

Copper Doped Ceria Porous Nanostructures towards Highly Efficient Bifunctional Catalyst for Carbon Monoxide and Nitric Oxides Elimination

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Experimental Section

Materials. The initial chemicals, including $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aescar Chemical Co.), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Alfa Aescar Chemical Co.), benzene-1,3,5-tricarboxylic acid (BTC) (98%, Alfa Aescar Chemical Co.), terephthalic acid (BDC) (98%, Alfa Aescar Chemical Co.) 4,4'-Biphenyldicarboxylic acid (BPDC) (98%, Alfa Aescar Chemical Co.) and ethanol (A. R., Beijing Fine Chemical Company, China), were used without further purification.

Preparation.

CeO₂ nanorods: In a typical procedure, the reaction of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) and BTC (1 mmol) in a 1:1 stoichiometry in ethanol-water solution (50 mL, v/v = 1:1) was carried out under vigorous stirring at room temperature. The reaction mixture was then refluxed at 90 °C under constant stirring for 2 h, and a large amount of white precipitate occurred. At last, the precipitate was collected by centrifugation, washed several times with ethanol and water, and dried at 60 °C for 24 h in atmosphere. In addition, the conversion of $\text{Ce}(\text{BTC}) \cdot 6\text{H}_2\text{O}$ into CeO_2 was carried out in an oven at 600 °C for 3 h in air.

CeO₂ nanobundles: the procedure for the synthesis of CeO_2 nanobundles is similar with the procedure for the synthesis of CeO_2 nanorods. The only different is reducing the concentrations of reactant (1 mL of 0.5 M $\text{Ce}(\text{NO}_3)_3$ aqueous solution was added into BTC (0.5 mmol) water-ethanol solution (40 mL, v/v = 1:1)).

Cu²⁺-doped CeO₂ nanorods and nanobundles: Cu²⁺-doped CeO_2 nanorods and nanobundles were prepared by the same treatment as the undoped sample except that 0.1 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.9 mmol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used instead of 1 mmol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

The procedure for the synthesis of other Cu²⁺-doped CeO_2 nanostructures obtain from Ce(Cu)-BDC and Ce(Cu)-BPDC is similar with the procedure for the synthesis of Cu²⁺-doped CeO_2 nanorods.

Characterization.

Powder X-ray diffraction (XRD) patterns were performed on a D8 Focus (Bruker) diffractometer (continuous, 40 kV, 40 mA, increment: 0.02 degree). Thermogravimetric analysis and differential thermal analysis (TGADTA) data were recorded with a thermal analysis instrument (SDT2960, TA Instruments, New Castle, DE) at the heating rate of 10 °C min⁻¹ in an air flow of 100 mL min⁻¹. The morphology and composition of the samples were inspected using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi) equipped with an energy dispersive X-ray spectrum (EDX, JEOL JXA-840). Transmission electron microscopy (TEM) images were obtained using a JEOL 2010 transmission electron microscope operating at 200 kV. The X-ray diffraction patterns of the products were collected on a Rigaku-D/max 2500 V X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$), with an operation voltage and current maintained at 40 kV and 40 mA. Transmission electron microscopic (TEM) images were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. 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.

Catalytic test: 8 mg catalyst was mixed with 20 mg SiO₂. The mixture was put in a stainless steel reaction tube. The experiment was carried out under a flow of reactant gas mixture (1 % CO, 20 % O₂, balance N₂) at a rate of 30 mL/min. The composition of the gas was monitored on-line by gas chromatography (GC 9800).

Micromeritics ASAP2020 surface area analyzer was used to measure gas adsorption.

