

Tuning the C_1/C_2 Selectivity of Electrochemical CO_2 Reduction on Cu– CeO_2 Nanorods by Oxidation State Control

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Ceria (CeO_2) is one of the most extensively used rare earth oxides. Recently, it has been used as a support material for metal catalysts for electrochemical energy conversion. However, to date, the nature of metal/ CeO_2 interfaces and their impact on electrochemical processes remains unclear. Here, a Cu– CeO_2 nanorod electrochemical CO_2 reduction catalyst is presented. Using operando analysis and computational techniques, it is found that, on the application of a reductive electrochemical potential, Cu undergoes an abrupt change in solubility in the ceria matrix converting from less stable randomly dissolved single atomic Cu^{2+} ions to (Cu^0, Cu^{1+}) nanoclusters. Unlike single atomic Cu, which produces C_1 products as the main product during electrochemical CO_2 reduction, the coexistence of (Cu^0, Cu^{1+}) clusters lowers the energy barrier for C–C coupling and enables the selective production of C_{2+} hydrocarbons. As a result, the coexistence of (Cu^0, Cu^{1+}) in the clusters at the Cu–ceria interface results in a C_{2+} partial current density/unit Cu weight 27 times that of a corresponding Cu-carbon catalyst under the same conditions.

drawing attention as a promising technology to mitigate excess anthropogenic CO_2 emissions because it can convert carbon dioxide into high-value-added chemicals and fuels in an eco-friendly and economical way.^[2] Among suitable metals, Cu (and its compounds) is the only one capable of producing high value-added C_{2+} products, such as C_2H_4 and C_2H_5OH , with high selectivity through CO dimerization.^[3] However, the C_{2+} selectivity of Cu-based electrocatalysts can be further improved by tailoring the active sites of Cu through doping,^[4] tuning the catalyst particle shapes and sizes,^[5] and increasing the number of low coordination sites, for example, the grain boundary density.^[6] In particular, the use of mixed oxidation states (i.e., Cu^+ and Cu^0) has been suggested as an effective means to achieve high C_{2+} product selectivity by lowering

1. Introduction

The continuous emission of greenhouse gases, including carbon dioxide, is causing changes to the climate that threaten human life.^[1] Therefore, electrochemical carbon dioxide reduction reaction (CO_2RR) technology using renewable energy is

the energy barrier for CO dimerization.^[7] However, Cu^+ is not stable and is easily converted to metallic Cu (Cu^0) at the negative applied potentials used for the CO_2RR . As a result, many strategies have been developed to sustain the mixed oxidation state of Cu during the CO_2RR .^[8] For instance, doping Cu with B atoms can induce the formation of Cu^+ under CO_2RR conditions, and increase its stability.^[4a,9] Nevertheless, it is still challenging to achieve controllable Cu^+ coverage at the catalytically active Cu top-surface.

Ceria (CeO_2) is a reducible metal oxide and an excellent support for metal catalysts in many catalytic processes, such as the water-gas shift reaction,^[10] CO oxidation,^[11] and CO_2 hydrogenation reaction.^[12] As a catalyst support, CeO_2 can disperse metals at various scales uniformly, from the nanometre in scale to single atoms.^[13] In addition, CeO_2 forms strong metal–support interactions (SMSIs) with the active metals, which allows the formation of a partially charged metal at the metal– CeO_2 interface.^[14] These unique characteristics of CeO_2 can also promote the electrocatalytic CO_2RR activity of metals such as Au and Cu supported on CeO_2 . In particular, Cu on ceria (Cu– CeO_2) shows wide tunability in CO_2RR product selectivity, and this is dependent on the sizes and compositions of Cu– CeO_2 . For example, CeO_2 can stabilize a single-atom (SA) Cu in the Cu^{2+} valence state and generate CH_4 with a faradaic efficiency (FE) of

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up to 58%.^[15] In addition, enhanced selectivity for ethylene and ethanol production has been reported for a catalyst comprising interconnected CuO and CeO₂ nanocrystals in a Cu/Ce ratio of 0.95: the high C₂₊ selectivity is attributed to the Cu–CeO₂ interfacial active sites.^[16] However, colloidal Cu–CeO_{2-x} nanoparticles (NPs) having a well-defined Cu–CeO_{2-x} interface show dominant CH₄ formation.^[17] This discrepancy indicates that the characteristics of the Cu–CeO₂ interface are a key to modulating the CO₂RR activity and are heavily influenced by catalyst synthesis processes. Although the structural and chemical properties of the Au- and Pt–CeO₂ interfaces have been well-established,^[18] those of Cu/CeO₂ interface for the electrochemical CO₂RR require further study.^[16,17]

Here, we present a Cu–CeO₂ nanorod (NR) electrochemical CO₂RR catalyst having a well-controlled Cu/CeO₂ interface. The abrupt transition from Cu SAs to a few atom-thick Cu nanoclusters in/on CeO₂ near about 3% Cu doping was identified using in operando analysis, as well as computational techniques, including high resolution transmission electron microscopy (HR-TEM), atom probe tomography (APT), in operando X-ray absorption near-edge structure (XANES), and density functional theory. In addition, the SMSI of CeO₂ results in the formation of a mixed valence state of Cu⁰/Cu¹⁺ on the Cu nanoclusters on the Cu–CeO₂ surface, which catalyzes the dimerization of CO and enhances selectivity for C₂ products. Our Cu–CeO₂ NRs with SA and NP Cu enable the tunable production of CH₄ (C₁) and C₂H₄ (C₂) products with FEs of 45.5% and 43.2%, respectively, at an applied potential of –0.9 V versus the reversible hydrogen electrode (RHE) in a gas-fed flow cell.

2. Results

2.1. Structural Characterization of As-prepared Cu–CeO₂ NR Catalysts

A Cu–CeO₂ NR catalyst was prepared by loading Cu into CeO₂ NRs prepared by hydrothermal synthesis, as reported previously.^[19] After loading with Cu, the Cu–CeO₂ NRs were calcined in air at 400 °C. The Cu loading was varied from 1 to 5 wt.% with respect to CeO₂. X-ray diffractometry (XRD) analysis was carried out to investigate the crystal structure of the as-prepared *x*% Cu–CeO₂ NRs (Figure 1a), where *x* denotes the degree of Cu doping in weight percent, as measured by inductively coupled plasma optical emission spectroscopy (ICP-OES), and the exact value according to the Cu contents is shown in Table S1 (Supporting Information). The diffraction peaks in all the catalyst corresponds to the fluorite structure of CeO₂, consistent with the standard diffraction pattern of CeO₂ (JCPDS No. 034–0394). No Cu peak ($2\theta = 43^\circ$) was found in the XRD patterns of any sample. A closer look at the CeO₂ peaks revealed a slight shift in 2θ toward higher angle as the Cu contents increased, followed by a plateau (Figure S1a and Table S2, Supporting Information). Accordingly, the CeO₂ lattice constant decreased from its bulk value of 5.4292 Å and then plateaued at 5.4116 Å at 4% Cu content (Figure 1b). This shift in the peaks is a result of the incorporation of Cu²⁺ ions into the CeO₂ lattice; because these ions have a relatively smaller ionic radius (87 pm) than Ce⁴⁺ ions (101 pm), the unit cell shrinks, resulting in a shift to higher scattering angle.^[20] In addition,

