

# Carbon Nanotube Templated Synthesis of CeF<sub>3</sub> Nanowires

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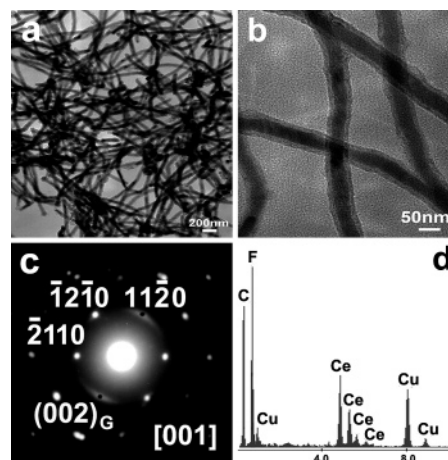
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Lanthanide fluorides have attracted considerable attention in the past decade because of their outstanding luminescent characteristics that originate from good coordination capability of hosted lanthanide ions in fluoride lattices and the wide band gap and very low vibrational energies induced by the high ionicity of the lanthanide to fluoride bond.<sup>1</sup> With precise shape and compositional control, the bonding state of the lanthanide fluorides is expected to be modified, which would help to further improve the performance of lanthanide fluoride nanostructures. Up to now, great efforts have been made on the synthesis of lanthanide fluoride nanostructures with specific shape and unique properties such as the nanoparticles,<sup>1c,2</sup> monodisperse nanocrystals,<sup>1h,3</sup> and well-defined nanoplates.<sup>4</sup> This was mainly achieved using the wet chemical approach in diverse solution systems. Nevertheless, the progress in the fabrication of one-dimensional (1D) lanthanide fluoride nanostructures such as nanotubes and nanowires remains a challenge, though their formation has been predicted to be possible in terms of the crystallographic structure.<sup>2c</sup>

Carbon nanotubes (CNTs) have been used as ideal nanotemplates or space confined nanoreactors for making 1D nanowires in the past decade. Their fascinating structures including well-defined 1D morphology, small diameters, and hollow interior cavities make it possible to govern and direct the growth of nanowires. More recently, the CNT-encapsulated Mg<sub>3</sub>N<sub>2</sub>,<sup>5</sup> Sn,<sup>6</sup> and Ge<sup>7</sup> nanowires have been made via the chemical vapor deposition (CVD) technique with CNTs



**Figure 1.** (a and b) TEM images of CNT-encapsulated CeF<sub>3</sub> nanowires; (c) corresponding SAED pattern; and (d) EDX spectrum, in which the Cu signals are from the grid used for TEM examination.

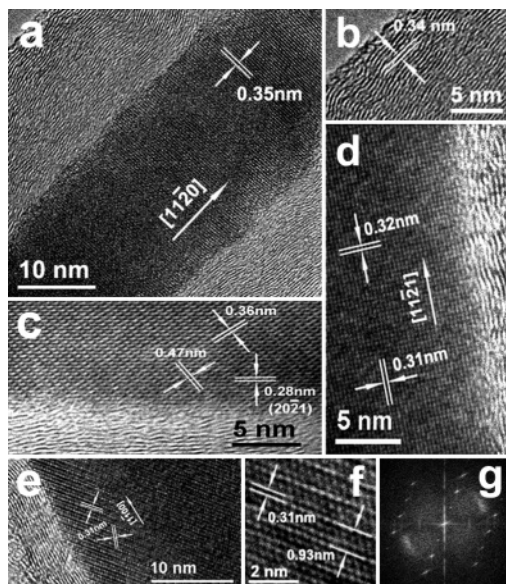
as the nanotemplate. Here, we report on the synthesis of CeF<sub>3</sub> nanowires with CNTs formed in situ as the nanotemplate, which was achieved by a novel polymer-involved arc discharge method. The approach could yield abundant CNT-encapsulated CeF<sub>3</sub> nanowires with high crystalline quality. After removing the CNT sheath by air oxidation, a large quantity of naked CeF<sub>3</sub> nanowires could be obtained with their 1D shape and crystalline nature remaining unchanged.

