

## Supporting Information

### **Electrochemical CO<sub>2</sub>-to-CO via enriched oxygen vacancies at gold/ceria interfaces**

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## Experimental Section

### General materials

Cerium(III) nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\geq 99\%$ ), ammonium aqueous ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , 25%~28%), trisodium phosphate ( $\text{Na}_3\text{PO}_4$ ,  $\geq 98\%$ ), and sodium hydroxide ( $\text{NaOH}$ ,  $\geq 98\%$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd. Potassium bicarbonate ( $\text{KHCO}_3$ ,  $\geq 99.7\%$ ), isopropyl alcohol ( $\geq 99.7\%$ ), and Nafion<sup>®</sup> perfluorinated resin solution (5 wt.%) were obtained from Sigma-Aldrich. All the chemicals were used as received without further purification. The aqueous solutions were prepared with DI water (18.2 M $\Omega$  cm).

### Preparation of $\text{CeO}_2$ support with different morphologies

The c- $\text{CeO}_2$ , r- $\text{CeO}_2$ , and o- $\text{CeO}_2$  were prepared by following modified approaches reported previously.<sup>1,2</sup> Typically, to prepare c- $\text{CeO}_2$ , 0.651 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 5 mL of DI water. 20 mL of aqueous solution containing 7.2 g of  $\text{NaOH}$  was added dropwise into the above  $\text{Ce}(\text{NO}_3)_3$  aqueous solution under vigorous stirring. The final volume of the mixed solution reached 30 mL by adding DI water. This mixture was stirred for an additional 1 hour at room temperature and hydrothermally treated in a stainless-steel vessel autoclave at 180°C for 24 h. After cooling in air, the white precipitate was collected by centrifugation and washed with water until the pH value of supernatant was neutral. Finally, the product was vacuum dried at 40°C overnight. The synthesis method of r- $\text{CeO}_2$  was similar to that of c- $\text{CeO}_2$ , except that the hydrothermal temperature was 100°C. To prepare o- $\text{CeO}_2$ , 0.3474 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 32 mL of  $\text{Na}_3\text{PO}_4$  (0.25 mM) aqueous solution. After stirring for 1 hour, the mixture was hydrothermally treated in sealed Teflon bottle at 170°C for 10 h. The precipitates were collected by centrifugation, washed with DI water and ethanol three times, and then vacuum dried at 40 °C overnight. All these three  $\text{CeO}_2$  nanoparticles were calcined at 500°C for 3 h in air.

### **Preparation of Au/CeO<sub>2</sub> catalysts**

Au/CeO<sub>2</sub> catalysts were prepared by a modified deposition-precipitation (DP) method.<sup>3</sup> The prepared CeO<sub>2</sub> with different shapes (50 mg) were dispersed in 20 mL of DI water. The slurry was sonicated for 30 minutes and stirred for 1 hour at room temperature. Subsequently, 2 mL of HAuCl<sub>4</sub> (10.16 mM) aqueous solution was added dropwise. After stirring for 15 minutes, 5 mL of aqueous ammonia (3 M) was slowly added. The mixture was then kept in water bath at 60°C for 4 hours with constant stirring. The light-yellow precipitates were collected by centrifugation at 8,000 rpm and washed several times with diluted ammonia aqueous solution (0.1 M). After vacuum dried at room temperature overnight, the obtained powder was calcined in muffle furnace at 200°C for 1 hour under air with the heating rate of 1°C min<sup>-1</sup>. The catalyst preparation process was carried out under light shielding.

### **Materials characterization**

The morphologies of CeO<sub>2</sub> catalysts were observed using scanning electron microscope (SEM, S4800). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a FEI F20 with an acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded using a Rigaku SmartLab diffractometer equipped with Cu-K $\alpha$  radiation. The X-ray photoelectron spectroscopy analysis was conducted on a Thermo Fisher Scientific NEXSA instrument. The Raman spectra were collected using a LabRAM HR Evolution Raman spectrometer (HORIBA) at 325 nm (1 mW). The Au loading contents of Au/CeO<sub>2</sub> catalysts were determined by inductively coupled plasma mass spectrometry (ICP-MS, Elementar Vario EL).

