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Boosting CO₂ electroreduction to multicarbon products via tuning of copper surface charge

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ABSTRACT: Electrochemical CO₂ reduction (ECR) to multicarbon compounds holds great potential but remains plagued with large overpotential, low faradaic efficiency (FE), and debilitating competition from the evolution of hydrogen and C₁ product. The design and development of advanced catalytic systems is required to overcome these problems. Here we demonstrate the selective cathodic CO₂ conversion to C₂₊ chemicals (C₂H₄, C₂H₅OH, and *n*-C₃H₇OH) by optimizing the surface charge of Cu via fine-tuned annealing of CuSiO₃@SiO₂. Stabilization of Cu⁺ by forming Cu–O–Si bonds is attained, as predicted by density functional theory (DFT) calculations and evidenced by multiple experiments. The C₂₊ selectivity is readily regulated by adjusting the surface content of Cu⁺, underpinning its significance during the ECR. The resulting Cu^{δ+}@SiO₂ with a Cu⁰-to-Cu⁺ surface ratio of ~0.5 achieves a remarkable C₂₊ FE as high as ~70%, C₂₊ partial geometric current density of about 9.0 mA cm⁻², and large C₂₊-to-C₁ ratio of ~10, using an H-type cell in aqueous CsBr electrolytes at mild overpotentials. The high C₂₊ FE and current density persist over 12 h of continuous CO₂ electrolysis. In addition, a respectable C₂₊ FE of ~52% can still be attained even under a large current density (500 mA cm⁻²) in a flow reactor system. DFT computations reveal that the oxidized copper species Cu⁺ boosts C–C coupling by lessening the formation energy of the key *OCCOH intermediate. This work underscores the prominent role of support-catalyst interaction and the modulation of Cu oxidation states in steering the ECR selectivity.

INTRODUCTION

The continued consumption of fossil fuels and accompanying excessive CO₂ emissions, with projections that atmospheric CO₂ levels could reach nearly 600 ppm by 2100, have intensified risks from global warming.¹⁻³ To overcome these disruptive consequences and avoid a potential tipping point, we should try to prevent global temperatures rising beyond 2 °C above pre-industrial levels, and instead work to an aspirational 1.5 °C limit. Thus much endeavour has been focused on the capture and utilization of CO₂.⁴ Electrochemical CO₂ reduction (ECR), powered by renewable energy, provides an appealing route to convert the abundant carbon source (CO₂) into fuels and valuable chemicals, which can close the anthropogenic carbon cycle and also facilitate an energy sector transformation that more sustainably handles CO_2 emissions.^{5–8} Compared to C_1 compounds, C_{2+} (composed of two or more carbon atoms) hydrocarbons and oxygenates, such as ethanol (C₂H₅OH), ethylene (C_2H_4), and *n*-propanol (*n*- C_3H_7OH), are more intriguing owing to their higher energy densities and economic value, and crucially their widespread uses as feedstocks in chemical industry.⁹ However, it is still challenging to efficiently catalyze ECR to C_{2+} species due to 1) the parasitic proton or water reduction reaction in proton solvents (that occurs concurrently and competitively under similar or even lower overpotentials); 2) the sluggish kinetics of the C-C coupling and its high activation barrier; 3) the ubiquitous competition of C-C bonding with single C-O and C-H bond creation; and 4) the potential gap between C_{2+} products and the essential *CO (* denotes the adsorption site) intermediate species.¹⁰

Similar surface–C bonds are formed regardless of the varied ECR intermediates (e.g., *CO, *COOH, and *COH),¹¹ rendering it challenging to tailor for the adsorption affinity of one intermediate without impacting the others in light of the Sabatier principle. Cu possesses a unique capacity to catalyze the deep reduction of CO₂ to valuable C_{2+} products because it has a suitable *CO adsorption energy (neither too weak nor too strong), enabling an adequate coverage for further stepwise transformation.¹¹ However, the corresponding activation barriers also rise with an increase in *CO binding. To circumvent such energetic linearity constraints, optimization of the binding energy of *CO is required for efficient CO₂-to-C₂₊ conversion. Protocols such as heteroatom doping,^{12,13} alloying,¹⁴ structure (e.g., morphology and exposed facet) alteration,^{15,16} oxidation treatment,¹⁷ and surface/interface modification^{18–21} have been employed to regulate the electronic properties of Cu and improve its performance for C₂₊ formation. Despite much effort devoted in this regard, the efficiency and selectivity of CO₂ to C₂₊ products are still unsatisfactory, largely owing to the formidable C–C coupling barriers.

