

Supporting information

Engineering CeO₂-ZrO₂-CuO_x nanocatalysts with abundant surface Cu species and oxygen vacancies toward high catalytic performance in CO oxidation and 4-nitrophenol reduction

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1. The characterization of catalyst

X-ray powder diffraction (XRD) of samples was obtained by Bruker D8 employing Cu-K α radiation (1.54056 Å) with an operating voltage of 40 kV and a beam current of 40 mA. The morphologies of samples were observed by high-resolution transmission electron microscopes (HRTEM) with an accelerating voltage of 200 kV (JEOL JEM-2010F electron microscope). The element component of catalysts was measured by the energy disperse X-ray spectrum (EDS, EDAXTLS). The surface components and valence states of samples were characterized by X-ray photoelectron spectra (XPS) (Thermo Fisher Scientific ESCALAB250Xi) employing Al K α (1486.6 eV). The structural properties of samples were recorded with Raman spectra (Bruker Senterra) at ambient temperature under an excitation of 488 nm. The specific surface area, pore size and pore volume of the samples were obtained by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods through N₂ adsorption-desorption isotherms (Quantachrome, Autosorb-iQ2). Before testing, all samples were degassed at 200°C for 6 h to remove the moisture and physical adsorbed gases.

2. Determination of the redox properties of CeO₂-ZrO₂-CuO_x catalysts before/after N₂O oxidation

The reducibility of CeO₂-ZrO₂-CuO_x (CZC) catalysts was investigated by H₂ temperature-programmed reduction (H₂-TPR) (Thermo TPDRO 1100 series) measured in a quartz reactor. Typically, 50 mg of samples were pretreated in He stream at 100°C with a flow rate of 40 ml min⁻¹ for 30 min before testing, and then they were cooled to room temperature. After that, a flow of 5% H₂/Ar (40 ml min⁻¹) was employed and tested from room temperature to 400°C with a heating rate of 10°C min⁻¹. The amount of H₂ consumption (A₁) and the TPR profile was monitored and recorded by a thermal conductivity (TCD) detector. Afterward, the reduced sample was cooled to 50°C in He (40 ml min⁻¹) and was purging for 1 h. Secondly, the samples were oxidized by 5 vol % N₂O (99.995% purity) in N₂ (99.999% purity) balance at this temperature with the flow rate of 40 ml min⁻¹ for 1 h. Lastly, the sample was purged again with He using the same condition and then to start an H₂-

TPR run. The amount of H₂ consumption (A₂) was also recorded by a TCD detector.

3. The test of CO catalytic oxidation

The catalytic performance of catalysts for CO oxidation was evaluated in a fixed bed quartz reactor at atmospheric pressure. Typically, 100 mg of catalyst without any pretreatment was loaded in a quartz reactor. The mixed feed gas is composed of 1 vol% CO, 20 vol% O₂ with N₂ balance. The total flow rate of the synthetic feed gas is 50 ml min⁻¹ (space velocity = 30000 ml g cat⁻¹ h⁻¹). The change of gas concentration was monitored with an online gas chromatography system (Agilent 7890B) equipped with a TCD. The CO conversion was calculated based on the following formula:

$$CO \text{ conversion } (\%) = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100\% \quad (1)$$

where [CO]_{in} and [CO]_{out} are the CO concentration in the inlet and outlet gas, respectively.

4. The test of 4-nitrophenol reduction

Typically, 2 mg of catalysts (0.04 mg/mL), 76 mg of NaBH₄ (2 mmol) and 50 mL of aqueous solution of 4-nitrophenol (4-NP) (0.1 mM) was added into a conical flask. After uniformly shake, 1 mL of the above solution was withdrawn per 2 min. The part of the solution was transferred into a quartz cuvette at room temperature. The absorbance spectra were recorded via a UV-vis spectrophotometer. In 4-NP reduction reaction, the aqueous solution of 4-nitrophenol 4-NP was constantly stirring, so as to ensure full mass transfer and eliminate the diffusion effect as much as possible. The conversion rate of 4-NP was calculated from the following equation:

$$4\text{-NP conversion } (\%) = [(C_0 - C_t)/C_0] \times 100\% \quad (2)$$

In addition, as the amount of NaBH₄ is excessive in the catalytic system, the kinetics information was obtained by the following equation:

$$dC_t/dt = -k_{app} C_t \quad (3)$$

$$\ln(C_t/C_0) = -k_{app} t \quad (4)$$

where, C_t, C₀, k_{app} and t are the concentration of the 4-NP solution in different time, the initial concentration of 4-NP in the solution, the apparent constant of reaction rate,

and the time of reaction, respectively.

