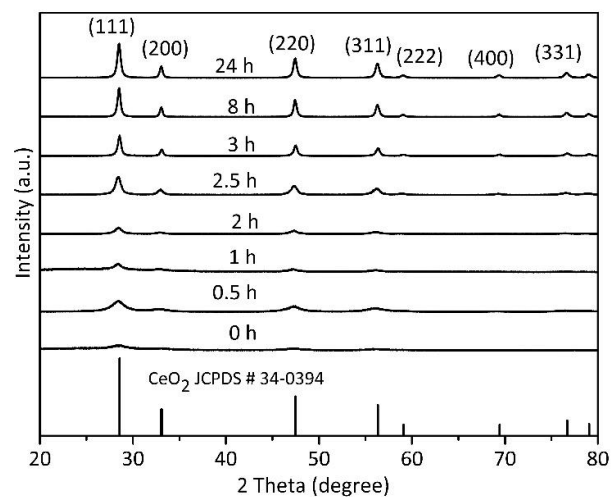


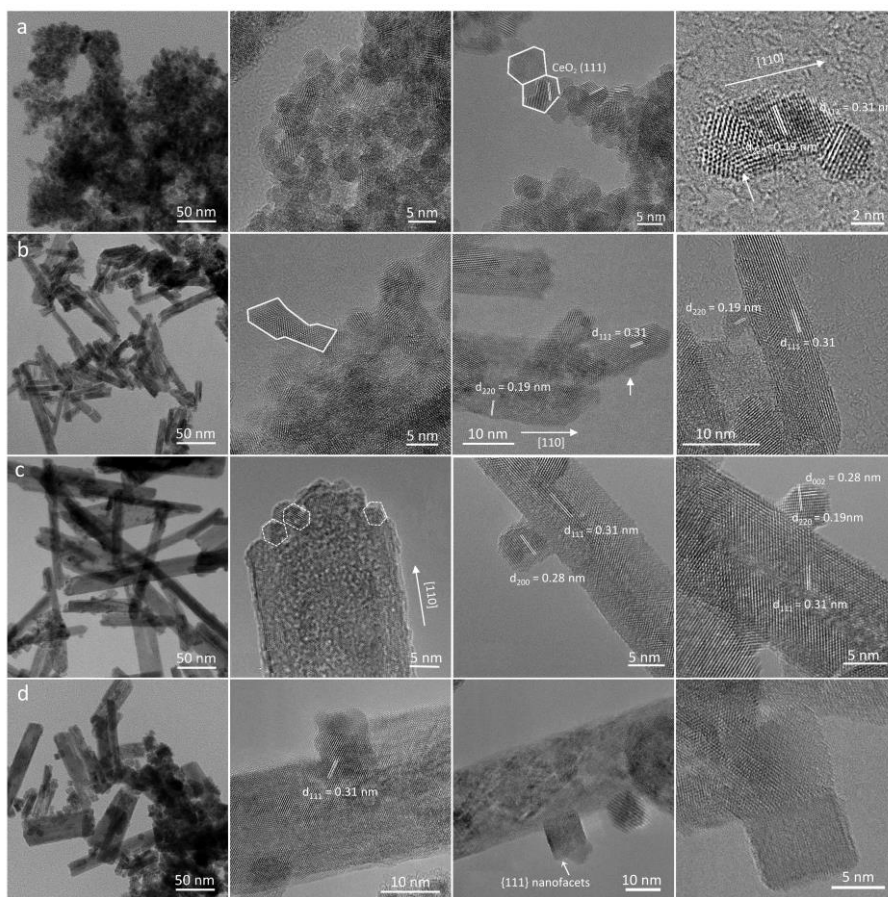
## Electronic Supplementary Information

The initially formed  $\text{Ce}(\text{OH})_3$  species, including the precipitate upon mixing cerium source with aqueous NaOH solution at room temperature and the short nanorods assembled by the amorphous precipitate at the early stage of hydrothermal synthesis, were very sensitive to air and easily oxidized into  $\text{CeO}_2$ . The intermediate samples, formed under the typical hydrothermal conditions (155 °C,  $\text{OH}^-/\text{Ce}^{3+}$  of 100), were dried in air at 80 °C overnight. The structural characters of these dried samples were investigated by XRD and HRTEM.

