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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.

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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

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indicate that preferential conversion of CO_2 to C_{2+} products can be achieved using Cu-based materials doped with foreign atoms,²² Cu alloys,^{23,24} or through control of exposed crystal lattice,^{25,26} oxidation state,^{27,28} and surface morphology.^{25,29–31} 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 KHCO_3 .²⁵ A recent study showed that CuAg bimetallic catalysts have enhanced selectivity to C_{2+} products, which was attributed to the suppression of the hydrogen evolution reaction (HER) due to the formation of compressively strained CuAg surface alloys.³² In addition, Cu/oxide interfaces are regarded to be critical to inhibit the parasitic HER during electrocatalytic CO_2 reduction.^{33,34} 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.³¹ Some computational studies have suggested that the coexistence of a Cu^+/Cu^0 mixture synergistically promotes CO_2 reduction to C_{2+} products due to improved CO_2 activation and CO dimerization.^{35,36} Experimentally, however, evidence for the stability of the active Cu^+ species during CO_2 reduction remains unclarified thus far.

Herein, we report on the stabilization of Cu^+ by controlling the interplay between lattice-mismatched CuO and CeO_2 . This scheme allows one to design an efficient and selective catalyst for electrocatalytic CO_2 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– CeO_2 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 CeO_2 changes the oxidation state of Cu atoms to Cu^+ at the CuO– CeO_2 interface.

Results and discussion

The X-ray diffraction (XRD) patterns of CuO– CeO_2/CB together with individual CuO/CB and CeO_2/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 CeO_2/CB and CuO– CeO_2/CB , corresponding to the (111), (220), and (311) planes of CeO_2 (PDF# 34-0394). These indicate the formation of fluorite ($Fm\bar{3}m$) CeO_2 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– CeO_2/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

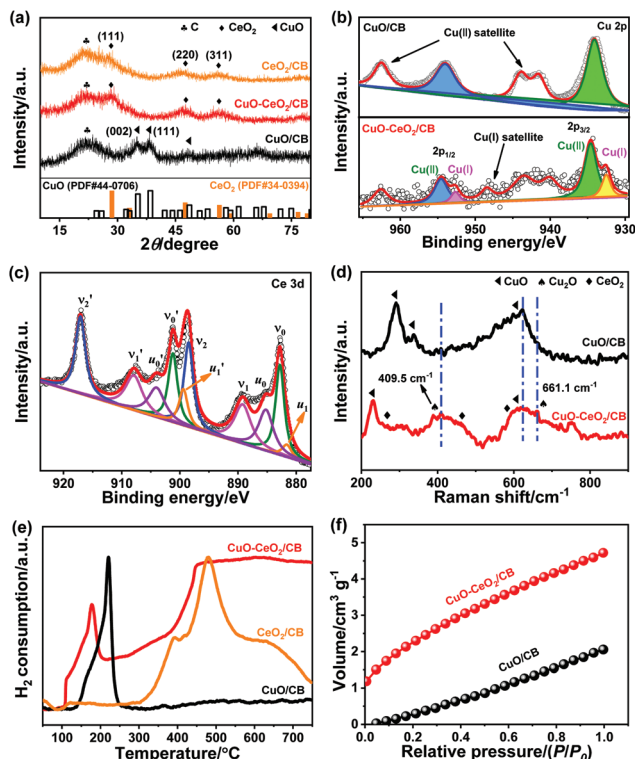


Fig. 1 (a) XRD patterns of CeO_2/CB , CuO/CB , and $\text{CuO-CeO}_2/\text{CB}$. (b) Cu 2p XPS spectra of CuO/CB and $\text{CuO-CeO}_2/\text{CB}$. (c) Ce 3d XPS spectrum of $\text{CuO-CeO}_2/\text{CB}$. (d) Raman spectra of CuO/CB and $\text{CuO-CeO}_2/\text{CB}$. (e) H_2 -TPR profiles of CeO_2/CB , CuO/CB , and $\text{CuO-CeO}_2/\text{CB}$. (f) CO_2 adsorption isotherms of CuO/CB and $\text{CuO-CeO}_2/\text{CB}$.

