3% could establish a stable Cu-SiOₓ catalyst before and after the reaction, showing an oxidation state of +2 and +1, respectively (denoted Cu-SiOₓ–M, where M represents the silica loading percentage) by varying the Si/Cu atomic ratio in the precursor solution. The silica loading was quantified by inductively coupled plasma optical emission spectrometry (ICP-OES, Supplementary Table 2).

Transmission electron microscopy and scanning electron microscopy images show nanoparticles in an aggregated form and a mean size of ~50 nm. The Cu morphology is unchanged with silica loading (Fig. 2a and Supplementary Fig. 20). The catalysts with/without silica loading lead to similar Cu patterns, seen in X-ray powder diffraction (XRD) measurements (Supplementary Fig. 21). We examined and compared the structure of the Cu-SiOₓ catalyst before and after CO₂RR using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray (EDX) mapping. We found that the Si species are evenly distributed on the Cu catalyst surface, and that the structure of Si species remains intact before and after the reaction, showing an oxidation state of +2 as revealed by X-ray photoelectron spectroscopy (XPS, Fig. 2b–f and Supplementary Figs. 22–27)³⁰. Using HAADF-STEM and XPS, we also characterized the Cu-SiOₓ catalysts with silica loadings of 2.5% (Figs. 2) and 5% (Supplementary Figs. 28–31), and found similar silica structures in both samples and detected no aggregation of silica, suggesting that silica clusters are uniformly distributed on the Cu surface. We note that characterizations of catalyst morphology were performed under ex-situ conditions.

Materials synthesis and characterization. We pursued a one-pot coprecipitation method to prepare the silica-modified Cu catalysts, dissolving silicon tetrachloride and copper chloride in ethanol. A Cu-SiOₓ catalyst was then coprecipitated by adding NaBH₄ directly into the precursor solution. We tuned the silica loading in the Cu structure from 0 to 5% (denoted Cu-SiOₓ–M, where M represents the silica loading percentage) by varying the Si/Cu atomic ratio in the precursor solution. The silica loading was quantified by inductively coupled plasma optical emission spectrometry (ICP-OES, Supplementary Table 2).

Transmission electron microscopy and scanning electron microscopy images show nanoparticles in an aggregated form and a mean size of ~50 nm. The Cu morphology is unchanged with silica loading (Fig. 2a and Supplementary Fig. 20). The catalysts with/without silica loading lead to similar Cu patterns, seen in X-ray powder diffraction (XRD) measurements (Supplementary Fig. 21). We examined and compared the structure of the Cu-SiOₓ catalyst before and after CO₂RR using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray (EDX) mapping. We found that the Si species are evenly distributed on the Cu catalyst surface, and that the structure of Si species remains intact before and after the reaction, showing an oxidation state of +2 as revealed by X-ray photoelectron spectroscopy (XPS, Fig. 2b–f and Supplementary Figs. 22–27)³⁰. Using HAADF-STEM and XPS, we also characterized the Cu-SiOₓ catalysts with silica loadings of 2.5% (Figs. 2) and 5% (Supplementary Figs. 28–31), and found similar silica structures in both samples and detected no aggregation of silica, suggesting that silica clusters are uniformly distributed on the Cu surface. We note that characterizations of catalyst morphology were performed under ex-situ conditions.
Although the extent of any catalyst reconstruction due to the potential removal after CO2RR is not expected to be major, the development of in-situ TEM capabilities will be useful to assess the impact of potential removal on catalyst reconstruction, if any.

Electrochemical CO2 conversion. We evaluated the CO2RR performance of the Cu-SiO2 catalysts in a 5 cm2 MEA electrolyzer (Fig. 3a), in which ethylene was produced according to the overall reaction of 2CO2 + 2H2O → C2H4 + 3O2 (E* = 1.15 V). In this system, a humidified CO2 feedstock was fed through the cathode without the presence of catholyte, and the Cu-SiO2 catalyst of interest was sandwiched between a PTFE gas diffusion layer and an anion exchange membrane (AEM) to enable sufficient CO2 reactants and abundant reaction interfaces, whereas 0.1 M KHCO3 aqueous solution was interfaced with anode catalysts (IrO2 coated onto a Ti mesh) to initiate the oxygen evolution reaction (OER). The ohmic loss was minimized, due to the absence of catholyte and direct contact between the catalyst and the AEM.