### **Working electrode preparation**

8 mg of prepared Au/CeO<sub>2</sub> catalysts, 1.6 mg of Ketjenblack EC300 carbon black, and 48  $\mu$ L

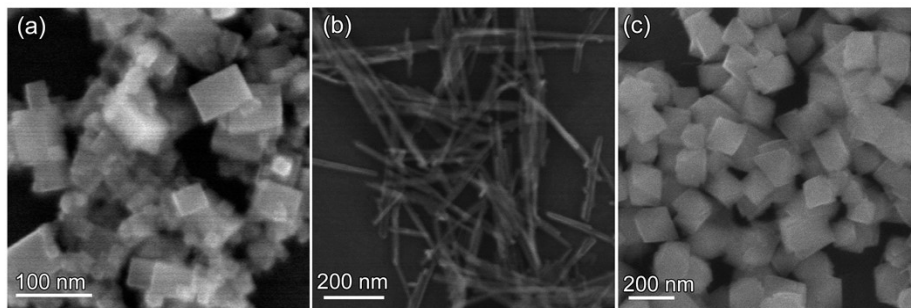
of Nafion perfluorinated resin solution (5 wt.%) were added into 1.6 mL of isopropyl alcohol, and then ultrasonically dispersed for 2 hours. The suspension was spray coated on carbon-based GDL (Sigracet 39BB) with catalyst/carbon black loading amount of 2.4 mg cm<sup>-2</sup>. The prepared GDE was dried vacuum at room temperature. Similarly, the CeO<sub>2</sub> ink was prepared by mixing 8 mg of CeO<sub>2</sub>, 1.6 mg of Ketjenblack EC300 carbon black, 48 μL of Nafion perfluorinated resin solution (5 wt.%), and 1.6 mL of isopropyl alcohol. Nickel foam and Ag/AgCl reference electrode (3 M KCl, BASi) were used as anode and reference electrode, respectively.

### CO<sub>2</sub>RR measurements

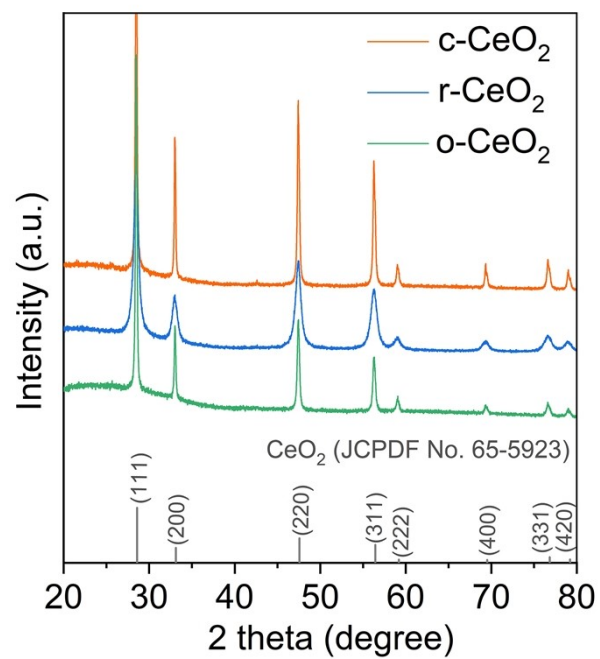
CO<sub>2</sub>RR was conducted in a flow cell setup with a three-electrode configuration using electrochemical station (CHI660E). The cathode chamber and anode chamber were separated by an anion exchange membrane (Fumasep FAB-PK-130). The geometric area of the cathode is 1 cm<sup>2</sup>. 1 M KOH was used as catholyte and anolyte and circulated using peristaltic pump, respectively. CO<sub>2</sub> (Linde, 99.9%) was supplied to gas chamber at a rate of 20 mL min<sup>-1</sup>. The CO<sub>2</sub>RR performance of cathodes were evaluated using constant-current electrolysis. All the potentials were converted to values versus RHE by the equation:  $E_{RHE} = E_{Ag/AgCl} + 0.210 \text{ V} + 0.0591 \text{ V} \times \text{pH}$ . CO<sub>2</sub>RR gas products were detected by a gas chromatograph (Shanghai Ramiin GC2060) equipped with thermal conductivity and flame ionization detectors. The liquid products generated in CO<sub>2</sub>RR were quantified using a high-performance liquid chromatography (HPLC) (Waters Arc HPLC; Aminex HPX-87H 300 × 7.8 mm column) with an aqueous solution of 0.005 M H<sub>2</sub>SO<sub>4</sub> as an eluate. The  $j_{CO, \text{mass}}$  is calculated as follows:

$$j_{CO, \text{mass}} \left( \text{mA mg}_{Au}^{-1} \right) = \frac{\text{Total current (mA)} \times FE_{CO}}{\text{weight percentage of Au (wt.\%)} \times \text{catalyst loading on electrode}}$$

