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Supporting Information

Correlating Morphology and Doping Effects with the Carbon Monoxide Catalytic Activity of Zn doped CeO_2 Nanocrystals

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1. EXPERIMENTAL

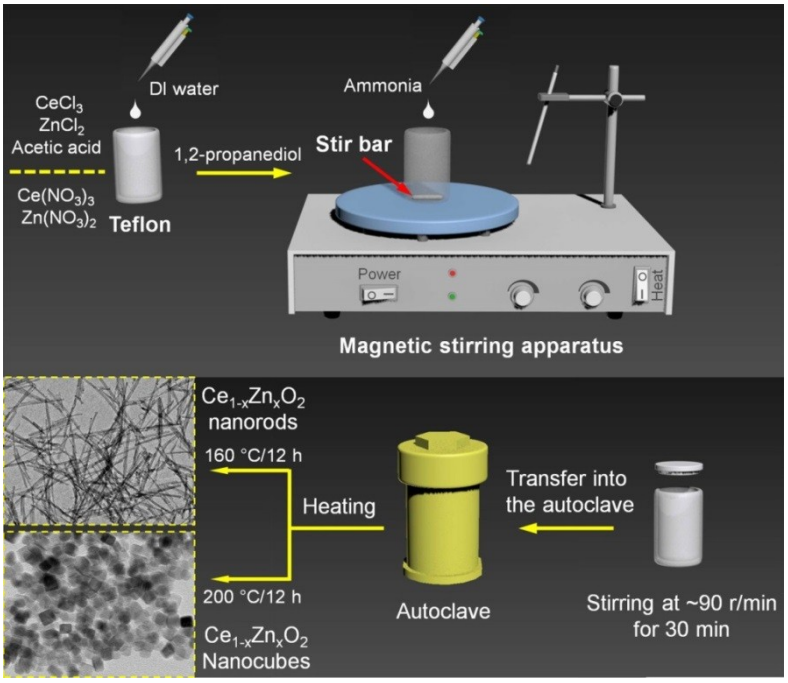
1.1 Materials

Cerium chloride heptahydrate ($CeCl_3 \cdot 7H_2O$, M_w: 372.58), cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, M_w: 434.22), zinc nitrate ($Zn(NO_3)_2$, M_w: 297.49), zinc chloride ($ZnCl_2$, M_w: 136.3), 1,2-propanediol (ρ: 1.036 g/mL), acetic acid (CH_3COOH, M_w: 60.05) and ammonia hydroxide solution (ρ: 0.9 g/mL) were purchased from Sigma-Aldrich without further purification.

1.2 Synthesis of $Ce_{1-x}Zn_xO_2$ nanocubes and nanorods (Scheme S1)

Synthesis of $Ce_{1-x}Zn_xO_2$ nanocubes: to produce neat CeO_2 or $Ce_{1-x}Zn_xO_2$ nanocubes, $Ce(NO_3)_3 \cdot 6H_2O$ and $Zn(NO_3)_2$ (the latter not present during neat CeO_2 nanocube preparation) with a total concentration of 0.3 M were weighed stoichiometrically and dissolved in 5 mL deionized (DI) water. Next, 15 mL of 1,2-propanediol was added to the solution. After stirring for 5 min, 10 mL of ammonia hydroxide solution was added dropwise to the solution under magnetic stirring over 30 min. The solution was then transferred to a Teflon flask which was sealed tightly in a stainless-steel autoclave. Hydrothermal treatment was conducted at 200 °C for 12 h. After cooling, the precipitate was collected and washed with DI water and then centrifuged at 5000 rpm for 2 min for five cycles, and then dried in an oven at 70 °C for 24 h.

Synthesis of $Ce_{1-x}Zn_xO_2$ nanorods: to obtain neat CeO_2 or $Ce_{1-x}Zn_xO_2$ nanorods, $CeCl_3 \cdot 7H_2O$ and $ZnCl_2$ (the latter not present during neat CeO_2 nanorod preparation) with a total concentration of 0.3 M were weighed stoichiometrically and dissolved in 5 mL DI water. Next, 200 μL of acetic acid and 15 mL of 1,2-propanediol were added to the solution (in that order). The presence of Cl^- is beneficial for forming nanorods and promoting higher catalytic activity.[1, 2] The neat CeO_2 and $Ce_{1-x}Zn_xO_2$ nanorods were synthesized using a similar process as described above with a modified hydrothermal treatment temperature of 160 °C.



