



## Fabrication of LaF<sub>3</sub> Nanochains via A Reverse Microemulsion-Solvothermal Route†

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A novel LaF<sub>3</sub> nanochain has been successfully prepared by the self-assembly of LaF<sub>3</sub> nanoparticles via a reverse microemulsion-solvothermal method. The products were characterized by XRD, TEM and HRTEM. A possible formation mechanism of nanochain was proposed.

**Key Words:** LaF<sub>3</sub>, Nanochain, Self-assembly, Solvothermal.

### INTRODUCTION

One-dimensional (1D) nanostructures such as wires, rod and tubes had also become the focus of intensive research owing to their unique applications in the mesoscopic physics and preparation of nanoscale devices. In order to fabricating one-dimensional nanostructures, a variety of techniques such as dictation by the anisotropic crystal structure, confinement by a liquid droplet in the vapour-liquid-solid process, template-directed synthesis, kinetic controlled by a capping reagent, size reduction of a one-dimensional microstructure and self-assembly of zero-dimensional (0 D) nanostructure were provided<sup>1,2</sup>. In fact, self-assembly was an effective approach for overcoming the limitations of the conventional techniques.

Lanthanum fluoride (LaF<sub>3</sub>) was well-known as an excellent host matrix for luminescent materials due to its low phonon energies. LaF<sub>3</sub> doped with other rare earths could act as X-ray storage phosphor<sup>3</sup>. Surface -modified LaF<sub>3</sub> nanoparticles had also been served as solid lubricant under high temperature due to its low hardness, high melting point and good resistance to thermal and chemical attack<sup>4</sup>. Lanthanum fluoride solid solution electrolytes could be used as oxygen sensors, having higher conductivities than zirconia<sup>5</sup>.

Recently there were many reports about the synthesis of LaF<sub>3</sub> nanoparticles<sup>6</sup>. In comparison, few papers were been reports to prepare one-dimensional LaF<sub>3</sub> nanostructure. Wang *et al.*<sup>7</sup> reported a LaF<sub>3</sub> cylinder architecture stacked by the micro-plates through oriented aggregation. Zhao *et al.*<sup>8</sup> demonstrated the synthesis of lanthanide-doped LaF<sub>3</sub> nanowire arrays with the two-dimensional symmetry by using La(CF<sub>3</sub>COO)<sub>3</sub> as precursors. Li *et al.*<sup>9</sup> reported uniform and novel (LaF<sub>3</sub>) nanodisks and donut-shaped nanostructures were

successfully synthesized in ionic liquids media. In this paper, we reported the novel LaF<sub>3</sub> nanochains had been successfully prepared by the self-assembly of LaF<sub>3</sub> nanoparticles via a reverse microemulsion-solvothermal method.

### EXPERIMENTAL

A quaternary reverse microemulsion, CTAB/water/cyclohexane/*n*-butanol, was selected for this research. As a typical preparation, two identical solutions were prepared by dissolving CTAB (2 g) in 25 mL of cyclonhexane and 10 mL *n*-pentanol. The mixing solution was stirred for 0.5 h until it became transparent under heating at 40-50 °C. Next, 1 mL of 0.1 M La<sup>3+</sup> aqueous solution and 1 mL of 0.3 M F<sup>-</sup> aqueous solution were added to the solutions and substantial stirring for 0.5 h, respectively. The optically transparent La<sup>3+</sup> microemulsion solution was slowly added into the transparent F<sup>-</sup> microemulsion solution under stirring for 0.5 h at same temperature. The resulting microemulsion was then transferred into a 50 mL stainless. Teflon-lined autoclave and heated at 100 °C for 3 h. The resulting suspension was cooled to room temperature after the heating. After the samples were centrifuged and washed several times with absolute ethanol and distilled water, the samples were collected.

### RESULTS AND DISCUSSION

Fig. 1 shows the X-ray powder diffraction pattern of productions. It was used to identify the phase and to assess phase purity. All diffraction peaks can be indexed as the hexagonal phase LaF<sub>3</sub> (JCPDS. No. 32-0483) and no other phase or obvious impurity were detected. The broadening of the diffraction peaks implied the nanocrystalline nature of the

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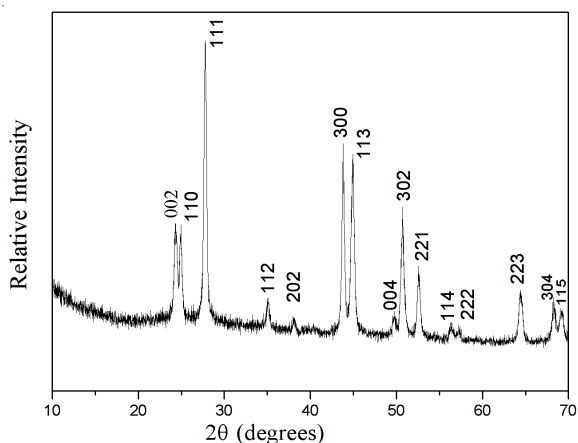


Fig. 1. X-ray powder diffraction pattern of productions

samples. The average size of as-prepared particles is about 30 nm according to the Scherer's equation.