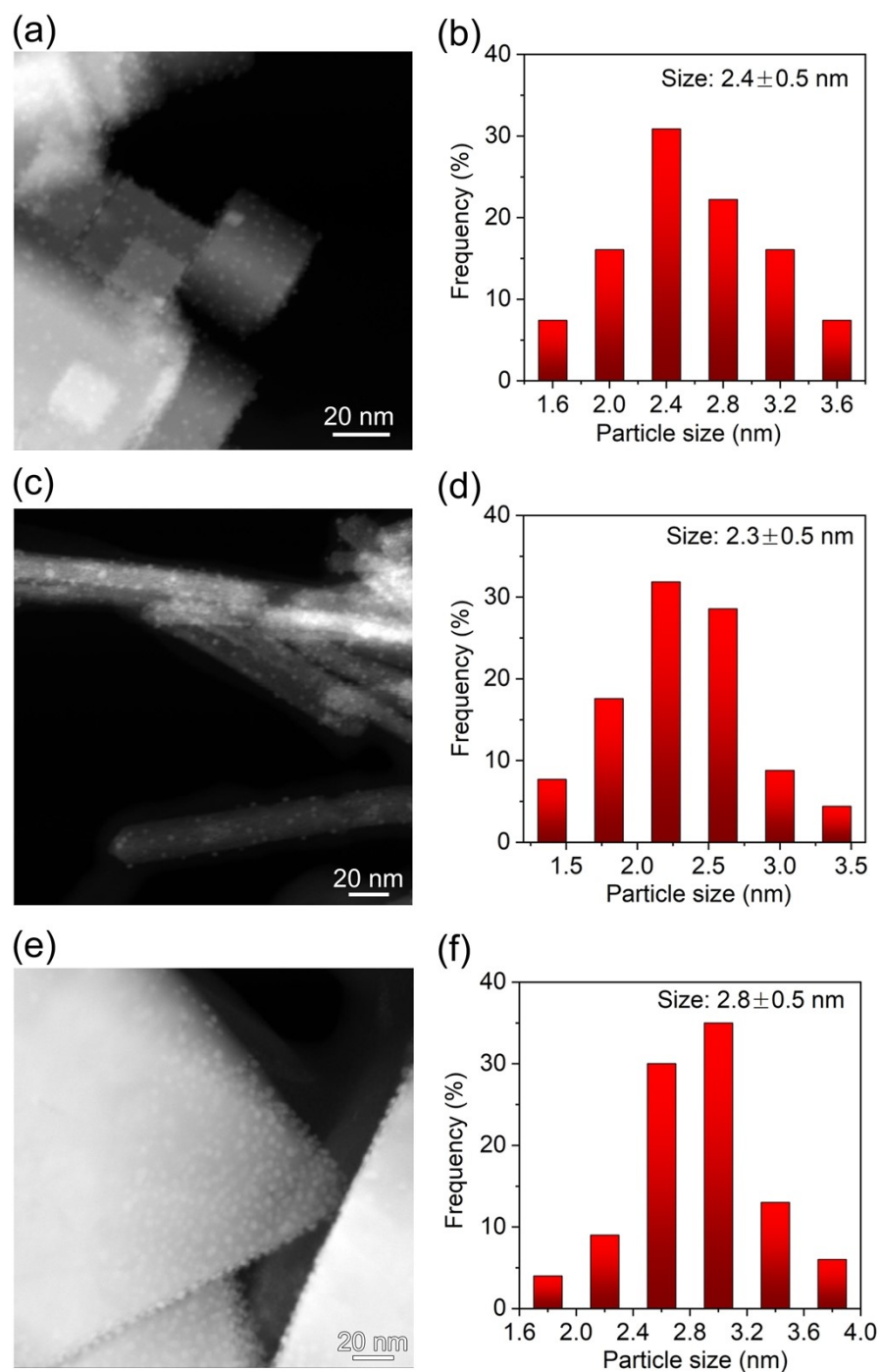
where  $FE_{CO}$  is the CO Faradaic efficiency in percentage, and  $A_{GDE}$  is the geometric area of the electrode.