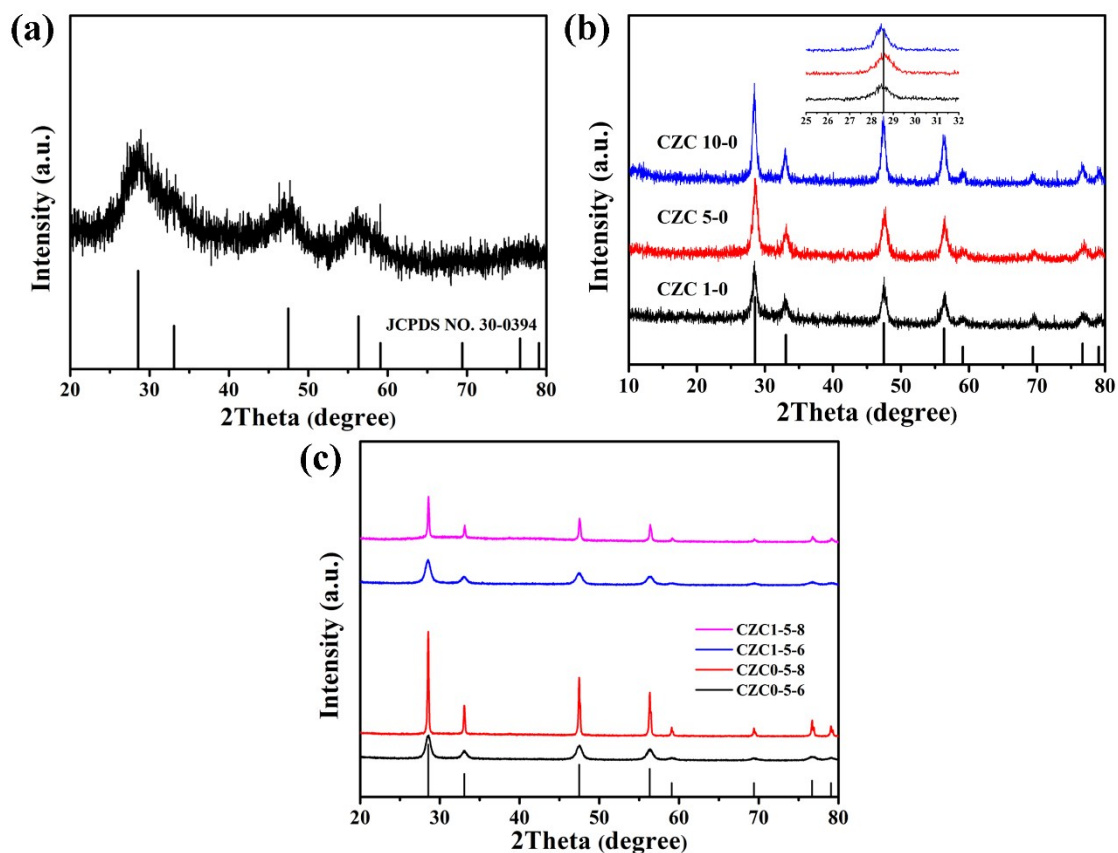


Fig. S1 The XRD patterns of CZC samples: (a) the CZC nanocatalysts acquired by straightforward grinding using metal salt and KOH; (b) the CZC samples with different ZrO₂ doping; (c) the CZC nanocatalysts calcined at different temperature.