In a silica loading range of 0–5% on Cu, we found a strong correlation between the silica loading and ethylene formation (Fig. 3b and Supplementary Fig. 32). We observed a gradual increase in FEethylene and a decrease in FE CO with increasing silica loading up to 2.5%, whereas we noted a decrease in FEethylene with a further increase in the silica loading from 2.5 to 5%, accompanied by an enhancement in FE CO. The volcano relation between FEethylene and the silica loading agrees well with the volcano correlation between the formation energy of OCCOH and the silica loading ranging from 0 to 5% (equivalent to a silica coverage of 0–3/16 ML) predicted by DFT calculations (Fig. 1b). We observed that the total and hydrogen current densities do not vary significantly in the range of silica loadings tested (Supplementary Fig. 33), implying similar physical availability (i.e., mass transport) of CO2.

We then focused on the 2.5% silica-loaded Cu catalyst (Cu-SiO2-2.5) and observed that FEethylene of the Cu-SiO2-2.5 catalyst outperforms that of the bare Cu catalyst across the full-cell potential range of −3.0 V ~ −4.25 V (Fig. 3c). The Cu-SiO2-2.5 catalyst reaches a peak FEethylene of 65% at a cell potential of −4.1 V, whereas a peak FEethylene of 50% of the bare Cu catalyst is achieved at −4.2 V. The ethylene current densities of the Cu-SiO2-2.5 and bare Cu catalysts increase with increasing cell potential in the negative direction and peak at 215 and 160 mA cm−2 at cell potentials of −4.2 and −4.25 V, respectively (Fig. 3d).

This performance exceeds prior MEA reports with a two-fold enhancement in ethylene current density (Supplementary Table 3). The Cu-SiO2-2.5 catalyst shows considerably lower FE CO and CO current density than the bare Cu catalyst (Fig. 3e and Supplementary Fig. 34), in agreement with our DFT results that the silica addition facilitates the C–C coupling reaction (Fig. 1). A further analysis of liquid products (Fig. 3f), using 1H nuclear magnetic resonance (1H-NMR) spectroscopy, reveals that the Cu-SiO2-2.5 catalyst also yields lower FEs toward multicarbon oxygenate products (i.e., acetate, ethanol, and 1-propanol) than the bare Cu catalyst.

Investigating the Cu-SiO2 interaction. To understand the role of silica in promoting ethylene production at the Cu-SiO2 catalyst, we performed in-situ Raman spectroscopy (Supplementary Table 4). At a range of applied cell potentials from −1.5 to −2.0 V (Fig. 4a, b), we observed one band at 280 cm−1 on the bare Cu electrode starting from −1.8 V, attributable to the Cu-CO frustrated rotation at metallic Cu surface31,32. On the Cu-SiO2-2.5 electrode, the same band emerged at the cell potential of −1.8 V, together with the emergence of a new band at 365 cm−1. This additional band is due to the Cu–O stretch at the metallic Cu surface, indicating that a silica addition increases CO coverage at...
In addition, we also observed a strong band at 530 cm$^{-1}$ on the Cu-SiO$_x$ electrode throughout the cell potentials applied, which we attribute to the presence of Cu$^+$ promoted by the Cu–O–Si interaction.

To further assess the role of silica, we carried out in-situ Raman measurements on the Cu-SiO$_x$ catalysts (Supplementary Fig. 35). While we observed the stable Cu–O–Si band at 530 cm$^{-1}$ in both cases throughout the cell potentials applied, the Cu–O stretch band at 365 cm$^{-1}$ emerged at a cell potential of $-2.0$ V on Cu-SiO$_x$-1 and $-2.2$ V on Cu-SiO$_x$-5. This shift in onset potential of the 365 cm$^{-1}$ band indicates the tuning of CO content on Cu in response to silica loading. The Cu-SiO$_x$-2.5 catalyst shows the lowest onset potential of $-1.8$ V, suggesting the highest CO concentration at the Cu-SiO$_x$-2.5 catalyst surface during CO$_2$RR. This finding is consistent with our DFT predictions of the formation energy of OCOH*—an intermediate in CO$_2$-to-CO conversion—at the Cu-SiO$_x$ interface (Supplementary Figs. 5–7). The Cu-SiO$_x$ catalyst with optimal CO coverage at a silica loading of 2.5% accelerates the C–C coupling by lowering the formation energy of OCCOH* at the Cu-SiO$_x$ interface, facilitating the formation of ethylene (Fig. 1b).