Scheme S1 Equipment and process used to synthesize neat CeO_2 and $Ce_{1-x}Zn_xO_2$ nanostructures.

1.3 Characterization

Structural analysis of the as-synthesized $Ce_{1-x}Zn_xO_2$ nanostructures was performed using an X-ray diffractometer with Cu Kα radiation (λ = 0.1541 nm). The microstructures were visually observed by transmission electron microscopy (TEM) on FEI Tecnai G2 and Philips CM200 instruments. Raman spectra were collected on a Renishaw inVia Raman Microscope with a 514 nm laser. The chemical bonding states were investigated by X-ray photoelectron spectroscopy (XPS) on ESCALAB250Xi spectrometer. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method using a Micromeritics ASAP 2000 Gas Sorption Analyser. Electron paramagnetic resonance (EPR) experiments were performed on a Bruker EMS X-Band EPR spectrometer with a quartz sample tube of 3.8 mm.

H_2 temperature-programmed reduction (H_2-TPR) measurements: H_2-TPR measurements were conducted on a Micromeritics Autochem II. Approximately 30 mg of sample was added to a quartz U-cell and placed in the instrument. The sample was initially flushed with 40 mL/min air at room temperature for 20 min after which it was heated to 300 °C for 30 min with heating rate of 15 °C/min. The sample was then cooled to 50 °C and flushed with argon to remove the air. A 5 vol%

H_2 in Ar gas mix, flowing at 40 mL/min, was introduced to the sample where it was kept at 50 °C for 20 min. The sample was then heated to 900 °C at 15 °C /min. It was held at this temperature for a further 5 min and then cooled to room temperature. H_2 consumed during reduction was measured by a thermal conductivity detector (TCD) located within the instrument.

1.4 Catalytic activity evaluation

CO oxidation catalytic activity was evaluated using a fixed-bed quartz tubular microreactor (i.d. = 6.0 mm) at atmospheric pressure. 50 mg catalyst was first pre-treated in pure oxygen (30 mL/min) at 300 °C for 2 h and then in pure nitrogen (30 mL/min) until cooling to RT. Afterwards, the reactant gas mixture, consisting of 5 vol% CO + 30 vol% O_2 + 65 vol% N_2, was introduced to the reactor at a total flow of 40 mL/min, giving a gas hourly space velocity of ca. 48,000 ml (g h)$^{-1}$. The concentrations of the reactants and products in the reactor effluent were monitored on-line by a gas chromatograph (Young Lin 6500) equipped with a TCD and a Carboxen-1010 PLOT column. The catalytic activities of the samples were assessed by the temperatures $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ corresponding to 10%, 50% and 90% CO conversions, respectively. CO oxidation was quantitatively determined using $(c_{inlet}-c_{outlet})/c_{inlet} \times 100\%$, where c_{inlet} and c_{outlet} are the CO concentrations in the inlet and outlet feed streams, respectively.

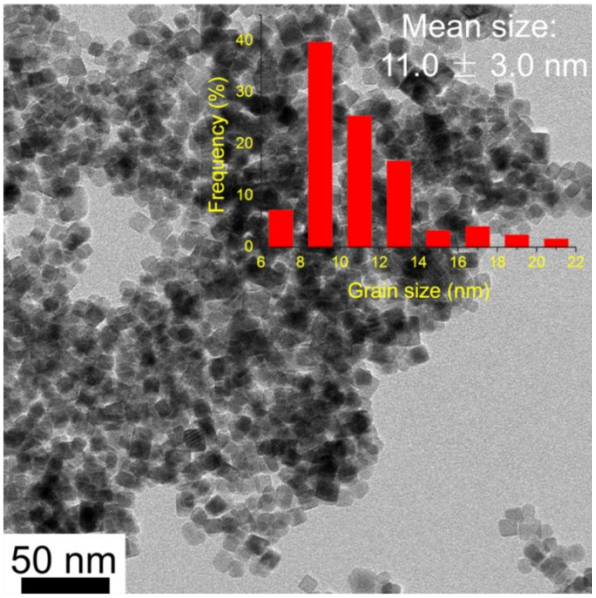


Fig. S1 TEM image and particle size distribution of $Ce_{0.9}Zn_{0.1}O_2$ nanocubes.