Prior literature suggests that Cu^+ can work cooperatively with Cu^0 to boost C_{2+} formation.²² Specifically, Cu^0 can promote CO_2 activation by reducing the thermodynamic energy barrier, while Cu^+ facilitates stronger adsorption of *CO, thereby jointly enhancing C–C coupling. From this scenario, some protocols have been developed to stabilize Cu^+ under reducing potentials, such as oxygen plasma treatment, elemental doping, electro-redeposition, and engineering of mixed metal oxide interfaces.^{17,22} Varied mechanisms were put forth to elucidate the stabilization of Cu^+ . The highly roughened surfaces with low-coordinated regimes and strains in the surface are speculated to bind oxygen strongly, thereby stabilizing Cu_2O during the ECR reaction.²³ Alternatively, the high local pH generated during the ECR could negatively shift the overpotential for Cu_2O reduction to help stabilize Cu^+ .²⁴ Among other strategies, introducing a reducible oxide such as CeO_2^{20} and ZrO_2^{19} can act as an "oxygen store" and release oxygen to inhibit the reduction of Cu^+ . Nonetheless, Cu^+ ions are unstable and prone to being reduced under ECR conditions, consequently degrading the C–C coupling for C_{2+} production. Additionally, the optimal Cu^0 -to- Cu^+ ratio for maximizing the ECR to C_{2+} products is unknown, warranting further exploration.

In this work, we report manipulating C_{2+} selectivity by tailoring the surface concentrations of oxidized and reduced Cu species on silica. SiO₂ is selected as a support since it is stable and also exhibits a remarkable CO₂ adsorption ability.^{25,26} Besides, it possesses strong affinities to Cu. Cu⁺ is found to be effectively protected against reduction by forming Cu–O–Si bonds, as suggested by density functional theory (DFT) computations combined with a range of experiments. An optimized balance between Cu⁺ and Cu⁰ for C–C coupling is achieved, giving rise to a marked improvement in faradaic efficiency (FE) toward forming C₂₊ products, reaching as high as ~70% with a C₂₊ selectivity exceeding 90% at –1.1 V versus the reversible hydrogen electrode (*vs.* RHE). This is among the most competitive ECR performances over Cu-based electrocatalysts for C₂₊ production in H-cells (Table S1). Equally importantly, the C₂₊ FE remains at a high level of ~52% even at a large current density of 500 mA cm⁻² in a flow cell. Further DFT calculations reveal that the existence of Cu⁺ substantially lowers the Gibbs free energies for the generation of the key intermediate *OCCOH, thus favoring the CO₂-to-C₂₊ conversion.

RESULTS AND DISCUSSION

DFT calculations were first performed on optimized structures to explore the electronic properties of $Cu^{\delta+}@SiO_2$ for enhanced ECR. It is recognized that the generation of *CO intermediate is essential to obtain multicarbon products *via* dimerization and/or trimerization pathways. Therefore, the relevant reaction barriers are investigated. For C–C coupling, the reaction barrier on the $Cu^{\delta+}@SiO_2$ surface was calculated to be 0.62 eV, which is markedly lower than that of $CuSiO_3@SiO_2$ (1.36 eV) (Figure

1A). This suggests that the ECR activity toward C_{2+} products can be enhanced by introducing an appropriate content of Cu⁺. As presented in Figure 1B, the free energy change of H adsorption ($\Delta G(*H)$) on Cu^{$\delta+a$}@SiO₂ and CuSiO₃@SiO₂ are determined to be 0.32 and -0.1 eV, respectively, implying that the parasitic hydrogen evolution reaction (HER) is greatly suppressed on Cu^{$\delta+a$}@SiO₂ relative to CuSiO₃@SiO₂.