copper and cerium oxides. Fig. 1b shows the Cu 2p signal of CuO/CB and $\text{CuO-CeO}_2/\text{CB}$. The Cu 2p core-level spectrum of CuO/CB reveals pronounced CuO features, that is, Cu $2p_{1/2}$ and $2p_{3/2}$ peaks with binding energies (BEs) at 954.0 and 934.0 eV, respectively. Strong Cu^{2+} satellites at 962.6, 944.0, and 941.6 eV were also clearly observed.³⁷ Nevertheless, no apparent peaks assigned to Cu^+ can be identified. In contrast, two peaks located at 954.3 and 951.9 eV were observed in $\text{CuO-CeO}_2/\text{CB}$, which can be attributed to $\text{Cu}^{2+} 2p_{1/2}$ and $\text{Cu}^+ 2p_{3/2}$, respectively.¹⁰ This unambiguously verifies the formation and stabilization of Cu^+ , likely owing to electron transfer from Ce^{3+} to Cu^{2+} . The relative Cu^+ percentage was determined to be 23.4% in $\text{CuO-CeO}_2/\text{CB}$, based on the peak area ratio of all copper oxidation states in the Cu 2p regions. Fig. 1c depicts the Ce 3d signals of $\text{CuO-CeO}_2/\text{CB}$ having a satellite structure due to the hybridization of Ce 3d orbitals with O 2p orbitals and partial occupation of the 4f levels.³⁸ The $3d_{5/2}$ and $3d_{3/2}$ 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) .³⁹ The peaks of ν_0 and ν_1 were attributed to a mixing configuration of the $3d^9 4f^2$ (O $2p^4$) and $3d^9 4f^1$ (O $2p^5$) Ce^{4+} states and ν_2 to the $3d^9 4f^0$ (O $2p^6$) Ce^{4+} state.³⁸ The same assignment could be applied to the ν' structures, which correspond to the Ce $3d_{3/2}$ level. This illustrates the major valence of Ce(IV) in the sample, consistent with the

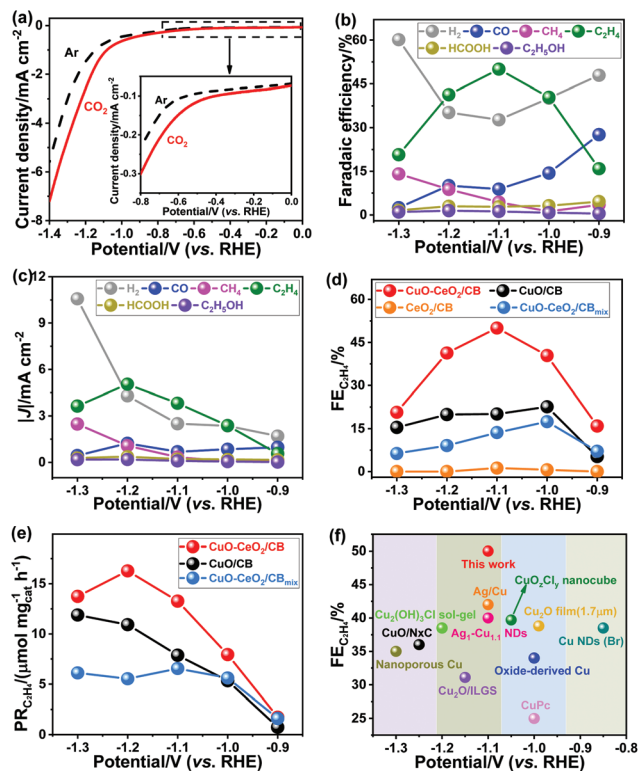


Fig. 3 (a) LSV results of CuO–CeO₂/CB on a glassy carbon electrode in Ar- (dashed black line) or CO₂ (solid red line)-saturated 0.1 M KHCO₃ solutions at a scan rate of 5 mV s⁻¹. (b) Faradaic efficiencies and (c) partial current densities for ECR products over CuO–CeO₂/CB at various applied potentials. (d) C₂H₄ FEs of CuO–CeO₂/CB, CuO/CB, CeO₂/CB, and CuO–CeO₂/CB_{mix} in the potential range from –0.9 to –1.3 V. (e) Production rates of C₂H₄ at different potentials over CuO–CeO₂/CB, CuO/CB, and CuO–CeO₂/CB_{mix}. (f) C₂H₄ FEs of CuO–CeO₂/CB and other reported Cu-based electrocatalysts.

at overpotentials larger than 0.97 V, the highest FE for ECR was below 32.0%, with the selectivity for C₂₊ products being less than 23.0%. It is worth noting that the CuO–CeO₂/CB nanocomposites substantially promoted the activity toward CO₂ reduction with an FE > 63.0%.

