Supplementary Information

Cuprous ions embedded in ceria lattice for selective and stable electrochemical reduction of carbon dioxide to ethylene

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1. Experimental Details

1.1. Materials

Cerium nitrate (Ce(NO₃)₃•6H₂O) and copper nitrate (Cu(NO₃)₂•3H₂O) were purchased from Heowns Biochem Technologies. Sodium hydroxide (NaOH) was purchased from Aladdin Industrial Corporation. Sodium carbonate (Na₂CO₃) was obtained from Tianjin Kermal Chemical Reagent Factory. All of reactants are analytically pure and without further purification.

1.2. Synthesis of CeO₂ nanorods

The ceria nanorods were prepared by hydrothermal synthesis. In a typical procedure, 0.65 g of $Ce(NO_3)_3 \cdot 6H_2O$ and 7.20 g of NaOH were dissolved in 10 and 20 mL ultrapure water, respectively, and then the two solutions were mixed in a beaker and stirred for 30 min. The solution was then transferred to a 45 mL Teflon bottle in a stainless steel vessel autoclave. Next, the autoclave was put into an oven and maintained at 100 °C for 24 h. After reaction was completed, the autoclave was cooled down naturally. The precipitates were separated by centrifugation, washed with ultrapure water and ethanol more than three times, and then dried in vacuum freeze dryer overnight.

1.3. Synthesis of CumCeOx catalysts

The Cu_mCeO_x catalysts were prepared by a deposition-precipitation (DP) method according to previous studies.¹ Briefly, The as-prepared ceria nanorods (0.50 g) and 20 mL ultrapure water were mixed by ultrasonic and stirred to form a pale yellow suspension. Copper nitrate solution with different concentrations was added dropwise to the ceria suspension. The pH value was kept around ca. $9\sim10$ by adding aqueous solution of 0.50 M Na₂CO₃. The suspension were further stirred 1 hour at room temperature and then centrifuged and washed by ultrapure water. The powder was calcinated at 500 °C for 3 h in a muffle furnace to obtain Cu_mCeO_x. The as-prepared sample was further annealed with a heating rate of 10 °C/min in H₂/Ar (5% v/v) or N₂ atmosphere at 500 °C for 3h.

1.4. Characterization

The copper and cerium amount in $Cu_m CeO_x$ catalyst were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) in Agilent 7700x instrument. The structure and crystal phase were determined by XRD (Siemens-Bruker D5000). TEM and high-resolution TEM was carried out by using JEOL 2100 Cryo microscope at an acceleration voltage of 200 kV equipped with a field-emission gun and a high angle annular dark field detector. Grazing incidence X-ray photoelectron spectroscopy (XPS) for Cu Auger LVV was conducted in BL11U beamline in national synchrotron radiation laboratory (NSRL). XPS analysis for Cu 2p, Ce 3d and O 1s was conducted on an Al k-alpha Thermo fisher spectrometer (ThermoFisher Scientific) at 15mA and 15kV, and the spot size is 0.5 mm, respectively. The binding energies were calculated with reference to the energy of C 1s peak of contaminant carbon at 284.6 eV and the highest binding energy peak for Cu²⁺ and Cu⁺ ions with their Cu 2p3/2 peaks located at 934.1 eV and 932.4 eV. The surface composition of all samples in terms of atomic ratios was calculated, using a Shirley-type background and empirical cross section factors for XPS. Raman spectra were measured on DXR Microscope using a laser with an excitation wavelength of 532 nm at laser powder of 4 mW. CO₂ temperature programmed desorption (CO₂-TPD) and CO temperature programmed desorption (CO-TPD) tests were carried out using an AutoChem II 2920 apparatus.

1.5. Electrochemical measurement

The catalyst ink was prepared by mixing 4 mg Cu_mCeO_x catalysts, 0.2 mL isopropanol, 0.2 mL ultrapure water and 10 μ L of Nafion solution (5 wt%) in cool water (~10°C) under sonication for 30 min. 10 μ L catalyst ink was dropped onto a glassy carbon (GC) electrode (φ = 5mm) by a pipette and dried at room temperature with a loading of 1 mg cm⁻².

