Controlled Synthesis and Self-Assembly of CeO$_2$ Nanocubes

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Supporting Information

Detailed preparation and Characterization

(1) Typically, 15 mL of 16.7 mmol/L cerium (III) nitrate aqueous solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave, and then 15 mL toluene, 1.5 mL oleic acid and 0.15 mL tert-butylamine were added to the autoclave in the ambient environment without stirring, respectively. The sealed autoclave was transferred to a 180 °C oven and held there for 24 h, and then cooled to room temperature naturally. It should be noted that tert-butylamine hydrolyzes in water to generate OH$^-$ and in such a basic environment, the oxidation transfer of Ce(III)$\rightarrow$Ce(IV) takes place because of the dissolved oxygen from air. The crude solution was centrifugated to remove the solid impurities, and then the upper brown supernatant solution containing the nanoparticles was precipitated with the minimum volume of ethanol and further isolated by centrifugation without any further size sorting process. The purified nanoparticles were easily dispersed in nonpolar solvent (toluene, hexane, chloroform, etc).

(2) For the small-sized nanoparticles, the one-step precipitation operation could precipitate all the nanoparticles from the solution. For the mixture of large-sized and small-sized nanoparticles, the upper brown supernatant solution after the first step of precipitation-centrifugation could be re-precipitated with ethanol for the second time, resulting in the small-sized nanoparticles (the so-called two-step precipitation operation). It should be noted that only two-step precipitation operation and no further size sorting process were applied in our experiments.

(3) A typical proportion of reagents for the ceria nanorods: 15 mL of 33.3 mmol/L cerium (III) nitrate aqueous solution, 15 mL toluene, 2 mL oleic acid and 0.2 mL tert-butylamine.

(4) The low water/toluene ratio in our experiments: 10 mL water to 20 mL toluene.

(5) XRD measurements were performed on a D/max 2550V with Cu K$\alpha$ radiation. Data in Figure 1e and S11c were recorded with the power of 8 kW (40kV, 200mA), others with the power of 1.6 kW (40kV, 40mA). Samples were prepared by dropping nanoparticle solution in toluene on single-crystalline Si wafer and evaporating the solvent. TEM and HRTEM images were gained by a JEOL 2100F microscope. Samples were generally prepared by depositing a drop of dilute nanoparticle solution in toluene onto carbon-coated Cu grids, evaporating for 30 s, and wicking away the excessive solvent with a filter paper. Specially, samples for 3D self-assembly arrays were prepared by evaporating nanoparticle solution in a mixed solvent of toluene and ethanol (1v:1v) with the same procedure.
Mixture of polyhedral and cube-like ceria NPs — the role of OLA

Figure S1. (a) TEM image of mixture of polyhedral and cube-like ceria NPs from the decreased amount of OLA. (b) SAED pattern. (c) HRTEM image of several NPs. (d) HRTEM image of an individual polyhedral ceria NP. (e) HRTEM image of an individual cube-like ceria NP.
The role of tert-butyamine

**Figure S2.** (a-d) TEM images of the samples prepared with the tert-butyamine of (a) 0.1, (b) 1.0, (c) 1.8, and (d) 2.5 mL with 1.5 mL OLA used. The lower is the XRD patterns corresponding to them; the relative intensity ratio of (200)/(111) can be used to estimate the proportion of cubic NPs. Neither low nor high concentration of tert-butyamine favors the formation of nanocubes, and the proper amount is 0.15 ~ 0.3 mL when 1.5 mL OLA is used.
Bimodal size distribution in the whole reaction system by mixing the large-sized and small-sized NPs from twice precipitation

Figure S3. (a) TEM image of the mixture of large-sized and small-sized nanocubes by mixing the NPs from the two steps of precipitation. (b) Bimodal size distribution of the whole reaction system (~1000 NPs). (c) HRTEM image of the large-sized nanocubes; the lattice fringes corresponding to cubic ceria {200} planes (spacing 0.271 nm) dominate the image and occasionally observed {220} lattice fringes run face-diagonally in the cube. (d) HRTEM image of the small-sized nanocubes; 1 and 2 marks {111} and {220} lattice fringes, respectively, and the unmarked are {200} lattice fringes, which dominate the image.

