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Single-Crystalline and Monodisperse LaF_3 Triangular Nanoplates from a Single-Source Precursor

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The synthesis of colloidal inorganic nanocrystals (NCs) with controlled shape, size, composition, internal structure, and surface chemistry is of fundamental and technological interest for mapping their shape/size-dependent material properties and for consolidating their promising applications in optics, catalysis, biosensing, and data storage.[1] In this area, many efforts have focused on inorganic 0D (dots) and 1D (rods and wires) nanostructures,[2] whereas 2D ones have rarely been explored, except for plate- or disk-shaped Ag, Co, Cu_2S, NiS, Gd_2O_3, and TiO_2.[3] So far, the organometallic approach and its alternatives in diverse surfactant solutions have been demonstrated as versatile pathways toward such shape-controlled NCs, using either multiple-source precursors or single-source precursor (SSP).[2,3b−e] However, it still remains a challenge to identify a suitable reaction system for growing high-quality NCs in terms of monodisperse, well-shaped, and single-crystalline NCs. The keys to a successful synthesis are to select suitable precursors, to control the coordinating behavior of the ligand, and to sustain a balance between the nucleation and growth stages. [2,3b−e]

The NCs of rare earth and alkaline earth fluorides have attracted recent interest due to their potential uses in optics and optoelectronics (e.g., lighting and displays, optical amplifiers, and lasers), microelectronics, and tribology.[4] The available synthetic approaches involving modified precipitation,[4a,b] microemulsion,[4c] polyol,[4d] and hydrothermal methods[4e,f] are all based on the liquid precipitation reaction between metal nitrates/chlorides and HF/NaF/NH_4F. Herein, we report the first synthesis of single-crystalline and monodisperse LaF_3 triangular nanoplates via a SSP ($La(CF_3COO)_3$) route. The nanoplates are characterized by 2.0 nm in thickness and 16.0 nm in edge length and can self-assemble into large-area superlattices.

In a typical synthesis, a slurry containing $La(CF_3COO)_3$ hydrate (1 mmol, prepared by literature method),[5] oleic acid (20 mmol, Aldrich), and octadecene (20 mmol, Acros) in a three-necked flask (100 mL) was heated to 100 °C to remove water and oxygen, with vigorous magnetic stirring under vacuum for several minutes in a temperature-controlled electromantle, and thus to form an optically transparent solution. The solution was then heated to 280 °C at a heating rate of 18 °C/min and kept for 1 h under an Ar atmosphere, and thus a light-yellow colloidal solution was obtained. As the solution was cooled to room temperature, the NCs were precipitated by adding a mixture of hexane/acetone (v/v in 1:4) into this colloidal solution, followed by washing with ethanol and drying in air at 60 °C. The as-prepared NCs could be easily redispersed in various nonpolar organic solvents, such as hexane, toluene, and dichloromethane.

From the large-angle X-ray diffraction (XRD, Rigaku D/MAX-2000) pattern shown in Figure 1a, we can see that all of the reflections well match the trigonal tysonite LaF_3 structure with lattice parameters of $a = 7.232$ Å and $c = 7.285$ Å (JCPDS 32-0483; $P\bar{3}c1$). In this structure, each La is on a 2-fold axis and has nine coordinating fluorine atoms.[6] The broadening of the diffraction peaks reveals the nanocrystalline nature of the sample. However, the (110) and (300) reflections, which have an included angle of 30°, show distinct peak widths that are narrower than those of the others, indicating the larger sizes perpendicular to them for the NCs, which also conform to the triangular plate shape of the NCs determined by the following microscopic analysis.