To reveal the electronic interaction between Cu and silica, we conducted X-ray absorption spectroscopy (XAS) measurements at the Cu K- and Si K-edges of the Cu-SiO$_x$ catalysts. In-situ X-ray absorption near-edge structure (XANES) at the Cu K-edge shows the metallic nature of Cu active sites, corroborated by the extended X-ray absorption fine structure (EXAFS, Supplementary Fig. 36a–c). Although the presence of Cu$^+$ from the Cu–O–Si interaction is evidenced by in-situ Raman analysis, the Cu K-edge XAS recorded in fluorescence yield probes further into the bulk interactions.
The predominantly metallic Cu states of the Cu-SiO\textsubscript{x} catalysts revealed by XAS further supports our view that silica clusters are deposited at the surface of Cu nanoparticles. This finding is also in line with the HAADF-STEM results (Supplementary Fig. 27).

The Si K-edge XANES of the Cu-SiO\textsubscript{x} catalysts reveals an average +2 oxidation state of the Si species (Fig. 4c), with absorption onset energy (1s → 2p transition) and spectral characteristics analogous to the Si K-edge XANES of the molecular SiO deposited on highly oriented pyrolytic graphite, reported elsewhere\textsuperscript{35}. Increasing the silica loading on Cu from 1 to 5% results in an enhancement of the Si K-edge white-line intensity and a blue shift of the absorption onset (Supplementary Fig. 37). A broadening of the white line indicates an overall Si p-charge depletion due to charge redistribution at the Cu-SiO\textsubscript{x} interface with increasing silica loadings, and a positive energy

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**Fig. 4 Spectroscopy studies of the Cu-SiO\textsubscript{x} catalysts.**

- **a, b** In-situ Raman spectra of the bare Cu (a) and Cu-SiO\textsubscript{x}-2.5 (b) catalysts at a cell potential range of −1.5 ~ −2.0 V. Current density recorded at each condition is listed in Supplementary Table 4.
- **c** Ex-situ Si K-edge XANES spectra of different Cu-SiO\textsubscript{x} catalysts and the Si standards (i.e., Si wafer and SiO\textsubscript{2}).
- **d** The Si K-edge EXAFS spectra (solid lines) and corresponding fitting curves (open circles) of different Cu-SiO\textsubscript{x} catalysts. The Si K-edge EXAFS spectra of Si wafer and SiO\textsubscript{2} standards are included for comparison.
- **e** Simulated coordination number (e) and Si–Si bond distance (f) of different Cu-SiO\textsubscript{x} catalysts extracted from their Si K-edge EXAFS. In-situ Raman analysis was performed during CO\textsubscript{2}RR, whereas ex-situ Si K-edge XAS was measured upon completion of CO\textsubscript{2}RR at a full-cell potential of −4.1 V in 0.1 M KHCO\textsubscript{3}.
shift of Si 1s absorption onset suggests a potential increase of the Si oxidation state from the charge redistribution process.

The Si K-edge EXAFS of the Cu-SiO₂ catalysts shows a strong peak at 1.3 Å, attributable to the Si–O bond in the first shell of Si atoms (Fig. 4d). We fit the Si K-edge EXAFS spectra of different Cu-SiO₂ catalysts with the relevant DFT models having similar silica loadings. We found that the Si local structures (i.e., coordination number and bond distance) extracted from the EXAFS fitting align well with those obtained from the DFT models (Fig. 4d, Supplementary Fig. 38 and Supplementary Table 5), indicating a general agreement between experimental and computational trends herein. From EXAFS fits, we also found a decrease in the Si–Cu coordination from 3 to 2 with the silica loading increasing from 2.5 to 5% (Fig. 4e), indicating that an increase in the silica loading to 5% diminishes the interaction between Cu and silica. Increasing the silica loading from 2.5 to 5% also results in the growth of silica molecules, evidenced by an increase in the Si–O coordination from 2 to 3, an increase in the Si–Si coordination from 1 to 2, and a ~7% contraction in the Si–Si bond length from 3.0 to 2.8 Å (Fig. 4e, f).