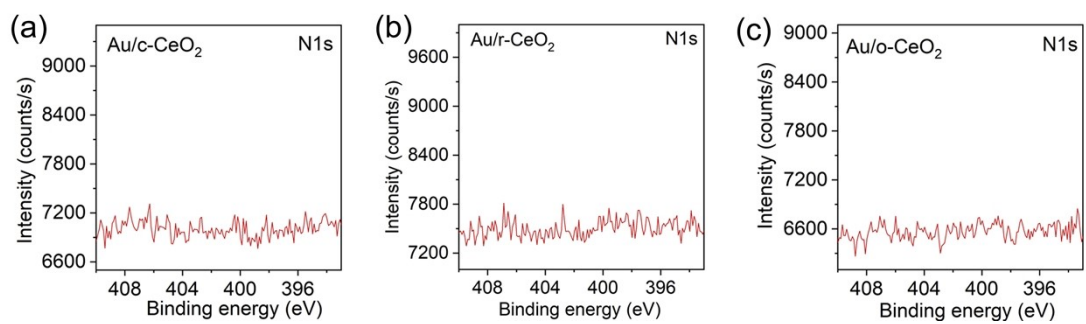
**Fig. S1.** SEM images of CeO<sub>2</sub> nanoparticles with different morphologies: (a) cube, (b) rod, and (c) octahedron.



**Fig. S2.** XRD patterns of CeO<sub>2</sub> catalysts.

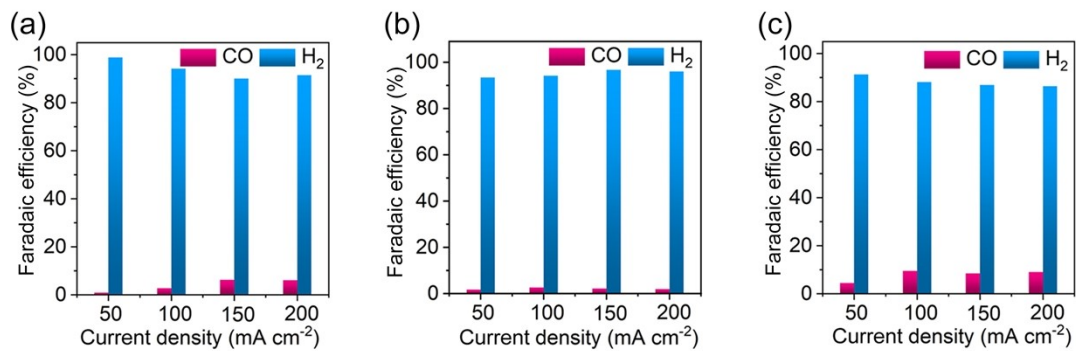


**Fig. S3.** The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and the corresponding particle size distribution histograms of Au for (a,b) Au/c-CeO<sub>2</sub>, (c,d) Au/r-CeO<sub>2</sub>, and (e,f) Au/o-CeO<sub>2</sub> catalysts.

