Supporting information

Electrocatalytic CO_2 reduction to ethylene over CuO_x with boosting CO_2 adsorption by lanthanide neodymium

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S1 Experimental section

S1.1 Materials

$Cu(NO_3)_2·3H_2O$ (99%), $Nd(NO_3)_2·6H_2O$ (99.5%), and KCl (99%) were obtained from Adamas-Beta. Toray carbon paper (CP, TGP-H-060) was applied as the catalyst backing layer, and Nafion 115 membrane and Nafion D-521 (5%) were provided by Alfa Aesar. CO_2 (99.999%), N_2 (99.999%), and Ar (99.99%) were purchased by Xi'an Xincheng Nuomin Electrical Equipment Co., Ltd. Other reagents and chemicals were purchased from commercial sources.

S1.2 Catalyst preparation

The Cu-Nd bimetallic catalysts were prepared by a hydrothermal method. Taking the Cu_2NdO_x catalyst as an example, 6 mmol $Cu(NO_3)_2·3H_2O$, 3 mmol $Nd(NO_3)_2·6H_2O$, and 20 mmol glucose were dissolved in 60 mL of deionized water under stirring. The solution was transferred into a Teflon-lined stainless steel autoclave (100 mL) and then heated to 160 ^oC and maintained for 12 h. Upon reaction completion, a precipitate was formed and collected by centrifugation. After washing with ethanol and deionized water repeatedly, a black solid was obtained. The obtained sample was dried at 80 ^oC for 12 h, calcined at 500 ^oC at a rate of 5 ^oC/min, and then kept for 2 h in a muffle furnace to obtain the catalyst, denoted as Cu_2NdO_x. The other Cu-Nd bimetallic catalysts with different Cu/Nd molar ratios such as Cu_5NdO_x, Cu_2NdO_x, $CuNdO_x$, $Cu_{0.5}NdO_x$, $Cu_{0.2}NdO_x$, *etc*., and the sole CuO and Nd_2O_3 were prepared by the same preparation method.

S1.3 Catalyst characterization

To disclose the catalyst characteristics, the samples were analyzed by XRD, SEM, TEM, XPS, *in-situ* Raman, N_2 adsorption/desorption, and CO_2 adsorption. The XRD patterns were studied on an X-ray diffractometer (Bruker D8 Advance) under Cu target Kα radiation. X-ray electron spectroscopy (XPS) was studied by using AXIS SUPRA ray photoelectron energy Spectrometer (monochromatic Ag Lα X-ray source). Prior to the test, the catalyst adhered to the conduction tape. All the binding energies were referenced by C1s XPS peak at 284.8 eV. SEM tests were carried out

on FEI Verios 460 high-resolution field emission scanning electron microscope. TEM images were recorded on a Titan G260-300 electron microscope using a voltage of 200 kV. N_2 adsorption/desorption and CO_2 adsorption were tested on Micromeritics ASAP 2460. Prior to tests, 100 mg of the sample were purged at 150 °C for 12 h. Pore sizes of the samples were analyzed by the Barrett-Joyner-Halenda (BJH) method. The surface areas were obtained by using the Brunauer-Emmett-Teller (BET) method.

In-situ Raman spectra were tested on Renishaw-inVia Micro-confocal Laser Raman Spectrometer under 532 nm He-Ne laser light in 0.5 M KCl electrolyte.

H_2-TPR and CO_2-TPD tests were carried out on an AutoChem II 2920 (Micromeritics, USA). In H_2-TPR tests, 40 mg of the catalysts were heated to 300 °C in He flow (50 mL/min) and kept for 60 min to remove the adsorbed impurities. After the temperature was cooled to 50 °C, the gas was changed to 10% H_2/Ar (50 mL/min) and kept for 60 min, then the catalysts were heated to 800 °C at 10 °C/min, and the H_2 consumption was recorded on a thermal conductivity detector (TCD). For CO_2-TPD tests, 60 mg of the catalysts were heated to 300 °C in a He atmosphere (50 mL/min) and held for 60 min to remove the adsorbed impurities. After the temperature was cooled to 50 °C, the gas was switched to 10% CO_2/He (50 mL/min) and kept for 60 min until the adsorption was completely saturated. Then, the mixed gas was replaced with He at the same flow rate to remove weakly adsorbed and residual CO_2. After 60 min, the catalysts were heated from 50 °C to 750 °C at 10 °C/min, and the desorbed CO_2 was recorded by a TCD detector.

S1.4 Electrode preparation

The procedures for the preparation of Cu_aNdO_x bimetallic electrodes are similar to our recent work.[36] In typical operations, 5 mg of catalyst were added into the solution of 45 μL of Nafion solution and 500 μL of isopropanol under ultrasound irradiation for 1 h to uniformly disperse the catalyst. The mixed solution was dropped on carbon paper (TGP-H-060), which was then dried for use.