The synthesis of CeF<sub>3</sub> nanowires was conducted in an arc-discharge reactor in helium at 0.08–0.09 MPa. A high-purity graphite tube (10 mm o.d., 6 mm i.d.) filled with a mixture of polyetherimide (PEI)<sup>8</sup> and CeF<sub>3</sub> powders (<150 μm) in a weight ratio of 3:7 was used as the consuming anode while the cathode was a high-purity graphite rod (15 mm o.d.). The arc discharge was conducted with a direct current of 70–90 A and voltage of 20–30 V for 10 min. After the reaction, the black deposits on the cathode were collected and separated into two parts. One part was directly examined using transmission electron microscopy (TEM, JEM-2000EX; HRTEM, Philips Tecnai G<sup>2</sup> 20) and X-ray diffraction (XRD, Rigaku, Cu Kα). Another part was heated in an electric furnace in air at 773 K for 3 h, resulting in pure CeF<sub>3</sub> nanowires.

The XRD analysis (Supporting Information, Figure S1) reveals that the as-made black deposits are mainly made of hexagonal CeF<sub>3</sub> (JCPDS 08-0045) and graphitic carbon phase, as well as a small amount of cerium carbide (CeC<sub>2</sub>) phase. The TEM examination reveals the presence of a large amount of CNTs with uniform size, as shown in Figure 1. On average, over 90% of the nanotubes are completely filled with continuous CeF<sub>3</sub> nanowires with a length of several micrometers and a diameter of 10–30 nm. The selected area

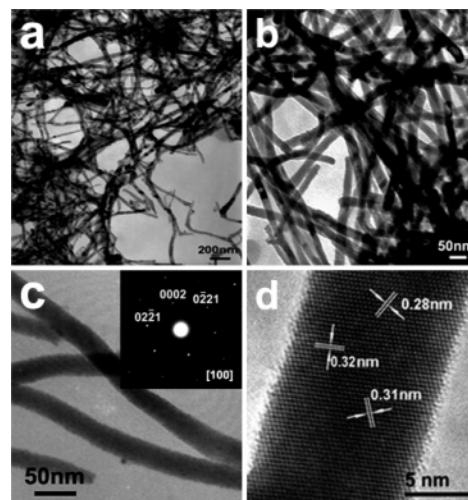
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**Figure 2.** (a–e) HRTEM images of CNT-encapsulated  $\text{CeF}_3$  nanowires with different growth directions; (f) the enlarged view of part e; and (g) the corresponding fast Fourier transform image of part e.

electron diffraction (SAED) analysis (Figure 1c) presents the pattern as a superpose diffraction of regular spots from  $\text{CeF}_3$  along the  $\langle 001 \rangle$  zone axis and a pair of short arcs from CNT (002) diffraction, evidencing the encapsulation of well-crystallized  $\text{CeF}_3$  nanowires inside the CNTs. The energy-dispersive X-ray (EDX) analysis of the entire nanowire further confirms the presence and domination of the Ce and F elements in the nanowires, as seen in Figure 1d. The typical high-resolution TEM (HRTEM) images of the  $\text{CeF}_3$  nanowires are shown in Figure 2, showing that the crystalline  $\text{CeF}_3$  nanowires are completely wrapped by graphitic carbon layers with a 0.34 nm spacing of the (002) atomic plane, which can be clearly seen in Figure 2b and Figure S2 in Supporting Information. The clear lattice fringes with approximately 0.35 nm spacing due to the (1120) planes of hexagonal  $\text{CeF}_3$  ( $d_{1120} = 0.3550$  nm) can be clearly seen in Figure 2a, and the (1120) crystallographic direction is parallel to the long axis direction of the wire, that is, the growth direction. In Figure 2c, the lattice fringes with approximately 0.28, 0.36, and 0.47 nm spacing due to the (2021), (1120), and ( $\bar{1}101$ ) planes of  $\text{CeF}_3$  ( $d_{2021} = 0.2836$  nm,  $d_{1120} = 0.3550$  nm,  $d_{\bar{1}101} = 0.4702$  nm) are described, and the growth direction of the wires is perpendicular to the (2021) crystallographic direction. Figure 2d shows the lattice fringes with approximately 0.31 and 0.32 nm spacing due to the (2200) and (1121) planes of  $\text{CeF}_3$  ( $d_{2200} = 0.3080$  nm,  $d_{1121} = 0.3195$  nm), respectively; the (1121) crystallographic direction is parallel to the wire's growth direction. Figure 2e shows the lattice fringes with approximately 0.31 nm spacing due to the (2020) and (0220) planes of  $\text{CeF}_3$  ( $d_{2020} = d_{0220} = 0.3080$  nm), and the ( $\bar{1}100$ ) crystallographic direction is parallel to the growth direction of the wire. More interestingly, 1D superlattice parallel to the (2020) or (0220) planes could be observed in some of the  $\text{CeF}_3$  nanowires. The superlattice has a periodicity of 0.93 nm, and one period consists of three (2020) or (0220) planes, as shown in Figure 2f. The presence of the superlattice is confirmed by corresponding fast Fourier transform image (Figure 2g), in which the distance between

