Supplementary Material (ESI) for CrystEngComm

## Electronic Supplementary Information

# Facile Synthesis and Catalytic Properties of $CeO_2$ with Tunable Morphologies from Thermal Transformation of Cerium Benzendicarboxylate Complexes

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## Experimental Section

**Materials.** Aqueous solutions of $Ce(NO_3)_3$ was obtained by dissolving $Ce(NO_3)_3{\cdot}6H_2O$ in deionized water. benzene-1,3-dicarboxylic acid (1,3-BDC) (98%, Alfa Aescar Chemical Co.), benzene-1,4-dicarboxylate (1,4-BDC), 1,10-phenanthroline, $HNO_3$, and ethanol (all with purity of A. R., Beijing Fine Chemical Company, China), were used without further purification.

**Synthesis of 1D Cerium benzene-1,3-dicarboxylate nanowires.** Under vigorous stirring, 1 mmol of $Ce(NO_3)_3$ aqueous solution was added into 1.5 mmol of 1,3-BDC ethanol-water solution (50 mL, v/v = 4:1). Then $NH_3{\cdot}H_2O$ (V/V = 1:1) was added to adjust the pH to 7 and a large amount of white precipitate occurred immediately. After constant stirring for 1 h, the precipitate was collected by centrifugation, washed several times with ethanol and water, and dried at 60 $^{o}$C for 24 h in atmosphere. In a comparative experiment, we added 0.5 mmol 1,10-phenanthroline to the ethanol-water solution before the addition of $Ce(NO_3)_3$ while keeping other conditions identical.

**Synthesis of 3D Cerium benzene-1,4-dicarboxylate microflowers.** 1.5 mmol of 1,4-BDC was dispersed in 50 mL deionized water and the pH was adjusted to 7 by $NH_3{\cdot}H_2O$ (V/V = 1:1) to form a homogeneous and transparent solution. Then 1 mmol of

$Ce(NO_3)_3$ aqueous solution was added into the solution under vigorous stirring. A large amount of white precipitate occurred immediately. The following procedures were identical to those mentioned in the section above.

**Thermal Conversion from the Coordination Compounds to $CeO_2$.** The obtained samples were annealed at 500 $^oC$ for 2 h in air with a heating rate of 2 $^oC$ min$^{-1}$ to obtain corresponding $CeO_2$ with specific morphologies.

**Characterization.** The samples were characterized by powder X-ray diffraction (XRD) performed on a D8 Focus diffractometer (Bruker). Elemental analysis of Ce, C, and H in the solid samples were carried out on VarioEL (Elementar Analysensysteme GmbH) and inductive coupled plasma (ICP) atomic emission spectrometric analysis (POEMS, TJA), respectively. Fourier transform infrared spectroscopy (FT-IR) spectra were measured with a Perkin-Elmer 580B infrared spectrophotometer with the KBr pellet technique. The morphology and composition of the samples were inspected using a scanning electron microscope (FE-SEM, Hitachi S-4800). Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were obtained using a JEOL 2010 transmission electron microscope operating at 200 kV. The surface area was measured using a Micromeritics (NOVA 4200e) analyzer. All the measurements were performed at room temperature.

**Catalytic Activity Evaluation.** The catalytic activity for $CH_4$ oxidation was evaluated in a fixed-bed quartz tubular reactor at atmospheric pressure. In a typical test, 50 mg of the samples were placed in the reactor. Then the test was carried out at a rate of 12 mL min$^{-1}$ flows of reactant gases (1.0% $CH_4$/Air). The composition of the outflow gases were analysed by an on-line QIC-20 quadrupole mass spectrometer (Hiden Analytical Ltd, detection limit: 5 ppb), controlled by MASsoft software.

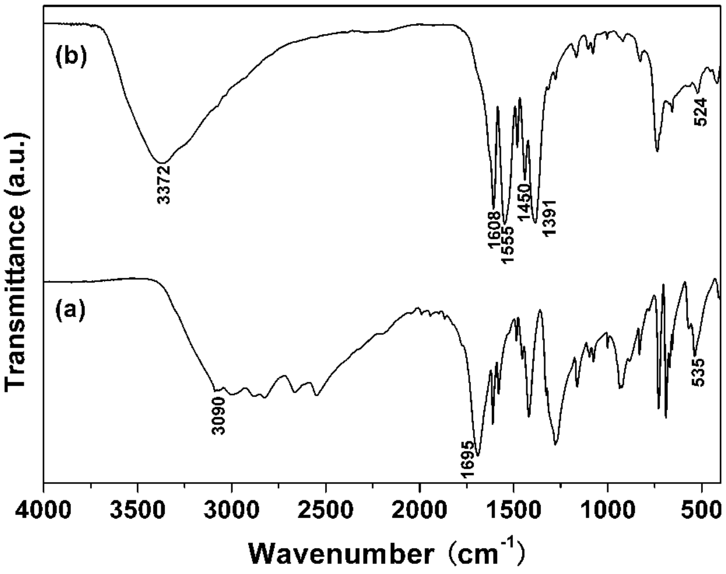

**Fig. S1.** FT-IR spectra of (a) pure 1,3-BDC powder and (b) the obtained Ce(1,3-BDC)$_{1.5}$·6H$_2$O nanowires, respectively.