Taken together, these results suggest that while Cu predominantly remains in a metallic state in the Cu-SiO₂ catalyst, the Si species preserve an oxidation state of ~+2 via Cu–O–Si interaction. An increase in the silica loading from 1 to 2.5% promotes the formation of stable Cu-SiO₂ interface sites with enhanced CO coverage to promote C–C coupling toward ethylene production, whereas a further increase in the silica loading to 5% diminishes the Cu and silica interaction due to the growth of silica molecules, destabilizing the Cu-SiO₂ interface and decreasing the CO content and therefore ethylene production on the electrode surface.

**System performance and catalyst stability.** To challenge the versatility of the Cu-SiO₂ catalyst, we assessed CO₂RR performance using dilute input gas streams with CO₂ concentrations in a range typical of flue gas36. We tested the CO₂RR performance of the Cu-SiO₂-2.5 catalyst across a cell potential window of −3.4 to −4.2 V by co-feeding CO₂ and N₂ gas feeds with the CO₂ concentrations ranging from 10 to 100%. We found that reducing the CO₂ concentration induces a slight decrease in current density (Supplementary Fig. 39), due to reduced CO₂ availability at the catalyst layer, evidenced by the increasing H₂ current densities at reduced CO₂ concentrations.

Regulating the CO₂ concentration in the full-cell potential window of −3.6 to −4.2 V results in a high FEethylene of >50% with varied FEH₂ and FEH₃ (Fig. 5a–c). At −3.6 V, we achieved a 52% FEethylene (15% FEH₂) with 10% CO₂ feed, in contrast to a 37% FEethylene with an increase of FEH₂ to 26% using 100% CO₂ at similar conditions. The sharp increase of FEH₂ at increasing CO₂ concentrations can be attributed to excessive local CO₂ in the catalyst layer, blocking active catalyst surface sites for C–O dimerization toward ethylene formation and promoting instead CO production17.

Increasing the potential to −4.2 V leads to a high FEethylene of 64% (13% FEH₃) with 100% CO₂ feed, whereas the FEethylene decreases to 30% with a dramatic increase of FEH₃ to 58% using 10% CO₂ at the same applied potential. A shift of product selectivity to H₂ at low CO₂ concentrations and at high negative potentials can be attributed to the CO₂ mass transport limitations (Fig. 5c and Supplementary Fig. 39). Taken together, these findings show that FEethylene increases when we constrain CO₂ availability, which can be linked to modulation of the surface coverage of *CO₂, *CO, and *H at the catalyst layer17. As a result, we achieve a high FEethylene from CO₂RR by tuning the local CO₂ concentration and applied potential/current density. Tuning conditions for high FEethylene and low cell potential, we achieve an 18% full-cell energy efficiency (EE) toward ethylene production across a broad range of CO₂ concentrations, 10–100% (Fig. 5d).

We also assessed the stability of the Cu-SiO₂-2.5 catalyst at different CO₂ concentrations to demonstrate stable selective ethylene electroproduction at industrial-scale reaction rates from various CO₂ feedstocks. We performed CO₂RR at 10, 40 and 100% CO₂ concentrations and achieved stable FEethylene of >60% at 125, 250, and 300 mA cm⁻², respectively, over the course of continuous 55-h operation (Fig. 5e and Supplementary Fig. 40). We noted fluctuations in the first 5 h of stability testing with high CO₂ concentrations, a phenomenon we attribute to forming stable cathode:AEM:anode interfaces and stabilizing rates of gas, ion, and water transports with the MEA.

**Discussion**

In this work, we show that introducing silica enables CO₂ activation and steers the reaction toward ethylene at the Cu-SiO₂ interface, at which silica might act as a dopant to promote Cu⁺ sites and the formation of Cu–Cu⁺ interface to assist C–C coupling4,37. However, in-situ Raman results show only two strong CO adsorption bands assigned to the metallic Cu–CO interactions. Neither any shifts of the Cu–CO Raman peaks nor additional Raman peaks related to the Cu²⁺–CO adsorption are observed on the Cu-SiO₂ catalyst. These findings suggest that the Cu⁺ sites promoted by silica deposition does not contribute to the CO adsorption, and the CO adsorption energetics do not change with and without silica addition, consistent with our DFT calculations (Supplementary Figs. 8–12). We, therefore, conclude that silica, in this case, acts as a structural promoter to assist the electrochemical CO₂-to-ethylene conversion at the Cu-SiO₂ catalyst interface.