The C₁ products were obtained at similar yields for CuO/CB and CuO–CeO₂/CB, but C₂₊ product selectivity and C₂H₄ FE and production rate (Fig. 3e) were remarkably boosted for the latter sample. C₂H₄ emerged at an onset potential of –0.7 V (vs. RHE) over CuO–CeO₂/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 CeO₂/CB, respectively (Fig. 3b and d). The C₂H₄ 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 C₂H₄ FE is 32.0%)^{45,46} and Ag–Cu nanodimers (maximum C₂H₄ FE is 40.0%).²⁴

The ECR activity was tunable by adjusting the amounts of CeO₂ and CuO (Tables S1 and S2†). As seen in Fig. 4a, incorporation of CeO₂ at various amounts was found to thwart hydrogen evolution and facilitate C₂H₄ generation. The

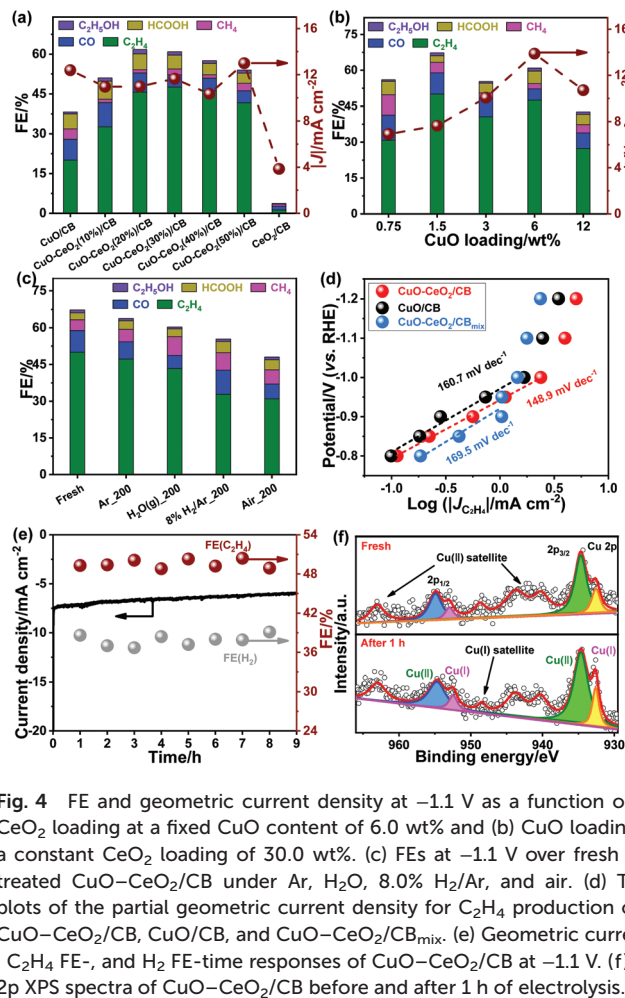


Fig. 4 FE and geometric current density at –1.1 V as a function of (a) CeO₂ loading at a fixed CuO content of 6.0 wt% and (b) CuO loading at a constant CeO₂ loading of 30.0 wt%. (c) FEs at –1.1 V over fresh and treated CuO–CeO₂/CB under Ar, H₂O, 8.0% H₂/Ar, and air. (d) Tafel plots of the partial geometric current density for C₂H₄ production over CuO–CeO₂/CB, CuO/CB, and CuO–CeO₂/CB_{mix}. (e) Geometric current-, C₂H₄ FE-, and H₂ FE-time responses of CuO–CeO₂/CB at –1.1 V. (f) Cu 2p XPS spectra of CuO–CeO₂/CB before and after 1 h of electrolysis.

optimal loading of CeO₂ was 30.0 wt%. A continuous increase in CeO₂ loading led to a slight decrease in ECR activity, probably owing to the reduction in electrical conductivity. Likewise, the ECR activity to yield C₂H₄ increased with the mass percentage of CuO in the range of 0.75–1.5 wt%. The C₂H₄ 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 C₂H₄ 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 Ce³⁺ impacted the ECR, the synthesis of catalysts was performed in an air-free glove-box under otherwise similar conditions. The resulting CuO–Ce₂O₃/CB provided a much lower C₂H₄ FE (22.4% at –1.1 V vs. RHE) compared to CuO–CeO₂/CB. This indicates that Ce³⁺ is unlikely to contribute to the enhanced ECR.

The role of Cu^+ during ECR was investigated by treating $\text{CuO-CeO}_2/\text{CB}$ at 200 °C under different atmospheres. The relative fractions of Cu^0 , Cu^+ , and Cu^{2+} in the treated $\text{CuO-CeO}_2/\text{CB}$ 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^{2+} to Cu^+ and Cu^+ to Cu^0 (Table S4 and Fig. S5a†). The C_2H_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_2H_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 $\text{Cu}^+/\text{Cu}^{2+}$ (Table S4 and Fig. S5d†) upon exposure of the sample to air at elevated temperatures degraded C_2H_4 production, accompanied by substantially more H_2 evolution.