From Fig. S1, one can see that the spectra of (a) the pure 1,3-BDC and (b) the obtained Ce(1,3-BDC)$_{1.5}$·6H$_2$O nanowires are difform. The characteristic bands of the nonionized carboxyl group of 1,3-BDC in Fig. S1a disappear ($\nu_{C=O}$: 1695 cm$^{-1}$; $\delta_{C=O}$: 535 cm$^{-1}$; $\nu_{-OH}$: 3090 cm$^{-1}$), and instead many new bands appear in the spectrum of our sample (Fig S1b). The bands located at the regions of 1479–1608 cm$^{-1}$, 1450–1391 cm$^{-1}$, and 524 cm$^{-1}$ are attributed to the stretching vibrations $\nu_{as}$(–COO$^-$), $\nu_s$(–COO$^-$) of the ionized carboxylate groups, and the characteristic Ce–O stretching vibration, respectively.[1] From the variety in the spectra, we can conclude that the Ce$^{3+}$ ions have been coordinated with the 1,3-BDC ligands to form a complex. Additionally, the bands $\nu_{-OH}$ in Figure S1b at about 3372 cm$^{-1}$ proved that water molecules has incorporated into the product as a reactant.[2]

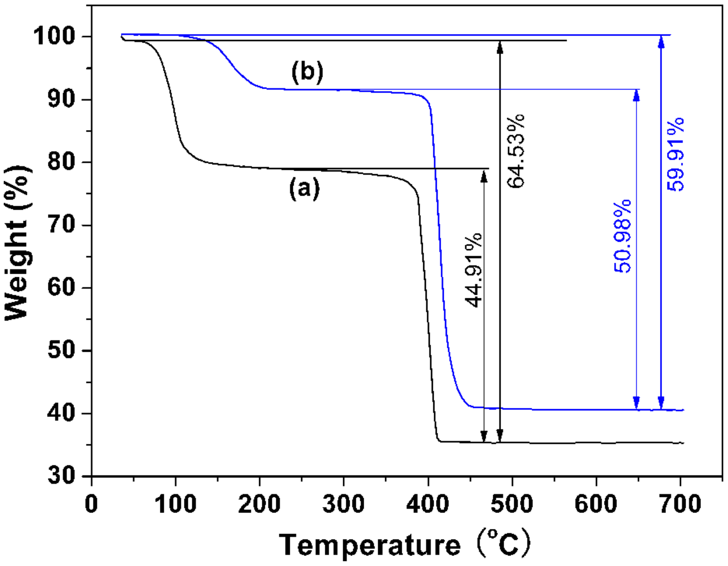

**Fig. S2.** TGA curves of the as-synthesized Ce(1,3-BDC)$_{1.5}$·6$H_2O$ nanowires (a) and Ce(1,4-BDC)$_{1.5}$·2$H_2O$ microflowers (b), respectively.

For Ce(1,3-BDC)$_{1.5}$·6$H_2O$, the first weight loss of 20.09% occurs at about 96.0 °C, which is due to the dehydration of six $H_2O$ molecules (theoretical value: 21.86%). The second sequential weight loss displays an even rapid curve at 398.0 °C and is measured to be 64.53%, attributing to the release of organic ligand (theoretical value: 65.19%) (Fig. S2a). Similarly, there are also two weight losses of 8.70 and 50.98% at about 164.0 and 412.0 °C in the TGA plot of Ce(1,4-BDC)$_{1.5}$·2$H_2O$, which are in agreement with the theoretical value of two water molecules (8.53%) and organic ligand (50.72%), respectively (Fig. S2b). These results give more evidence to support our speculation on the compositions and provide information of the conversion temperature to $CeO_2$.

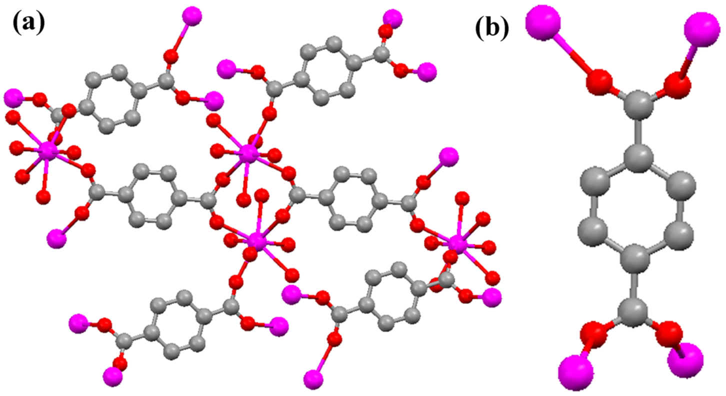

**Fig. S3.** (a) Crystal structure of the as-synthesized $Ce(1,4\text{-}BDC)_{1.5}\cdot 2H_2O$ microflowers and (b) coordination modes of the carboxylate groups.