To demonstrate the universality of our oxide modulation strategy, we theoretically assessed the role of GeOₓ—an analogous oxide to silica—on the C–C coupling reaction at the Cu-GeOₓ interface (Supplementary Figs. 41 and 42). By changing the GeOₓ loading ranging from 0 to 5%, we find a similar volcano-shaped dependence of the OCCOH* formation energy based on the GeOₓ loading. The Cu catalyst with a GeOₓ loading up to ~3% decreases the OCCOH* formation energy by ~0.6 eV compared to the bare Cu catalyst, which we attributed to the formation of the Ge–O bond between O³⁻ of the OCCOH* intermediate and GeOₓ at the Cu-GeOₓ interface.

In summary, we show an efficient oxide modulation strategy that modifies the activity and intermediate binding characteristics of Cu catalysts by creating active Cu-SiO₂ surface step sites. The MEA electrolyzer equipped with the Cu-SiO₂ catalyst enables FEethylene of >60%, current densities of up to 300 mA cm⁻², ethylene full-cell EEs of 18%, and continuous stable operation of 55 h with a wide range of input CO₂ concentrations (10–100%). With the aid of spectroscopic and electrochemical tools as well as DFT calculations, we reveal that the silica addition can decrease the formation energies of OCCOH* and OCCOH⁺ by forming strong Si–O or Si–C bonds at a stable Cu-SiO₂ step site, and thereby accelerate ethylene production. The improved reaction energetics achieved in the oxide-promoted Cu catalyst would motivate new catalyst design strategies for CO₂RR.

**Methods**

**DFT calculations.** Density functional theory calculations were carried out with the Vienna Ab Initio Simulation Package (VASP) code30,39. Perdew–Burke–Ernzerhof (PBE) functionals40 were used to treat the exchange-correlation interactions, and the projector-augmented wave (PAW) method41 was used to solve the ion-electron interactions in the periodic system. All the configurations were first optimized under vacuum calculations and then converged under implicit solvation conditions. Details of DFT calculations were included in Supplementary Note 1.
Catalysts preparation. For the synthesis of 2.5% silica-loaded Cu catalysts, 0.5984 g of CuCl2·2H2O (Sigma-Aldrich, ACS reagent, ≥ 99.0%) was dissolved into 180 mL ethanol under magnetic stirring. Then 90 μL of silicon tetrachloride (Sigma-Aldrich, 99.998% trace metals basis) was injected into the Cu(II) solutions. Afterward, 0.6 g of sodium borohydride (Sigma-Aldrich, powder, ≥ 98.0%) dispersed in 120 mL of ethanol was added into the above-mentioned solution under stirring. The color of the solutions changed from blue to darkish. After stirring for 5 min, precipitates formed in the solution were kept for 30 mins and then centrifuged. The as-prepared Cu-SiO_x precipitates were washed with ethanol under intense ultrasonication at least three times to remove all unreacted reagents. The Cu-SiO_x catalysts were then dried under vacuum at room temperature overnight.

The silica-loaded Cu catalysts with different Si/Cu ratios of 0, 0.01, and 0.05 were synthesized by following a procedure similar to that described above, except for changing the amount of silicon tetrachloride.