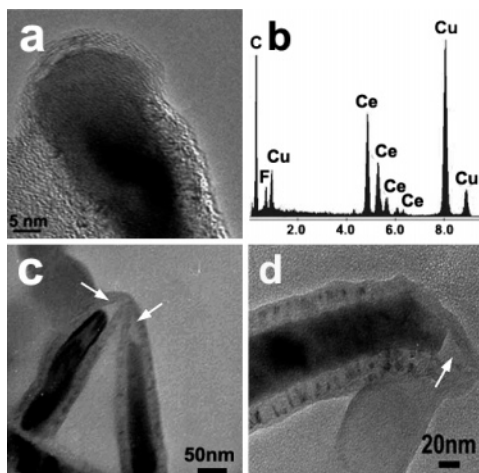


**Figure 3.** Un-coated pure  $\text{CeF}_3$  nanowires obtained by oxidizing the CNT-encapsulated  $\text{CeF}_3$  nanowires in air: (a) an overview; (b) and (c) zoom fraction, with the inset in part c being the SAED pattern; and (d) HRTEM image of one naked wire.

two basic spots is subdivided into three equal parts along the (2020) or (0220) direction. It is believed that the diverse growth mode of  $\text{CeF}_3$  nanowires is due to the confining effect of the CNTs in situ formed. The presence of CNT sheath retards the lateral growth of  $\text{CeF}_3$  crystals by preventing the formation of free surface and enforces the formation of 1D  $\text{CeF}_3$  nanowires inside the tube, whereas for uncoated nanowires the surface energy and facet formation plays crucial role for their intrinsic anisotropic growth. Despite of the diversity in growth mode, long-range order crystalline  $\text{CeF}_3$  nanowires can be observed within most of the CNTs (Supporting Information, Figure S2), indicating the good crystalline quality of  $\text{CeF}_3$  nanowires.

The synthesis of continuous and crystalline  $\text{CeF}_3$  nanowires inside the CNTs offers a new opportunity for the production of naked pure  $\text{CeF}_3$  nanowires. Inspired by the large difference between graphitic carbon and  $\text{CeF}_3$  in thermal oxidative stability, the CNT-encapsulated  $\text{CeF}_3$  nanowires were oxidized in air, which yielded abundant naked pure  $\text{CeF}_3$  nanowires whose dimensions fully inherited the 1D nanotube cavities. The length of these naked pure  $\text{CeF}_3$  nanowires could reach several micrometers. From the TEM examination, it can be clearly seen that after the air oxidation, the  $\text{CeF}_3$  wire's morphology and crystalline nature remain unchanged (Figure 3). The SAED analysis (inset, Figure 3c) reveals the regular diffraction spots from  $\text{CeF}_3$  crystals along the  $\langle 100 \rangle$  zone axis without CNT (002) diffraction due to the removal of CNT sheaths. HRTEM images (Figure 3d) also evidence the formation of well crystalline  $\text{CeF}_3$  nanowires after complete removal of CNT sheath, which was further confirmed by the XRD examination. In the XRD patterns, the peaks from carbon phase have disappeared completely (Supporting Information, Figure S3).