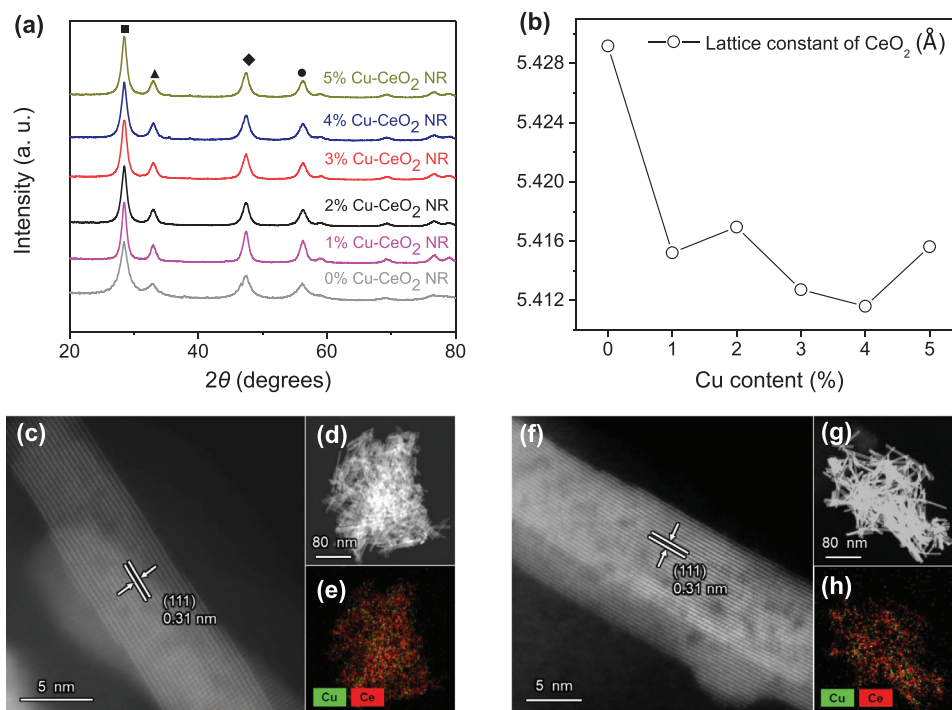


Figure 1. Structural characterization of as-prepared Cu–CeO₂ NRs. a) XRD patterns of *x*% Cu–CeO₂ NRs; CeO₂ lattice planes ■ = (111), ▲ = (200), ◆ = (220), and ● = (311). b) Lattice constants of *x*% Cu–CeO₂ NRs calculated from the XRD peaks. c) HAADF-STEM image of the 2% Cu–CeO₂ NR. d, e) HAADF-STEM image of 2% Cu–CeO₂ NRs and corresponding energy-dispersive spectroscopy (EDS) maps. f) HAADF-STEM image of the 4% Cu–CeO₂ NRs. g, h) HAADF-STEM image of 4% Cu–CeO₂ NRs and corresponding EDS maps.

low intensity peaks consistent with CuO ($2\theta = 35.5^\circ$ and 38.7°) began to emerge in the XRD patterns of the Cu–CeO₂ NRs once the copper doping exceeded 4% (Figure S1b, Supporting Information). According to the CuO–CeO₂ phase diagram, CuO and CeO₂ are immiscible;^[21] therefore, the precipitation of CuO in the CeO₂ matrix is anticipated even at low CuO concentration. Cu is loaded more than the solubility limit, the excess Cu no longer incorporates in CeO₂ lattice and affects the CeO₂ lattice constant as it precipitates out as CuO (Figure 1a,b). In our work, the solubility limit for CuO in CeO₂ is about 2%, and, above this concentration, CuO precipitates out in the CeO₂ NRs. Below the solubility limit, CuO is homogeneously mixed in CeO₂ without segregation.

TEM analyses were performed to investigate the structure of the Cu–CeO₂ NRs in detail. The as-prepared Cu–CeO₂ NRs had an average width of 9.8 nm and an aspect ratio ranging from about 1:1.5 to 1:15 (Figure S2, Supporting Information). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images show that the CeO₂ support is single crystalline with a (111) crystal plane parallel to the long axis of the rod (Figure 1c,f). However, CuO is not visible in the HAADF-STEM images, even though microscopic observation was carried out at multiple locations with many independent samples. This could be attributed to the poor crystallinity and the low contrast of CuO compared to that of CeO₂.^[16,17] Elemental analysis indicates that Cu is uniformly distributed both in the 2% and 4% Cu–CeO₂ samples (Figure 1c–h). However, the segregation of Cu was not observed in the images of the 4% Cu–CeO₂ sample, despite the fact that the precipitation of CuO is expected based on the XRD results. The structure and elemental distribution of the Cu–CeO₂ NRs was maintained even after the CO₂RR (Figures S3 and S4, Supporting Information). In the electron energy loss spectroscopy (EELS) spectra, small peaks at the Cu L_{2,3} position were found at/near the CeO₂ surface, probably arising from CuO clusters (Figure S5, Supporting Information). However, the presence of these peaks is not sufficient to prove the presence of CuO clusters on the CeO₂ surface. Therefore, we conclude that the

precipitated CuO in 4% Cu–CeO₂ is smaller than the resolution of the HR-TEM device used in this study.

The presence of CuO clusters was investigated further using atom probe tomography (APT). APT provides a quantitative 3D atomic distribution of nanostructures at near-atomic resolution.^[22] Thus, we analyzed the atomic distribution of as-prepared 5% Cu–CeO₂ NR, which is expected to contain CuO precipitates throughout the CeO₂ matrix. Because the NRs themselves are too small to be fabricated into needle-shaped APT specimens, the NRs were embedded in a Co matrix using electrodeposition (see Experimental Section).^[23] The mass spectrum acquired from the APT analysis shows clear peaks corresponding to Co, Ce, and Cu ions, as expected for the Cu–CeO₂ NRs (Figure S6, Supporting Information). The measured atomic ratio of Ce and Cu in the NR is 6.9:1, in agreement with the target composition of 5 wt.% Cu–CeO₂ NR in atomic percent (Ce:Cu = 7:1).

