



# Synthesis and characterization of novel flower-like $\text{CeF}_3$ nanostructures via a rapid microwave method

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## ABSTRACT

Novel flower-like  $\text{CeF}_3$  nanostructures with a mean diameter of 190 nm were successfully synthesized via a rapid and facile microwave irradiation route using ethylenediaminetetraacetic acid disodium as the complexing reagent. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and photoluminescence (PL). XRD patterns showed that the  $\text{CeF}_3$  nanoflowers were hexagonal phase and had good crystallinity and purity. TEM and SEM images showed that the as-prepared  $\text{CeF}_3$  samples displayed 3D flower-like nanostructures and had uniform sizes and morphologies. The experimental results revealed that the as-prepared  $\text{CeF}_3$  nanoflowers might be assembled by nanodisks. The formation process of the  $\text{CeF}_3$  nanoflowers was preliminarily investigated.

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## 1. Introduction

In recent years, great effort has been devoted to the synthesis of inorganic micro- and nanostructures of controlled size and shape using various methods driven primarily by the fact that the shape and size of inorganic nanocrystals have tremendous effects on their properties [1–3]. Rare-earth compound nanomaterials with controllable shapes and sizes have received intense research attention during the past few years because of their potential applications in optics, optoelectronics, biological labeling, catalysis, and so forth [4–8]. Such immense interests stem from their 4f electrons.

Cerium fluoride ( $\text{CeF}_3$ ) has been attracting increasing attention because of its technological importance as an inorganic scintillating crystal [9].  $\text{CeF}_3$  has obvious advantages over other conventional scintillators in their high density, fast response and high radiation resistance and is therefore considered as one of the most promising scintillators for the next generation experiments in high-energy physics. Furthermore, it is also an important fluorescent host material owing to its low vibrational energies and the subsequent minimization of the quenching of the excited state of the rare-earth ions [10]. Up to now, great efforts have been made on the synthesis of  $\text{CeF}_3$  nanostructures with specific shape and unique properties such as nanoparticles [11], nanocrystals [12,13], nanoplates [14] and nanowires [15]. Various methods including polyol methods [11], hydrothermal route [12], ultrasound method [13] and reverse micelles or microemulsions [16] have been developed to synthesize  $\text{CeF}_3$  nano-

and microstructures. However, it is still a challenge to fabricate some novel structures of  $\text{CeF}_3$  with the controlled morphologies in mild reaction conditions.

The application of microwave irradiation in synthetic chemistry is a fast growing research area. Up to now, microwave irradiation has been accepted as a promising method for rapid volumetric heating, higher reaction rate and selectivity, reducing reaction time often by orders of magnitude, and increasing yield of products compared to conventional heating methods.  $\text{Pr}(\text{OH})_3$  nanorods and hollow  $\text{PrF}_3$  nanoparticles were prepared by microwave irradiation method in previous works [17,18]. In this paper, we report a facile rapid microwave irradiation method to prepare flower-like  $\text{CeF}_3$  nanostructures using  $\text{Na}_2\text{H}_2\text{EDTA}$  as a complexing reagent. The products were characterized by XRD, TEM, SEM and PL.

## 2. Experimental procedure

### 2.1. Microwave-assisted synthesis of flower-like $\text{CeF}_3$ nanostructures

All the chemical reagents used were of analytical grade. In a typical synthesis, 2 mmol of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 50 ml deionized water to form a solution. Then 4 mmol of ethylenediaminetetraacetic acid disodium ( $\text{Na}_2\text{H}_2\text{EDTA}$ ) was added to above solution under vigorous stirring to form a clear solution. After that, 50 ml 0.64 M KF solution was slowly added to the above solution under vigorous stirring. The pH of the final solution was adjusted to 6.0 with 10%  $\text{HNO}_3$  solution. After stirring about 30 min, the solution was finally transferred into a 250 ml round flask and placed in a microwave oven (650 W, 2.45 GHz) with a refluxing apparatus. The mixture was heated by microwave irradiation for 26 min at 80% of the