To obtain more information about the formation of CNT-encapsulated  $\text{CeF}_3$  nanowires, the growth ends of the tubes and the nanowires were scrutinized by EDX analysis. The spectrum shown in Figure 4b reveals the domination of the Ce and C elements ( $\text{CeC}_x$ ) in the chemical composition of the wire's end section (Figure 4a), implying the formation of CNT-encapsulated  $\text{CeF}_3$  nanowires may proceed via a Ce-



**Figure 4.** (a) TEM image of the growth end of one CNT-encapsulated  $\text{CeF}_3$  nanowire, of which the EDX spectrum is shown in Figure 4b; (c and d) the images of the tip of CNT-encapsulated  $\text{CeF}_3$  nanowires.

catalyzed growth process, in which  $\text{CeC}_x$  species function as the seed for the formation of CNTs; meanwhile, the in situ formed CNTs serve as templates for the continuous growth of  $\text{CeF}_3$  nanowires. Moreover, the tip section of CNT-encapsulated  $\text{CeF}_3$  nanowires was also examined in detail by TEM, as shown in Figure 4c,d. In general, hollow cavities with dimensions of 10–20 nm can be observed inside the upper tip of the nanotubes, as marked in the images with white arrows, implying the growth of outside CNT layers is faster than the encapsulated nanowires; that is, the formation of  $\text{CeF}_3$  nanowires inside the CNTs follows a templated growth mechanism.

The successful synthesis of CNT-encapsulated  $\text{CeF}_3$  nanowires is strongly dependent on the use of PEI, a unique macromolecular carbon source, which was evidenced by the fact that few  $\text{CeF}_3$  nanowires could be made under identical conditions without the use of PEI. The chemical structure of the PEI (Supporting Information, Figure S4) may give the clues for the crucial role of the PEI in the present study. The PEI is a macromolecular polymer consisting of abundant simple aromatic units that are joined together by binding links such as aliphatic bridges and ether linkages. Under the effect of the arc plasma, the PEI molecules would undergo a fast pyrolysis step in which they are broken up to release a variety of activated hydrocarbon fragments, transforming the arc to an analogy of “flash CVD”<sup>9</sup> in the absence of active gas (such as hydrogen, methane or acetylene, etc.). At the initial stage of the reaction, these activated hydrocarbon species could be readily adsorbed on preformed  $\text{CeC}_x$  seed and be

subsequently converted to graphitic carbon layers via a “dissolution-precipitation mechanism”<sup>10</sup> after spontaneous dehydrogenation, leading to the formation of a growth nucleus of CNTs. During the subsequent CNT growth, the  $\text{CeF}_3$  vapor enters the cavities of growing nanotubes under the driving force of capillarity, where it deposits as the nucleus for the further growth of the  $\text{CeF}_3$  crystal. With the continuous penetration of  $\text{CeF}_3$  clusters into the nanotubes,  $\text{CeF}_3$  nanowires are formed finally, and the template CNTs also self-seal. In this process, a high-temperature CVD mechanism instead of the traditional ones involved in the graphitic arc discharge<sup>11</sup> may be responsible for the formation and in situ filling of the CNTs, as schematically illustrated in Figure S5 in Supporting Information.

The strategy reported here not only is successful to synthesize high quality  $\text{CeF}_3$  nanowires but also can be extended to make the nanowires of other lanthanide fluorides with similar chemical properties and crystalline structure. One example is the successful fabrication of CNT-encapsulated and naked  $\text{LaF}_3$  nanowires by using  $\text{LaF}_3$  as starting materials instead of  $\text{CeF}_3$ , evidenced by Figures S6 and S7 in Supporting Information.

In conclusion, CNT-encapsulated  $\text{CeF}_3$  nanowires have been successfully synthesized for the first time via a PEI-involved arc-discharge method. The as-made nanowires are crystalline materials with a uniform diameter of 10–30 nm and a length of over several micrometers. A simple yet controllable oxidation in air could remove the carbon sheaths wrapped around the  $\text{CeF}_3$  nanowires, yielding un-coated pure  $\text{CeF}_3$  nanowires while their 1D morphology and crystalline nature remain unchanged. This novel strategy could be extended to produce nanowires of other lanthanide fluorides such as  $\text{LaF}_3$  nanowires. It is expected that the present technique may be generalized for the production of CNT-encapsulated and naked lanthanide fluoride nanowires, which will provide a fresh impetus not only to the fundamental study on CNT templated synthesis of 1D nanomaterials but also to the fabrication and practical use of lanthanide fluoride nanowires.

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**Supporting Information Available:** XRD patterns and TEM images of CNT-encapsulated and naked  $\text{LnF}_3$  ( $\text{Ln} = \text{La}, \text{Ce}$ ) nanowires; the formula of PEI; and schematic illustration of the growth process of the CNT-encapsulated  $\text{CeF}_3$  nanowires (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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