

Co₃O₄/CeO₂ Multi-shelled Nanospheres Derived from Self-templated Synthesis for Efficient Catalytic CO Oxidation

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Experimental details

Synthesis of Co-IPA . All chemicals and solvents are purchased from commercial sources and used without purification. In a typical synthesis, 0.5 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.5 mmol of isophthalic acid (H_2IPA) are dissolved in a mixture of DMF (25 mL) , ethanol (20 mL) and deionized water (5 mL) to form a clear solution by stirring for 6 h. The solution is then transferred to a Teflon-lined stainless steel autoclave and kept at 160 °C for 4 h. After cooling to room temperature, the obtained Co-based coordination polymer spheres (Co-IPA) are separated by centrifugation.

Synthesis of Co_3O_4 . The Co_3O_4 particles are generated through a thermal treatment in air at the temperature of 400 °C for 30 min with a heating rate of 15 °C min⁻¹ .

Synthesis of n-Co-Ce-IPA. All chemicals and solvents are purchased from commercial sources and used without purification. In a typical synthesis, 0.5 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.5 mmol of isophthalic acid (H_2IPA) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ are dissolved in a mixture of DMF (25 mL) , ethanol (20 mL) and deionized water (5 mL) to form a clear solution by stirring for 6 h. The solution is then transferred to a Teflon-lined stainless steel autoclave and kept at 160 °C for 4 h. After cooling to room temperature, the obtained Co-based coordination polymer spheres (Co-Ce-IPA) are separated by centrifugation. And other precursor solutions with different mole ratio of Co/Ce could be prepared by varying the content of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

Synthesis of $\text{Co}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$. The $\text{Co}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$ particles are generated through a thermal treatment in air at the temperature of 400 °C for 30 min with a heating rate of 15 °C min⁻¹.

Characterization. X-ray diffraction patterns were obtained on a Bruker D8 X-ray diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm). The images of FESEM were measured by Hitachi S4800 scanning electron microscope. Transmission electron microscopic (TEM) images were obtained with a TECNAI G2 high-resolution transmission electron microscope, operating at 200kV. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analyses were performed with a Varian Liberty 200 spectrophotometer to determine the contents. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al K α X-ray radiation as the X-ray source for excitation. H_2 -Temperature-programmed reduction (H_2 -TPR) is treated in 100 mL/min argon at 100 °C for 1 h to remove any adsorbed gases or water. After cooling to 50 °C, the flowing gas was switched to 10 % H_2/Ar , and then the samples were heated from 50 to 900 °C at a ramping rate of 3 °C min⁻¹ . N_2 adsorption–desorption isotherms were measured using an Autosorb-iQ system, and the products were degassed at 300 °C in a nitrogen atmosphere before the measurements. The specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method. The average pore size and pore size distribution were determined by the Barrett–Joyner–Halenda (BJH) method using desorption branches. The thermal weight loss (TGA) curves were measured on the Netzsch STA 449F3 TG/DTA pyrogravimetric analyzer, and the samples were heated from 25 to 850 °C at a ramping rate of 10 °C min⁻¹ in 50 mL/min air atmosphere. Carbon monoxide temperature programmed desorption (CO-TPD) was carried out in a full automatic instrument (XQ TP-5080, China) and performed in the following procedure: Firstly, 70 mg of the catalyst was mounted in a quartz tube and calcined under a helium stream (30 mL/min) at 200 °C for 1 h. After the catalyst was cooled down to 25 °C, 10 % CO-He was introduced into the system at the

rate of 30 mL/min for 1 h. Then the catalyst was flushed in He flow (30 mL/min) to remove physisorbed CO at 25 °C. Finally, the sample was gradually heated from 25°C to 700°C at a ramp of 10 °C/min. The CO desorption was monitored by a thermal conductivity detector (TCD) and MS.

Performance Evaluation of CO Catalytic Oxidation: The activity for CO catalytic oxidation of the samples was evaluated in a continuous fixed bed reactor coupled online with a gas chromatograph (GC-2014C). The operation conditions were as follows: 50 mg of catalysts, a gas mixture of 1% CO and 20% O₂ in N₂ at a total flow rate of 30 mL min⁻¹, with programmed-temperature rate of 1 °C min⁻¹. The composition of the gas mixture was monitored by gas chromatography.