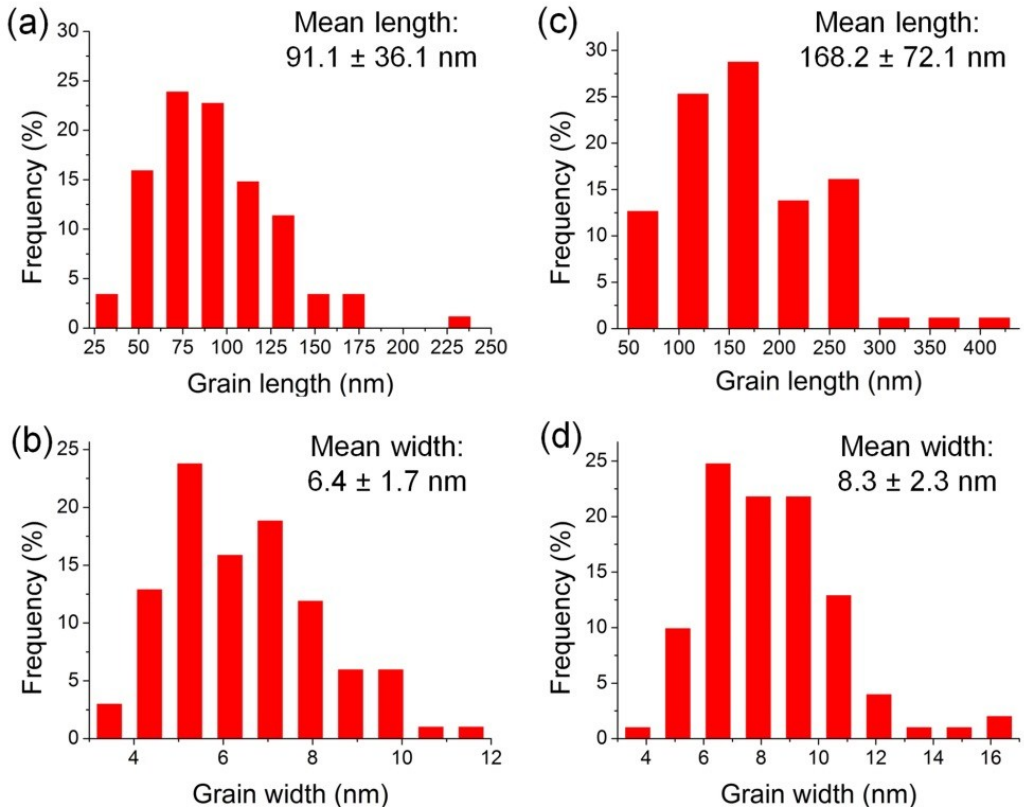


Fig. S2 Grain length and width distributions of $Ce_{1-x}Zn_xO_2$ nanorods: CeO_2 (a, b) and $Ce_{0.8}Zn_{0.2}O_2$ (c, d).