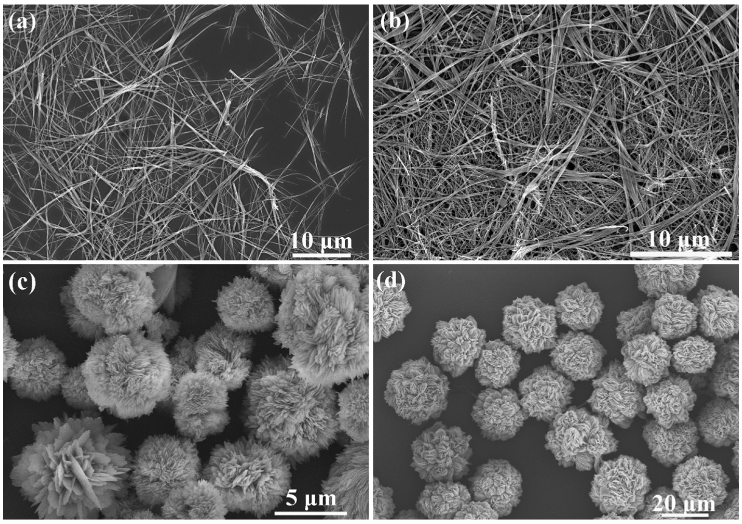

**Fig. S4.** SEM images of the as-synthesized $Ce(1,3\text{-}BDC)_{1.5}\cdot 6H_2O$ nanowires obtained after the reaction for (a) 1 min and (b) 2 h; SEM images of $Ce(1,4\text{-}BDC)_{1.5}\cdot 2H_2O$ microflowers obtained after the reaction for (c) 1 min and (d) 2 h.

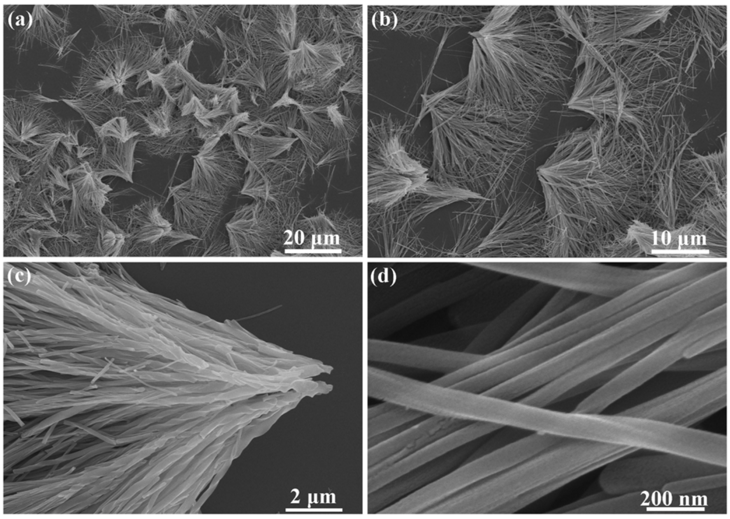

**Fig. S5.** SEM images of the Ce(1,3-BDC)$_{1.5}$·6H$_2$O fan-like architectures obtained in the presence of 0.5 mmol of 1,10-phenanthroline.

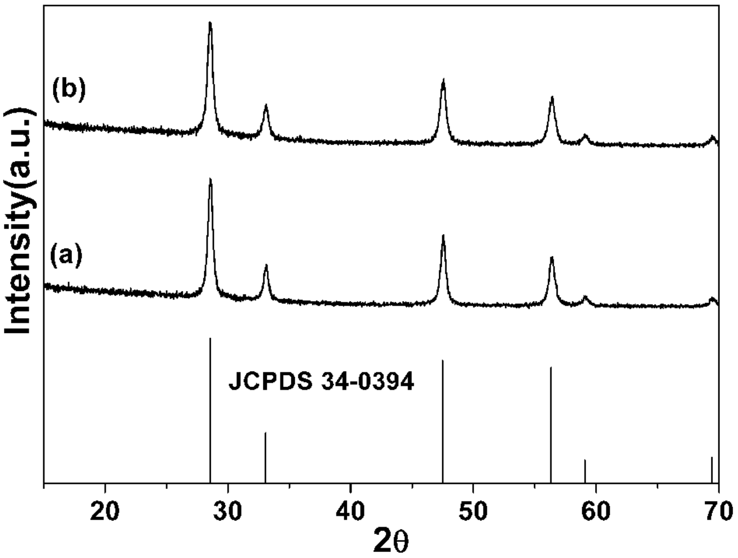

**Fig. S6.** XRD patterns of the as-synthesized samples after calcinations of Ce(1,3-BDC)$_{1.5}$·6H$_2$O nanowires (a) and Ce(1,4-BDC)$_{1.5}$·2H$_2$O microflowers (b), respectively. The standard data for CeO$_2$ (JCPDS card 34-0394) are presented in the figure for comparison.

1. G. Jia, Y. Huang, Y. Song, M. Yang, L. Zhang and H. You, *European Journal of Inorganic Chemistry*, 2009, **2009**, 3721.
2. J. Yang, Q. Yuo, G. D. Li, J. J. Cao, G. H. Li and J. S. Chen, *Inorganic Chemistry*, 2006, **45**, 2857.