Stabilization of Cu⁺ by tuning a CuO–CeO₂ interface for selective electrochemical CO₂ reduction to ethylene†

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Electrochemical conversion of carbon dioxide (CO₂) into multi-carbon fuels and chemical feedstocks is important but remains challenging. Here, we report the stabilization of Cu⁺ within a CuO–CeO₂ interface for efficient and selective electrocatalytic CO₂ reduction to ethylene under ambient conditions. Tuning the CuO/CeO₂ interfacial interaction permits dramatic suppression of proton reduction and enhancement of CO₂ reduction, with an ethylene faradaic efficiency (FE) as high as 50.0% at −1.1 V (vs. the reversible hydrogen electrode) in 0.1 M KHCO₃, in stark contrast to 22.6% over pure CuO immobilized on carbon black (CB). The composite catalyst presents a 2.6-fold improvement in ethylene current compared to that of CuO/CB at similar overpotentials, which also exceeds many recently reported Cu-based materials. The FE of C₂H₄ remained at over 48.0% even after 9 h of continuous polarization. The Cu⁺ species are believed to be the adsorption as well as active sites for the activation of CO₂ molecules, which remain almost unchanged after 1 h of electrolysis. Further density functional theory calculations demonstrate the preferred formation of Cu⁺ at the CuO–CeO₂ interface. This work provides a simple avenue to convert CO₂ into high-value hydrocarbons by rational stabilization of Cu⁺ species.

Introduction

Electrochemical carbon dioxide (CO₂) reduction (ECR) shows promise in reducing greenhouse gas emissions, storing intermittent renewable electricity, as well as attaining energy security and sustainability.¹,² Although this energy conversion process can be conducted under mild temperatures and atmospheric pressure, there are still many challenges, such as low conversion efficiency and poor product selectivity, which have to be overcome.³,⁴ To enable progress towards this goal, the development of catalysts with high efficiency, sufficient selectivity, and low cost is necessary.⁵,⁶ The synthesis of valuable hydrocarbons and other chemicals through ECR has drawn significant attention as a potential scheme for recycling CO₂.⁷⁻¹⁸ In particular, C₂⁺ (containing two or more carbon atoms) compounds such as ethylene have high energy densities and enjoy global demand in comparison to C₁ products.¹⁹,²⁰ For instance, ethylene is widely used as an industrial feedstock for manufacturing plastics and diesel, and its selective production in lieu of methane is important.

Copper, with its unique electronic properties, has been shown to stabilize CO intermediates (*CO) and enable them to be further reduced to multi-carbon products via CO dimerization to yield an *OCCO adsorbate and subsequent hydrogenations.¹⁹ However, Cu is intrinsically limited by the scaling relations between the binding energies of various reaction intermediates on the metallic surfaces, which leads to wide product distributions and undesirable hydrogen evolution, thus hampering large-scale practical implementation.²¹ Selective reduction of CO₂ into industrially important C₂⁺ species remains an ongoing challenge. Recent investigations...
indicate that preferential conversion of CO₂ to C₂+ products can be achieved using Cu-based materials doped with foreign atoms, Cu alloys or through control of exposed crystal lattice, oxidation state, and surface morphology. For example, single-crystal Cu(100) was demonstrated to display good selectivity for ethylene evolution with a faradaic efficiency (FE) of about 40.0%, which can be further improved to 50.0% over Cu(711) at 5.0 mA cm⁻² in 0.1 M KHCO₃. A recent study showed that CuAg bimetallic catalysts have enhanced selectivity to C₂+ products, which was attributed to the suppression of the hydrogen evolution reaction (HER) due to the formation of compressively strained CuAg surface alloys. In addition, Cu/oxide interfaces are regarded to be critical to inhibit the parasitic HER during electrocatalytic CO₂ reduction. Oxides of copper exhibit enhanced ECR activity and increased selectivity towards multi-carbon products. The selectivity of these catalysts is dependent on the copper oxidation state. Some computational studies have suggested that the coexistence of a Cu⁺/Cu⁰ mixture synergistically promotes CO₂ reduction to C₂+ products due to improved CO₂ activation and CO dimerization. Experimentally, however, evidence for the stability of the active Cu⁺ species during CO₂ reduction remains unclarified thus far.