A CHI 660E potentiostat was used for all electro-chemical experiments under room temperature (25 °C). A piece of platinum foil (0.5 cm \times 0.5 cm) was used as the auxiliary (counter) electrode and is thoroughly rinsed with diluted nitric acid and deionized water, respectively, prior to electrochemical experiments. All electrolysis was conducted in a gastight custom made two-compartment three-electrode electrochemical cell separated by a piece

of anion exchange membrane (Nafion®, 115). Each compartment contained 20 mL electrolyte and approximately ~10 mL headspace.

All applied potentials were measured against a saturated calomel electrode (SCE) and converted to reversible hydrogen electrode (RHE) reference scale using *E* (vs. RHE) = *E* (vs. SCE)+ 0.2415 V+ 0.0591×pH. Unless otherwise stated, electrolyte used for CO₂ electrochemical reduction experiments was 0.1 M KHCO₃ (Aladdin Industrial Corporation) (pH 6.8) at room temperature in this work. Before electrolysis, the electrolyte in the cathodic compartment was degassed and saturated with CO₂ by bubbling CO₂ gas at a rate of 40 sccm for 40 min. Prior to collecting data, the pre-electrolysis was performed for 30 min. During the CO₂ reduction processes, CO₂ gas was delivered to the cathodic compartment at an average rate of 20 sccm. The gaseous products of CO₂ electrocatalytic reduction were detected by an online gas chromatography (GC) (Agilent 780B). The KHCO₃ solution after electrolysis was collected and analyzed on a Bruker AVANCE III 400 MHz NMR spectrometer to quantify liquid products. Standard Dimethyl sulfoxide (DMSO Sigma-Aldrich), 0.5 mL sample of the KHCO₃ solution after electrolysis was mixed with the addition of 0.1 mL D₂O and 0.05 mL DMSO solution as an internal standard. The 1H spectrum was measured with water suppression by a pre-saturation method.

The cyclic voltammetry measurements were conducted in a three-electrode cell equipped with an SCE reference electrode and a Pt counter electrode from 0 V to -1.4 V vs. RHE with a scan rate of 50 mV s⁻¹. Constant-potential electrolysis, at the potential of -0.8 V, -0.9 V, -1.0 V, -1.1 V and -1.2 V vs. RHE, respectively, for multiple hours are performed under steady-state conditions in 0.1 M KHCO₃ saturated with CO₂ at ambient temperature.

The Faradaic efficiency (FE, %) for gaseous species i (H₂, CO, CH₄ and C₂H₄) was calculated according to the formula as below:

$$FE_i = \frac{nFv_i Gp_0}{RT_0 i_{total}} \times 100\%$$

where, n= the number of electron transferred in CO₂ reduction;

 $v_i(\%)$ = molar ratio of species *i* in the exist gas from the electrochemical cell, calculated from GC measurement;

G(ml/min)= exhaust gas volume flow from the electrochemical cell monitored using an electronic meter (Omega Engineering);

 $i_{total}(mA)$ = steady-state cell current.

The constant number: $p_0=1.01 \times 10^5$ Pa, $T_0=273.15$ K, F=96485 C• mol⁻¹, R=8.314 J• mol⁻¹•K⁻¹.

The Faradaic efficiency (F.E. %) for liquid species j (HCOOH and C₂H₅OH) is calculated by

 $FE_j = \frac{nFm}{Q} \times 100\%$

where n= electrons transferred number; F= Faraday's constant; m= desires product moles number; Q= all charge passed.

1.6. In situ XANES measurement

The *in situ* experiments were conducted at the BL 14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF), operated at 3.5 GeV under "decay" mode with currents of 160-300 mA. The powder sample was loaded into carbon fibers as working electrode in situ flow cell. In 0.1 M KHCO₃ electrolyte pre-saturated CO₂ gas more than 1 h. The in situ CO₂ reduction reaction was carried out under a potential of -1.1V vs. RHE, pre-reduction more than 30 min. The XANES spectrum was taken under fluorescence mode. The XANES data have been analyzed *via* Athena and Artemis programs.