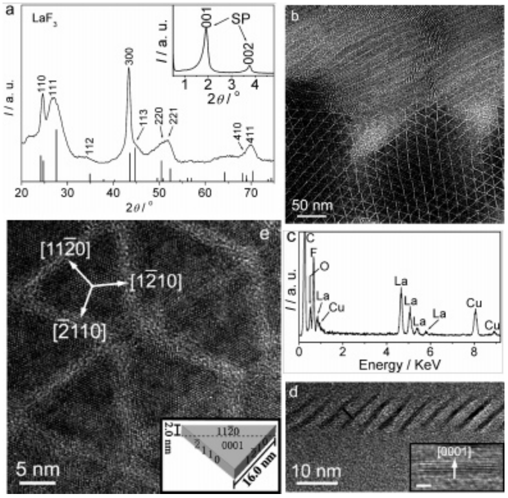

Figure 1. (a) Large-angle XRD pattern of the as-dried LaF_3 nanoplate powder; inset is the small-angle XRD pattern of the NC superlattices (SP) formed on a glass substrate from a toluene/hexane solution. (b) TEM image of the LaF_3 nanoplates. (c) EDAX spectrum of the LaF_3 nanoplates. (d) HRTEM image of an aligned LaF_3 nanoplate (standing on the edge) array; inset is the HRTEM image of an individual nanoplate (scale bar = 2 nm). (e) HRTEM image of an aligned LaF_3 nanoplate (lying flat on the face) array; inset is the schematic diagram of an individual nanoplate.

Transmission electron microscopy (TEM, Philips Tecnai F30 FEG-TEM, 300 kV) was used to map the shape, size, lattice structure, and arrangement of the NCs dispersed on a carbon-coated copper grid from toluene/hexane solutions. Figure 1b shows that the LaF_3 NCs consist of highly aligned triangular nanoplate arrays, either standing on the edge or lying flat on the face, demonstrating the high uniformity of the crystallite size and the retention of the oleic acid capping ligand, which was further confirmed by ^1H NMR measurement (Supporting Information). Energy-dispersive X-ray analysis (EDAX) confirmed the presence of La and F in the nanoplates (Figure 1c). According to the high-resolution TEM (HRTEM) image of Figure 1d, the side plane of the standing aligned triangular nanoplates comprises six (0002) layers with an interplanar spacing of 0.36 nm and shows a thickness of 2.0 ± 0.1 nm. The interparticle distance is ca. 2.4 nm, which seems to fit the thickness of one monolayer of the capping oleates. Figure 1e shows that

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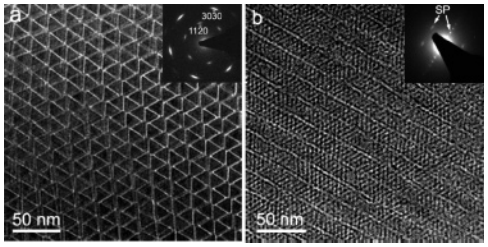

Figure 2. TEM images of the edge-to-edge (a) and face-to-face (b) superlattices (SP) of LaF_3 nanoplates. Insets are the SAED patterns.

the triangular nanoplates are highly uniform, with three equilateral edges in the length of 16.0 ± 0.4 nm, and are single crystalline, showing an interplanar spacing of 0.35 nm along [−2110], [1−210], and [11−20] directions. The nanoplate surfaces are perfect without any stacking faults and clean without any sheathed amorphous phase even at the edges. Totally, {0001} and {11−20} facets are determined to enclose the triangular nanoplate (see inset in Figure 1e).

The high uniformity of these nanoplates allows the formation of nanoarrays arranged with long-range translational and orientational order in several microns. After slow evaporation of a concentrated LaF_3 nanoplate solution in toluene/hexane at the volume ratio (R) of 1:3, a hexagonally close-packed (*hcp*) superlattice formed on the TEM grid, as verified by the 6-fold symmetric spots of (11−20) and (30−30) planes ascribed to trigonal LaF_3, shown in the selected area electron diffraction (SAED) pattern with the [0001] zone axis (inset in Figure 2a).[7] In this *hcp* superlattice, the nanoplates lay flat on the face and self-assemble into nanoarrays via edge-to-edge formation. By manipulating the solvent/substrate combination, ribbonlike nanoarrays were generated at $R = 1{:}5$, in which the nanoplates stood on the edge and self-assembled into nanoarrays via face-to-face formation (see Figure 2b). The SAED pattern inserted in Figure 2b showed two sets of diffraction spots, representing a periodicity length of 17.6 (inter-ribbon distance) and 4.3 nm (interparticle distance) and indicating the highly ordered arrangement of the nanoplates.[7] The value of 4.3 nm corresponds well to the layer distance of the NCs' lamellar stacking determined by the small-angle XRD pattern (inset in Figure 1a). Interestingly, the self-assembly direction of the nanoplate shows an included angle of ∼30° with its c-axis.