CuSiO₃@SiO₂ shows semiconducting electronic properties by DFT modelling (Figure 1C). In contrast, the integrated densities of states (DOS) of Cu^{$\delta+$}@SiO₂ is predicted to be close to the Fermi level, signifying the role of the created catalyst-support interface and the strikingly improved electron transfer. The convoluted Cu *d*-band center (*E_d*) of Cu@SiO₂ is calculated to be -2.489 eV. Based on the *d*-band center theory, the optimized binding energy should not be too high or too low, and the binding strength between adsorbate and adsorbent should be closely associated with the highly localized metal *d* states. Meanwhile, the total occupied electrons (Ne) of the Cu *d* band in Cu^{$\delta+$}@SiO₂ is larger (582) relative to that of CuSiO₃@SiO₂ (450), implying an optimized adsorption energy (Figure 1C). We also found that the Cu total charge gradually decreases but the O total charge increases in both Cu^{$\delta+$}@SiO₂ and CuSiO₃@SiO₂, indicating charge accumulation around the O side (Figure 1D), consistent with the charge distribution map of Cu^{$\delta+$}@SiO₂ and CuSiO₃@SiO₂ (SI Figure S1A,B). Compared with CuSiO₃@SiO₂, the lower valence copper species in Cu^{$\delta+}$ @SiO₂ is better for C-C coupling. This electronic analysis points to the interactions among Cu, O, and Si, and that the formed Cu–O-Si bond can protect the Cu⁺ from further reduction.</sup>



Figure 1. The Gibbs free energy diagrams for (A) *OCCO formation and (B) HER on $Cu^{\delta+}@SiO_2$ and $CuSiO_3@SiO_2$. (C) Comparison of PDOS of the Cu d-band for $Cu^{\delta+}@SiO_2$ and $CuSiO_3@SiO_2$. (*E*-*E*_F) refers to the energy relative to the Fermi level. (D) Computed Bader charges of Cu, O, and Si atoms in $Cu^{\delta+}@SiO_2$ and $CuSiO_3@SiO_2$.

To validate the prediction of the DFT calculations, we prepared Cu supported on SiO₂ with tailored surface Cu charges by reaction of SiO₂ with cupric acetate (Cu(CH₃COO)₂·H₂O), followed by thermal treatment in 8% H₂/Ar at different temperatures. The resulting Cu^{$\delta+a$}@SiO₂ was first characterized by X-ray diffraction (XRD) (Figure 2A). Apart from the typical reflections from SiO₂ (JCPDS no. 43–0784), another two diffraction peaks at 42.6 and 43.3° were discernible, which could be assigned to the (200) plane of Cu₂O (JCPDS no. 34–1354) and (111) plane of Cu (JCPDS no. 04–0836),

respectively. The diffraction peaks are weak in intensity, indicating the high dispersion of the formed Cu species on the surface of SiO₂. Upon elevating the annealing temperature, the diffraction peaks became more intense indicating the increased content of crystalline Cu⁺ and Cu⁰. The formation of Cu⁺ in Cu^{$\delta+a$}@SiO₂ was also observed by Raman spectroscopy whereas only Cu²⁺ exists in CuSiO₃@SiO₂ before annealing (Figure 2B). The peak at ~677.2 cm⁻¹corresponds to the A_g mode while the band at ~380.1 cm⁻¹ is related with the B_{2g} mode of CuSiO₃.²⁷ The Raman bands at ~295.5 and 603.1 cm⁻¹ are attributed to Cu⁺ species promoted by the Cu–O–Si interaction, which became more intense with increased annealing temperature.²⁸ This verifies that CuSiO₃ was partially converted to Cu₂O, consistent with the aforementioned XRD results.

The surface oxidation state of Cu species was further analyzed by X-ray photoelectron spectroscopy (XPS) (Figure 2C,D and SI Figure S2). The wide-scan XPS spectra of $Cu^{\delta+}@SiO_2$ and $CuSiO_3@SiO_2$ reveal the existence of Cu, O, and Si elements without other impurities in the samples (SI Figure S2). A spin-orbit split doublet with binding energies (BEs) at ~955.6 (Cu $2p_{1/2}$) and 935.6 eV (Cu $2p_{3/2}$) originating from Cu^{2+} moieties (Figure 2C) was observed for $CuSiO_3@SiO_2$ and $Cu^{\delta+}@SiO_2$ samples.¹⁹ There also exist three pronounced Cu^{2+} satellites with BEs at ~942.2, 944.2, and 963.1 eV.¹⁹ For $Cu^{\delta+}@SiO_2$, a doublet with BEs at ~952.5 (Cu $2p_{1/2}$) and 933.1 eV (Cu $2p_{3/2}$) could be identified, corresponding to Cu^+ species.¹⁹ The surface concentration of Cu^+ is seen to increase upon raising the annealing temperature. The Cu LMM Auger primary excitation spectra (Figure 2D) confirm the presence of both Cu^+ and Cu^0 with characteristic BEs of ~571.1 and 568.8 eV, respectively. The additional peak at ~574.5 eV originates from Auger transitions involving Cu^+ .¹⁸ The surface fraction of Cu^{2+} , Cu^+ , and Cu^0 species were determined by the corresponding ratio of the peak areas relative to the overall Cu oxidation states in the Cu 2p and Cu LMM regimes. Upon elevating the annealing