2. Computational details

All electronic structure calculations were performed by density functional theory with Vienna ab initio simulation package (VASP) code,² making use of the PBE exchange-correlation functional and the projector augmented-wave (PAW). Calculations were performed on the basis of the obtained equilibrium lattice constants with full relaxation using a plane-wave cut-off of 408 eV and vacuum layer was over 15 Å. The structures of the bulk and extended surface were fully relaxed until the force on any atom was smaller than 0.05 eV/Å. A minimum of $5 \times 5 \times 5$ k-points was used in the Brillouin zone of the conventional

cell for bulk and $5 \times 5 \times 1$ k-points for surface. In order to account for the strong localization of the Ce 4f electrons, a Hubbard-like U term was used, (GGA+U), which makes use of an effective parameter U=5 eV and J = 3 eV for Ce, and U=7 eV and J = 2 eV for Cu.

Gibbs free energies (G) for each gaseous and adsorbed species were calculated at 298.15 K and 101325 Pa, according to the following expression:

$$G = E_{DFT} + E_{ZPE} + \int C_p dT - TS$$
(4)

where ${}^{E}_{DFT}$ is the electronic energy calculated with VASP; ${}^{E}_{ZPE}$ is the zero-point energy; $\int C_{P} dT$ is the enthalpic temperature correction; -TS is the entropy contribution to *G*. As previously described, standard ideal gas method was used to calculate ${}^{E}_{ZPE}$, $\int C_{P} dT$ and -TS from temperature, pressure, and calculated vibrational energies. Free energies of each adsorbate on the surfaces were calculated by treating all 3N degrees of freedom of the adsorbate as frustrated harmonic vibrations given that the contribution from the vibrations of the substrate is negligible. All vibrations were treated in the harmonic oscillator approximation.

The computational hydrogen electrode (CHE) model was employed to determine free energies of reaction intermediates under an applied external potential (*U*).³ In the CHE model, each electrochemical reaction step occurring at a catalyst surface involves a simultaneous proton-electron transfer. The chemical potential of a proton-electron pair, μ [H⁺+e⁻], is equal to a half of the chemical potential of gaseous hydrogen at *U*=0 vs. the reversible hydrogen electrode (RHE), 101325 Pa of H₂, 298.15 K, and all pH values, μ [H⁺ + e⁻] = 0.5 μ [H₂]. When the external bias voltage *U* is applied, the chemical potential of the proton-electron pair r is shifted by -eU, that is [H⁺ + e⁻] = 0.5 μ [H₂] -eU.

Sample	Annealing	Copper contents ^a	m=
	atmosphere	[Cu/(Cu _m CeO _x)×100%]	$[Cu^+/(Cu_mCeO_x)\times 100\%]$
Cu _{3.02} CeO _x	N_2	9.21	3.02
Cu _{3.12} CeO _x	N_2	6.90	3.12
Cu _{3.37} CeO _x	H ₂ /Ar	5.57	3.37
Cu _{3.86} CeO _x	H ₂ /Ar	9.21	3.86
Cu _{4.16} CeO _x	H_2/Ar	6.90	4.16

Table S1. The contents of $\mathbf{Cu^{+}}$ in different $\mathbf{Cu_{m}CeO_{x}}$ samples.

^a Determined by ICP-AES.