Figure 2a shows a 3D atom map of the as-prepared 5% Cu–CeO₂ NR embedded in the Co matrix. In the atom map, a single CeO₂ NR is included (visualized with isolated Cu atoms and Cu clusters). The isolated Cu atoms, i.e., Cu SAs, are assumed to be the dissolved solutes in the CeO₂ lattice and the Cu clusters appear to originate from the precipitation of CuO. The coexistence of the surface CuO NPs and the Cu SAs in the NR is more clearly shown in the enlarged atom maps (Figure 2b,c). Such clustering behavior of Cu is also reflected in a Cu nearest neighbor distribution (NND) (Figure S7, Supporting Information). The Cu NND from the atom map shows a clear deviation from a random Cu distribution, indicating the presence of Cu clusters in the NRs.^[24] The clustering behavior of Cu in 5% Cu–CeO₂ NR is more clearly confirmed by the χ^2 -statistical test and also from the additional APT dataset of 5% Cu–CeO₂ NRs (Figure S8, Supporting Information). In addition, to confirm if these Cu clusters exist as CuO, we obtained radial distribution functions (RDFs) for Cu and O (Figure S9, Supporting Information). The Cu RDF shows that Cu–O, as well as Cu–Cu, are positioned close together, likely as a result of the aggregation of Cu and O atoms in the NRs.^[24] Likewise,

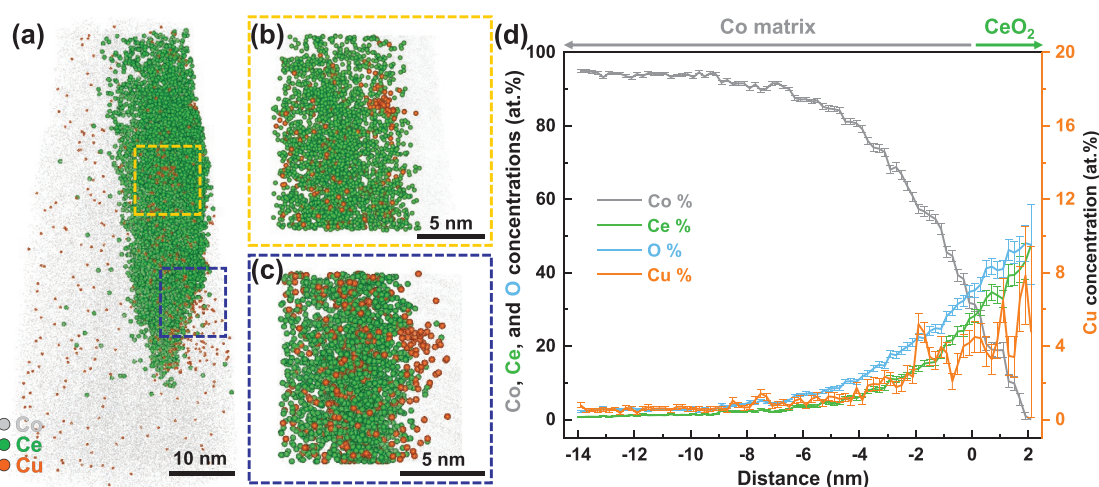


Figure 2. APT reconstruction of as-prepared 5% Cu–CeO₂ NRs. a) 3D atom map of CeO₂ NR in a Co matrix. b,c) Enlarged atomic view of Cu clusters on CeO₂ surface. d) Proximity histogram consistent with 25 at.% Ce iso-concentration surface. Error bars represent the standard deviation (σ).

the O RDF shows the strong correlation between O–O and O–Cu, suggesting that Cu is present as CuO clusters within the CeO₂ bulk, as well as on the surface; this is consistent with the XRD pattern of the 5% Cu–CeO₂ NR (Figure S1b, Supporting Information). To confirm the absence of Cu clusters in lower-doped CeO₂ NRs, we also conducted the APT analyses on the as-prepared 1% Cu–CeO₂ NR (Figure S10, Supporting Information). The resulting data shows well-matched composition with the 1 wt.% Cu–CeO₂ NR (i.e., Ce:Cu = 37:1 in atomic ratio), and no remarkable Cu clusters are detected from the 3D atom map (Figure S10a–c, Supporting Information). In addition, the reasonable fit between random and experimental Cu distribution from the Cu NND, (Figure S10d, Supporting Information) and the χ^2 -statistical test further supports that the Cu clusters are unlikely to exist in the lower doped CeO₂ nanorods as expected from the XRD pattern and solubility limit of CuO in CeO₂ (≈ 2 wt.%).

The presence of surface CuO clusters was also identified from a proximity histogram, which was obtained for an iso-concentration surface of 25 at.% Ce, which is half the maximum concentration of Ce in the NRs (Figure 2d).^[25] The proximity histogram shows the interface between CeO₂ and the Co matrix, and the Cu concentration increased by ≈ 2 at.% ≈ 2 nm from the interface before it dropped. Because the proximity histogram provides the average atomic concentration with respect to distance from the interface,^[26] this result indicates the presence of CuO clusters at the CeO₂ interface.

2.2. Valence State Characterization of the Cu–CeO₂ Interface

The abrupt transition in the structure of Cu from SAs to NPs on the CeO₂ surface, which is a result of the low solubility of CuO in CeO₂, can produce dramatic differences in the valence state of Cu, and this affects the CO₂RR activity. Accordingly, we attempted to determine the valence state of the Cu atoms constituting the x % Cu–CeO₂ catalyst using in operando XANES analysis. The analysis was performed with a constant current in a gas-diffusion electrode (GDE) flow cell (Figure S11, Supporting Information). The normalized Cu K-edge XANES spectra of the 2% and 4% Cu–CeO₂ NR samples were measured under open-circuit conditions (dotted lines) and during the CO₂RR at -100 mA cm⁻² (solid lines) to allow the valence state changes to be compared (Figure 3a). Under open-circuit conditions, both the 2% and 4% Cu–CeO₂ catalysts have characteristic peaks (8986.0 and 8997.7 eV) of Cu²⁺,^[27] consistent with the reference CuO spectrum shown in lower panel of Figure 3a. When a constant current was applied to the Cu–CeO₂ NR catalysts, these catalysts showed different changes in their spectra. In the case of 2% Cu–CeO₂ NR, there was no significant change in the spectra during the reduction process, whereas, in the case of 4% Cu–CeO₂ NR, the peak at 8997.7 eV slightly decreased, and the edge also moved to lower energy during reduction. This indicates that the initial Cu²⁺ state changed to Cu⁰, Cu¹⁺ as the reaction proceeded. This is because CuO clusters on/near the CeO₂ surface in 4% Cu–CeO₂ NR were reduced to Cu¹⁺ and Cu⁰ during the CO₂RR. As a result, both Cu⁰ and Cu⁺ co-exist in the 4% Cu–CeO₂ NRs.