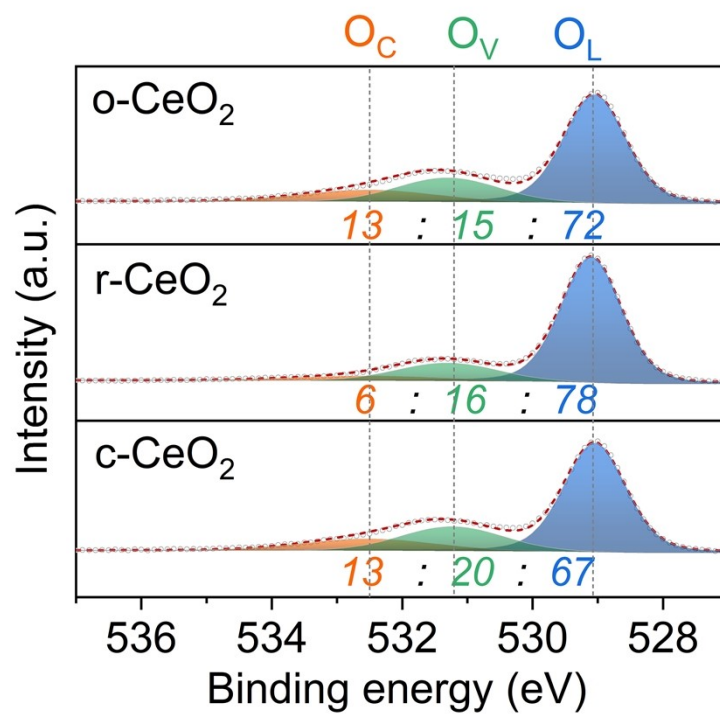


**Fig. S4.** N 1s XPS spectra of (a) Au/c-CeO<sub>2</sub>, (b) Au/r-CeO<sub>2</sub>, and (c) Au/o-CeO<sub>2</sub>.

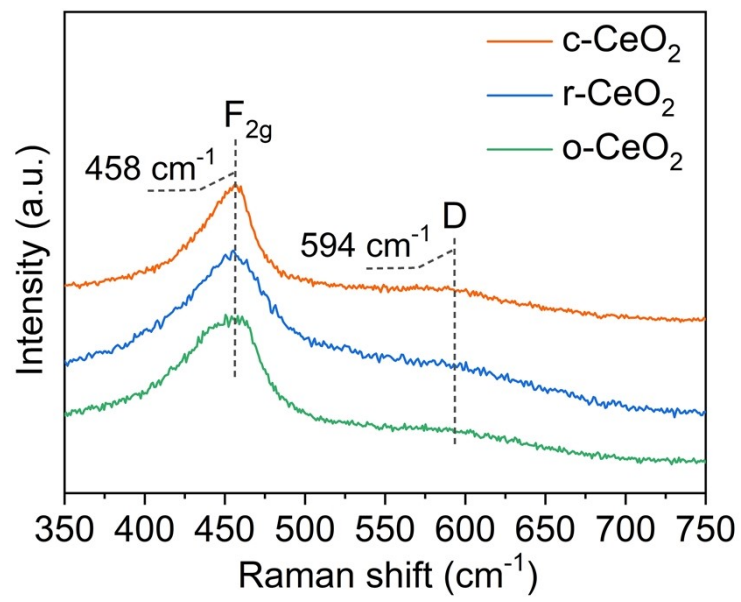




**Fig. S5.** CO<sub>2</sub>RR gas product distribution on (a) c-CeO<sub>2</sub>, (b) r-CeO<sub>2</sub>, and (c) o-CeO<sub>2</sub> under different applied current densities.



**Fig. S6.** O 1s XPS spectra of CeO<sub>2</sub> catalysts.



**Fig. S7.** UV Raman spectra of CeO<sub>2</sub> catalysts.

**Table S1.** Comparison of different Au-based electrocatalysts for CO<sub>2</sub> electroreduction to CO in a flow cell.

<b>Catalysts</b>	<b><math>j_{\text{CO, mass}}</math> (mA mg<sub>Au</sub><sup>-1</sup>)</b>	<b><math>j</math> (mA cm<sup>-2</sup>)</b>	<b>Ref.</b>
Au/c-CeO <sub>2</sub>	678	200	This work
Au <sub>81</sub> Ga <sub>19</sub> aerogel	29	28	4
Au/carbon	75	100	5
4H/fcc Au-MMT	478	200	6
Au-Ag hollow nanocubes	294	107	7
H <sub>2</sub> O <sub>2</sub> -treated-AuMPs	516	102	8

**Table S2.** Formate FEs on Au/CeO<sub>2</sub> GDEs in CO<sub>2</sub>RR.

$j_{\text{total}}$ (mA cm <sup>-2</sup> )	Au/c-CeO <sub>2</sub> (%)	Au/r-CeO <sub>2</sub> (%)	Au/o-CeO <sub>2</sub> (%)
50	2	2	2
100	3	4	2
150	3	4	3
200	3	4	3

**Table S3.** Formate FEs on CeO<sub>2</sub> GDEs in CO<sub>2</sub>RR.

$j_{\text{total}}$ (mA cm <sup>-2</sup> )	c-CeO <sub>2</sub> (%)	r-CeO <sub>2</sub> (%)	o-CeO <sub>2</sub> (%)
50	1	1	1
100	1	1	1
150	1	1	1
200	1	1	1

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