TEM tilted angle analysis of the nanocube
**Figure S4.** (a, b) TEM tilting experiment of the nanocube, indicating that the \(\{220\}\) fringes (spacing 0.191 nm) run face-diagonally in the cube.

**3D self-assembly of 15 nm nanocubes**

**Figure S5.** (a) TEM image of the 3D self-assembly of 15 nm nanocubes. (b) HRTEM image of a brim of the self-assembled pattern, indicating double layers of nanocubes.
**Cubic mesocrystals**

**Figure S6.** (a-e) TEM tilting experiment of a cubic mesocrystal; the cubic shape of the mesocrystal can be clearly seen. (f) SAED pattern, indicating that it is nearly single-crystal. (g) Low magnification TEM image of the cubic mesocrystals.
Fourier analysis of several large-sized nanocubes in 4.43 nm nanocubes

Figure S7. (a, b) HRTEM images of the large-sized nanocubes in the dominant amount of small-sized nanocubes. They can be easily separated from the small-sized nanocubes by the precipitation-centrifugation operation. (c) The power spectrum (PS) of the marked area in Figure S7b. (d, e) and (f, g) masked PS and back Fourier transform of the area marked by white square in Figure S7b; the circle marks a typical dislocation, the pair of parallels and the ellipsoid highlight typical displacements. There exist different domains in the images.

Fourier analysis of NPs from low water/toluene ratio
Figure S8. (a) TEM image of imperfect nanocubes from a low water/toluene ratio, indicating the inadequacy of growth from the molecular precursors (lack of Ce(III) reactant). There apparently exist pits in the nanocubes. (b) HRTEM image of a typical NP. (c) The power spectrum (PS) of the marked area in Figure S8b, (d) masked PS, and (e) back Fourier transform of the area marked by white square in Figure S8b; the circle marks a typical dislocation and the two ellipsoids highlight typical displacements. There exist dislocations and displacements which are not marked in the image. So, there are displacements (sometimes dislocations) and domains in the imperfectly shaped nanocube, although the whole nanocube is single-crystalline. (f) XRD pattern.

NPs from a shortened reaction time (6 h) with the low water/toluene ratio
Figure S9. (a) HRTEM image of NPs from the low water/toluene ratio with a shortened reaction time (6 h). (b) HRTEM image of a typical area. (c) FFT pattern of the marked area in Figure S9b. Low contrast between crystalline regions (from lattice fringes) shows spacing between primary particles, but lattice fringe orientations and FFT pattern indicate that particles are attached to share the same crystallographic direction. After a long reaction time (the stage of growth from the molecular precursors), the nanocubes become relatively integrated, as shown in Figure S8. (d) XRD pattern on the single-crystalline Si wafer.

Flowery NPs from low water/toluene ratio and high Ce(III) concentration (Low
Figure S10. (a) TEM image of flowery NPs from the increased Ce(III) concentration compared with the sample in Figure S8, and (b) HRTEM image of several NPs; it can be seen that the lattice planes of the primary particles are almost perfectly aligned and they go straight through the contact areas where the primary particles are epitaxially fused together, indicating the oriented aggregation-mediated growth. (c, d, e) Fourier analysis of nanoparticle 1, and (f, g, h) Fourier analysis of nanoparticle 2; the ellipsoid marks displacement and the circle marks dislocation. (i) XRD pattern.

Mixture of nanorods and nanocubes
Figure S11. (a) TEM image of the nanorods and nanocubes; arrows indicate the imperfectly shaped NPs. (b) HRTEM image of the NPs; the nanorods are along [100] and enclosed by {200} planes, which is different from the previous reports where the nanorods are along [110] and enclosed by two {200} and two {220}planes (ref.4b, 4c and 7c). (c) XRD pattern of the NPs. (d) The schematic illustrations of the facets of an individual cube, and the direction and facets of an individual rod.

UV-vis absorption spectrum and photoluminescence spectrum
**Figure S12.** (a) Typical UV-vis absorption spectrum, and (b) room temperature photoluminescence spectrum of dilute toluene solutions of ceria nanocubes.

**FT-IR spectrum**

**Figure S13.** FT-IR spectrum of ceria nanocubes. The bonds at 2921 and 2850 cm$^{-1}$ are the C-H antisymmetric and symmetric stretching vibrations, and the bands at 1538 and 1436 cm$^{-1}$ are the COO$^-$ antisymmetric and symmetric stretching vibrations.