X-ray photoelectron spectroscopy (XPS) was also carried out to compare the valence states change of the Cu and Ce atoms on the surface of the Cu–CeO₂ NRs before and after the CO₂RR (Figures S12 and S13, Supporting Information). The XPS spectra of the as-prepared 4% Cu–CeO₂ NR show the mixed oxidation states of Ce and Cu (Figure 3b,c). Although the as-prepared 4% Cu–CeO₂ NR was calcined in air, the partial reduction of CuO and CeO₂ was observed before the CO₂RR. Figure 3d,e shows the change of surface atomic ratio of Ce³⁺ and (Cu⁰, Cu⁺), respectively, by calculating the area ratio shown in the XPS spectrum of elements having different valences before and after CO₂RR. Relative amount of surface atom of each catalysts in Figure 3d,e is determined by dividing the amount of surface atom of the reference samples that are undoped CeO₂ and 2% Cu–CeO₂ NR, respectively (Tables S3 and S4, Supporting Information). The amount of partially reduced CuO and CeO₂ increased with increase in Cu concentration, although it decreased at higher Cu doping concentration (Figure 3d,e). Therefore, the Cu and Ce atoms on the Cu–CeO₂ surface interact closely, thus affecting their valence states.^[15,19b,28]

The changes in the valences of Cu and Ce were strongly dependent on the Cu doping concentration and showed dramatic differences after the CO₂RR. When the Cu doping concentration was 3% or more, the ratio of Ce³⁺ and (Cu⁰, Cu¹⁺) increased after the CO₂RR (Figure 3d,e). This can be attributed to the fact that the CuO clusters segregated on the surface of the catalyst and were reduced to metallic Cu clusters as the CO₂ reduction reaction proceeded. At the same time, electrons from the reduced Cu clusters are transferred to form Ce³⁺ and Cu¹⁺ at the Cu/CeO₂ interface, allowing them to exist in a stable state on the CeO₂ surface. The adsorbed Cu atoms on the CeO₂ surface can be stabilized via bonding with the oxygen vacancies (V_O) of CeO₂ in a form Cu⁺–V_O–Ce³⁺ at the Cu/CeO₂ interface.^[14,28a] These results are consistent with the in operando XANES results. Notably, the valence state of Cu varies more significantly than that of Ce: the relative amount of surface (Cu⁰, Cu⁺) increases ≈ 2.8 -times, whereas that of surface Ce³⁺ increases only $\approx 25\%$ in 4% Cu–CeO₂ (Table S4, Supporting Information). Because the formation of Cu⁺ and Ce³⁺ is coupled at the Cu/CeO₂ interface and CeO₂ itself is inert during CO₂RR, this indicates that the Cu clusters consist of more than a few atomic layers, as revealed in the APT analysis (Figure 2c). This also means that a layer of stacked Cu⁺–Cu⁰ species would form along the perimeter of the interface, and, thus, the structure of the CuO–CeO₂ interface can lower the energy barrier for C–C coupling.

2.3. Insights from Density Functional Theory Calculations

To gain further insights into the formation of different oxidation states and clusters under operating conditions, we performed extensive spin-polarized density functional theory (DFT) calculations using the RPBE+U method.^[29] All calculated formation energies are summarized in the Tables S5–S8 (Supporting Information). We first considered the pristine CeO₂ catalyst and investigated the probability of oxygen vacancy (V_O) formation by searching for the most stable configuration. For this, we

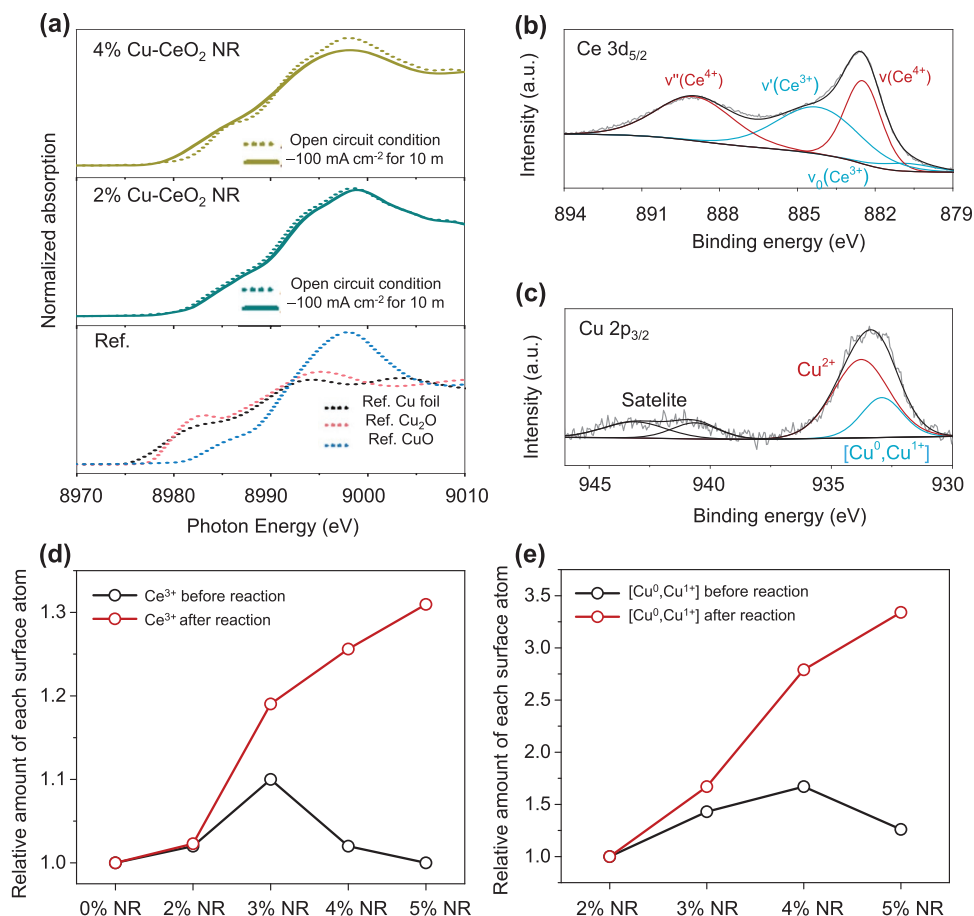


Figure 3. Analysis of valence state changes of atoms at the surface of Cu–CeO₂ NRs. a) Normalized Cu K-edge XANES spectra of 2% and 4% Cu–CeO₂ NR catalysts recorded under open-circuit conditions and at -100 mA cm^{-2} for 10 min. Spectra of a Cu foil and Cu₂O and CuO powder samples are shown at the bottom as references. b,c) XPS spectra of the Ce 3d_{5/2} and Cu 2p_{3/2} in as-prepared 4% Cu–CeO₂. Note that v'' , v' indicate the peaks corresponding to Ce³⁺, and v'' , v' indicate peaks corresponding to Ce⁴⁺. d) Relative amount of Ce³⁺ in x% Cu–CeO₂ NR catalysts determined from Ce 3d_{5/2} XPS compared to pure CeO₂ NR. e) Relative amount of (Cu⁰, Cu¹⁺) in x% Cu–CeO₂ NR catalysts from Cu 2p_{3/2} XPS compared to 2% Cu-NR. The relative amount of surface atoms is the ratio at which the amount of surface atoms increases based on the reference sample having the lowest Cu content. In the Ce 3d_{5/2} and Cu 2p_{3/2} XPS data, pure CeO₂ NR (0% NR) and 2% NR were used as references, respectively.

considered both bulk CeO₂ and the (111) facet, as well as two different environmental conditions: *ambient* gas phase conditions with atmospheric O₂ playing the role of the oxidant and *reducing* electrochemical conditions, for which H₂O facilitated by an applied bias potential results in oxidation (the computational hydrogen electrode, CHE approach was used for this).^[30] Under *ambient* air conditions, we found that vacancy formation was not thermodynamically feasible at the considered vacancy concentration, neither on the CeO₂ crystal nor on the surface (positive formation energy relative to the pristine materials). However, at smaller vacancy concentrations, the configurational entropy reduces the formation energy so that we can expect the formation of vacancies at low concentrations. Under *reducing* conditions, we saw the expected strongly favourable formation of oxygen vacancies.^[31] The vacancies were most stable in the bulk of CeO₂ rather than on the (111) surface, Figure S16a,b (Supporting Information) show all plotted vacancy formation energies and the first row of Figure 4a summarizes these findings.