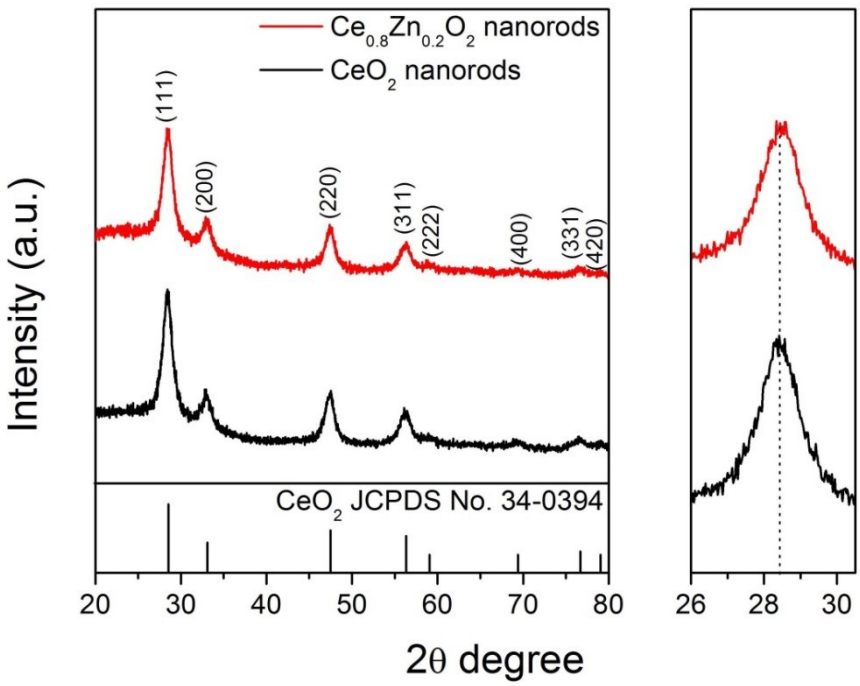


Fig. S3 XRD profiles of CeO_2 and $Ce_{0.8}Zn_{0.2}O_2$ nanorods.

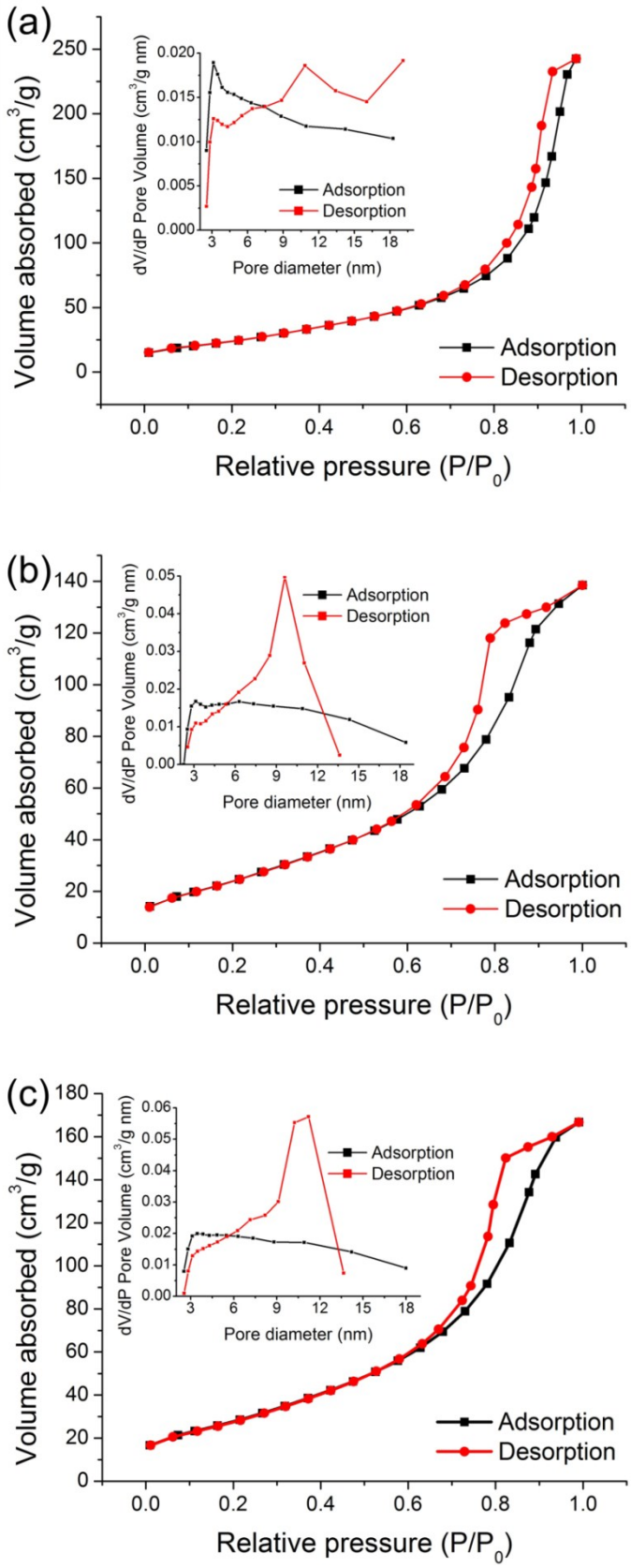


Fig. S4 Nitrogen adsorption–desorption isotherms and pore size distributions (insets) of nanocubes: (a) CeO_2, (b) $Ce_{0.9}Zn_{0.1}O_2$ and (c) $Ce_{0.8}Zn_{0.2}O_2$.

