

Supercritical Hydrothermal Synthesis of Organic-Inorganic Hybrid Nanoparticles

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Introduction

As one of the most important rare earth oxides, ceria nanocrystals have been extensively applied in catalysis, electrochemistry and optics. Structural, optical, electronic and catalytic properties of ceria nanocrystals are strongly dependent on their crucial geometrical parameters: size and shape. The preparation of high quality ceria nanocrystals of desired morphology is of great fundamental and technological interest. Recently, the organic solution phase and liquid-solid-solution phase transfer synthetic routes have been demonstrated as versatile pathways toward the uniform nanocrystals with controlled morphology [1]. These nanocrystals are often referred to as "nanoblock" to build superlattice patterns via self-assembly, which is a prerequisite for the generation of nanodevices and nanosystems. Despite these recent reports, up to now, it is still a great challenge for us to control the nanocrystal morphology at sub-10nm, and realize various self-assembly modes of nanocrystal building blocks for 0-D (dimension) to 3-D to reveal the underlying self-assembly principles. Here, we report a novel synthesis approach to control ceria nanocrystals at sub-10nm, especially for tailor-made crystal plane. This strategy is based on the miscibility of the organic ligand molecules with supercritical water due to the lower dielectric constant of the water; and the nanocrystal shape control by selective reaction of organic ligand molecules to the specific inorganic crystal surface. Additionally, the important pioneering studies on the assembly of shape-controlled nanocrystals into ordered superlattices are discussed.

Experimental

In a typical synthesis, the cerium oxide precursor was prepared by mixing 100 ml of 0.1M Ce(NO₃)₃ solution with 100 ml of 0.3M NaOH. After the reaction mixture had been stirred for about 6 h, the precursor was centrifuged and washed several times with distilled water. Then 2.5 ml of the 0.02M precursor was transferred into a pressure-resistant SUS316 vessel (inner volume, 5 ml). To modify the surface of the nanocrystals and induce anisotropic growth of the nanocrystals, an appropriate amount of decanoic acid and decanoic amine (0.05- 1g) was also loaded into the vessel reactor. The hydrothermal reaction was performed in the reactor at 400°C for 10 min and terminated by submerging the reactor in a water bath at room temperature. The organic ligand-modified nanocrystals were extracted from the product mixture with 3 ml of hexane. The final products were precipitated from the resulting hexane phase by the addition of 10 ml of ethanol as an anti-solvent reagent, and then were separated by centrifugation. The obtained nanocrystals could be redissolved in some organic solvents such as hexane, toluene and tetrahydrofuran.

Results and Discussion

Crystal structure and morphology of the synthesized ceria nanocrystals were characterized by means of powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). The XRD patterns of the nanocrystals indicated that they had a fluorite cubic structure. When decanoic acid (mol ratio to ceria precursor, 24:1) was added to the reaction system, the TEM image in Fig. 1a exhibited that the resulting 6nm nanocrystals were truncated octahedron enclosed by the {111} and {200} planes. They were self-assembled with a nearest neighbour spacing of ~ 2nm maintained by the decanoic acid capping group. To understand the interaction between the ceria nanocrystals and the organic ligand molecules, FTIR of these ceria nanocrystals were analysed. Bands in the 2800–2960 cm⁻¹ region were attributed to the C–H stretching mode of methyl and methylene groups. The bands at 1532 and 1445 cm⁻¹ corresponded to the stretching frequency of the carboxylate group, which suggest that carboxylate group from decanoic acid is chemically bonded to the surface of the ceria nanocrystals and the other hydrocarbon groups

oriented outward. This result is an evidence for possible organic-inorganic reactions to form chemical bonds between the nanocrystal surface and organic ligand molecule in the unique reaction of supercritical water, which is essential for arranging individual nanocrystal into superlattices via self-assembly.

In our synthesis, adding decanoic acid and decanoic amine led to tune the supercritical water media. When the ratio of decanoic acid to decanoic amine is reduced, the nanocrystal morphology change from truncated octahedron to cubic. The HRTEM image (Fig. 1d) displayed ceria nanocubes with exposed (200) surfaces, which was due mostly to the much faster growth of {111} planes than {200} planes of the cubic phase of ceria by the selective interaction of decanoic acid.

As shown in Fig. 1, the self-assembly patterns transfer from hexagonal to cubic like packing structure, with the nanocrystal shape change from truncated octahedron to cube. These suggest that the packing fashion is influenced by nanocrystals shape, especially, the strong interactions from the exposed crystal planes can control the superlattice pattern, when the average size of nanocrystals and surface ligand molecules are similar.

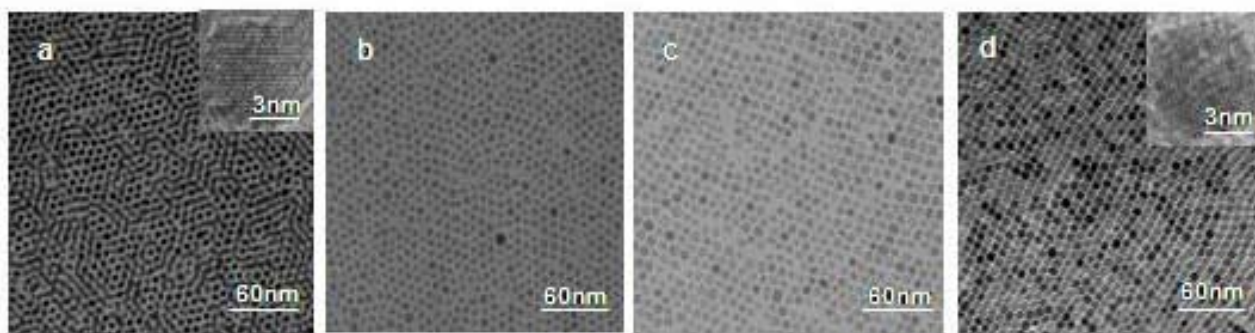


Fig. 1. TEM of ceria nanocrystals by organic ligands-assisted supercritical hydrothermal synthesis. The mol ratios of decanoic amine-to-decanoic acid were (a) 0, (b) 1:5, (c) 1:1, (d) 2:1

In summary, the study offers a simple and green chemistry approach to controlling the shape of ceria nanocrystals by tuning organic ligands assisted-supercritical hydrothermal process. Shape-controlled ceria nanocrystals and their self-assembly patterns are intriguing for various applications, including photonics and catalysis.

References

[1] J. Zhang, S. Ohara, M. Umetsu, T. Naka, Y. Hatakeyama, and T. Adschiri, "Novel approach to colloidal ceria nanocrystals: tailor-made crystal shape in supercritical water", *Adv. Mater.*, (in press).

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