Starting from the pristine CeO₂ crystal, we prepared a 1.6 mass% Cu-doped CeO₂ crystal containing both substitutional (Cu_S) and interstitial (Cu_I) defects, as reported in earlier works.^[31] We first evaluated the formation energies of the Cu defects (Figure S17a,b, Supporting Information). Under *ambient* conditions, we found Cu_I to be more favorable than Cu_S and preferably located on the surface rather than the bulk. We further found vacancy formation in the case of the Cu_I defects to occur randomly throughout CeO₂ without preference for the Cu_I site (Figures S15 and S19, Supporting Information) indicating decoupled vacancy and defect formation. Therefore, the Cu_I site maintains its oxidation state, which we estimated from Bader charge analysis,^[32] of between +1 and +2 on the surface and +1 in the bulk, and the oxidation state of the neighbouring Ce is reduced to stabilize the lower oxidation state of the cationic defects (Figure S19, Supporting Information). In contrast to the Cu_I defect, we found that Cu_S had a sufficiently high energetic driving force to induce the formation of a nearby oxygen vacancy (Figures S14 and S18, Supporting

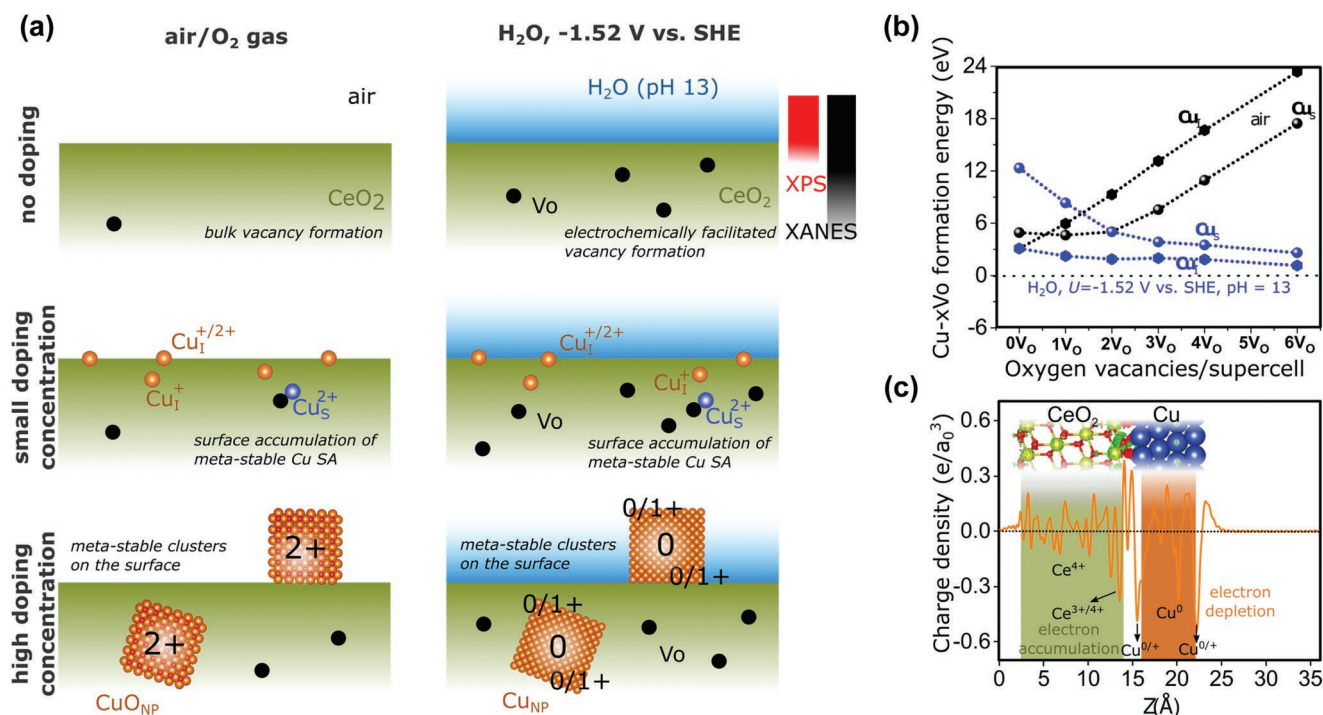
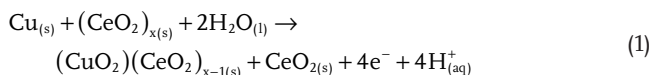


Figure 4. Computational insights into the thermodynamic stability of Cu/CeO₂ systems. a) Schematic of the combined theoretical and experimental findings concerning the thermodynamic stability of Cu/CeO₂ systems under different environmental and doping conditions. b) Energetic cost of forming substitutional and interstitial Cu single atom defects from metallic Cu, as well as oxygen vacancies, in a pristine CeO₂(111) surface. Formation energies under ambient conditions/air are shown in black and those under electrochemical conditions are shown in blue. c) CeO₂(111)/Cu(111) interface: *xy*-plane averaged electronic charge density difference $\Delta\rho(Z)$ relative to the isolated components. Inset: Isosurface of $\Delta\rho$ at 0.003 e a_0^{-3} . Green, blue, and red balls represent the Ce, Cu, and O atoms.

Information), possibly because of the smaller possible oxidation state (+2) of Cu compared to that of Ce (+4), which can be stabilized by introducing an oxygen vacancy. Indeed, as shown in Figure 4b and Figure S17c (Supporting Information), the formation of a Cu_s-V_O pair in the bulk of CeO₂ is energetically comparable to the formation of Cu_i in the bulk, and both could, thus, be present. However, we expect surface Cu_i formation to be dominant; therefore, Cu defects should accumulate in the surface region. Under reducing conditions, the energetic cost of forming a Cu_s defect increases. For demonstration, if a Cu defect originates from metallic Cu and is inserted into the pristine CeO₂ structure, four electrons must be released during the oxidation reaction:



Here, x depicts the formula units of CeO₂ per supercell and, thus, represents the doping concentration. Reducing conditions will shift this equilibrium to the left so that the formation of Cu_s becomes increasingly energetically unfavorable. This energetic penalty can be reduced by increasing the vacancy concentration because the reference system converges to a less oxidized state and the number of electrons released during the oxidation reaction decreases. However, as shown in Figure 4b and Figure S17c (Supporting Information), Cu_i is expected to be energetically preferable in all cases based on our calculations, although the formation energies on the surface suggest greater

stability here. Consequently, interstitial Cu defects are mostly expected close to the surface, whereas oxygen vacancies are expected randomly in the bulk of CeO₂, as summarized in the second row of Figure 4a.

