# Facile synthesis of hybrid hexagonal $CeF_3$ nano-disks on $CeO_2$ frustum pyramids

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## ARTICLE INFO

## ABSTRACT

A hybrid architecture comprising two types of cerium compound nanoparticles is synthesized via a facile surfactant- and template-free hydrothermal process. The prepared hybrid materials show an unusual morphology with small hexagonal nano-disks dispersed on relatively larger frustum pyramids. Microscopic analyses identify the chemical composition of the nano-disks as $CeF_3$ and the frustum pyramids as $CeO_2$. Apart from absorption on the $CeO_2$ supports, the $CeF_3$ nano-disks are self-assembled as well to form ordered one-dimensional chain nanostructure. Such unique hybrid architecture may open an avenue for the scientific and technological application in the rapidly emerging catalytic field.

## 1. Introduction

Rare-earth compound nanocrystals have been investigated extensively over the past few years because of the hopes they raise for diverse technological applications, e.g., in optics, optoelectronics, biological labeling, and catalytic field [1–4] and also for their fundamental scientific significance. A well-known rare-earth compound is ceria ($CeO_2$), which is currently the subject of intensive research for its promise as three-way catalysts [5], oxygen sensors [6], solid fuel cells [7,8], and absorbents to toxic matter as well as due to its ability to filter ultraviolet rays. Apart from oxide nanocrystals, nanostructured fluoride $CeF_3$ is also one of the important rare-earth compounds due to its widespread uses as ionic conductors [9], nano-composite scintillators for detection of gamma-ray [10], additives to lubricating oils [11], and so forth.

Great effort has been devoted to date to the synthesis of inorganic micro- and nano-crystals with controllable size and morphology. The interest is driven primarily by the fact that shape and size of inorganic nanocrystals impose tremendous impact on their physical and chemical properties. To date, a number of approaches have been attempted to prepare cerium compound nanocrystals, in particular $CeO_2$ nanostructures, including high-intensity ultrasound [12], rapid microwave [13], hydrothermal synthesis method [14] and so forth [15–17]. However, it remains a nontrivial task to fabricate the nanocrystals with unique morphologies in a tunable way using a simple method, especially for the two cerium compounds, $CeO_2$ and $CeF_3$. For example, the well-defined $CeO_2$ nanostructures with morphologies of nano-cubes, nanorods and nano-octahedra, and the $CeF_3$ with the nano-plates and nano-flower-like morphology have been successfully synthesized through a variety of complicated methods [18–20]. Among all of the applied methods, hydrothermal synthesis technique has attracted the broadest attention because many of its own merits are relevant for the one-step low-temperature synthesis including a simple operation, low energy consumption, and the possibility for large-scale industrialization [21]. Here, we fabricate a hybrid architecture comprising unusual hexagonal $CeF_3$ nano-disks dispersed on $CeO_2$ frustum pyramids using a facile one-step hydrothermal synthesis process, and discuss underlying growth mechanism. The interesting hybrid system prepared with a facile, economical, and effective method holds substantial technological promise for many applications, e.g., in the catalytic field.

## 2. Experimental

All chemical reagents were of analytical grade (purity of 99.99%, Sigma-Aldrich Co., Ltd.) and utilized with no further

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purification. The hybrid samples were synthesized via the hydro-thermal method. First, cerium nitrate hexahydrate (Ce(N-O$_3$)$_3$·6H$_2$O) and sodium fluoride (NaF) were dissolved in distilled water, followed by an intense stirring for 15 min to produce precursors. The solution was then transferred into auto-claves, where it was subsequently heated at 200 °C for 12 h under autogenous pressure. White products were eventually harvested by centrifuging, washing with distilled water and ethanol to remove unexpected ions, and drying at 60 °C in air. Fractionation technique was taken in order to separate nanoparticles. Micro-structure analyses were conducted using x-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). For the XRD, a Rigaku Smart Lab diffractome-try with the Cu Kα radiation operated at 45 kV and 200 mA was employed. Surface morphologies were characterized with a field-emission Hitachi SU8000 SEM. Microstructures were also inves-tigated using a JEOL JEM-2010F electron microscope operated at an accelerating voltage of 200 keV.