temperature from 200, 250 to 300 °C, the Cu⁰-to-Cu⁺ increased from 0.45, 0.5 to 1.21. This allows for tuning of the Cu⁰/Cu⁺ interface for optimizing ECR performance.



Figure 2. (A) XRD patterns, (B) Raman, (C) Cu 2p XPS, and (D) Cu LMM Auger electron spectra of CuSiO₃@SiO₂ (unreduced) and Cu^{$\delta+$}@SiO₂ obtained at 200, 250, and 300 °C.

The morphology and crystallography of the resulting samples were deciphered by aberrationcorrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) along with energy-dispersive X-ray spectroscopy (EDS). As shown in Figure 3A, a large density of interconnected Cu and Cu₂O nanoparticles with a diameter of about 3 nm (SI Figure S3) are homogeneously distributed on the surface of SiO₂ spheres of 300 nm in diameter. The high exposure of Cu species as well as the created intact interface between Cu and SiO₂ support provide benefits for access of reactants/intermediates and also desorption of products. The EDS maps of Cu^{$\delta+}@SiO₂$ reveal the good dispersion of Cu species mainly on the outer layer of SiO₂, as displayed in Figure 3B–D. High-resolution STEM images (Figure 3E,F) together with fast Fourier transform (FFT) (inset of Figure 3E) show good crystalline nature of the nanoparticles. Most Cu crystals are observed to be in close contact with Cu₂O nanoparticles, resulting in large interfaces (Figure 3F). The interplanar spacing fringes of ~2.1 and 2.5 Å illustrated in Figure 3F can be ascribed to the (111) planes of monoclinic Cu and cubic Cu₂O, respectively. A relatively bigger lattice distance of >3.7 Å was also seen, which is likely due to the nonstoichiometric Cu–O–Si species (SI Figure S4).</sup>



Figure 3. (A) HAADF-STEM image of $Cu^{\delta+}@SiO_2$ obtained at 250 °C. EDS elemental maps of (B) Si, (C) Cu, and (D) overlapped Si and Cu. (E,F) High-resolution STEM images of $Cu^{\delta+}@SiO_2$ obtained at 250 °C. The inset of (E) denotes the FFT of the region of the image.

The generation of Cu–O–Si was verified by Si magic angle spinning nuclear magnetic resonance (²⁹Si MAS NMR), where a chemical shift of Si occurred when the surface Si–OH was replaced by Cu– O–Si entities (SI Figure S5). This indicates the marked Cu–O–Si interfacial interactions which also facilitates uniform dispersions of Cu species.

The ECR properties of the resulting $Cu^{\delta+}$ @SiO₂ were evaluated in a standard H-type reactor cell, separated by a Nafion 117 membrane under continuous CO₂ bubbling using 0.1 M KHCO₃ as catholyte and 0.1 M H₂SO₄ as anolyte (unless stated otherwise).²⁹ The gas products were identified by gas chromatography (GC), and the liquid products were detected by proton nuclear magnetic resonance