S1.5 The CO₂ electrochemical reduction

The CO₂ER was conducted in an H-type electrolytic cell. A working electrode containing Cu-Nd bimetallic catalysts, an Ag/AgCl reference electrode, and a counter electrode (Pt mesh electrode) composed the three electrodes system. Prior to the reaction, the electrolyte (0.5 M KCl) was purged with Ar or CO₂ for at least 30 min. After the catalyst was activated by the linear cyclic voltammetry method, the CO₂ER was conducted through potentiostatic polarization test, and after 1 h, the products were collected. In all measurements, the potential (*vs.* Ag/AgCl) was converted to RHE using the following equation:

$$E_{vs.\ RHE} = E_{vs.\ Ag/AgCl} + 0.059 \times pH + 0.197$$

The gas product was analyzed by GC-9790 II gas chromatograph (Fuli Chromatography Analysis Technology Co., Ltd.). Alkanes and olefins were analyzed by an FID, and H₂ was analyzed by a TCD detector. CO was methanated, and then analyzed by an FID detector.

S1.6 DFT calculation

The DFT calculations were conducted using the Vienna *ab initio* simulation (VASP5.4.4) code.[1] The exchange-correlation was simulated with PBE functional and the ion-electron interactions were described by the PAW method.[2,3] The vdWs interaction was included by using empirical DFT-D3 method.[4] The Monkhorst-Pack-grid-mesh-based Brillouin zone k-points were set as 2×2×1 for all periodic structure with the cutoff energy of 450 eV, and the convergence criteria were set as 0.01 eV A⁻¹ and 10⁻⁵ eV in force and energy, respectively. To avoid interlayer interference, a 20 Å vacuum layer along the *z* direction was employed.

The binding energy calculation of species (E_b) is based on $E_b = E_{total} - E_{substrate} - E_{adsorbate}$, where E_{total}, $E_{substrate}$, and $E_{adsorbate}$ are the electronic energies of adsorption system, substrate, and adsorbate (such as *CO₂, *COOH, and *CO), respectively. The free energy change is based on the equation

$\Delta G = \Delta E_b + \Delta ZPE - T\Delta S$, where the ΔZPE is zero point energy of adsorbate and the $T\Delta S$ is the change of product of temperature and entropy. The entropy of $H^+ + e^-$ pair is approximately regarded as half of H_2 entropy in standard condition.[5]

Table S1. Catalytic performances of the CO_2ER over diverse bimetallic catalysts.