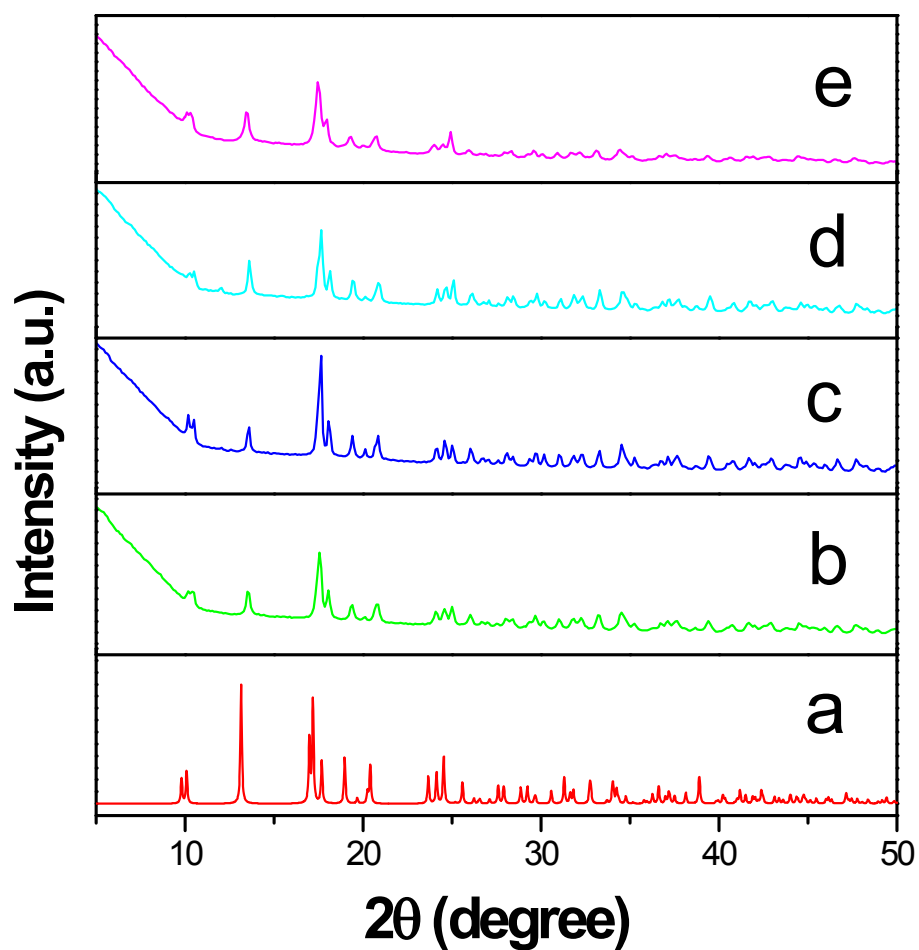


Fig. S1. The XRD patterns of $\text{Ce}(\text{BTC})(\text{H}_2\text{O})_6$ and Cu^{2+} doped (10% content with Ce) $\text{Ce}(\text{BTC})(\text{H}_2\text{O})_6$ nanocrystals (a: simulated $\text{Ce}(\text{BTC})(\text{H}_2\text{O})_6$; b: $\text{Ce}(\text{BTC})(\text{H}_2\text{O})_6$ nanorods; c: $\text{Ce}(\text{BTC})(\text{H}_2\text{O})_6$ nanobundles; d: $\text{CeCu}(\text{BTC})(\text{H}_2\text{O})_6$ nanorods; e: $\text{CeCu}(\text{BTC})(\text{H}_2\text{O})_6$ nanobundles).

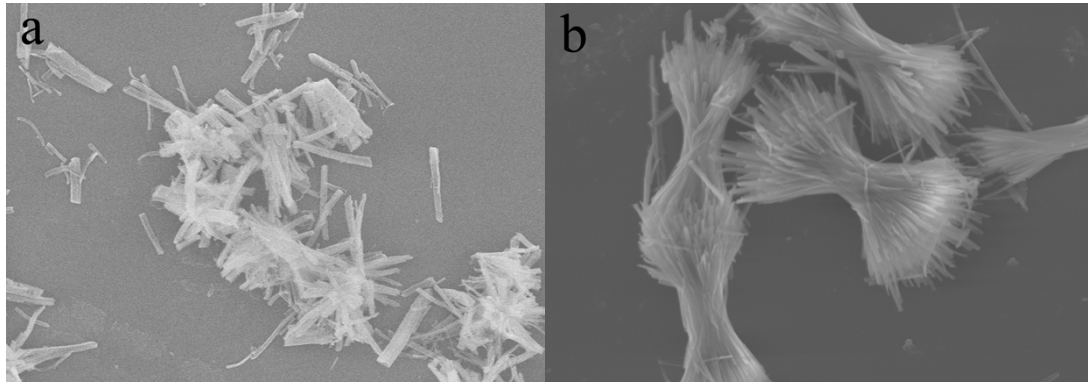


Fig. S2. The morphology of Ce-MOF nanorods (a) and nanobundles (b).