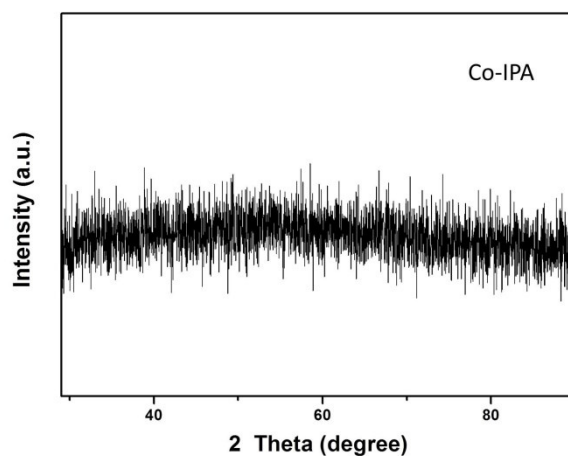


Figure. S1. XRD pattern of Co-IPA coordination polymer spheres.

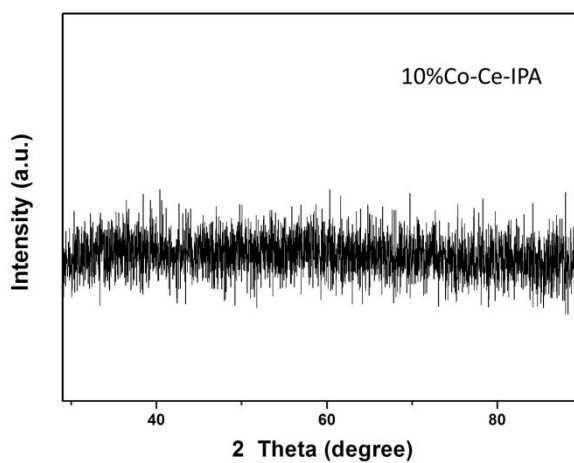


Figure. S2. XRD pattern of 10 % Co-Ce-IPA catalyst.

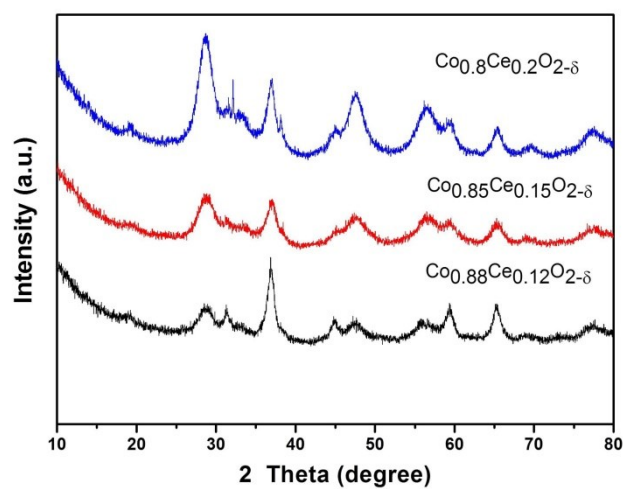


Figure. S3. XRD patterns of Co_{1-x}Ce_xO_{2-δ} catalysts (x = 12 %, 15 %, 20 %).

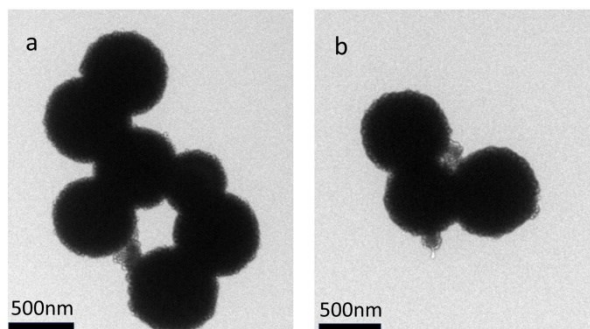


Figure. S4. TEM images of Co-IPA coordination polymer spheres.