The typical TEM, ED and HRTEM images of the sample are illustrated in Fig. 2. Fig. 2a and b displays the TEM image of the sample. Each  $\text{LaF}_3$  nanocrystal had nearly hexagonal-like shapes and similar sizes. It could be observed that the average size of the particles is about 30 nm. It is interesting that the nanocrystals back-to-back self-assembly into a nanochain each other. The electron diffraction pattern of the particles is showed in Fig. 2b, which was carried out to identify the phase of the sample. These diffraction circles can be indexed as (111), (300), (221) of the hexagonal phase  $\text{LaF}_3$ , respectively. They are in good consonant with the results of XRD.

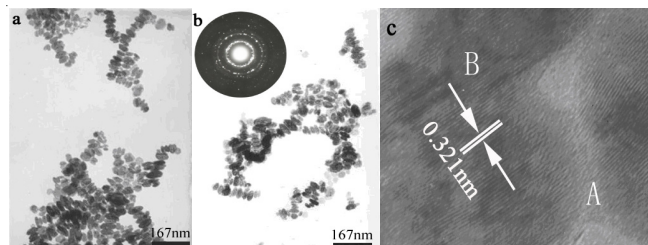


Fig. 2. (a) TEM image, (b) ED pattern and (c) HRTEM image of the nanochains

The HRTEM images were demonstrated in Fig. 2c. It indicates that the sample is of high crystallinity and that the fringe spacing is about 0.321 nm, which corresponds to the (111) of hexagonal phase  $\text{LaF}_3$ . From the HRTREM images, there were two kinds of the nanoparticles connecting methods. In the "A" area of image, two nanoparticles connected with noncrystalline, but with (111) planes of nanoparticles in the "B" area of image.

To uncover the self-assembly mechanism of nanochain, the effects of temperature, reaction time, the pH values, the solution concentration and the composing of reverse microemulsion on the production were investigated. It was found that the amount of surfactant CTAB in reverse microemulsion was very important to successful self-assembling the nanochain. As too much or too little surfactant CTAB in reverse microemulsion, the nanochains were not product, but the separate nanoparticles were been prepared even though other conditions were unvaried in the experiment. Obviously,

surfactant CTAB acted as the key in the self-assembly process. The reaction temperature and the reaction time little affected the size of as-prepared product.

The possible self-assembly mechanism from nanoparticles to a nanochain is schematically illustrated in Fig. 3. At first,  $\text{La}^{3+}$  and  $\text{F}^-$  were restricted in the very small water pool of reverse microemulsion, respectively. When the two different reverse microemulsions were mixed,  $\text{LaF}_3$  colloids formed in the water pool because of the microemulsion collision and inosculation. It was clear that the size of water pool restricts the size of  $\text{LaF}_3$  colloids. In the latter high temperature and high-pressure solvothermal process, the colloids were be improved the degree of crystallinity into  $\text{LaF}_3$  nanoparticles while reverse microemulsion were be destroyed. Then, cationic surfactant  $\text{CTA}^+$  adsorbed the surface of nanoparticles by static force.  $\text{LaF}_3$  nanoparticles adsorbed  $\text{CTA}^+$  assembled into the chain by intertwisting fatchain of  $\text{CTA}^+$  on the interface of oil and water. Finally,  $\text{LaF}_3$  nanoparticles connected by non-crystalline or (111) planes in ripening process as demonstrated in Fig. 2h and nanochain were product. Surfactant CTAB acted as the key in self-assembly mechanism.

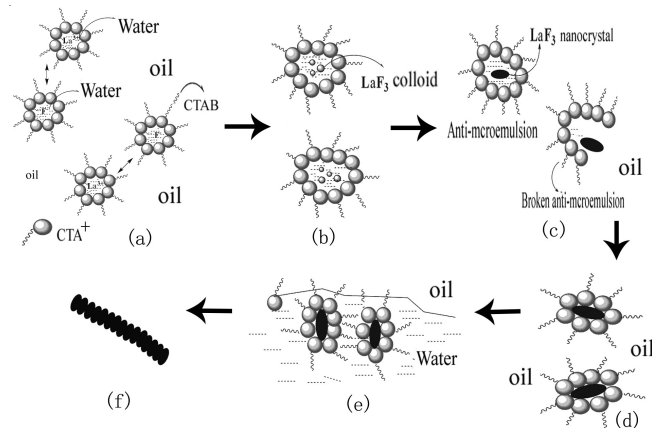


Fig. 3. Possible self-assembly mechanism from nanoparticles to a nanochain

In conclusion, a novel  $\text{LaF}_3$  nanochain has been successfully prepared *via* a reverse microemulsion-solvothermal method.

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