| Entry	Catalyst	Electrolyte	E(V, *vs*. RHE)	j (mA cm^{-2})	FE$_{C2H4}$ (%)	Ref.
1	Cu/CeO$_2$(110)	0.1 KHCO$_3$	-1.13	2.8	39.1	[6]
2	Cu-Pd/CP	0.1 KCl	-1.2	17.2	45.2	[7]
3	Cu$_4$Zn Alloy	0.1 KHCO$_3$	-1.1	2.01	33.3	[8]
4	Sn–CuO NSs	0.5 KHCO$_3$	-1.0	40	22	[9]
5	Cu/Au	0.1 M KHCO$_3$	-1.05	42.9	39	[10]
6	Au/CuO–CuO	1 M KOH	-1.5	78.77	32	[11]
7	CuNi	0.5 M NaHCO$_3$	-0.97	18	24	[12]
8	Phase-separated CuPd	1 M KOH	-0.74	—	48	[13]
9	Cu-Sb alloys	0.1 M KCl	-1.19	28.5	49.7	[14]
10	CuO-CeO$_2$/CB	0.1 M KHCO$_3$	-1.1	7.5	48	[15]
11	Ag/Cu	0.5 M KHCO$_3$	-1.2	8.45	41.3	[16]
12	Ag-Cu Nanodimers	0.1 M KHCO$_3$	-1.1	32.5	40	[17]
13	Cu$_3$Pd$_7$	0.5 M KHCO$_3$	-1.07	1.7	14.1	[18]
14	ZrO$_2$/Cu-Cu$_2$O	0.1 M KCl	-1.28	24	62.5	[19]
15	Cu$_2$NdO$_x$	0.5 M KCl	-1.19	28.4	54.4	This work
16	Cu$_2$CeO$_x$	0.5 M KCl	-1.19	10.1	15	This work (for comparison)
17	Cu$_2$LaO$_x$	0.5 M KCl	-1.19	11.3	13.6	This work (for comparison)
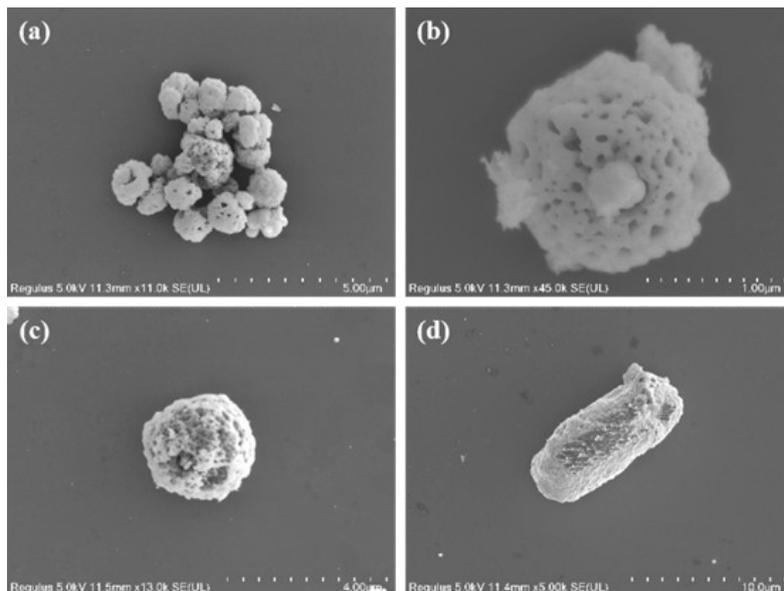
Fig. S1 SEM images of the Cu_2NdO_x(a,b), $CuNdO_x$ (c) and Cu_5NdO_x catalysts (d), respectively.
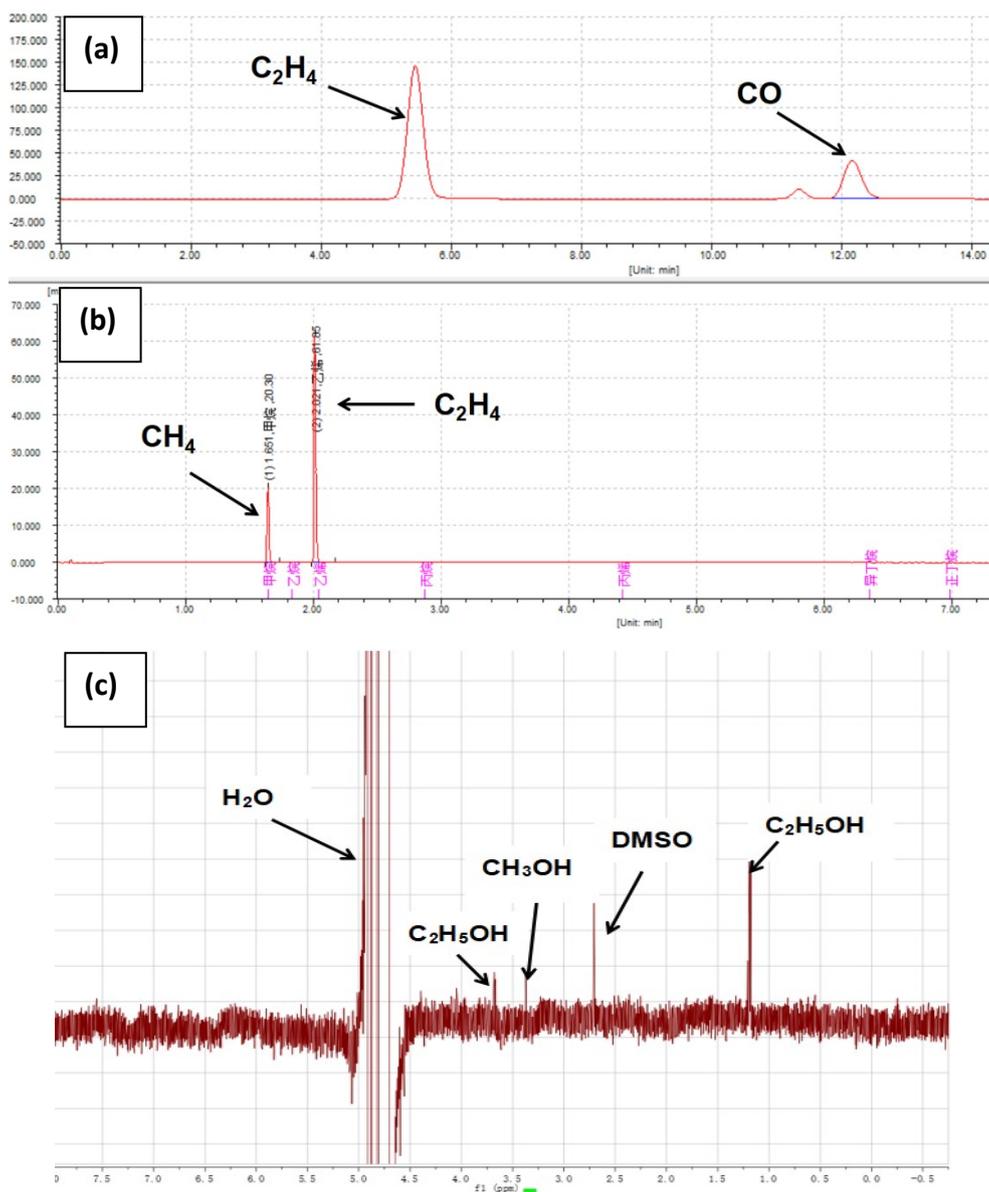
Fig. S2 The GC spectra (a and b) of the obtained products such as C_2H_4, CH_4, CO, H_2, and (c) the ^1H NMR spectrum of liquid products over Cu_2NdO_x in 0.5 M KCl electrolyte.
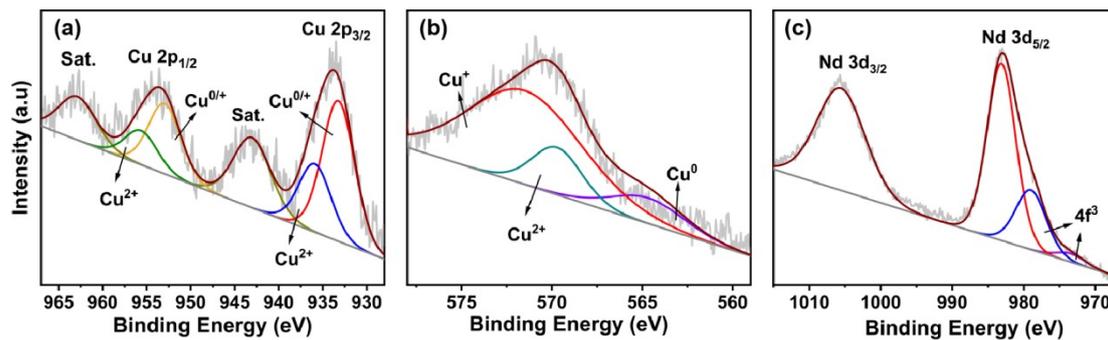
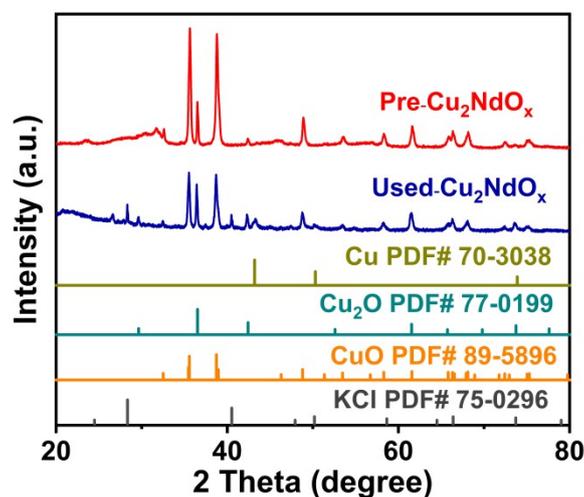**Fig. S3** XPS spectra of the used Cu_2NdO_x catalyst. (a) Cu 2p, (b) Cu LMM, and (c) Nd 3d, respectively.