At higher Cu doping concentrations, Cu cluster formation will unavoidably occur because of the higher stability of the phase-separated system compared to the SAs.^[21] As shown in Figure 4b, all Cu formation energies are positive relative to the reference system, i.e., bulk metallic Cu. Note that copper oxide phases are more stable compared to Cu under *ambient* conditions (Figure S17d, Supporting Information). We also evaluated the energetic costs of forming solid–solid copper oxide–CeO₂ interfaces. Tables S7 and S8 (Supporting Information) show that, although energy is required to form a free-standing Cu, copper oxide, or CeO₂ surface, energy is released when forming a CeO₂/Cu or CeO₂/Cu oxide interface as a result of attractive interactions. Following standard nucleation theory, this result indicates that there is practically no nucleation barrier, and NPs can grow freely in the bulk. Because of the large size of the NPs, we also expect the formation of metastable NPs on the surface. In general, a reduction in the radii of NPs exposes more surface facets to the environment (CeO₂ or gas/water), which stabilizes Cu NP formation.^[33] For all considered radii, the formation energy of Cu in NPs is much lower than the formation energy of a Cu_i SA (Figure S17a,b,d, Supporting Information). Under *ambient* conditions, CuO NPs with Cu in the oxidation state +2 will form as the most stable phase (Figures S17d and S21, Supporting Information). Under *reducing* conditions, these NPs are

readily reduced to Cu(0) (Figure S17d, Supporting Information) and vacancies form in the bulk of CeO₂, as discussed above. We also considered the possible formation of oxygen vacancies at the Cu (oxide)/CeO₂ interface. Although the surface tension of Cu(111)/CeO₂(111) in the presence of oxygen vacancies is less negative, indicating still formation of vacancies in the bulk, the copper oxide interface could be subject to some vacancy formation (Table S8, Supporting Information). Next, we analyzed the oxidation state of metallic Cu NPs adsorbed on the CeO₂(111) surface by considering an overlayer structure (Figure 4c). We found a slightly increased oxidation state of Cu close to the interface, in between Cu(0) and Cu⁺, as also evidenced by the charge distribution. The bottom layer of the Cu cluster contains slightly oxidized Cu atoms that are bonded to O sites on reduced CeO₂(111); this is consistent with literature.^[28a,34]

Overall, our computational findings are consistent with the XPS and XANES data. At low doping concentrations, there is no change in the Cu oxidation state, neither in the bulk (XANES) nor the surface (XPS), even under *reducing* conditions because

Cu₁ is most stable and its stability is independent of vacancy formation. At higher doping concentrations, Cu is thermodynamically prone to form NPs via phase separation. In contrast, under *ambient* conditions, Cu will form Cu²⁺O clusters, which can be reduced to Cu^{0/+} under electrochemical conditions; this is an oxidation state change that was confirmed experimentally for both the bulk (XANES) and surface (XPS), showing that the clusters are present both at the surface and the bulk.

2.4. Performance of Cu–CeO₂ NRs for CO₂RR

The electrocatalytic performance of all Cu–CeO₂ NR catalysts was evaluated in a GDE based flow electrolyzer.^[35] As reference, the performance of the pure CeO₂ NRs was evaluated, and they were found to be inactive for the CO₂RR: that is, hydrogen production was observed at all current densities (Figure S23, Supporting Information). Figure 5a shows the CO₂RR partial current densities of Cu–CeO₂ NRs at various

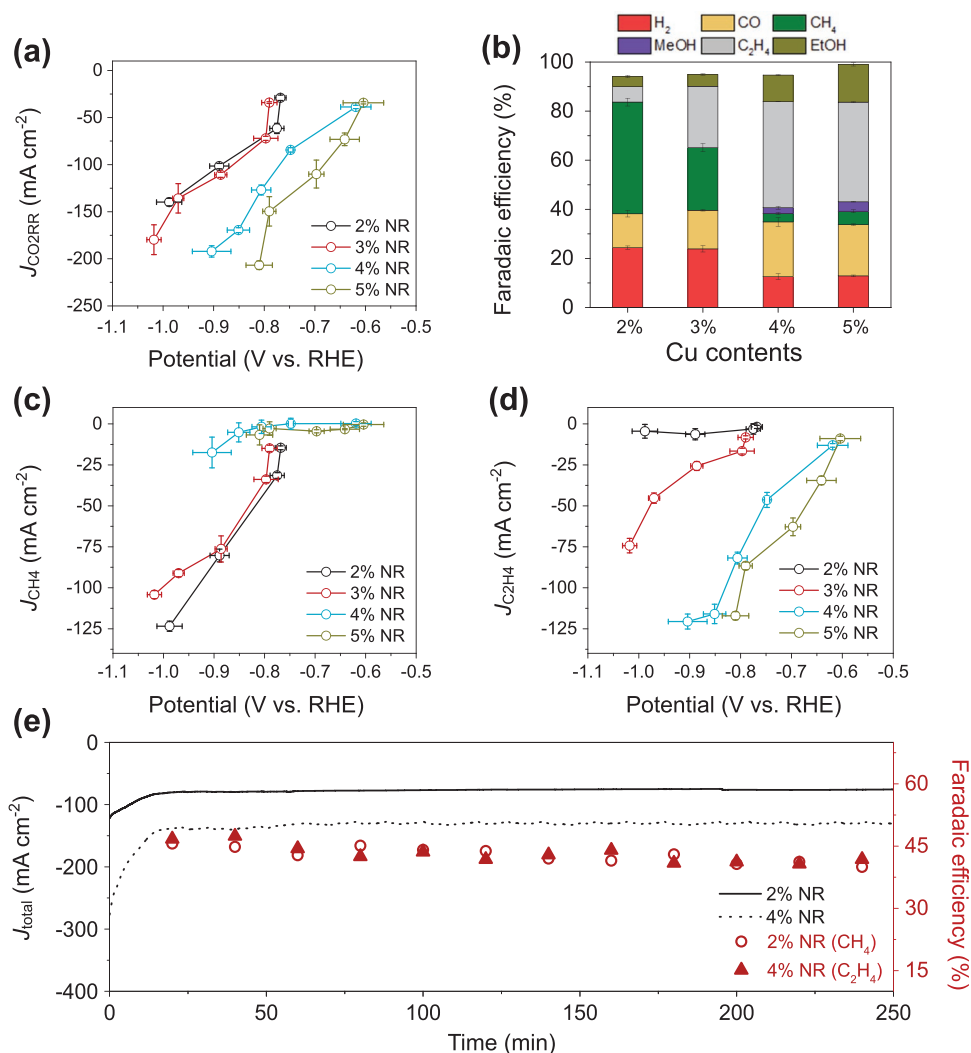


Figure 5. Electrochemical CO₂ reduction performances of x% Cu–CeO₂ NR. a) Partial current density for CO₂ reduction of the x% Cu–CeO₂ NR catalysts. b) Faradaic efficiency of x% Cu–CeO₂ NR catalysts at -0.9 V versus RHE. c,d) Partial current density for CH₄ and C₂H₄ of the x% Cu–CeO₂ NR catalysts. e) Stability test results of 2% and 4% Cu–CeO₂ NR at -0.9 V versus RHE.