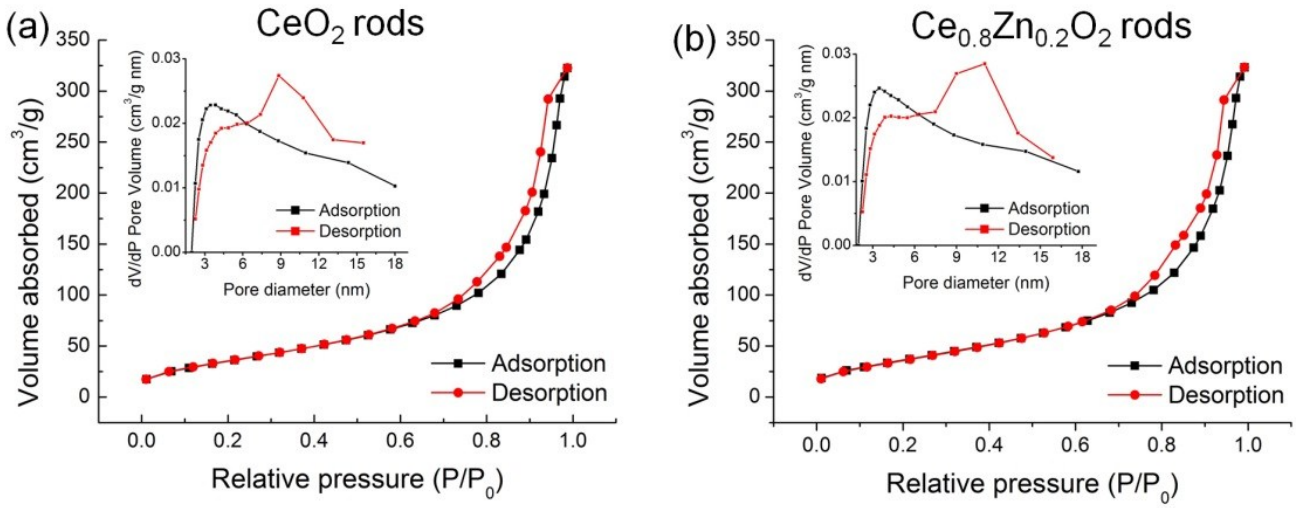


Fig. S5 Nitrogen adsorption–desorption isotherms and pore size distributions (insets) of nanorods (a) CeO_2 and (b) $Ce_{0.8}Zn_{0.2}O_2$.