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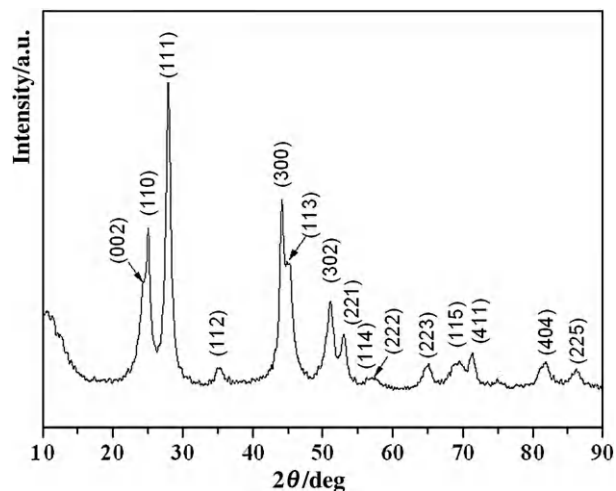


Fig. 1. XRD pattern of flower-like  $\text{CeF}_3$  nanostructures prepared by microwave irradiation.

maximum power under refluxing. The resulting product was collected by centrifuge and washed three times using deionized water and absolute ethanol, then dried 12 h under vacuum at 60 °C.

$\text{CeF}_3:\text{Tb}$  samples were prepared by the same procedure, except that an additional  $\text{Tb}_4\text{O}_7$  was dissolved in concentrated  $\text{HNO}_3$  first, then evaporating the solvent and added to the  $\text{Ce}^{3+}$ -containing solution.

## 2.2. Characterization of $\text{CeF}_3$ samples

XRD analysis was performed on a D/Max-2550 X-ray diffractometer with monochromatized  $\text{CuK}\alpha$  radiation ( $\lambda = 0.1540562$  nm). TEM was recorded using a transmission electron microscope (TEM, JEOL JEM-200CX). Samples for TEM were obtained by dispersing the products in ethanol with 15 min ultrasonicating, and then dropping a few drops of the resulted suspension onto a copper grid precoated with amorphous carbon and allowing them to dry naturally. SEM images were taken with a FEI SIRION-100 field-emission scanning electron microscope. The emission spectra was recorded on a Hitachi-

F2005 luminescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The  $\text{CeF}_3:\text{Tb}$  samples were dispersed into absolute ethanol with 15 min ultrasonicating for PL measurements.

## 3. Results and discussions

The crystal structure and the phase purity of the products were determined by X-ray diffraction (XRD). A typical XRD pattern of the as-prepared sample is presented in Fig. 1. The major detectable diffraction peaks can be readily indexed to the pure hexagonal phase of  $\text{CeF}_3$  consistent with the standard powder diffraction file of  $\text{CeF}_3$  (JCPDS 85-1343). No impurity phase could be found. The high and sharp peaks indicate that the sample was well crystallized. The XRD patterns indicate that the pure well-crystallized  $\text{CeF}_3$  products can be easily obtained in our synthetic route.

The morphology and microstructure details of the as-prepared  $\text{CeF}_3$  samples were investigated with SEM and TEM. Fig. 2A–B show the typical SEM images with different magnifications. The SEM image clearly demonstrates that the majority of the  $\text{CeF}_3$  samples have a uniform flower-like spherical shape with an average diameter of about 190 nm. The nanoflowers are constructed with several petals intercrossed together to form complex nanostructures. The yield of the flowers is closed to 100%. Fig. 2C–D are the typical TEM images which could further reveal the inner structures of the as-prepared  $\text{CeF}_3$  nanoflowers. It can be seen that several petals inside the flower with a thickness of about 14 nm intercross together and stretch out towards the edges of the flower. The TEM results agree well with the SEM observation.