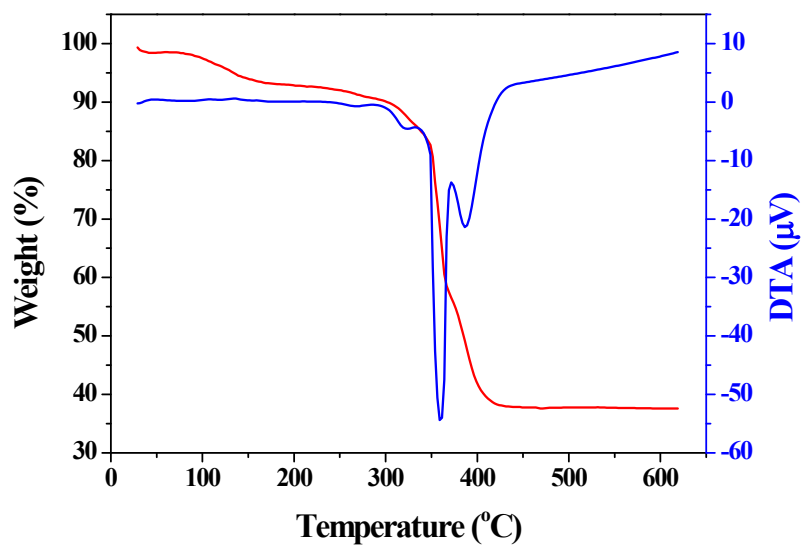


Fig. S3. TG-DTA analysis of CeCu-BTC nanocrystals.

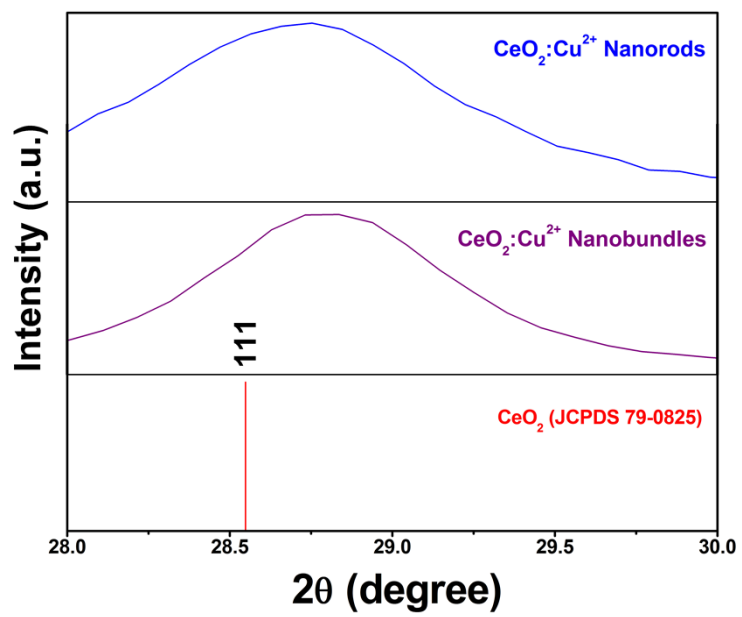


Fig. S4. XRD patterns of Cu²⁺ doped samples.

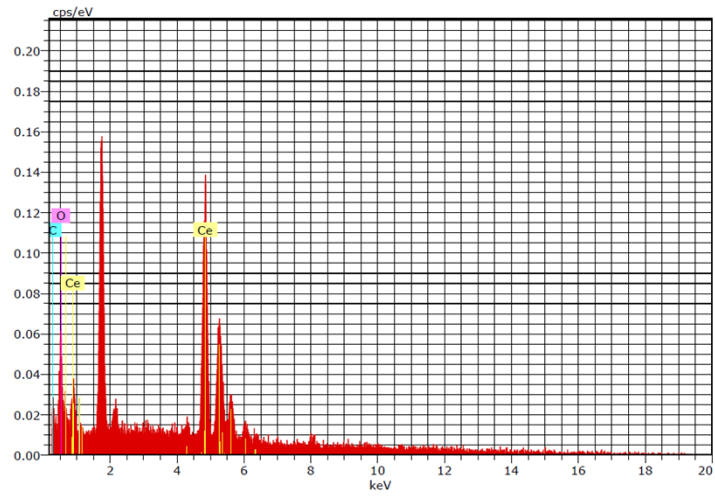


Fig. S5. The representative EDX patterns recorded from the $\text{CeO}_2:\text{Cu}^{2+}$.