## 3. Results and discussion

Fig. 1(a) shows morphology of the samples prepared free from surfactants, where two utterly different types of particles are readily seen: small particles covering larger ones with a regular shape. The small particles, which are separated independently using the fractionation technique at high speed, exhibit corner-truncated pyramidal morphology (named hexagonal nano-disks hereafter) with an average size of ∼30 nm (Fig. 1(b) and (g)). Moreover, the polygon faces on the both sides of the nano-disks are flat. These nano-disks with a flat face are self-assembled to a one-dimensional chain nanostructure. In contrast, the larger particles, which have a size of up to ∼800 nm, exhibit a frustum pyramid morphology with well-defined edges (Fig. 1(c) and (d)). The nano-disks are dispersed on the surfaces of frustum pyramids (Fig. 1(e) and (f)). Such unusual hybrid architecture may act as solid catalysts where the larger frustum pyramids serve as supports to the smaller nano-disks, holding thereby technological promise for catalytic applications [22].

To determine individual chemical composition of the hybrid particles, we performed the XRD analysis, as shown in Fig. 2, where textural orientations of the detected matters are shown as well for easy reference. Upon close indexing, the diffraction peaks are identified as belonging to the CeO$_2$ and the close-packed hexagonal CeF$_3$. To further identify every individual particle, we conducted TEM investigations. Fig. 3(a) shows a typical TEM image of the frustum pyramid, which is in line with the above SEM observation (Fig. 1(d)). The corresponding selected-area diffraction pattern (SADP; Fig. 3(b)) identifies the particle with frustum pyramid shape as face-centered cubic CeO$_2$. Fig. 3(c) shows a representative TEM image of an individual hexagonal nano-disk, which is in close agreement with the SEM observation (Fig. 1(f) and (g)). A careful indexing of its SADP clarifies the nano-disks as CeF$_3$ and reveals that normal of their hexagonal faces is [001] direction (Fig. 3(d)). Fig. 3(e) gives a cross-section view of the nano-disks, where one can see that there are triangles at the corners of the nano-disks, indicating that the nano-disks are sharp. The thickness of the nano-disks is measured to be ∼30 nm. Fig. 3(f) gives a model of CeF$_3$ nano-disk having sharp corners and well-defined edges. The high-resolution TEM (HRTEM) image is taken from the corner area of the nano-disk (Fig. 3(c)), as shown in Fig. 3(g), from which the lattice spacing is determined to be ∼0.35 nm, in line with that of the ($2\bar{1}0$) plane of CeF$_3$, suggesting that the exposed lateral hexagon surfaces are {$2\bar{1}0$}.

Upon the aforementioned observations, we propose a possible growth mechanism for the hybrid architecture. First, all the NaF are ionized to F$^-$ and hydrolyzed to produce OH$^-$ ions. These OH$^-$ ions react with the hydrated Ce$^{3+}$ ions, forming milky Ce(OH)$_3$·nH$_2$O precursor. The precursor is then oxidized at high temperature and pressure during hydrothermal process, resulting in the nucleation of CeO$_2$ particles. The CeO$_2$ crystal nuclei are eventually aggregated and self-assembled, shaping the unique
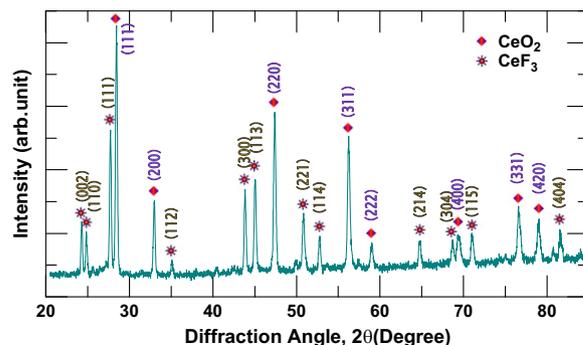