(¹H NMR). The applied potentials are all referred to the RHE scale, unless specified otherwise. Linear sweep voltammetry (LSV) plots of $Cu^{\delta+}$ @SiO₂-250 and CuSiO₃@SiO₂ in Ar- and CO₂-purged 0.1 M KHCO₃ solutions are given in Figure 4A. Both samples exhibit larger current densities in a CO₂environment rather than when under an Ar condition over the entire potential window (from -0.2 to -1.4 V), implying the occurrence of CO₂ reduction. Notably, Cu^{$\delta+a$} @SiO₂-250 imparts substantially higher reduction currents than CuSiO₃@SiO₂, indicating its superior ECR activity. Moreover, constant potential polarization was conducted in the voltage regions from -0.85 to -1.25 V with an interval of 0.05 V for 1 h. The FE_{C2+} displays a volcano-type dependence on applied potential (Figure 4B). Note that C₂H₅OH is attained at a potential of -0.85 V on Cu^{$\delta+a$} SiO₂-250, in stark contrast to CuSiO₃@SiO₂ that produces C_2H_5OH at a more negative bias (-1 V). Through the voltage range from -0.85 to -0.95 V, the only liquid product detectable is HCOOH on CuSiO₃@SiO₂ (SI Figure S6). C₂H₄ is generated at potentials below -1 V on Cu^{$\delta+$} @SiO₂-250 with a lower onset overpotential than CuSiO₃@SiO₂. Especially, some amounts of *n*-propanol (FE_{*n*-C3H7OH} \approx 6.3% at -1 V) were obtained on Cu^{$\delta+$}@SiO₂-250 whereas no C₃ products were detected on CuSiO₃@SiO₂. The as-made Cu^{δ +}@SiO₂-250 achieves a maximum FE_{C2+} of ~53.1% at -1.1 V (Figure 4B), accompanied with the highest partial C₂₊ geometric/mass current density (~3.9 mA cm⁻²/mA mg⁻¹, Figure S7A) and C₂₊ production rate (~32.7 µmol mg_{cat.}⁻¹ h⁻¹, Figure S7B), remarkably exceeding CuSiO₃@SiO₂. Evidently, the partial current density resulting from H₂ evolution on $Cu^{\delta+}$ @SiO₂-250 was markedly lower than that of CuSiO₃@SiO₂ (Figure 4C), consistent with the DFT results (Figure 1B). Furthermore, we calculated the C_{2+} cathodic energy efficiency (EE) from the C_{2+} FE and the ratio of the reaction thermodynamics over cell voltage. $Cu^{\delta+}$ @SiO₂-250 was observed to display higher C₂₊ cathodic EE than CuSiO₃@SiO₂ through all the potentials applied. A C₂₊ cathodic EE of up to ~26.6% on Cu^{$\delta+a$} @SiO₂-250 was accomplished at -1.1 V (Figure 4D). Under identical electrochemical conditions, $Cu^{\delta+}$ @SiO₂-250 also dramatically outperforms commercial Cu, CuO, Cu₂O, and Cu(OH)₂ in terms of C₂₊ FE, C₂₊ geometric/mass current density, and C₂₊ production rate (PR) (Figure 4E and SI Figure S8). The stability of $Cu^{\delta+}@SiO_2-250$ was evaluated by performing constant potential electrolysis at -1.1 V for 12 h. Note that Cu^{$\delta+$}@SiO₂-250 retains a nearly unchanged C_{2+} FE with 90% of its original current density even after 12 h of continuous CO₂ electrolysis, demonstrating its good durability (Figure 4F). To further validate the ECR occurs at the catalyst surface, identical potentiostatic measurements were conducted in a N₂purged electrolyte, and no ECR products were detectable by the GC and NMR at any voltage. Electrochemical impedance spectroscopy (EIS) measurements (Figure 4G) reveal a smaller chargetransfer resistance (R_{ct}) for Cu^{$\delta+$} @SiO₂-250 than for CuSiO₃@SiO₂, indicating its faster charge transfer rate and catalytic kinetics, eventually leading to the enhanced FE for ECR. Tafel plots (Figure 4H) based on the C₂H₄ partial current densities show that $Cu^{\delta+}$ @SiO₂-250 exhibits a drastically lower Tafel slope of 194.9 mV dec⁻¹ as compared to CuSiO₃@SiO₂'s 359.9 mV dec⁻¹, implying faster kinetics of CO₂ reduction on Cu^{δ +}@SiO₂. The partial C₂₊ products current density of Cu^{δ +}@SiO₂-250 normalized according to the electrochemical active surface area (ECSA) as reflected by double-layer capacitance (C_{dl}) (SI Figure S9), is higher than that of pure CuSiO₃@SiO₂, indicative of the superior intrinsic catalytic performance of $Cu^{\delta+}$ @SiO₂-250. Cycling assays by alternated polarization between Ar- and CO₂-purged catholytes signify that the C_{2+} FE can be maintained almost constant for at least 4 cycles (Figure 4I). This also supports that the C_{2+} produced originates from the feed gas CO_2 . We attempted to understand the influence of Cu surface charge on the ECR. We found that the ECR performance based on the metrics of C₂₊ FE, C₂₊ partial current density, and C₂₊ production rate (Figure 4J and SI Figures S10,S11) showed a volcano trend with the Cu⁰-to-Cu⁺ surface ratio and was maximized at the Cu^{0} -to- Cu^{+} surface ratio of 0.5.