In the monodisperse nanoplate synthesis, the combined use of SSP and coordinating and noncoordinating solvents seemed to play a key role. Experimentally, we observed that some tiny gas bubbles emitted from the reaction medium in a few minutes as the clear SSP solution was heated rapidly to 280 °C under an Ar atmosphere, whenever we used oleic acid, octadecene, or a combination of both as the solvent. The gas emission implied the instant decomposition of the $La(CF_3COO)_3$ precursor at 280 °C and the simultaneous formation of LaF_3 nuclei.[5] We also found that the sole use of oleic acid as the solvent yielded soluble but less uniform LaF_3 triangular nanoplates (22.5 ± 2.5 nm), while the sole use of octadecene produced insoluble, aggregated, and ill-shaped NCs. Further, it is known that the $c{:}a$ ratio of trigonal LaF_3 equals 1.02, while the ratio of edge length to thickness for the nanoplates is as large as 8:1. All of these results strongly suggest that the plate shape of our LaF_3 NCs should be attributed to the 2D growth of the homogeneous trigonal LaF_3 nuclei with the rigidly growth-blocked {0001} facets, related to the much stronger adsorption of oleic acid on them during crystal growth. In fact, the blocked growth phenomenon for particular facets due to the selective adsorption of surfactants was also observed in the synthesis of Co and Cu_2S nanodisks.[3b,c] The triangular geometry of the nanoplates is possibly due to the slow but equal growth rate of the three energetically equivalent {11−20} facets, which have the same surface atom density in the trigonal structure.[6] The low polydispersity of the nanoplates should be ascribed to a well-maintained balance between nucleation and growth stage during the synthesis,[2a,c,d] that is, the thermolysis of SSP at a suitable concentration generated a quick but short nucleation stage, and the proper use of noncoordinating solvent (octadecene), together with the concentration reduction of the coordinating ligand (oleic acid), created a slow but long growth stage without Ostwald ripening.[2d] We are currently exploring the detailed formation mechanism of the nanoplates.

The SSP synthesis of LaF_3 triangular nanoplates can readily be reproduced and scaled up and can be extended to the other rare earth fluorides. Grams of the LaF_3 nanoplates were obtained when using a large flask (250 mL) in synthesis. Starting from $Ce(CF_3COO)_3$ hydrate, we obtained high-quality CeF_3 triangular nanoplates [(1.7 ± 0.2) × (14.4 ± 0.5) nm] in trigonal tysonite structure ($a = 7.171$ Å, $c = 7.176$ Å) via the SSP approach.

In summary, single-crystalline and monodisperse LaF_3 triangular nanoplates (2.0 × 16.0 nm) in trigonal structure were synthesized via thermolysis of $La(CF_3COO)_3$ in a hot oleic acid/octadecene solution, which has merits of one-step, mass production, and easy operation. Their high quality should be more valuable for further theoretical and practical exploration of their shape/size-dependent properties. Their intriguing self-assembly capability enables them to serve as novel nano-building blocks for new nanodevice applications. Further considering that the precursor is available for many metal elements (e.g., alkaline earths), we expect that the present SSP route may be generalized to synthesize many other pure or doped fluorides NCs.

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Supporting Information Available: ^{1}H NMR spectrum of the LaF_3 product in $CDCl_3$, and more XRD and TEM results for LaF_3 and CeF_3 nanocrystals (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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