Materials characterization. A Hitachi S-5200 SEM/STEM operating at 1 kV was employed to analyze the surface morphology of catalysts. TEM analysis was performed using a Hitachi HF-3300 instrument with an acceleration voltage of 300 kV. An aberration-corrected FEI Titan 80–300 equipped with a CEOS probe and image corrector was used for high-resolution TEM images and EDX. The microscope was operated at an acceleration voltage of 200 kV and STEM micrographs were captured using a HAADF detector (Fischione). The microscope was equipped with four-quadrant windowless silicon drift detectors EDX (Super-X) which increased the angle of collection, and hence, collection efficiency. During EDX mapping, the electron beam used for STEM imaging was rastered over the particles and the characteristic X-rays (resulting from electron-matter interaction) were collected by EDX detectors (four of them available in this microscope). For each EDX map, the area was exposed to the electron beam for 10–15 min, depending on the number of counts collected and the qualitative signal-to-noise ratio. In general,
once the overall number of counts (detected X-rays) reached ~0.5 million (depending somewhat on the area size and elements), the maps and the elemental signals were clear. The Agilent SII ICAP-OES system was employed to determine the elemental composition. P-XRD was performed on a MiniFlex600 instrument with a copper target (λ = 1.54056 Å) at room temperature. XPS measurements were carried out on a K-Alpha XPS spectrometer (PHI 7000 ESCA System), using Al Kα X-ray radiation (1486.6 eV) for excitation. In-situ XAS measurements at the Cu K-edge were carried out at the 9BM beamline of Advanced Photon Source (APS, Argonne National Laboratory, Lemont, Illinois, USA) using a home-made flow cell. Ex-situ Si K-edge experiments were conducted at the Soft X-ray Microcharacterization Beamline (SRXMB) of the Canadian Light Source (CLS, Saskatchewan, Canada) by sequencing samples in Kapton tape after the CO2RR testing and vacuum drying. Ex-situ XAS measurements at the Cu K-edge were also recorded at the SRXRB beamline together with ex-situ Si K-edge testing to exclude material oxidation from ex-situ measurements (Supplementary Fig. 43). Fluorescence yield was recorded using silicon drift detectors at both the 9BM and SRXMB beamlines. XANES data were analyzed using Athena software included in a standardized IFEFFIT package43. EXAFS fittings were performed using the IFEFFIT software included in the IFEFFIT package. In-situ Raman experiments were performed using Renishaw via Raman microscope in a home-made flow cell (Supplementary Fig. 44) with a water immersion objective. During testing, CO2 with a constant flow rate of 20 sccm flowed through the gas compartment, whereas 0.1 M KHCO3 solution with a flow rate of 0.2 mL min−1 flowed through the electrolyte compartment. A Pt wire was used as the counter electrode, and a 785-nm laser was used for Raman testing. Signals were recorded using a 5× integration and averaging ten scans.

Electrode preparation. The cathodes were manufactured via a two-step fabrication procedure. The first step was evaporating Cu (Kurt J. Lasker Company) on a polytetrafluoroethylene (PTFE) substrate at a constant sputtering rate of 0.45 Å s−1 at 10−7 Torr until the sputtering thickness of 150 nm was achieved. The second step was spray-depositing a homogeneous ink of Cu catalysts, polymer binder (Aquivion, D79-25BS), and methanol until the catalyst loading of 1.25 mg cm−2 was achieved. The anodes for the OER were manufactured via a five-step fabrication procedure. The procedure involved (i) etching the titanium (Ti) mesh (Fuel Cell Store) in 5 M HCl at 70 °C for 30 min, (ii) preparing a catalyst ink of iodium (III) oxide dehydrate (Alfa Aesar, 99.99%), 2-propanol and HCl (iii) immersing the etched Ti mesh into the catalyst ink for 30 s, (iv) drying and sintering the resulting Ti meshes for 15 min at 100 and 500 °C, respectively, and (v) repeating the immobilizing, drying, and sintering steps until the total TiO2 loading of 1.5 mg cm−2 was achieved.

CO2RR electroreduction. The CO2RR performance assessments of the cathode Cu-SiO2 catalysts were made via a custom-made electrochemical test station. The station was equipped with a potentiostat and booster, CO2RR electrolyzer (a membrane electrode assembly electrolyzer purchased from Dioxide Materials), anolyte (0.1 M KHCO3) and reactant (CO2) over the electrolyte compartment. A Pt wire was used as the counter electrode, and a 785-nm laser was used for Raman testing. Signals were recorded using a 5× integration and averaging ten scans.

Data availability
The data that support the findings of this study are available from the corresponding author on reasonable request.

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Author contributions

E.H.S. and D.S. supervised the project. J.L. and A.O. conceived the idea, carried out all the experiments, and wrote the manuscript. F.C. supervised and M.W. performed the DFT simulations and both wrote the corresponding sections. Z.Y.W. assisted the DFT discussion. J.L. and Y.F.H. performed and analyzed synchrotron data. A.O. and J.L. performed the in-situ Raman measurements. Y.H.W., R.Z., D.R., and B.C. assisted in SEM and TEM analysis. D.-H.N. and J.W. conducted XRD and XPS measurements. F.W.L., Y.X., W.M.C., and M.G. assisted in electrochemical experiments and analysis. All authors discussed the results and assisted during manuscript preparation.

Competing interests

The authors declare no competing interests.

Additional information

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