Herein, we report on the stabilization of Cu⁺ by controlling the interplay between lattice-mismatched CuO and CeO₂. This scheme allows one to design an efficient and selective catalyst for electrocatalytic CO₂ reduction to produce ethylene, among other products (methane, carbon monoxide, formic acid, and ethanol). Catalytic selectivity can be greatly improved by taking advantage of the CuO–CeO₂ interactions in different composition regimes and interfacial structures. A remarkable FE for ethylene production of up to 50.0% was obtained at mild overpotentials, outperforming many previously reported Cu-based electrocatalysts. Furthermore, density functional theory (DFT) calculations revealed that CeO₂ changes the oxidation state of Cu atoms to Cu⁺ at the CuO–CeO₂ interface.

Results and discussion

The X-ray diffraction (XRD) patterns of CuO–CeO₂/CB together with individual CuO/CB and CeO₂/CB are shown in Fig. 1a. Apart from a broad peak at 22.2° originating from carbon black with low crystallinity, diffraction peaks at about 28.1, 47.6, and 56.0° were observed in both CeO₂/CB and CuO–CeO₂/CB, corresponding to the (111), (220), and (311) planes of CeO₂ (PDF# 34-0394). These indicate the formation of fluorite (Pnma) CeO₂ with a face-centered cubic (fcc) structure in the composites. Unlike the bare CuO/CB that displayed representative monoclinic CuO peaks (PDF# 44-0706), no diffraction peaks of any Cu compounds were discernible in the XRD pattern of CuO–CeO₂/CB, likely due to the low loading and/or small size of CuO in the composite.

X-ray photoelectron spectroscopy (XPS) was used to acquire information about the surface composition and chemical state of the Cu species, as well as possible interactions between copper and cerium oxides. Fig. 1b shows the Cu 2p signal of CuO/CB and CuO–CeO₂/CB. The Cu 2p core-level spectrum of CuO/CB reveals pronounced CuO features, that is, Cu 2p₁/₂ and 2p₃/₂ peaks with binding energies (BEs) at 954.0 and 934.0 eV, respectively. Strong Cu²⁺ satellites at 962.6, 944.0, and 941.6 eV were also clearly observed. Nevertheless, no apparent peaks assigned to Cu⁺ could be identified. In contrast, two peaks located at 954.3 and 951.9 eV were observed in CuO–CeO₂/CB, which can be attributed to Cu²⁺ 2p₁/₂ and Cu²⁺ 2p₃/₂, respectively. This unambiguously verifies the formation and stabilization of Cu⁺, likely owing to electron transfer from Ce⁴⁺ ions. The relative Cu⁺ percentage was determined to be 23.4% in CuO–CeO₂/CB, based on the peak area ratio of all copper oxidation states in the Cu 2p region. Fig. 1c depicts the Ce 3d signals of CuO–CeO₂/CB having a satellite structure due to the hybridization of Ce 3d orbitals with O 2p orbitals and partial occupation of the 4f levels. The 3d₅/₂ and 3d₃/₂ spin–orbit components (spin–orbit splitting, ~18.5 eV) are denoted as ν and ν′, respectively, which is in line with the previous literature on Ce(IV). The peaks of ν₀ and ν₁ were attributed to a mixing configuration of the 3d⁵ 4f⁰ (O 2p³) and 3d⁵ 4f¹ (O 2p²) Ce⁴⁺ states and ν₂ to the 3d⁵ 4f⁰ (O 2p³) Ce⁴⁺ state. The same assignment could be applied to the ν′ structures, which correspond to the Ce 3d₃/₂ level. This illustrates the major valence of Ce(ν) in the sample, consistent with the
XRD result. Four peaks \(u_0\) (BE \(\approx 885.8\) eV), \(u_1\) (BE \(\approx 880.6\) eV), \(u_2\) (BE \(\approx 904.1\) eV), and \(u_3\) (BE \(\approx 899.5\) eV) associated with Ce\(^{3+}\) were identified, indicating the presence of Ce\(_2\)O\(_3\) in the sample.\(^1\) The well-defined peak \(\nu_2\) typical of Ce\(^{4+}\) can be used to estimate the fraction of Ce\(^{4+}\).\(^40\) Given that the area of the \(\nu_2\) component comprises 14.0% of the overall area of the Ce 3d component, the deconvoluted O 1s XPS spectrum of CuO–CeO\(_2\)/CB (Fig. S1a) displays a predominant peak at 529.7 eV arising from the lattice oxygens in the metal oxides, and two less intense peaks at 531.2 and 532.6 eV that can be assigned to defective sites (surface oxygen vacancies) and physisorbed water, respectively.