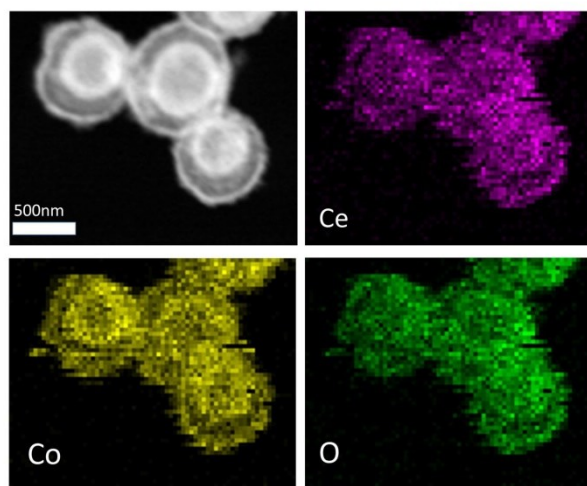


Figure. S5. EDX elemental mapping of Ce, Co, and O for $\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_{2-\delta}$ catalyst.

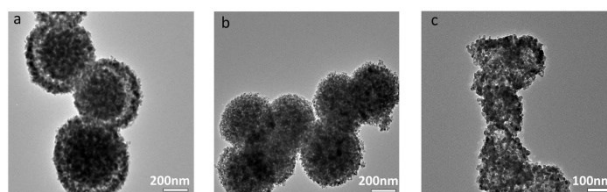


Figure. S6. TEM images of (a) $\text{Co}_{0.88}\text{Ce}_{0.12}\text{O}_{2-\delta}$, (b) $\text{Co}_{0.85}\text{Ce}_{0.15}\text{O}_{2-\delta}$, (c) $\text{Co}_{0.8}\text{Ce}_{0.2}\text{O}_{2-\delta}$.

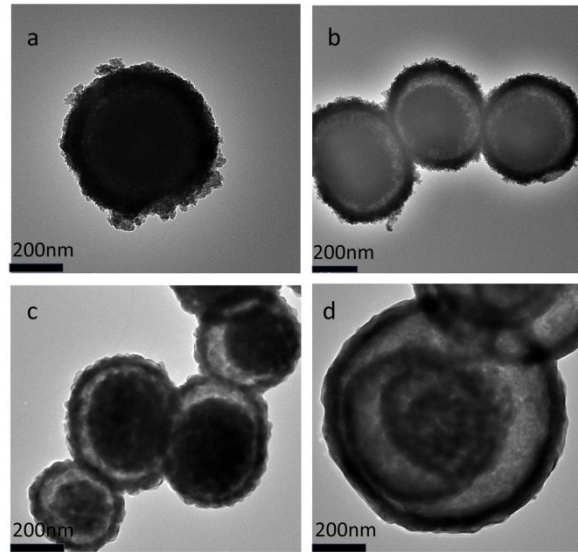


Figure. S7. TEM images at different heating stages: (a) Co-Ce-IPA nanospheres, (b) 300 °C, 5 min, (c) 400 °C, 5 min, (d) 400 °C, 30 min.

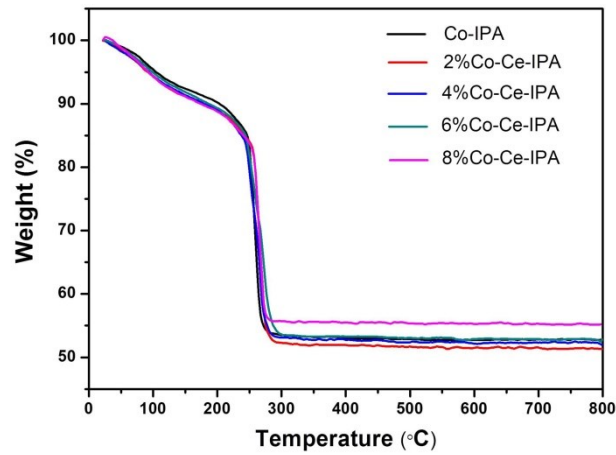


Figure. S8. TGA curves of n-Co-Ce-IPA (n = 2 %, 4 %, 6 %, 8 %).