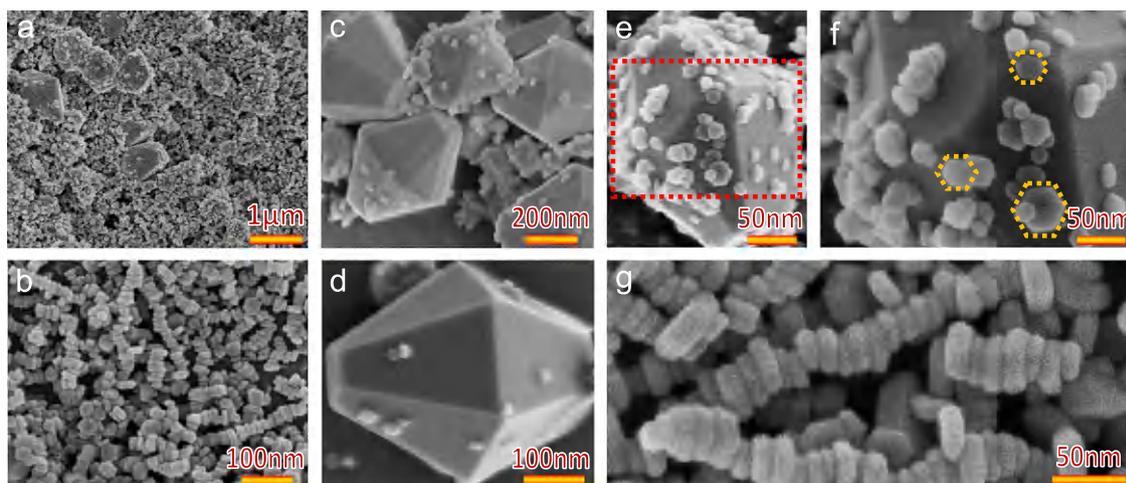**Fig. 2.** XRD spectrum of the products prepared with the sodium fluoride.



**Fig. 1.** SEM images of prepared samples: (a) mixed particles, (b) independently separated hexagonal nano-disks, (c) independently separated particles with the frustum pyramid morphology, (d) enlarged frustum pyramid, (e) and (f) enlarged hybrid system comprising nano-disks absorbed on the surface of frustum pyramid, and (g) self-assembly of the nano-disks into one-dimensional chains.
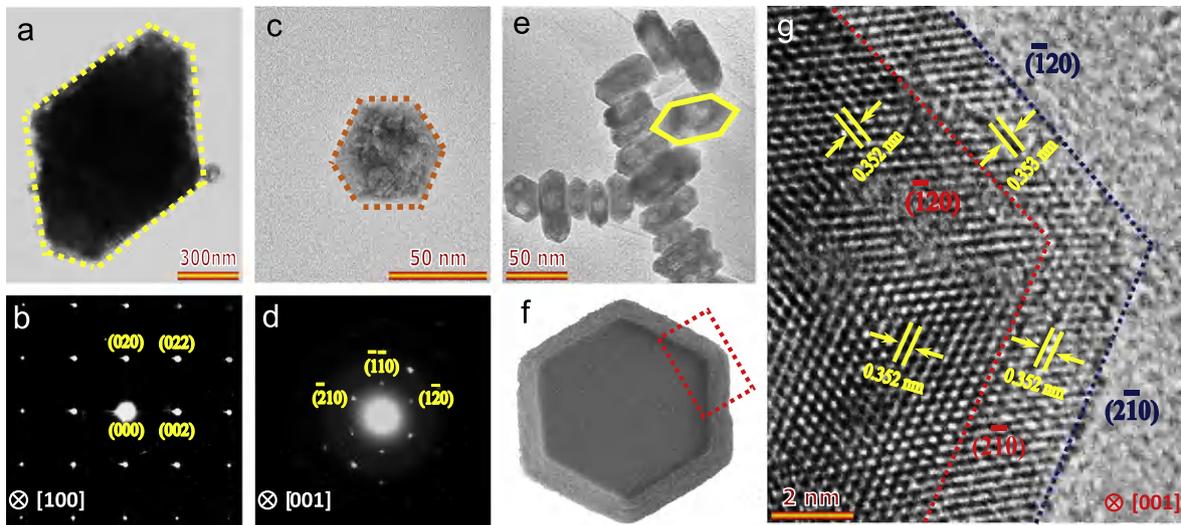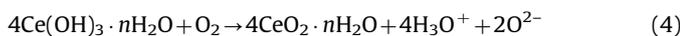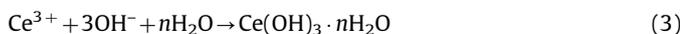
**Fig. 3.** (a) TEM image of a particle with the frustum pyramid morphology. (b) Corresponding SADP identifying the frustum pyramid particle as CeO$_2$. (c) TEM image of an individual hexagonal nano-disk. (d) SADP of the nano-disk, which identifies the nano-disk as CeF$_3$. (e) TEM image of the self-assembled nano-disks. (f) Model of the hexagonal nano-disk. (g) HRTEM image giving the corner region of the nano-disk.
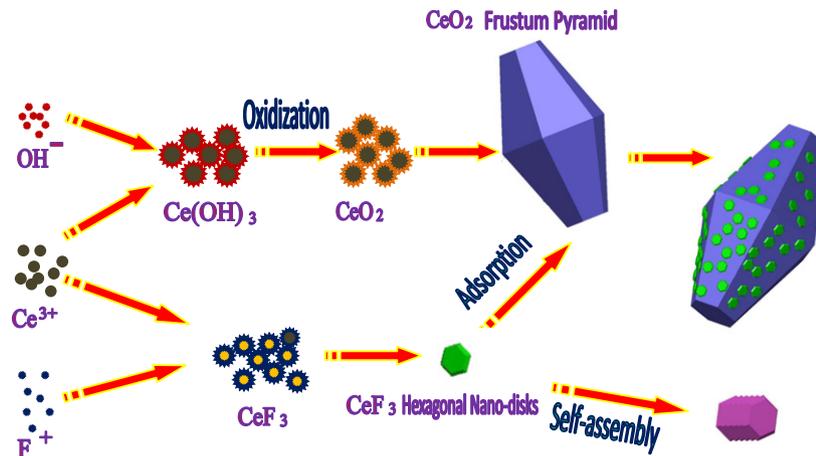