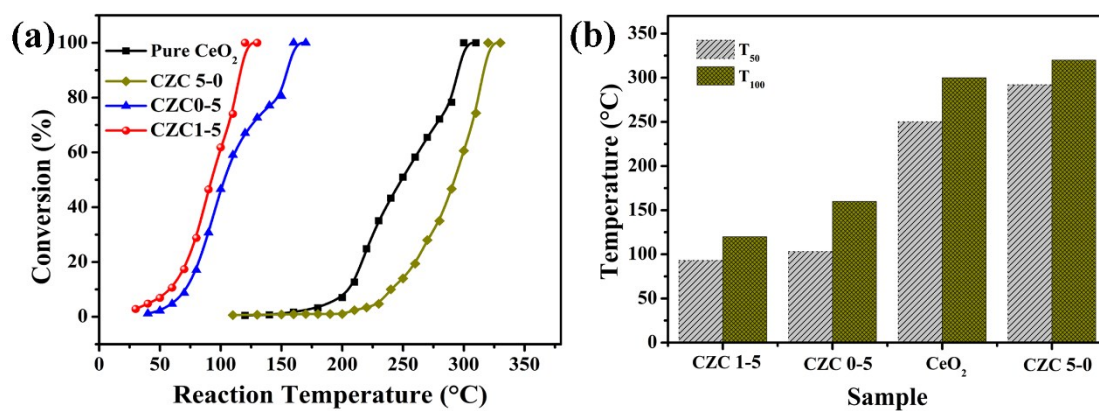


Fig. S2 (a) The CO conversion performance curve; (b) T₅₀ and T₁₀₀ values of CeO₂, CZC5-0 (Zr/Ce=0.05), CZC0-5 and CZC1-5 samples.

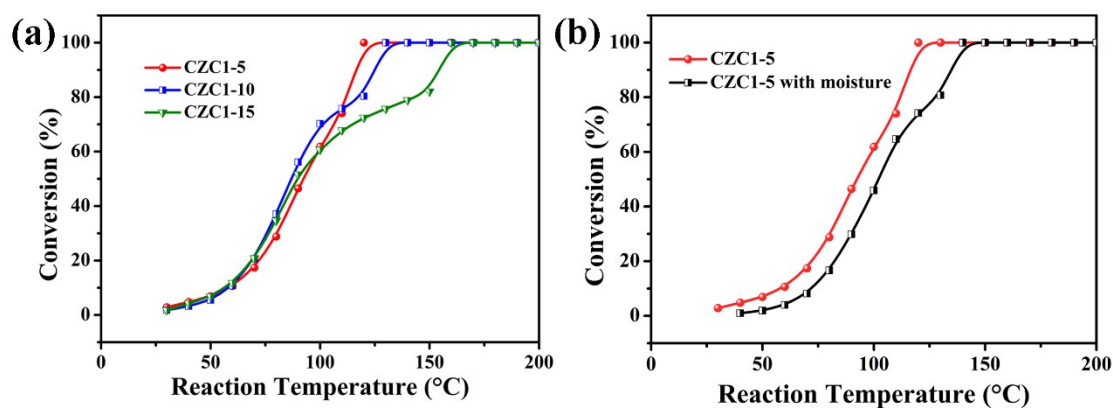


Fig. S3 (a) The CO conversion performance of samples with more Cu loading; (b) the water resistance test of CZC1-5 sample for CO oxidation.

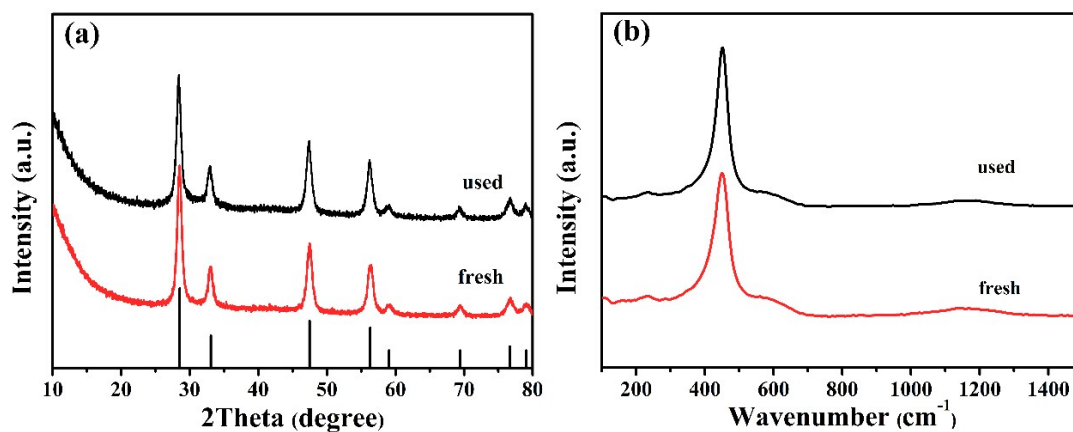


Fig. S4 (a) XRD patterns and (b) Raman spectra of the fresh and used CZC1-5 sample after a long-term stability test under moisture conditions for 120 h.