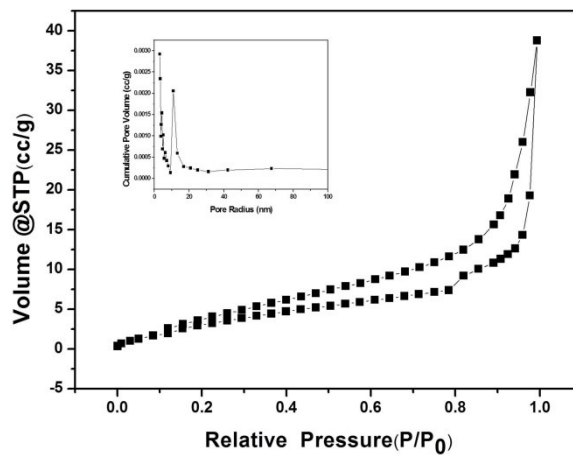


Figure. S9. N₂ adsorption–desorption curve and pore diameter distribution of Co₃O₄ catalyst.

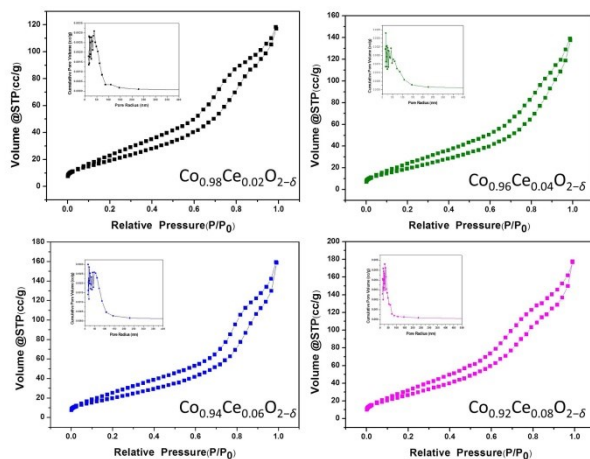


Figure. S10. N₂ adsorption–desorption curves and pore diameter distribution of Co_{1-x}Ce_xO_{2-δ} catalysts.

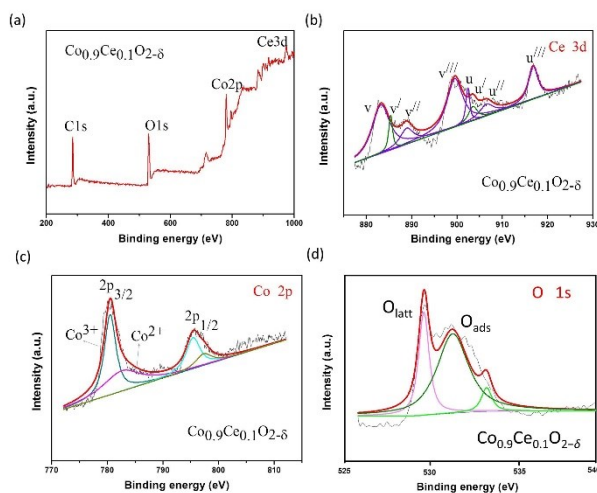


Figure. S11. (a) XPS spectra, (b) Ce 3d, (c) Co 2p and (d) O 1s XPS spectra of Co_{0.9}Ce_{0.1}O_{2-δ} catalyst.

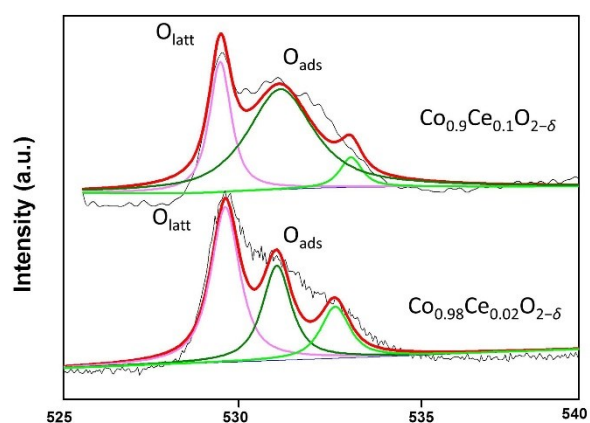


Figure. S12. O 1s XPS spectra of Co_{0.98}Ce_{0.02}O_{2-δ} and Co_{0.9}Ce_{0.1}O_{2-δ} catalysts.