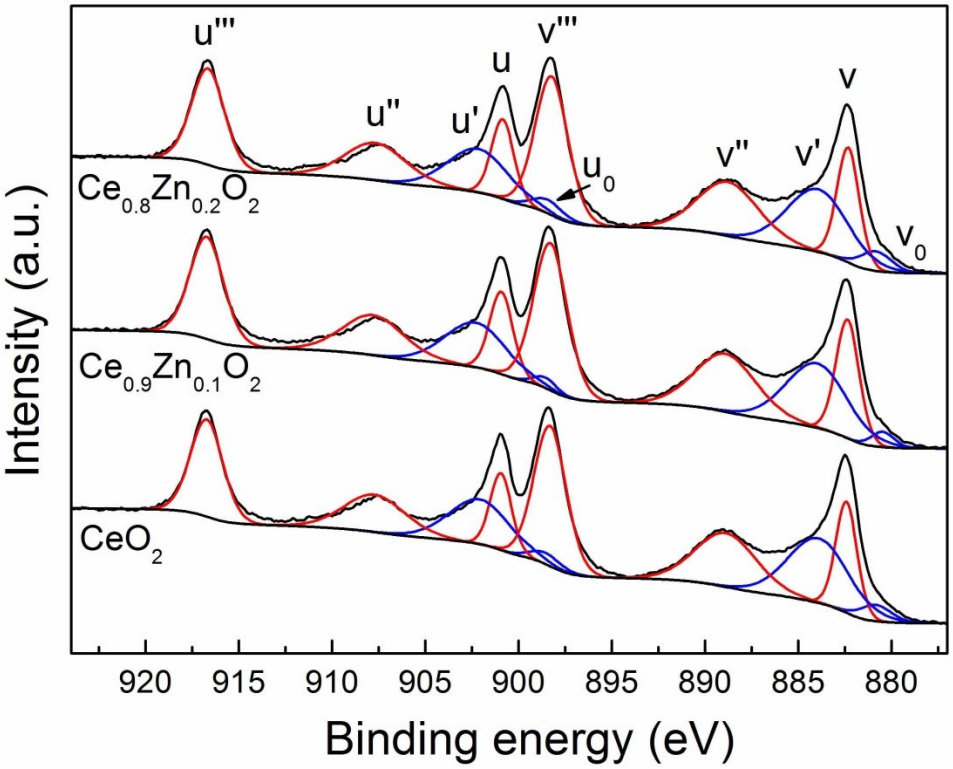


Fig. S6 XPS spectra of Ce 3d for the neat CeO_2 and $Ce_xZn_{1-x}O_2$ nanocubes.

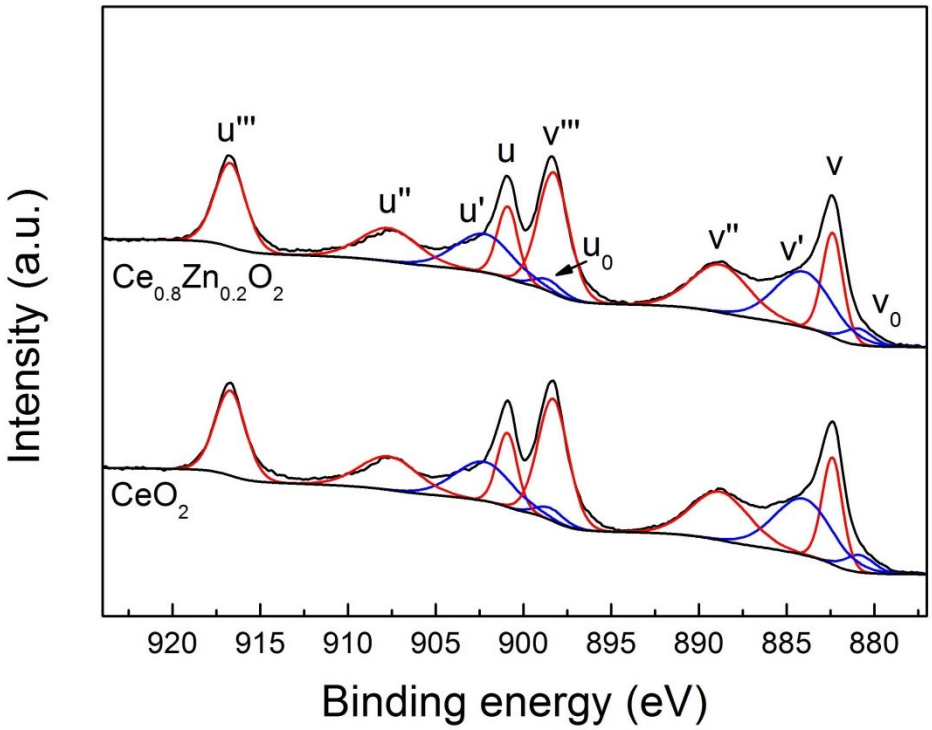


Fig. S7 XPS spectra of Ce 3d for the neat CeO_2 and $Ce_xZn_{1-x}O_2$ nanorods.