Cu doping concentrations (Table S9, Supporting Information). The CO₂RR activity at a given potential increased with increase in the Cu doping concentration, and the highest current density of $-206.8 \text{ mA cm}^{-2}$ was achieved at -0.81 V versus the RHE for 5% Cu–CeO₂ NR. This is because of the increasing number of active sites for the CO₂RR with increase in the Cu concentration.

Figure 5b shows the product distribution of all Cu–CeO₂ NRs at a constant potential of -0.9 V versus RHE (Table S10, Supporting Information). Interestingly, in the case of 2% Cu–CeO₂, CH₄ was the main product, having an FE of $\approx 45.5\%$. However, as the doping concentration of Cu gradually increased, the amount of CH₄ diminished, and the FE decreased below 5%. Further, C₂H₄ became the main product, having an FE of 43.2%. Similar transition from CH₄ to C₂H₄ with Cu doping concentration is apparent in other applied potentials (Figure S24 and Table S11, Supporting Information). Figure 5c,d show the partial current densities for CH₄ and C₂H₄ in x% Cu–CeO₂ as a function of applied potential. The 2% Cu–CeO₂ NRs yielded CH₄ with current density for CH₄ (J_{CH_4}) of $-123.4 \text{ mA cm}^{-2}$ at -0.99 V versus RHE, whereas 5% Cu–CeO₂ NR yielded a $J_{\text{C}_2\text{H}_4}$ of $-117.1 \text{ mA cm}^{-2}$ at -0.81 V versus RHE. Thus, both the abrupt suppression of CH₄ production and increase in C₂H₄ production at Cu concentrations larger than 4% are evident. For example, the ratio of the partial current density for C₂₊ production to that of C₁ is ≈ 0.09 for 2% Cu–CeO₂ NR, but it rapidly increased to 2.85 for 4% Cu–CeO₂ NR at a current density of -200 mA cm^{-2} ; that is, the selectivity toward C₂₊ products increased by 34-times when the Cu doping concentration was doubled (Figure S25, Supporting Information). This sudden change in product selectivity is attributed to the different structure and valence state of Cu in CeO₂ associated with the phase separation of CuO or Cu in CeO₂. Specifically, when Cu SAs exist as a random solid solution in the CeO₂ NRs, CO–CO dimerization is suppressed and CH₄ is produced dominantly. In contrast, when the amount of Cu is above the solubility limit in CeO₂, the CeO₂ support stabilizes the (Cu⁰, Cu¹⁺) cluster structure, thus resulting in a favored pathway to C₂ products, such as C₂H₄. Notably, the electrochemically active surface area (ECSA)-normalized CO₂RR activity shows a similar trend (Figures S26 and S27, Supporting Information).

To confirm the stabilizing effect of the ceria NR support on the mixed-valent Cu clusters at the Cu–ceria interface, comparison with a 4% Cu–carbon catalyst was carried out (Figure S28, Supporting Information). The CuO existing in the Cu–carbon structure is reduced to metallic Cu⁰ during the electrochemical reduction reaction, and these act as active sites. Therefore, by comparing the Cu–carbon catalyst containing the same amount of Cu as a reference, the effect of mixed-valent Cu clusters at the Cu–ceria interface could be identified. These experiments were conducted at constant potential (-0.9 V versus RHE), and, on comparing the FE of the C₂₊ product, the performance was found to be ≈ 5 -times better when the ceria support was used. Further, comparing the partial current density of the C₂₊ product per unit mass of Cu, the Cu–ceria NR showed 27-times higher performance than the Cu–carbon catalyst. This result underlines the notable (and positive) effect of mixed valent Cu at the Cu–ceria interface. These results indicate superior catalytic activity of the Cu–ceria NRs compared to Cu–ceria or

Cu-based catalysts reported so far in terms of properties and performance (Table S12, Supporting Information).

Stability is also a very important factor in the evaluation of catalyst performance. Therefore, stability tests were also performed at -0.9 V versus RHE for 2% and 4% Cu–CeO₂, which produce CH₄ and C₂H₄ as main products, respectively (Figure 5e). Both catalysts showed stable catalytic activity, and the FEs of CH₄ and C₂H₄ were maintained above 40% even after 250 min of CO₂RR.

3. Conclusions

In summary, we have reported the tunable CH₄/C₂H₄ selectivity of Cu–CeO₂ NRs during the electrochemical CO₂RR by precisely controlling the structure and valence state of the Cu active sites on CeO₂ NRs; the unique tunability is a result of the immiscible nature of the CuO and CeO₂ binary oxide system. Briefly, when the CuO content is less than the solubility limit in CeO₂, CuO is present as a single atomic, random solid solution in CeO₂ and is maintained as a stable state even at the large negative potentials used for the CO₂RR. In contrast, when the concentration of CuO exceeds the solubility limit of CeO₂, excess CuO precipitates out as CuO clusters throughout the CeO₂ NRs, and these can be observed by APT measurements. These results were obtained from both experimental analysis and extensive quantum chemical calculations. As the CO₂RR proceeds, the CuO clusters undergo phase transformation to metallic Cu clusters with a partially oxidized Cu⁺ layer at the Cu/CeO₂ interface, leading to the formation of mixed Cu⁺/Cu⁰ active sites along the perimeter of the Cu/CeO₂ interface. The oxidized form of Cu at the interface was also confirmed using quantum chemical calculations. Further, electrochemical CO₂RR evaluation in a gas-fed flow cell revealed that single atomic CuO in CeO₂ is unfavorable for C–C coupling and produces CH₄ as the main product. However, the coexistence of (Cu⁰, Cu¹⁺) in the clusters lowers the energy barrier for C–C coupling and enables the selective production of C₂₊ hydrocarbons. This work provides a rational and fundamental strategy for the fabrication of high-performance, highly efficient electrocatalysts through the precise control of the active sites and their structure on metal oxide supports.

4. Experimental Section

Catalyst Preparation: CeO₂ nanorods (NRs) was prepared by a hydrothermal synthesis method. After dissolving 16.8 g of NaOH (JUNSEI) in 70 mL of deionized (DI) H₂O for 10 min, 10 mL of DI H₂O in which 1.736 g of cerium(III) nitrate hexahydrate (99.99%, Sigma Aldrich) was dissolved with the dropwise addition and stirred for 30 min with 500 RPM. A total of 80 mL of the mixed solution was sealed in a hydrothermal reactor with a capacity of 100 mL and maintained at 100 °C for 24 h. Then, Cu was deposited on CeO₂: a desired amount of Cu(II) nitrate trihydrate (Sigma Aldrich) was added in the mixed solution, followed by stirring at 500 RPM at room temperature for 12 h. Finally, the catalysts were dried at 60 °C overnight and then calcined in a tube furnace in an air atmosphere at 400 °C for 2 h to obtain x% Cu–CeO₂ NR catalyst powder. For the Cu–CB sample, the same wt.% of Cu and carbon black (Sigma Aldrich) as that of the Cu–CeO₂ sample

was used, and the rest of the process was prepared in the same way except for hydrothermal synthesis. To make a catalyst ink, 50 mg of catalyst powder was mixed with 20 mL of isopropanol and 20 μ L of nafion (Sigma Aldrich). This catalyst ink was evenly sprayed on a carbon paper (Sigracet, 39BC) using a spray gun and the loading amount is $\approx 1.5 \text{ mg cm}^{-2}$ for all samples.