To further investigate the details of the formation of  $\text{CeF}_3$  nanoflowers, the growth processes of the final product were followed by time-dependent experiments. TEM images obtained after different reaction times show a growth process from the small nanoparticles to the final flowers. With microwave irradiation for 6 min, the solution became turbid and the oblate nanodisks with blurry outline appeared (Fig. 3A). It is seen that the surfaces of these nanodisks were covered with many small amorphous nanoparticles. After another 7 min, some nanodisks began to assemble to form flower-like structures (Fig. 3B). After 26 min, the growth of the flower-like products was completed.

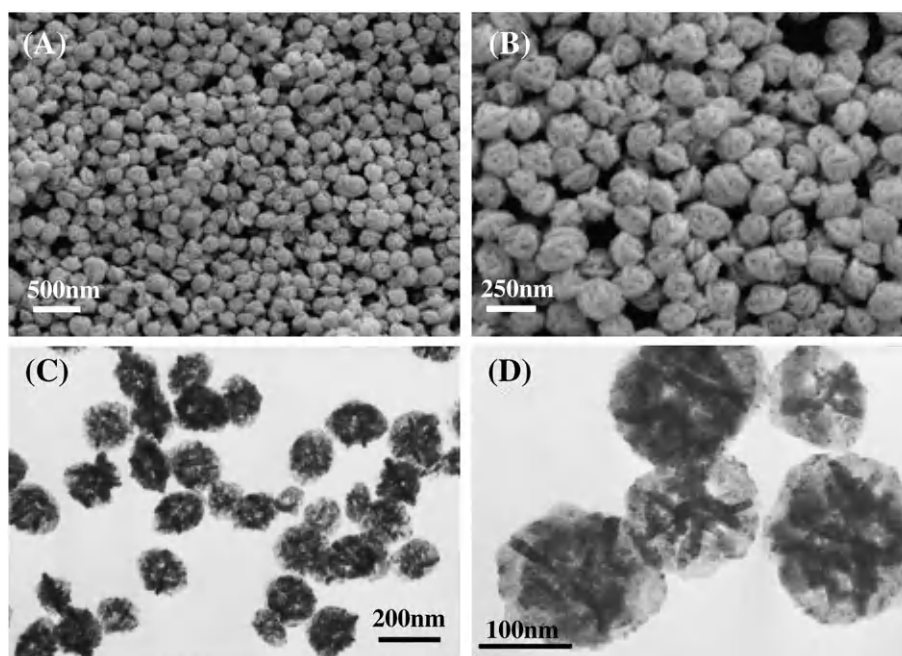


Fig. 2. SEM and TEM images of the  $\text{CeF}_3$  nanoflowers prepared by microwave irradiation.

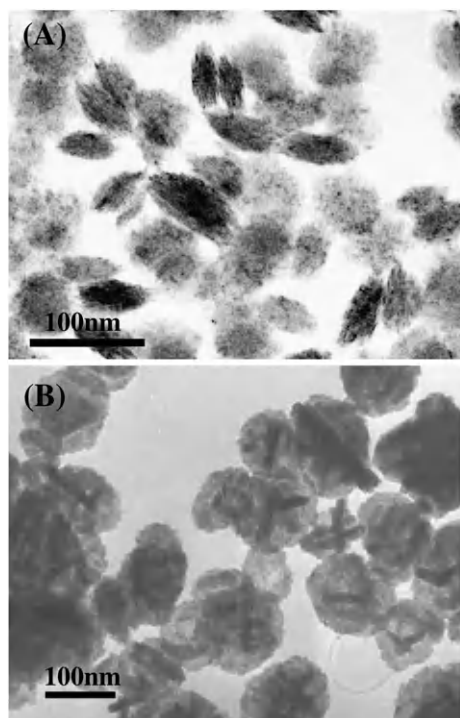
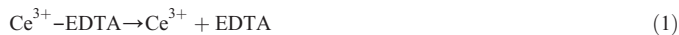


Fig. 3. TEM images of the  $\text{CeF}_3$  samples prepared by microwave irradiation for different time. (A) 6 min and (B) 13 min.