To probe the role of the CuO-CeO_2 interface, we made efforts to tailor the interfacial structure by fine-tuning synthetic parameters such as the feeding sequence of metal precursors. When the precursor $\text{Cu}(\text{Ac})_2$ was first added followed by the addition of $\text{Ce}(\text{NO}_3)_3$ to prepare the catalyst, only 22.0% of C_2H_4 FE was attained (Table S5†). Alternatively, a cascade addition of cerium precursor and copper precursor in sequence also increased C_2H_4 FE only to about 37.8%. In both cases, the accessible CuO-CeO_2 interfaces with exposed copper domains were markedly reduced, which accounted for the declined ECR performance. A physical mixture of CuO/CB and CeO_2/CB ($\text{CuO-CeO}_2/\text{CB}_{\text{mix}}$) with equivalent metal oxide loadings was also evaluated for ECR. It showed even worse CO_2 reduction activity than that of CuO/CB (Fig. 3d and e), most likely due to poor mass transport. Taken together, we conclude that an intelligent design of CuO-CeO_2 interfaces to yield and stabilize Cu^+ is essential to facilitate the CO_2 -to- C_2H_4 conversion.

The interfacial reaction kinetics was explored by Tafel analysis. A Tafel slope of 148.9 mV dec^{-1} was observed for $\text{CuO-CeO}_2/\text{CB}$, much lower than 160.7 mV dec^{-1} for CuO/CB and 169.5 mV dec^{-1} for $\text{CuO-CeO}_2/\text{CB}_{\text{mix}}$ (Fig. 4d). This indicates that $\text{CuO-CeO}_2/\text{CB}$ has a comparatively faster kinetics for CO_2 reduction. The formation of the $^*\text{CO}$ intermediate for tandem catalysis on the surface of the catalysts determines the reaction rate.

The long-term performances of the catalysts were examined by chronoamperometric measurements. The results (Fig. 4e) showed that the FE for C_2H_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 (Ce_3O_6) on the $\text{CuO}(100)$ surface.^{47,48} The (100) facet, which has been known as the active site for C_2 production in electrochemical CO_2 reduction, is considered.⁴⁹ We also considered the Cu-terminated surface of CuO since the surface O species would be reduced at the experimental electrode potential range ($-0.9 \sim -1.3$ V vs. RHE). Previous studies have shown that subsurface oxygen in copper oxides plays an important role in facilitating the CO_2 reduction,^{35,36} and hence, we focus on subsurface O rather than surface O.

We focused on the change/trend of the Bader charges⁵⁰ of 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 $\text{Cu}(100)$, $\text{Cu}_2\text{O}(100)$, and $\text{CuO}(100)$ correspond to the oxidation states of 0, +1, and +2, respectively, we obtained 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_2O 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_2O . 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_2O (*i.e.* Cu^+). This result agrees with the presence of Cu^+ in the XPS characterization of $\text{CuO-CeO}_2/\text{CB}$ (Fig. 1b), and indicates that CeO_2 plays an important role in stabilizing Cu^+ .

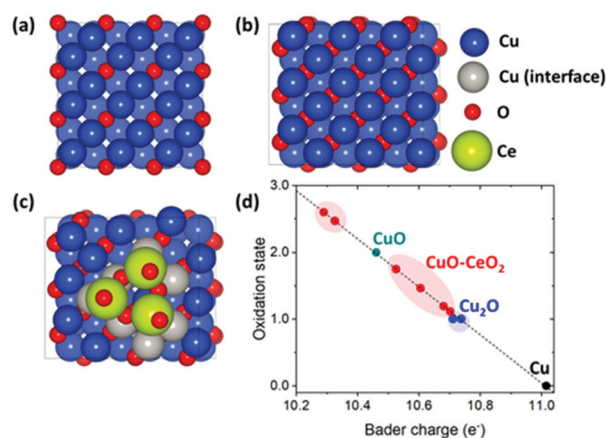


Fig. 5 Top view of the optimized geometries of (a) Cu_2O , (b) CuO , and (c) CuO-CeO_2 . (d) Oxidation states of surface Cu atoms obtained by Bader charge analysis. Only the surface Cu atoms adjacent to CeO_2 (denoted as grey balls in (c)) are considered for the Bader charge analysis of CuO-CeO_2 . In (d), black, blue, cyan, and red colors represent Cu, Cu_2O , CuO , and CuO-CeO_2 , respectively.

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 Cu⁺ 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 Cu⁺ species was confirmed by XPS, Raman spectroscopy, as well as TPR; Cu⁺ 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.

Acknowledgements

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