Materials Characterizations: The powder X-ray diffraction (XRD) patterns were acquired with X'Pert-PRO MRD diffractometer (PANalytical) equipped with Cu K-alpha light source. X-ray photoelectron spectra (XPS) were recorded with a K-alpha system provided by VG scientific and the peak deconvolution was done in an Advantage software. The HAADF-STEM and EELS analysis were performed at an acceleration voltage of 300 kV with Titan G2 60–300 which was equipped with a monochromator, aberration corrector and Gatan Quantum 965 spectrometer. ICP-OES 720 (Agilent) was used to measure the Cu concentration in Cu–CeO₂ catalysts. The operando XANES was conducted using 10C-Wide XAFS line using at the Pohang light source (PLS-II) in Republic of Korea. All experimental data were measured in the fluorescence mode and the references (CuO powder, Cu₂O powder, and Cu metal) were measured in transmission mode at Cu K-edges. Commercial products (CuO, Cu₂O : Sigma Aldrich) were used as references. During the operando XANES measurements, 1 M KOH solution (Liquid pump : Masterflex L/S) and 20 sccm of CO₂ gas (Mass flow controller : MFC KOREA) were continuously fed into the cathode part of the GDE cell. The operando test was performed under a constant current of -100 mA cm^{-2} . Data fitting was done using ATHENA and ARTEMIS software.

Atom Probe Tomography: As-prepared 5% Cu–CeO₂ NRs were spray coated on porous carbon substrate and electrodeposited by Co using the process reported by Kim et al. for enabling APT analysis.^[23] Co electrodeposition bath was prepared by dissolving 15 g of cobalt sulfate heptahydrate (CoSO₄·7H₂O, Sigma Aldrich), and 1.75 g of boric acid (H₃BO₃, Sigma Aldrich) in 50 mL of DI water. Electrodeposition was performed at a constant current of 2 mA for 1600 s. APT measurements were conducted using a CAMECA LEAP 4000X HR instrument with a pulsed-laser mode at evaporation rate of 0.003 atoms per pulse, base temperature of 57 K, pulse frequency of 125 kHz, and laser pulse energy of 100 pJ. Needle-shaped APT specimens were prepared by ultra-high resolution focused ion beam (Helios G4, FEI) according to the standard lift-out method.^[36] APT data were analyzed using IVAS 3.8.4 software developed by CAMECA instruments.

Electrochemical CO₂RR in a Flow Cell: All the electrochemical measurement were taken on an (SP-150, Biologic) in a three-electrode system. The three electrode system consists of a counter electrode (Ni–Fe–Mo alloy supplied from Sigma Aldrich), a references electrode (Ag/AgCl saturated with KCl), and a working electrode (catalyst sprayed on a GDE). The anodic and cathodic compartment of the flow cell were separated by a sustainion membrane (supplied by Dioxide material). The cathodic compartment filled with 7 mL of 1 M KOH was connected to an electrolyte reservoir of 93 mL. The whole electrolyte was circulated via a pump (Masterflex L/S) between the cathodic compartment and the reservoir at a rate of 10 mL min⁻¹. The cathodic gas compartment was continuously fed with 20 sccm of CO₂ flow controlled via a mass flow controller (MFC KOREA). The flow rate at the outlet of the GDE was monitor during each experiment and used to estimate the CO₂RR performances. The gas products such as hydrogen, CO, methane, and ethylene were quantified by using a gas chromatography (YL instrument, 6500 GC system) equipped with thermal conductivity (TCD) and flame ionization (FID) detectors. Liquid products collected from the cathode part were quantified by using a high performance liquid chromatography (HPLC, YL9100, Youngin Chroma). All measurement results were recorded after 20 m of reaction under each condition and reproducibility test was performed on three independent samples under the same conditions. All potentials used in this experiment were based on the RHE electrode after 90% iR compensation as shown below.

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059 \text{ pH} + V_{\text{Ag/AgCl}}^{\circ} \quad (2)$$

where $V_{\text{Ag/AgCl}}^{\circ}$ is 0.197 V in saturated KCl solution at room temperature. The calculation method of Faradaic efficiency (FE) used in this study is as follows.

$$\text{FE}(\%) = \frac{z \cdot n \cdot F}{Q} \quad (3)$$

where z is the number of electrons transferred, n is the number of moles of products, F is Faraday constant, and Q is the amount of charge.

ECSA values were analyzed by the Pb underpotential deposition (UPD) method in 0.1 M HClO₄ and 1 mM PbCl₂ at a scan rate of 10 mV s⁻¹. During the measurement, the solution was continuously purged with N₂ gas and charge was calculated by integrating the oxidation peak area of the Pb monolayer. ECSA values for all samples were calculated by dividing the stripping charge by the reported conversion factor (Figure S26, Supporting Information).^[3d]

Computational Framework: Structure relaxations were performed using the Vienna ab-initio simulation package (VASP).^[29a,b] The electron-ion interactions were described using the projector-augmented wave (PAW) method, primarily a frozen-core all-electron calculation.^[29c] Attractive van der Waals interactions included using Grimme's correction for the revised Perdew-Burke-Ernzerhof (RPBE) with the Pade method.^[29d,37] For structure optimization, the atoms were relaxed in the direction of the Hellmann-Feynman force using the conjugate gradient method with an energy cut-off of 520 eV until a stringent convergence criterion (of 0.001 eV Å⁻¹) was satisfied. The electrons in Ce and Cu metals were divided into two groups: strongly correlated ones usually localized on atomic d or f orbitals and subject to the Hubbard treatment.^[38] The remaining electrons were treated using standard density functional theory. Lattice constants and accurate electronic structure calculations were performed using the RPBE exchange-correlation functional by employing Hubbard U corrections for Ce f and Cu d orbitals with $U_{\text{Ce}} = 5 \text{ eV}$ and $U_{\text{Cu}} = 4 \text{ eV}$, respectively.^[39] The U parameter was chosen for Ce f orbitals because spin saturates in the Ce⁺³ oxidation state and accurately models chemical expansion in ceria and adsorption properties of reduced ceria.^[39a,40] However, the U parameter correctly predicted bandgap and formation enthalpy of CuO and Cu₂O.^[39b] Additional details are reported in Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

atom probe tomography, copper-ceria, electrochemical CO₂ reduction, gas diffusion electrodes, interface

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