The presence of Cu\(^+\) in CuO/CeO\(_2\) heterostructures was also evidenced by Raman scattering experiments. The bands centered at about 258.0, 462.9, and 595.0 cm\(^{-1}\) were identified as shown in Fig. 1d, which can be well assigned to the \(E_{2g}\) mode, second-order transverse acoustic (2TA) mode, and defect-induced (D) mode of fluorite CeO\(_2\), respectively.\(^41\) It is worth noting that the three peaks at 290.4, 337.0, and 622.8 cm\(^{-1}\) that appeared for CuO/CuO are attributed to the respective single \(A_g\) mode and two \(B_g\) optical modes of cupric oxide.\(^42\) However, for CuO–CeO\(_2\)/CB, the feature around 290.4 cm\(^{-1}\) disappeared and a new band at 230.4 cm\(^{-1}\) was observed being tentatively assigned to one-magnon scattering, which arose from the antiferromagnetic ordering of the Cu\(^{2+}\) ions.\(^42\) Two additional distinct peaks at 409.5 and 661.1 cm\(^{-1}\) were observed that were typical of Cu\(^+\) Raman fingerprints.\(^42\) This further confirms that CuO was partially converted to Cu\(_2\)O, possibly induced by adjacent CeO\(_2\) nanoparticles (NPs). These results are consistent with the XPS data in Fig. 1b.

Temperature-programmed reduction by hydrogen (H\(_2\)-TPR, Fig. 1e) manifested two marked H\(_2\) consumption peaks at 110.0 and 178.0 °C for CuO–CeO\(_2\)/CB, which were ascribed to the reduction of the subsurface Cu\(^{6+}\) to Cu\(^{2+}\) and further to Cu\(^0\), respectively, by consuming reducible oxygen from the CuO\(_2\) species. Notably, the TPR reduction peaks shifted to lower temperatures relative to CuO/CuO, which is likely a result of hydrogen spillover to CuO at the CuO/CeO\(_2\) interface. Furthermore, CuO–CeO\(_2\)/CB exhibited a CO\(_2\) uptake capacity of 4.7 cm\(^3\) g\(^{-1}\) (Fig. 1f), 2.3 fold as large as that of CuO/CB. This could lead to enriched CO\(_2\) on the local surface of the working electrode, thus boosting \(*\)CO coverage and dimerization. The significant enhancement in CO\(_2\) capture ability is due to the introduction of CeO\(_2\), which can effectively adsorb CO\(_2\), forming carbonates and hydrogen carbonates.\(^43\) It can be envisioned that the as-made hybrid catalyst may facilitate multiple interesting functionalities such as adsorption, electronics, activation, and catalysis, among others, based on the synergistic interaction between CuO and CeO\(_2\).

To decipher the morphological features of our catalyst, aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed on CuO–CeO\(_2\)/CB. Fig. 2a and b show the formation of many reticular NPs homogeneously distributed on carbon black. The (111) and (100) planes of CeO\(_2\) were indexed with the aid of fast Fourier transformation (FFT) (inset of Fig. 2b).

Furthermore, the energy-dispersive X-ray spectroscopy (EDS) maps (Fig. 2c–g and Fig. S2b–ff) along with the EDS spectrum (Fig. 2h) confirmed that the NPs were composed of CuO and CeO\(_2\) crystallities. EDS elemental mapping revealed an almost full overlap of the Cu-rich and Ce-rich domains, indicating large interfaces between the two metal oxides. The crystallite sizes of CuO and CeO\(_2\) were found to be similar with the sizes being less than 5 nm as found using high-resolution TEM (Fig. 2i and j). By FFT, the fcc CuO and CeO\(_2\) NPs were discerned (Fig. 2k and l). Most of the CuO crystals exhibited a faceted cuboidal morphology and were surrounded by CeO\(_2\) NPs (Fig. 2i and j).