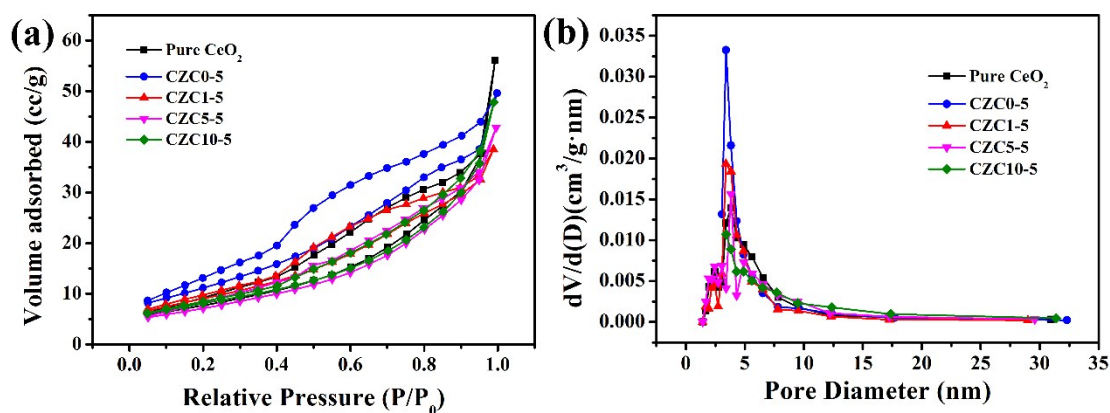


Fig. S5 (a) N₂ adsorption-desorption isotherms and (b) BJH pore size distribution curves of various CZC samples.

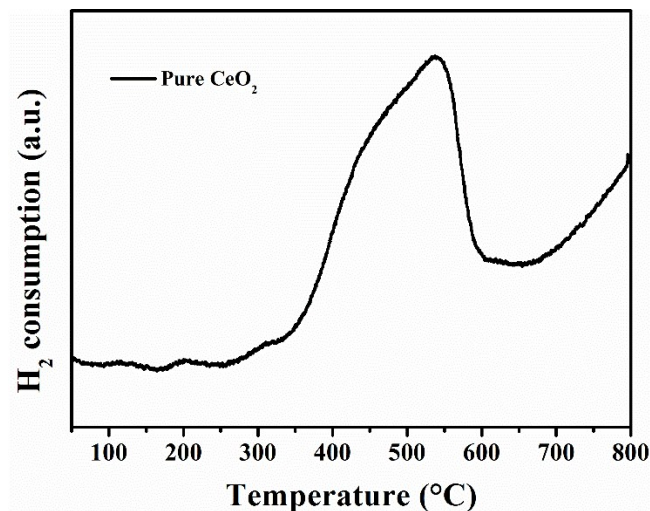


Fig. S6 H₂-TPR profile of the CeO₂.

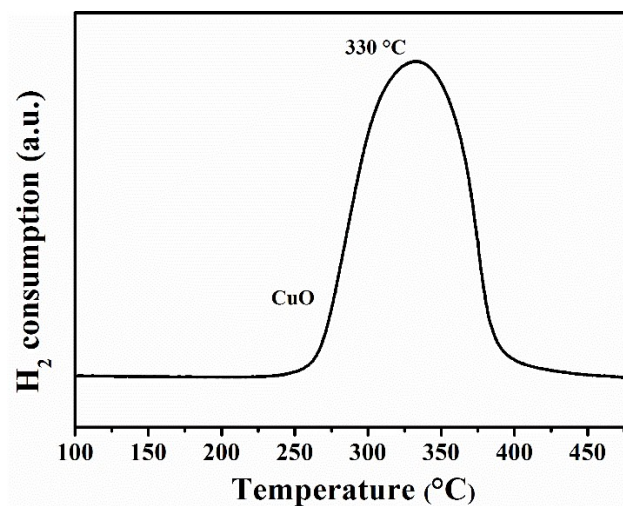


Fig. S7 H₂-TPR profile of the CuO.