Catalyst	Production	Faradic efficiency	Potential	electrolyte	Reference
Cu _m CeO _x	C_2H_4	47.6%	-1.1 V vs. RHE	0.1 M KHCO ₃	This work
Cu(1)GO/GC Cu(1)PG/GC	CH ₄	40%	−1.3 V vs. RHE	0.1 M NaHCO ₃	[4]
Cu ₂ O film deposited on Cu dis	C_2H_4	40%	−1.0 V vs. RHE	0.1 M KHCO ₃	[5]
Cu foil	CH_4	60%	−1.0 V vs. RHE	0.1 M KHCO ₃ and $0.3 M$ KI.	[6]
	C_2H_4	25%	−1.0 V vs. RHE	0.1 M KHCO ₃ and 0.3 M KCl	[6]
Cu Nanowire Arrays	C ₂ H ₄	20.3%	-1.1 V vs. RHE	0.1m KClO ₄	[7]
	CH ₄	72%	-1.4 V vs. NHE	0.2 M KHCO ₃	[8]
	C ₂ H ₄	36%	-1.4 V vs. NHE	0.05 M KHCO ₃	[8]
N-doped graphene quantum dots	C_2H_4	31%	-0.75 V vs. RHE	0.5 M KHCO ₃	[9]
Copper Nanofoams	C_2H_4	1.3%	-1.5 V vs. Ag/AgCl	0.5 M KHCO ₃	[10]
Cu Nanoparticles	C_2H_4	5%	-1.1 V vs. RHE	0.1 M KHCO ₃	[11]
copper(II)-5,10,15,20-tetrakis- porphyrin	C_2H_4	~17%	-0.976 V vs. RHE	0.5 M KHCO ₃	[12]
Cu nanoparticles on pyridinic-N rich grapheme	C ₂ H ₄	20%	-0.9 V vs. RHE	0.5 M KHCO ₃	[13]
Cu Nanowires	C_2H_4	~8%	-0.8 V vs. RHE	0.1 M KHCO ₃	[14]
plasma-activated copper	C_2H_4	60%	–0.8 V vs. RHE	0.1 M KHCO ₃	[15]
Cu ₂ O films	C_2H_4	33%	-1.1 V vs. RHE	0.1 M KHCO ₃	[16]
Densely packe Cu NP ensembles	C_2H_4	34%	–0.9 V vs. RHE	0.1 M KHCO ₃	[17]
Annealed Cu skeleton	C_2H_4	20%	-1.1 V vs.	0.5 M	[18]

Table S2. The performance of various catalysts for CO₂ electrochemical reduction

			RHE	NaHCO ₃	
avida dariyad Cu	CIL	280/	-1.1 V vs.	0.1 M	[19]
oxide-derived Cu	С2П4	28%	RHE	KHCO ₃	
Diagma Activisted Conner Nenesyle	C II	450/	-1.0 V vs.	0.1 M	[20]
Plasma-Activated Copper Nanocube	С2П4	43%	RHE	KHCO ₃	
Ovide derived compar	C_2H_4	21.00/	-0.95 V vs.	0.1 M	[21]
Oxide-derived copper		51.9%	RHE	KHCO ₃	
Thick Ouida Dariyad Conner	C H	26 70/	-0.98 V	0.1 M	[22]
Thick Oxide-Derived Copper	C_2H_4	20.7%	vs. RHE	KHCO ₃	[22]
	C II	400/	-0.5 V vs.	1М КОН [23	[22]
CuDA1-wire	C_2H_4	~40%	RHE		[23]
CaMaganan	C II	200/	-1.7 V vs.	0.1 M	[24]
Cumesopore	C_2H_4	38%	NHE.	KHCO ₃	
Debumatalline Compar	C II	400/	-1.1 V vs.	0.1 M	[25]
Polycrystalline Copper	C_2H_4	40%	RHE	KHCO ₃	[23]

S	Lattice Parameter (Å)		F _{2g} mode	
Sample	Experimental ^a	Theoretical ^b	frequency (cm ⁻¹)	
CeO ₂	5.4152	5.4451	479.60	
Cu _{4.16} CeO _x	5.4148	5.3606	429.11	

Table S3. Structural parameters of ceria and Cu_{4.16}CeO_x.

^aThe lattice parameters were obtained by rietveld refinement of XRD pattern using TOtal PAttern Solution (TOPAS) program. CeO₂ initial structure cell parameters are acquired by PDF 78-0694, cubic crystal system, a=b=c=0.54109 nm, $\alpha=\beta=\gamma=90^{\circ}$, Space group Fm-3m (225). During refinement thermal parameters constrained in fixed range and sum of occupancies have been set to 1.