We also investigated the effects of catholytes on ECR and obtained the trend of $Cs^+ > K^+$ and $Br^- > Cl^-$ based on the metrics of C_{2+} FE and partial current density. Strikingly, the C_{2+} FE (Figure 4K)

reached up to ~70% with a C₂₊ partial geometric current density of ~9.0 mA cm⁻² at -1.1 V with 0.1 M CsBr solutions (as both catholyte and anolyte), about 1.3 and 2.3 times that of 0.1 M KHCO₃ (as catholyte and 0.1 M H₂SO₄ as anolyte), respectively (SI Figure S12). This can be ascribed to the smaller cation radius of Cs⁺ and thus higher buffering capacity to offset the increase in local pH, thereby decreasing the loss of local CO₂ concentration during the reduction.¹¹ Meanwhile, halogen ions adsorbed on the electrode facilitate electron transfer to the empty orbital of CO₂, weakening the C–O bond for CO₂ activation.³⁰ It is also proposed that the adsorbed halide anions could impede proton adsorption, resulting in a larger hydrogen overpotential.³⁰ The superior ECR with Br⁻ compared to Cl⁻ is associated with the higher strength of the bond between adsorbed Br⁻ and working electrode.³⁰ Furthermore, the ECR was performed in a flow cell to facilitate the rapid diffusion of CO₂ to catalyst surface, and also alleviate the weak solubility and low diffusivity coefficient of CO₂ in water. Large current densities of over 700 mA cm⁻² were thus easily achieved in a flow reactor using 1 M aqueous KOH as the electrolyte, with the C₂₊ FE on Cu^{δ +} @SiO₂ approaching 52% at 500 mA cm⁻² (Figure 4L). Moreover, the catalyst loading was optimized at -1.1 V. It was found that the best performance regarding the C₂₊ FE was achieved with a catalyst loading of 1 mg cm⁻² (SI Figure S13A). This can be attributed to both the homogeneous dispersion of the catalyst and full coverage of the carbon paper at this catalyst loading level. To further probe the C–C coupling barrier over $Cu^{\delta+}$ @SiO₂-250 and CuSiO₃@SiO₂ experimentally, the electrochemical reduction of CO was performed (SI Figure S13B). C_2H_4 product started to form over $Cu^{\delta+}@SiO_2-250$ at a potential as low as -0.4 V while no product was detected over CuSiO₃@SiO₂. Through the voltage range from -0.4 to -0.8 V, Cu^{$\delta+$}@SiO₂-250 exhibited superior C₂H₄ FE with a maximum value of ~35.4% at -0.6 V, 1.8 times that of CuSiO₃@SiO₂. The results suggested that Cu^{$\delta+$}@SiO₂-250 could lower the C–C coupling barrier for the yield of C_{2+} products, which was in accordance with the DFT results (Figure 1A).



Figure 4. (A) LSV curves of $Cu^{\delta+}@SiO_2-250$ and $CuSiO_3@SiO_2$ in 0.1 M KHCO_3 solution purged with Ar (dashed line) or CO₂ (solid line). The scan rate is 5 mV s⁻¹. (B) C₂₊ FE against switched voltage on Cu^{$\delta+$}@SiO₂-250 (solid column) and CuSiO₃@SiO₂ (striped column). (C) Partial current density for H₂ and (D) C₂₊ cathodic EE on Cu^{$\delta+$}@SiO₂-250 and CuSiO₃@SiO₂ at various applied voltages. (E) C₂₊ FE and C₂₊ production rate over Cu^{$\delta+$}@SiO₂-250, commercial Cu, Cu₂O, CuO, and Cu(OH)₂. (F) Geometric current density- and C₂₊ FE (inset)-time responses of Cu^{$\delta+$}@SiO₂-250 for ECR at -1.1 V. (G) EIS profiles and (H) Tafel plots for C₂₊ production along with corresponding fitting lines on Cu^{$\delta+$}@SiO₂-250 and CuSiO₃@SiO₂. (I) C₂₊ FE (bar) and partial geometric current density (circle) for Cu^{$\delta+$}@SiO₂-250 versus alternate cycle with an interval of 1 h in CO₂- and Ar-saturated 0.1 M KHCO₃

at -1.1 V. (J) C₂₊ FE and partial geometric current density over different surface Cu⁰-to-Cu⁺ at -1.1 V. (K) C₂₊ FE over Cu^{δ^+} @SiO₂-250 in different 0.1 M electrolytes as both catholyte and anolyte at -1.1 V. (L) C₂₊ FE of Cu^{δ^+} @SiO₂-250 at different current densities from 100 to 700 mA cm⁻² in a flow cell using 1 M aqueous KOH as both catholyte and anolyte.