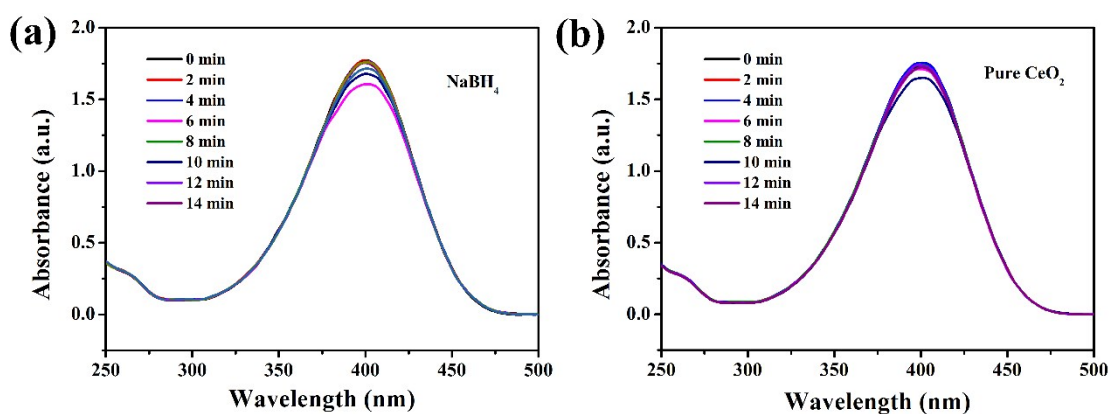


Fig. S8 UV-vis spectra of the 4-NP reduction reaction on as-prepared catalysts: (a) without catalyst, (b) CeO₂.

Table S1 Zr and Cu loadings determined by EDS measurement.

Sample	Ce content (At %)	Cu content (At %)	Zr content (At %)	O content (At %)	Zr/Ce molar ratio	Cu/Ce molar ratio
CZC0-5	32.93	1.88	--	65.24	--	0.057
CZC1-5	30.27	1.69	0.66	67.38	0.021	0.056
CZC5-5	30.65	2.04	2.08	65.23	0.068	0.067
CZC10-5	26.45	1.70	3.46	68.39	0.131	0.064

Table S2 The contents of Ce, Cu, Zr elements obtained by ICP.

Samples	Ce contents (mg/L)	Zr contents (mg/L)	Cu contents (mg/L)	Zr/Ce molar ratio	Cu/Ce molar ratio
CZC0-5	3.845	--	0.074	--	0.042
CZC1-5	3.852	0.019	0.079	0.008	0.045
CZC5-5	3.848	0.087	0.075	0.035	0.043
CZC10-5	3.837	0.186	0.076	0.075	0.043

Table S3 The BET surface area, pore volume and pore size over different catalysts.

Sample	S _{BET} (m ² g ⁻¹)	Pore volume (m ³ g ⁻¹)	Pore size (nm)
Pure CeO ₂	48	0.063	3.832
CZC0-5	52	0.065	3.408
CZC1-5	46	0.063	3.402
CZC5-5	43	0.057	3.820
CZC10-5	30	0.072	3.413

Table S4 Quantified differential CO conversion rates of the catalysts at 110°C.

Sample	R_w at 110°C (mol s ⁻¹ g ⁻¹) ($\times 10^{-5}$) ^a
CZC0-5	8.39
CZC1-5	10.52
CZC5-5	9.87
CZC10-5	8.98

^a R_w : CO conversion rates normalized by catalyst weights.**Table S5** H₂-TPR results of catalysts with different calcination temperature before/after N₂O oxidation.

Sample	A ₁	A ₂	A ₂ /A ₁	A ₁ total hydrogen uptake (mmol/g _{cat})	A ₂ total hydrogen uptake (mmol/g _{cat})
CZC0-5	5662.014	4907.533	0.866747	0.226554	0.196365
CZC1-5	6286.824	5896.635	0.937935	0.25605	0.240164
CZC5-5	7540.564	7372.683	0.977736	0.30712	0.300282
CZC10-5	7415.803	5837.628	0.787188	0.29615	0.233126