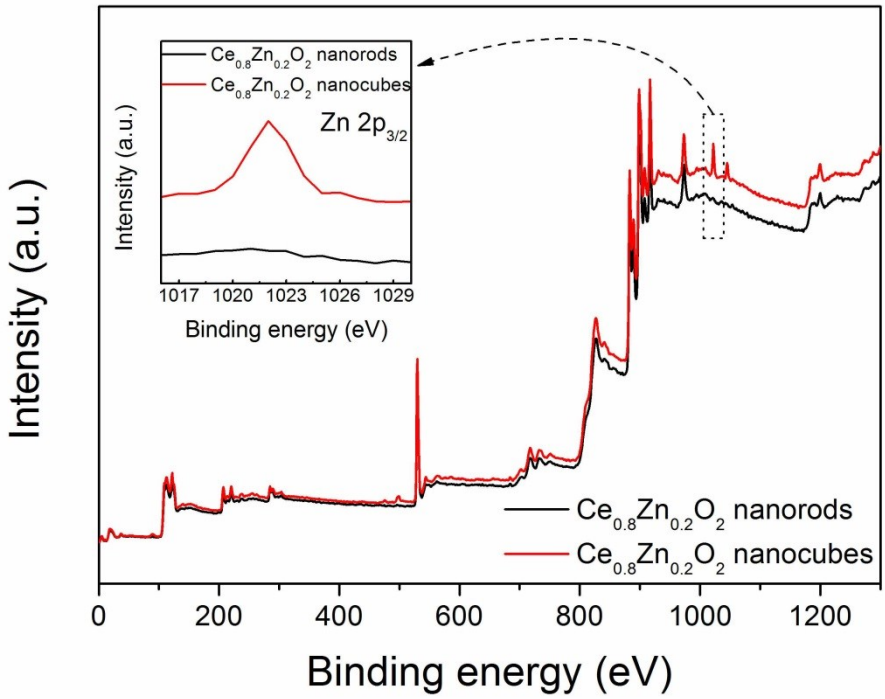


Fig. S8 XPS spectra across the entire energy range for $Ce_{0.8}Zn_{0.2}O_2$ nanocubes and nanorods. The insert figure: Zn $2p_{3/2}$ spectra.

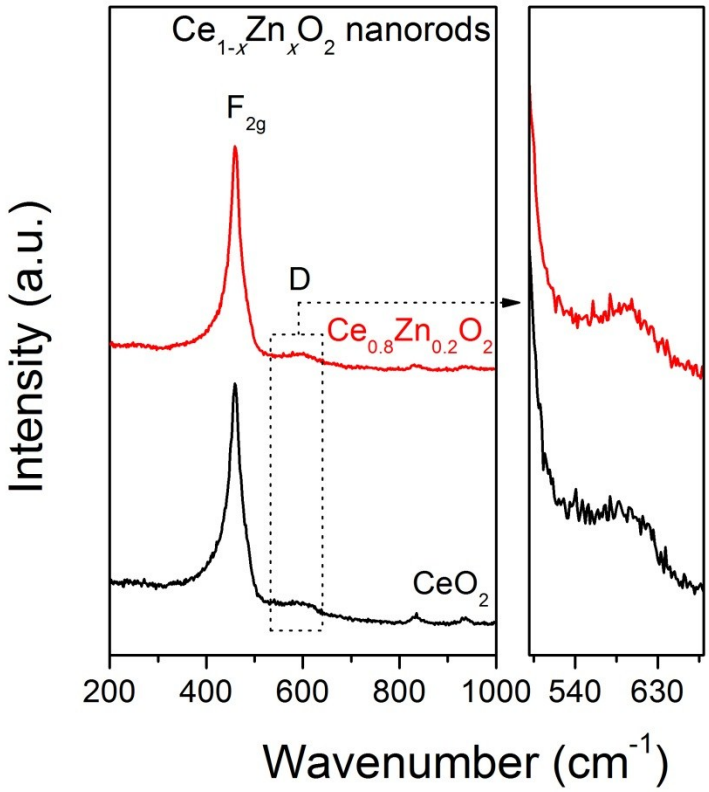


Fig. S9 Raman spectra of neat CeO_2 and $Ce_{1-x}Zn_xO_2$ nanorods.

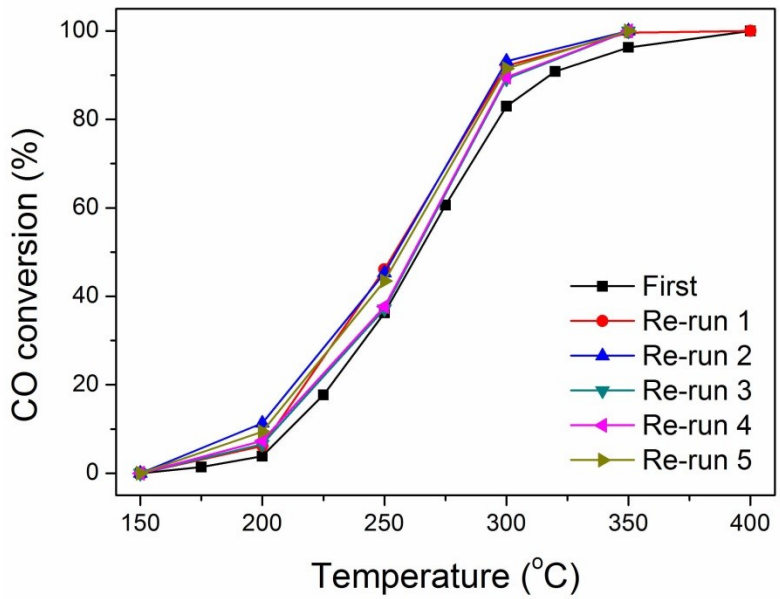


Fig. S10 Cycling performance of the $Ce_{0.8}Zn_{0.2}O_2$ nanocubes for the CO catalytic reaction.