On the basis of the experimental results, the probable reaction process in our current experiment can be summarized as following expressions:



As an efficient chelator for rare-earth ions,  $\text{Na}_2\text{H}_2\text{EDTA}$  could react with  $\text{Ce}^{3+}$  to form stable  $\text{Ce}^{3+}$ -EDTA complexes. Under microwave irradiation conditions,  $\text{Ce}^{3+}$  ions were continuously supplied at a convenient rate by gradual dissociation of the  $\text{Ce}^{3+}$ -EDTA complex and reacted with  $\text{F}^-$  to form  $\text{CeF}_3$  primary amorphous nanoparticles. This kind of  $\text{Ce}^{3+}$  feeding mode might be favorable to formation of uniform nanoparticles. In the following growth process, adjacent amorphous nanoparticles might be fused in a certain way to form nanodisks under microwave irradiation. The obtained nanodisks began to assemble together to form flower-like nanostructures. The exact mechanism for this flower-like nanostructure is not yet exactly clear and needs to be further investigated.

The luminescence properties of  $\text{CeF}_3$  doped with 5 mol% (molar ratio)  $\text{Tb}^{3+}$  ions were also investigated. Fig. 4 shows the room temperature photoluminescence spectra of the obtained  $\text{CeF}_3$  nanoflowers using the excitation line at 258 nm. It can be seen that the  $\text{CeF}_3:\text{Tb}^{3+}$  samples yield both weak emission of  $\text{Ce}^{3+}$  (300–400 nm) and strong emission of  $\text{Tb}^{3+}$  (450–650 nm) due to the transition between the excited  $^5\text{D}_4$  state and the  $^7\text{F}_j$  ( $j=6-3$ ) ground states of  $\text{Tb}^{3+}$  ions. This indicates that an energy transfer from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$  occurs in the  $\text{CeF}_3:\text{Tb}^{3+}$  nanoflowers, as observed in the result reported before [13]. The  $\text{Ce}^{3+}$  luminescence failed to be completely quenched by  $\text{Tb}^{3+}$  owing to the high  $\text{Ce}^{3+}$  concentration in the samples.

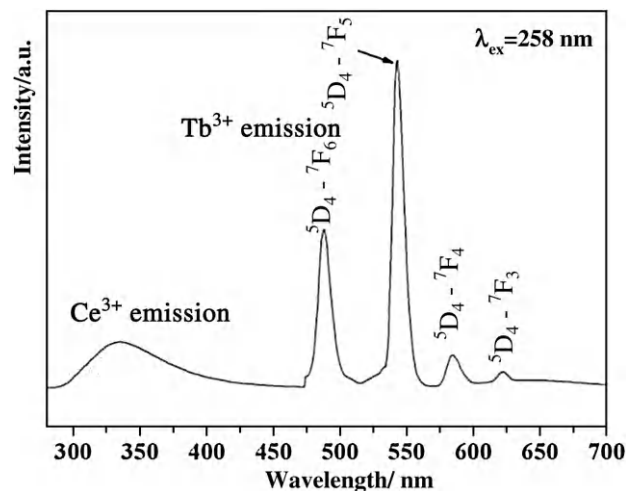


Fig. 4. Emission spectrum of the  $\text{CeF}_3:\text{Tb}^{3+}$  nanoflowers prepared by microwave irradiation.

#### 4. Conclusions

In summary, novel  $\text{CeF}_3$  nanoflowers with an average diameter of about 190 nm were successfully synthesized via a mild and facile microwave irradiation route using  $\text{Na}_2\text{H}_2\text{EDTA}$  as complexing reagent. The obtained  $\text{CeF}_3$  samples have good crystallinity and purity. The formation process of  $\text{CeF}_3$  nanoflowers was investigated. It was found that the as-prepared  $\text{CeF}_3$  nanoflowers were assembled by nanodisks. The strategy presented in this work is easily controllable and well reproducible and may be feasible to develop into the scale-up production.

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