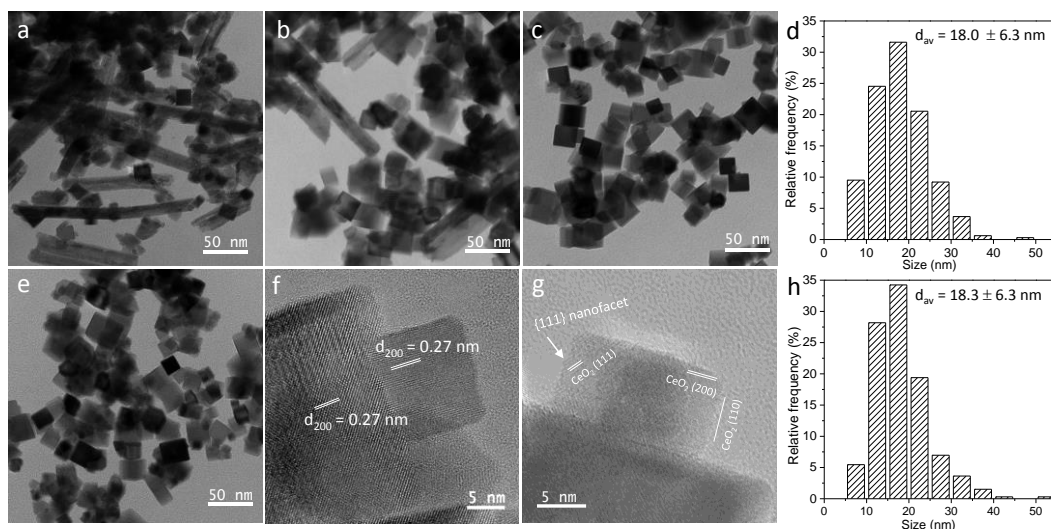
Typical diffraction peaks of ceria were observed for all the samples (Fig S1), illustrating that the  $\text{Ce}(\text{OH})_3$  species were readily oxidized to  $\text{CeO}_2$  upon drying in air. The sample, obtained by drying the initially formed  $\text{Ce}(\text{OH})_3$  precipitate, showed very weak diffraction lines and poor crystallinity and consisted of truncated octahedra that ranged from 2 to 6 nm and enclosed by eight {111} and six {001} planes (Fig. S2a). Most truncated octahedra connected to each other by the {111} or {100} planes joining at their planar interfaces and sharing the [110] crystallographic orientation. Under the hydrothermal conditions, the diffraction lines of  $\text{CeO}_2$  became narrower and sharper progressively with extending synthetic time, indicating the enhancing crystallinity and particle size. At 0.5 h, ceria nanorods with an average length of 42 nm and a mean diameter of 7 nm were formed dominantly (Fig. S2b). 2-6 nm particles were observed to attach on the surface of the growing nanorods, demonstrating that the nanorods grew mainly via the oriented attachment (OA) of small  $\text{CeO}_2$  particles along the [110] direction. At 1 h, the diameter of the ceria nanorods increased to around 14 nm while the average length extended to about 107 nm; irregular particles of 2-6 nm attached on the top of the nanorods; while a small fraction of polyhedra/nanocubes of 2-8 nm attached on the side surfaces of the nanorods and were epitaxially growing on the {111} or {100} facets (Fig. S2c). At 2 h, the mean diameter of the nanorods slightly increased to 16 nm but the average length decreased to 80 nm; the ceria cubes enlarged to about 10 nm and their relative proportion to the nanorods increased considerably (Fig. S2d). Meanwhile, small polyhedra attached on the surface of the growing cubes. The developed nanocube was dominated by the flat {001} facet but truncated at edges by the {110} plane consisting of sawtooth-like {111} facets. The average size of the cubes increased to 13.6 nm at 2.5 h (Fig. S3a) and 16.6 nm at 3 h (Fig. S3b), accompanied by an increasing proportion of cubes at the expense of rods. At 8-24 h,  $\text{CeO}_2$  cubes of around 18.0 nm were obtained as the only product (Fig. S3c-h), and the {111} nanofacets were further developed.



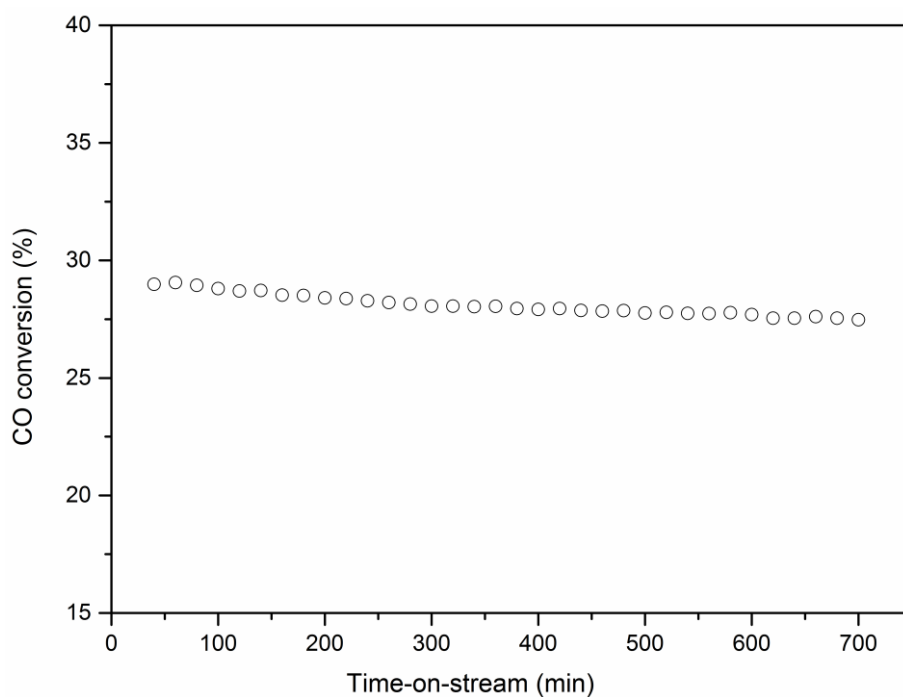
**Fig. S1** XRD patterns of the air-dried samples that were obtained at different intervals during the hydrothermal synthesis. The samples were dried in air at 80 °C overnight.



**Fig. S2** TEM images of the air-dried samples (CeO<sub>2</sub>) obtained during the hydrothermal synthesis at (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 2 h. The samples were dried in air at 80 °C overnight.



**Fig. S3** TEM images and size distributions of the air-dried samples obtained during the hydrothermal synthesis at (a) 2.5 h, (b) 3.0 h, (c, d) 8.0 h and (e-h) 24 h. The samples were dried in air at 80 °C overnight. The size distributions were derived by counting 330 particles.



**Fig. S4** CO oxidation over the air-dried ceria nanocubes (Fig. S3e-h). Reaction conditions: 350 °C, 1 vol. % CO/20 vol. % O<sub>2</sub>/He, 30000 ml g<sup>-1</sup> h<sup>-1</sup>. The conversion of CO was around 27.5% within 12 hours.