**Fig. 4.** Schematic illustration of the evolution of the CeF$_3$ and CeO$_2$ particles in the hybrid system.

frustum pyramid morphology. The reaction process is summarized as follows:

$$NaF \leftrightarrow Na^+ + F^- \tag{1}$$

$$F^- + H_2O \leftrightarrow OH^- + HF \tag{2}$$

$$Ce^{3+} + 3OH^- + nH_2O \rightarrow Ce(OH)_3 \cdot nH_2O \tag{3}$$

$$4Ce(OH)_3 \cdot nH_2O + O_2 \rightarrow 4CeO_2 \cdot nH_2O + 4H_3O^+ + 2O^{2-} \tag{4}$$

On the other hand, the growth of CeF$_3$ is simple by the reaction of Ce$^{3+}$ with F$^-$:

$$Ce^{3+} + 3F^- + nH_2O \rightarrow CeF_3 \cdot nH2O \tag{5}$$

Fig. 4 illustrates schematical evolution of the CeF$_3$ and CeO$_2$ nanoparticles in the hybrid system. A portion of CeF$_3$ nano-disks are adsorbed on the surface of CeO$_2$ frustum pyramids, while the rest of them are self-assembled, forming one-dimensional chain nanostructures. The CeF$_3$ nanoparticles are dispersed on the CeO$_2$ surface, which should be important for the performance enhancement of CeF$_3$. The self-assembly and adsorption of the CeF$_3$ onto the CeO$_2$ is attributable to the fact that the CeO$_2$ facets have a high activity energy and that such adsorption balances geometrical mechanics.

## 4. Conclusions

We have demonstrated the synthesis of a hybrid system comprising two kinds of cerium compounds by a facile approach: hexagonal CeF$_3$ nano-disks on CeO$_2$ frustum pyramid. The applied hydrothermal method is simple both technically as no surfactants and templates are used and in starting materials as only Ce(NO$_3$)$_3 \cdot 6H_2O$ is employed as the cerium resource and NaF as mineralizer. Further microscopic investigations identify the chemical composition of the hexagonal nano-disks as CeF$_3$ and the frustum pyramid as CeO$_2$. The CeF$_3$ nano-disks are found to be either self-assembled or adsorbed onto the surfaces of CeO$_2$ frustum pyramids owing to the high activity energy of their surfaces. Such an interesting architecture of nano-disks on frustum pyramid could be promising for wide technological applications and the results presented in this work demonstrate an economical route to synthesize more than one particle in one step.

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