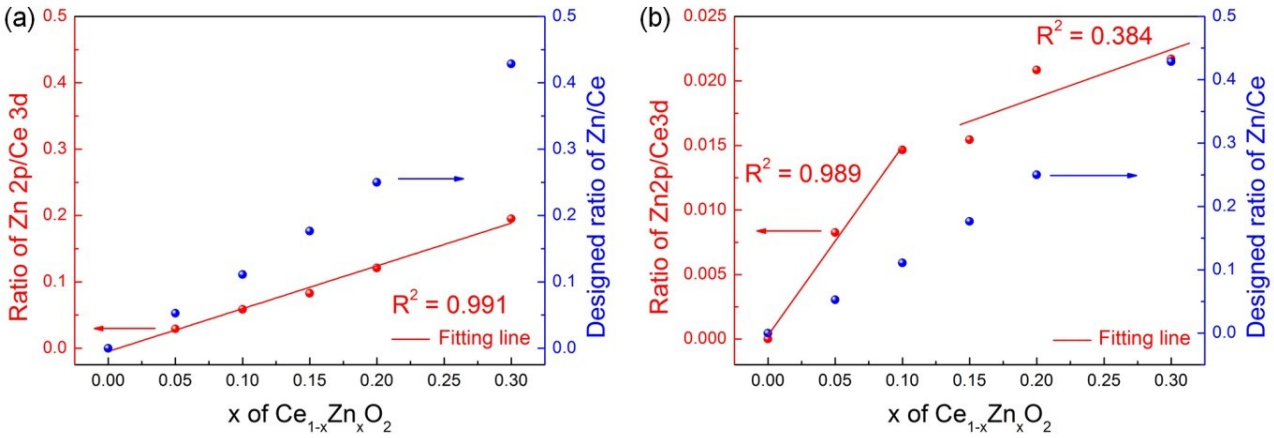


Fig. S11 Atomic ratio of Zn 2p/Ce 3d from XPS results: $Ce_{1-x}Zn_xO_2$ nanocubes (a) and nanorods (b). The intended Zn/Ce ratio for the starting materials is shown in blue.

Table S1 XRD lattice parameters, BET surface areas, conversion temperatures, Raman spectra analyses and XPS results for the neat CeO_2 and $Ce_{1-x}Zn_xO_2$ samples.

Sample		XRD	N_2 adsorption–desorption isotherms		CO conversion			Raman spectra	XPS		
		Lattice parameter (Å)	S_{BET} (m^2/g)	BJH adsorption average pore diameter (nm)	Temperature (°C)			A_D/A_{F2g}	Ce^{3+}/Ce_{tot} [a]	Binding energy (eV)	
					$T_{10\%}$	$T_{50\%}$	$T_{90\%}$			O_{latt}	O_{ads}
Nanocubes	CeO_2	5.4162	90	7.3	259	317	363	0.110	0.358	529.5	531.7
	$Ce_{0.8}Zn_{0.2}O_2$	5.4108	105	7.3	211	264	318	0.129	0.380	529.3	531.5
Nanorods	CeO_2	5.4228	136	6.7	252	298	344	0.131	0.369	529.4	531.6
	$Ce_{0.8}Zn_{0.2}O_2$	5.4200	140	6.7	252	304	357	0.142	0.375	529.4	531.6

[a] $$Ce^{3+}/Ce_{tot} = \frac{A(v_0 + v' + u_0 + u')}{A(v_0 + v' + u_0 + u') + A(v + v'' + v''' + u + u'' + u''')}$$

References

1. Q. Wu, F. Zhang, P. Xiao, H. Tao, X. Wang, Z. Hu and Y. Lu, *J. Phys. Chem. C*, 2008, **112**, 17076-17080.
2. X. Liu, K. Zhou, L. Wang, B. Wang and Y. Li, *J. Am. Chem. Soc.*, 2009, **131**, 3140-3141.