ECR is very sensitive to operating conditions, such as the nature and properties of the electrocatalyst, electrolyte composition, and electrochemical cell type. To evaluate the intrinsic catalytic properties of the as-prepared hybrids, we conducted the ECR in CO\(_2\)-saturated 0.1 M KHCO\(_3\) aqueous electrolyte (pH 6.8) using a reported design of liquid H-type cell with continuous CO\(_2\) bubbling.\(^44\) The potential-dependent geometric current densities of CuO–CeO\(_2\)/CB within the potential range of 0.0 to −1.4 V (vs. RHE) were recorded by linear sweep voltammetry (LSV), as shown in Fig. 3a. Significantly higher cathodic currents were observed in a CO\(_2\) environment than in an Ar environment within the entire potential region. CO, H\(_2\), HCHO, HCOOH, CH\(_4\), and C\(_2\)H\(_4\)OH were detected at applied potentials ranging from −0.9 to −1.3 V (vs. RHE) in a CO\(_2\)-saturated 0.1 M KHCO\(_3\) solution. The ECR preferably occurred over HER at potentials ranging from −0.9 to −1.2 V (vs. RHE), while HER dominated at more negative potentials (Fig. 3b and c). As demonstrated in Fig. 3d, CeO\(_2\)/CB generated exclusively H\(_2\) with a very small amount of ECR products (FE < 3.0%). Commercial Cu\(_2\)O decorated on CB exhibited an FE of 31.7% for ECR (vs. RHE) (Fig. S3†), whereas the FE for CH\(_4\) formation was as low as 8.5%. Although CuO/CB can reduce CO\(_2\),
at overpotentials larger than 0.97 V, the highest FE for ECR was below 32.0%, with the selectivity for C$_2$+ products being less than 23.0%. It is worth noting that the CuO–CeO$_2$/CB nanocomposites substantially promoted the activity toward CO$_2$ reduction with an FE > 63.0%.

The C$_1$ products were obtained at similar yields for CuO/CB and CuO–CeO$_2$/CB, but C$_2$+ product selectivity and C$_2$H$_4$ FE and production rate (Fig. 3e) were remarkably boosted for the latter sample. C$_2$H$_4$ emerged at an onset potential of −0.7 V (vs. RHE) over CuO–CeO$_2$/CB and rose to a maximum with FE up to 50.0% at −1.1 V (vs. RHE) in contrast to that of 22.6% and 1.2% for CuO/CB and CeO$_2$/CB, respectively (Fig. 3b and d). The C$_2$H$_4$ selectivity even outperforms many recently reported Cu-based electrocatalysts under similar overpotentials (Fig. 3f), such as the state-of-the-art Cu nanocubes with exposed (100) facets (maximum C$_2$H$_4$ FE is 32.0%)$^{45,46}$ and Ag–Cu nanodimers (maximum C$_2$H$_4$ FE is 40.0%).$^{24}$

The ECR activity was tunable by adjusting the amounts of CeO$_2$ and CuO (Tables S1 and S2†). As seen in Fig. 4a, incorporation of CeO$_2$ at various amounts was found to thwart hydrogen evolution and facilitate C$_2$H$_4$ generation. The optimal loading of CeO$_2$ was 30.0 wt%. A continuous increase in CeO$_2$ loading led to a slight decrease in ECR activity, probably owing to the reduction in electrical conductivity. Likewise, the ECR activity to yield C$_2$H$_4$ increased with the mass percentage of CuO in the range of 0.75–1.5 wt%. The C$_2$H$_4$ FE tended to diminish upon a further increase in CuO loading (Fig. 4b). This may be due to a combination of the less extended interface and formation of larger CuO particles, resulting in weakened binding of the reactants and intermediates. Furthermore, it was found that there is an optimum in the particle size of CuO, which maximized C$_2$H$_4$ generation (Table S3†), in line with the results observed for Cu in the literature.$^{24}$ The effect of electrolytic temperature on ECR was also explored. The FE for ECR was found to be maximized at 3 ± 3 °C (Fig. S4†), indicating that the HER tends to be inhibited at low reaction temperatures.