To monitor catalyst structural alteration and gain information on reaction intermediates during ECR, operando Raman spectroscopy was conducted. In the spectra obtained at the open-circuit potential (OCP), $Cu^{\delta+} @SiO_2-250$ and $CuSiO_3 @SiO_2$ display prominent signals at ~286.9, 363.0 cm⁻¹ and ~338.7, 675.8.0 cm⁻¹ assigned to $CuSiO_3$ (SI Figure S14). For $CuSiO_3 @SiO_2$, the peaks are retained with polarization time, suggesting the stability of Cu^{2+} during the CO_2 reduction reaction. A band located at ~299.7 cm⁻¹ appeared on $Cu^{\delta+}@SiO_2-250$ after 10 min of CO_2 electrolysis, with no such peak observed for $CuSiO_3@SiO_2$. The peak is related to the frustrated rotation of *CO bound to Cu^+ in an atop geometry.¹⁸ This supports that the $Cu^{\delta+}@SiO_2-250$ promotes the formation and high coverage of *CO, thus boosting the C–C coupling activity. Post characterization of the used catalysts by XPS (SI Figure S15) indicated that the surface concentrations of Cu^+ and Cu^0 remained almost unchanged after 1 h of reaction at –1.1 V, implying that the formed Cu–O–Si bond in $Cu^{\delta+}@SiO_2-250$ can protect Cu^+ and Cu^0 against reduction during the ECR in accordance with the DFT calculations.

CONCLUSION

We have demonstrated the fine-tuning of surface oxidation of Cu supported on silica associated with electrolyte regulation for optimizing ECR to C_{2+} compounds (C_2H_4 , C_2H_5OH , and *n*- C_3H_7OH). By virture of the strong Cu-SiO₂ interaction, the surface ratio of Cu⁰-to-Cu⁺ is readily tailored by annealing of the composite catalyst in a hydrogen environment with varying temperature. An appropriate surface content of Cu⁺ and Cu⁰ (Cu⁰-to-Cu⁺ molar ratio of ~0.5) is found to greatly facilitate C–C coupling by lessening the energy of formation of the key *OCCOH intermediate and also concurrently suppress

the parasitic HER. The designed $Cu^{\delta+}$ @SiO₂-250 electrocatalyst delivers a remarkable C₂₊ FE of ~70% with a C₂₊ partial geometric current density of about 9.0 mA cm⁻², and a large C₂₊-to-C₁ ratio of ~10 using an H-type cell in aqueous CsBr electrolytes at mild overpotentials. The C₂₊ FE achieves a high level of ~52% even when operated at a large current density of 500 mA cm⁻² in a flow reactor. The catalytic activity maintains good stability after 12 h of consecutive polarization. The existence and stability of Cu⁺ species was confirmed by XRD, XPS, Raman, NMR, and DFT calculations. This work shows a simple, low cost, and promising approach for efficient ECR toward multicarbon products.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: Experimental and DFT details; differential charge density diagrams; wide-survey XPS spectrum; particle size distribution diagram; STEM image; ²⁹Si MAS NMR spectra; the FE of ECR products; C_{2+} partial geometric current density; C_{2+} production rate; scan-rate dependence of cyclic voltammetric stripping; Operando Raman spectra; Cu 2p XPS and Cu LMM spectra after electrolysis; summary of C_{2+} FE performance over reported Cu-based electrocatalysts in an H-type cell.

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Author Contributions

Z.S. supervised the project. D.W. conceived the idea and conducted synthesis and electrochemical experiments. S.H. and A.W.R. helped with transmission electron microscopy measurements and

analysis. L.L. and Q.X. performed DFT calculations. Z.S. and D.W. wrote the manuscript. L.H. and A.W.R. polished the language. All authors reviewed the manuscript.

Notes

The authors declare no competing financial interest.

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