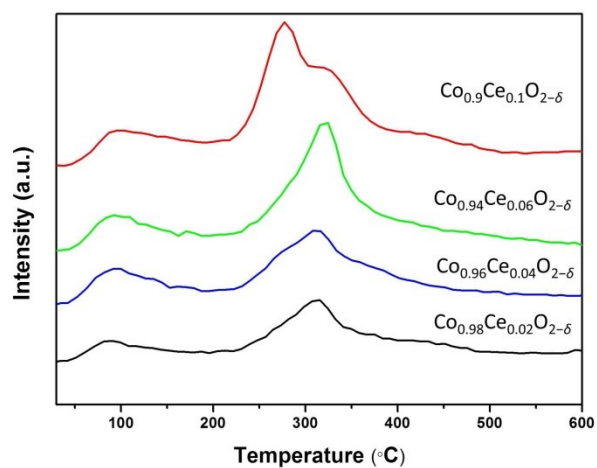


Figure. S13. CO-TPD profiles of $\text{Co}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$ catalysts.

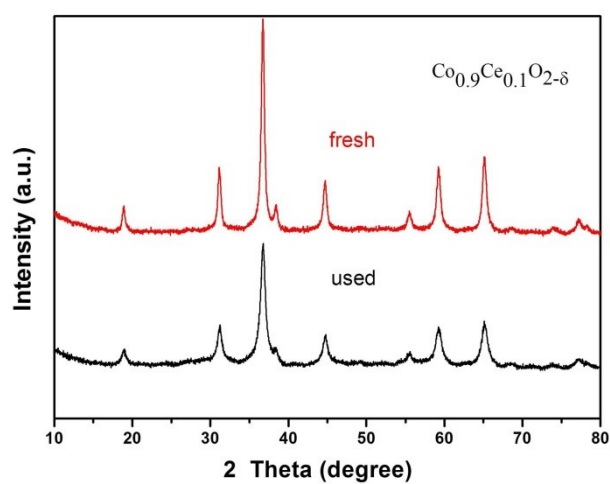


Figure. S14. XRD patterns of fresh and used $\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_{2-\delta}$ catalyst.

samples	Ce/Co
$\text{Co}_{0.98}\text{Ce}_{0.02}\text{O}_{2-\delta}$	0.021
$\text{Co}_{0.96}\text{Ce}_{0.04}\text{O}_{2-\delta}$	0.043
$\text{Co}_{0.94}\text{Ce}_{0.06}\text{O}_{2-\delta}$	0.065
$\text{Co}_{0.92}\text{Ce}_{0.08}\text{O}_{2-\delta}$	0.087
$\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_{2-\delta}$	0.111

Table S1. The Ce/Co ratio in the samples detected by ICP.

Catalysts	$S_{\text{BET}}(\text{m}^2\text{g}^{-1})$	pore volume (cc/g)	average pore radius (nm)
$\text{Co}_{0.98}\text{Ce}_{0.02}\text{O}_{2-\delta}$	73.268	0.208	53.85
$\text{Co}_{0.96}\text{Ce}_{0.04}\text{O}_{2-\delta}$	74.805	0.177	46.69
$\text{Co}_{0.94}\text{Ce}_{0.06}\text{O}_{2-\delta}$	80.707	0.260	61.07
$\text{Co}_{0.92}\text{Ce}_{0.08}\text{O}_{2-\delta}$	114.275	0.273	49.20
$\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_{2-\delta}$	115.568	0.340	46.03
Co_3O_4	26.02	0.058	16.04

Table S2. physical properties of the $\text{Co}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$ catalysts (x = 2 %, 4 %, 6 %, 8 %, 10 %) and Co_3O_4 .