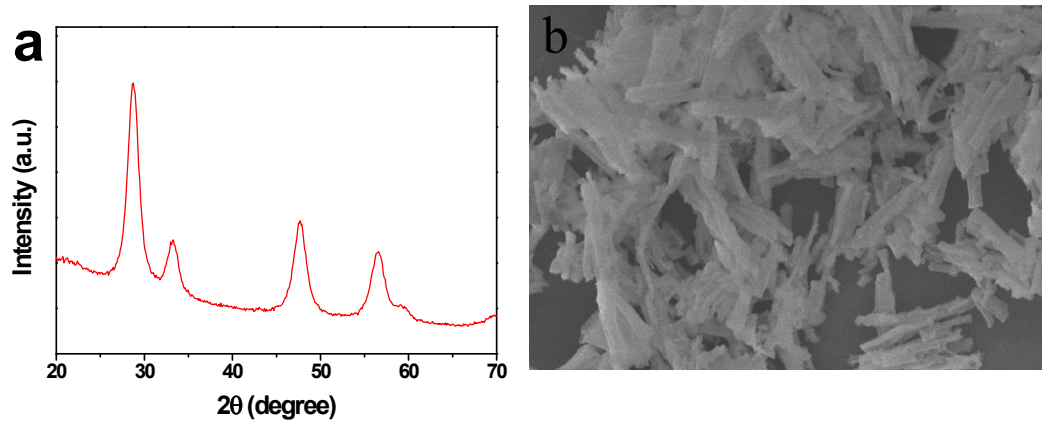


Fig. S6. The XRD pattern (a) and SEM image (b) of the nanorods after catalytic reaction.

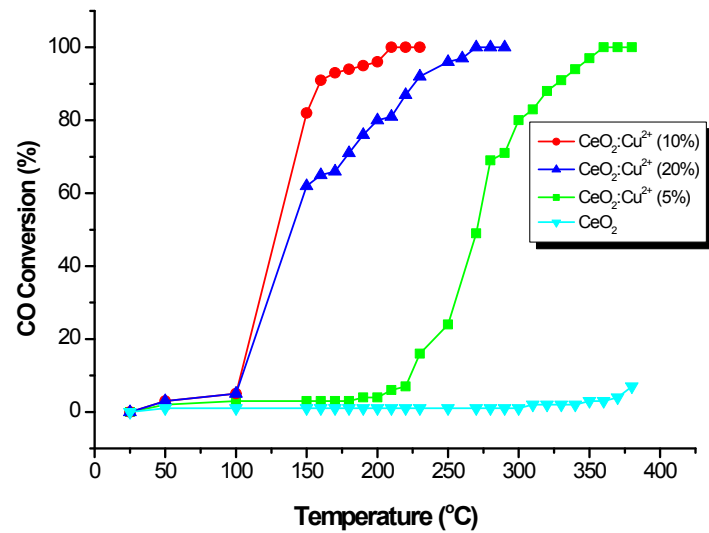


Fig. S7. The CO catalytic activity of CeO₂:Cu²⁺ porous nanomaterials with different Cu²⁺ content.