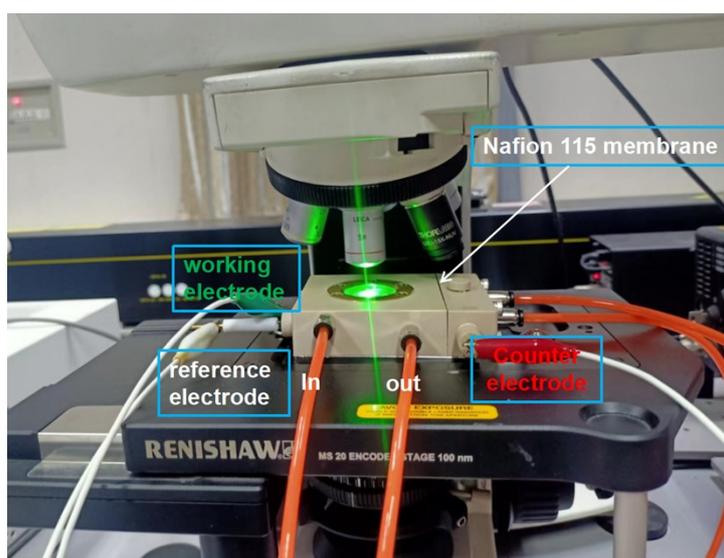**Fig. S4** XRD patterns of the fresh and used Cu_2NdO_x catalyst.

Fig. S5 Setup of the *in situ* Raman set of the CO_2ER over the Cu_2NdO_x catalyst

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