^bThe theoretical lattice parameter of CeO₂ and Cu_{4.16}CeO_x was attained by DFT calculation *via* VASP code. Geometrical optimization was performed to obtain lattice parameter of fully relaxed CeO₂ or Cu_{4.16}CeO_x, unit cell."



Fig. S1. (a) Cyclic voltammetry curves of $Cu_{4.16}CeO_x$, OD-Cu and CeO_2 in 0.1 M KHCO₃ saturated with CO₂; (b) constant-potential electrolysis for the above three catalysts at -1.1 V vs. RHE in 0.1 M KHCO₃ saturated with CO₂.



Fig. S2. FEs of the main products by $Cu_m CeO_x$ samples as a function of potential. (a) C_2H_4 , (b) CH₄.



Fig. S3. H_2 Faradaic efficiency of ceria as the function of potential in 0.1 M KHCO₃ saturated by CO₂.



Fig. S4. TEM and HRTEM (insert) images of Cu_mCeO_x . The nanorod displays a lattice spacing of 0.317 nm, corresponding to (111) plane of ceria.



Fig. S5. XRD patterns of CeO_2 and $Cu_{4.16}CeO_x$.



Fig. S6.TEM images of (a) CeO_2 and (b) $Cu_{4.16}CeO_x$. The insets are corresponding SAED patterns



Fig. S7. Raman spectra of CeO₂ and Cu_{4.16}CeO_x. The minor Raman peak at 574–598 cm⁻¹ is attributed to the presence of oxygen vacancies²⁶.



Fig. S8. XPS spectra of O 1s for $Cu_{4.16}CeO_x$ before and after CO_2 reduction. The oxygen vacancy (O_V) concentration in $Cu_{4.16}CeO_x$ is defined as the radio of $O_V/(O_v+O_L)$, where O_L represents lattice oxygen.



Fig. S9. XPS spectra of Ce 3d for $Cu_{4.16}CeO_x$ before and after CO_2 reduction. The Ce^{3+} concentration in $Cu_{4.16}CeO_x$ is defined as $Ce^{3+}/(Ce^{3+}+Ce^{4+}))$.



Fig. S10. In situ Cu K-edge XANES spectra of $Cu_{4.16}CeO_x$ before electrolysis and after 30 min electrolysis at -1.1 V vs. RHE. The standard spectra of Cu_2O , CuO and Cu are presented for comparison.



Fig. S11. CV profile for $Cu_{4.16}CeO_x$ at the scan rate of 50 mV s⁻¹ in 0.05 M sodium sulfate solution at ambient temperature (25 °C). The electrolyte was degassed by bubbling with N₂ prior to the measurement.



Fig. S12. Correlation of Cu⁺ contents with total current density at the potential of -1.1 V vs. RHE. The total current density is collected at 1.0 h after initiating CO₂ reduction.



Fig. S13. Correlation of Cu^+ (a) and Cu^{2+} (b) contents with FE and partial current density for CH_4 at the potential of -1.1 V vs. RHE.



Fig. S14. Optimized structures of Cu^{2+} -CeO_x(111) and Cu^+ -CeO_x(111) slabs. Two neighboring Ce atoms on the CeO₂(111) are replaced by two Cu atoms, considering that the generation of C₂H₄ results from C-C coupling that requires two neighboring Cu atoms. For charge balance, the symmetrical oxygen atoms bonded to Cu atoms are removed. To obtain surfacial Cu⁺, the oxygen atom connecting two Cu atoms is removed. The cyan circles represents the oxygen vacancy.



Fig. S15. TPD profile of $Cu_{4.16}CeO_x$, CeO_2 and Cu for (a) CO_2 , (b) CO.



Fig. S16. Schematic of the pathway of CO₂ reduction toward C_2H_4 *via* *C-*CO intermediate on the Cu⁺ doped CeO₂(111) surface. The inset shows the free-energy landscape for C₂H₄ and CH₄ generation. For each step, the configuration of intermediate adsorption on Cu⁺_mCeO_x is listed.



Fig. S17. The optimized configuration of two *CO intermediates adsorbed on the neighboring Cu atoms.

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