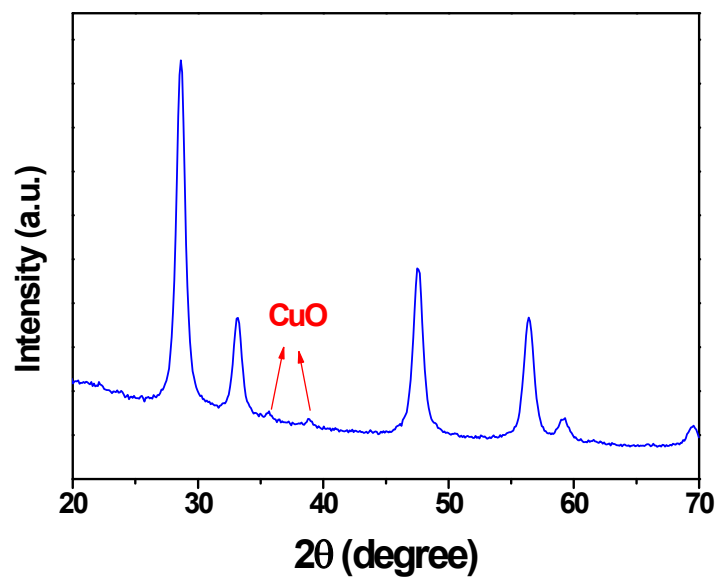


Fig. S8. The XRD pattern of $\text{CeO}_2:\text{Cu}^{2+}$ nanocrystals with 20% Cu^{2+} content.

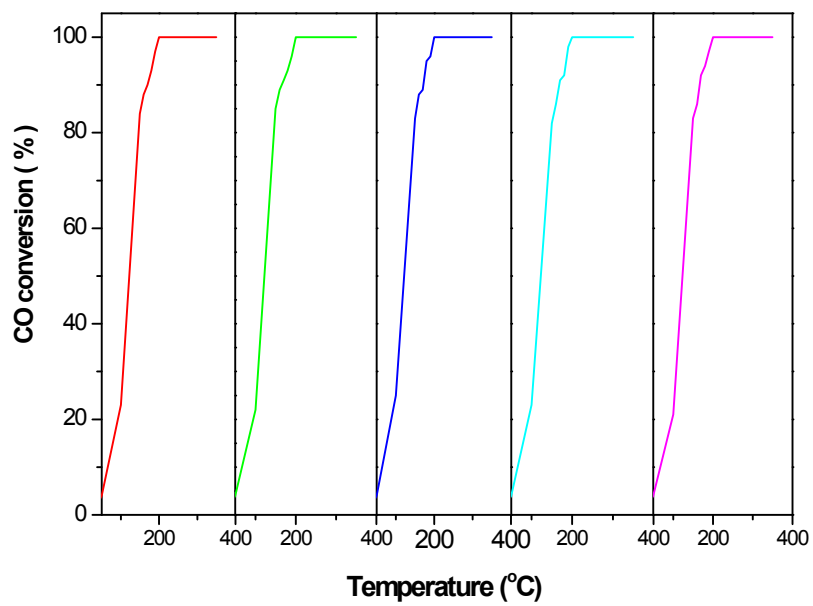


Fig. S9. Catalytic cycles of CeO₂:Cu²⁺ nanorods.

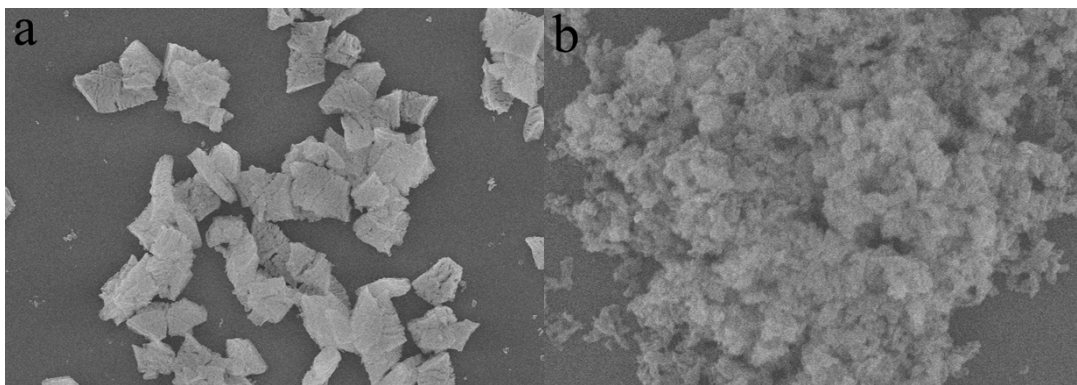


Fig. S10. The morphology of $\text{CeO}_2:\text{Cu}^{2+}$ nanocrystals obtained from CeCu-BDC (a) and CeCu-BPDC (b).