To check whether Ce$_{3+}$ impacted the ECR, the synthesis of catalysts was performed in an air-free glove-box under otherwise similar conditions. The resulting CuO–Ce$_2$O$_3$/CB provided a much lower C$_2$H$_4$ FE (22.4% at −1.1 V vs. RHE) compared to CuO–CeO$_2$/CB. This indicates that Ce$_{3+}$ is unlikely to contribute to the enhanced ECR.
The role of Cu$^+$ during ECR was investigated by treating CuO–CeO$_2$/CB at 200 °C under different atmospheres. The relative fractions of Cu$^{II}$, Cu$^+$, and Cu$^{IV}$ in the treated CuO–CeO$_2$/CB samples were probed using XPS (Table S4 and Fig. S5†). As observed in Fig. 4c, the CO$_2$ reduction activity and selectivity dropped slightly in an Ar environment, which may favor the transformation of a small fraction of Cu$^{IV}$ to Cu$^+$ and Cu$^+$ to Cu$^0$ (Table S4 and Fig. S5†). The C$_2$H$_4$ FE mildly decreased with a simultaneous increase in CH$_4$ FE, probably resulting from the aggregation of metal oxide NPs and the presence of Cu$^0$. This phenomenon became a little more pronounced after being subjected to water vapor, which may be due to the promotion of CH$_4$ formation by the adsorbed surface water molecules, in addition to the transformation of Cu$^+$ (Table S4 and Fig. S5b†). However, annealing of the catalyst in 8% H$_2$/Ar led to increased HER with a distinct drop in ECR performance. Despite CO FE being improved to 33.7%, the C$_2$H$_4$ FE dropped to 33.8%. This suggests that the reduction of Cu$^+/Cu^0$ ratio (Table S4 and Fig. S5c†) is detrimental to CO–CO coupling. In addition, the decrease in Cu$^+/Cu^{II}$ (Table S4 and Fig. S5d†) upon exposure of the sample to air at elevated temperatures would be reduced at the experimental electrode potential range (−0.9 ~ −1.3 V vs. RHE). Previous studies have shown that subsurface oxygen in copper oxides plays an important role in facilitating the CO$_2$ reduction, and hence, we focus on subsurface O rather than surface O.

We focused on the change/trend of the Bader charges in the surface Cu atoms with and without CeO$_2$ clusters since the Bader charge agrees with the oxidation state qualitatively (albeit not quantitatively). Assuming that the Bader charges of surface Cu atoms in Cu(100), Cu$_2$O(100), and CuO(100) correspond to the reduction state of Cu at Cu$^+$, Cu$^0$, and Cu$^{IV}$, respectively, we obtain a linear relationship between the Bader charge and oxidation state (Fig. 5d), and from the latter correlation, we obtained the oxidation state of Cu atoms in CuO–CeO$_2$.

This Bader charge analysis shows that the oxidation states of several Cu atoms at the CuO–CeO$_2$ interface lie between that of Cu$^0$ and CuO (Fig. 5d), indicating that the interfacial CeO$_2$ cluster changes the oxidation state of neighboring Cu atoms in CuO toward that of Cu$^0$. More specifically, the oxidation states of two Cu atoms at the CuO–CeO$_2$ interface are highly similar to those of surface Cu atoms in Cu$_2$O (i.e. Cu$^+$). This result agrees with the presence of Cu$^+$ in the XPS characterization of CuO–CeO$_2$/CB (Fig. 1b), and indicates that CeO$_2$ plays an important role in stabilizing Cu$^+$. The long-term performances of the catalysts were examined by chronocoulometric measurements. The results (Fig. 4e) showed that the FE for C$_2$H$_4$ remained steady, exceeding 48.0% even after 9 h of continuous polarization at −1.1 V (vs. RHE). XPS analysis (Fig. 4f and S1b†) indicated that the surface concentration of Cu$^+$ was preserved after 1 h of polarization at −1.1 V (vs. RHE), reflecting its good stability owing to the strong interplay between ceria and copper oxide.

To further investigate the role of CeO$_2$ in stabilizing Cu$^+$, we performed density functional theory (DFT) calculations (Fig. 5). We modeled the interface between CuO and CeO$_2$ (denoted as CuO–CeO$_2$) by constructing a small CeO$_2$ cluster (CeO$_2$) on the CuO(100) surface. The (100) facet, which has been known as the active site for C$_2$ production in electrochemical CO$_2$ reduction, is considered. We also considered the Cu-terminated surface of CuO since the surface O species would be reduced at the experimental electrode potential range (−0.9 ~ −1.3 V vs. RHE).
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Conclusions
In summary, we present CuO–CeO₂/CB as a highly promising electrocatalyst for enhancing the selective reduction of CO₂ to ethylene. By utilizing the strong synergistic interaction between CuO and CeO₂, stabilization of the Cu⁷⁺ species at the metal–oxide interface is realized, while H₂ production is simultaneously considerably suppressed, resulting in boosted ethylene production with a high FE of up to 50.0%. The existence of Cu⁷⁺ species was confirmed by XPS, Raman spectroscopy, as well as TPR; Cu⁷⁺ species are believed to be the adsorption as well as active sites for the activation of CO₂ molecules. This work provides a simple way to enhance the conversion of CO₂ into ethylene, and it is hoped that the findings will inspire the rational design of active copper domains for efficient electroreduction of CO₂.

Conflicts of interest
The authors declare no conflicts of interest.

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Notes and references

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