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Complexing reagent-assisted microwave synthesis of uniform and monodisperse disk-like CeF_3 particles

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Abstract

Highly uniform and monodisperse disk-like CeF_3 particles with diameter about 230 nm and thickness about 76 nm were successfully synthesized via a mild and facile microwave irradiation assisted by a complexing reagent, ethylenediamine tetraacetic acid disodium salt (Na_2H_2EDTA). The morphologies and crystal structure of the products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and scanning electron microscopy (SEM). XRD patterns showed that the as-prepared CeF_3 products have hexagonal structure and high crystallinity. SEM images showed that these disk-like CeF_3 nanocrystals had rough surfaces which were covered with many sheet-like structures. It was found that the reaction time and the complexing reagent played crucial roles on formation of uniform disk-like CeF_3 particles. A possible formation mechanism of the disk-like CeF_3 particles was preliminarily presented.

Keywords: Microwave; CeF_3; Microwave; Crystal growth; Nanomaterials

1. Introduction

In recent years, great effort has been devoted to the synthesis of inorganic micro- and nanocrystals 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]. Lanthanide compounds have been extensively investigated in diverse applications ranging from high-performance luminescent displays, optical communications and biochemical probes to laser materials [4–6]. Cerium fluoride (CeF_3) has been attracting increasing attention because of its technological importance as an inorganic scintillating crystal [7]. 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. Further more, 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 [8]. Studies also indicate that CeF_3 is a good solid lubricant for its layered structures [9]. Up to now, various methods including hydrothermal route [10], polyol methods [8,11] and reverse micelles or microemulsions [9,12,13] have been developed to synthesize CeF_3 nano- and microcrystals. However, it is still a challenge to fabricate some novel structures of CeF_3 with the controlled morphologies in mild reaction conditions.

As a quick, simple, uniform and energy efficient heating method, microwave irradiation has widely applied in chemical reactions and material synthesis due to its unique reaction effects such as rapid volumetric heating and the consequent dramatic increase in reaction rates [14]. Patra et al. have employed microwave heating approach to synthesis lanthanide orthophosphate nanorods under solvothermal conditions [15]. Zhu et al. synthesized copper and copper oxide nanocrystals with controllable morphology by a microwave-induced polyol process [16]. The Pt/C catalysts and hollow PrF_3 nanoparticles were also synthesized by microwave irradiation in our previous work [17–19]. In this paper, we report a facile method to prepare uniform disk-like CeF_3 particles by a complexing reagent-assisted

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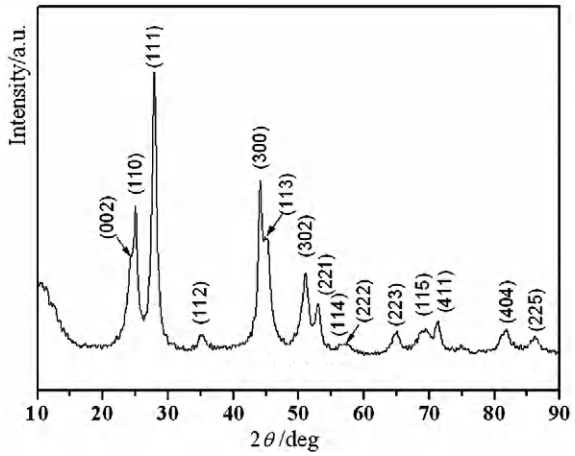

Fig. 1. XRD patterns of CeF_3 products prepared by microwave heating for 26 min.

microwave heating process. The products were characterized by XRD, TEM, SAED and SEM.

2. Experimental procedure

2.1. Microwave synthesis of disk-like CeF3 particles

In a typical procedure, 2 mmol of $Ce(NO_3)_3{\cdot}6H_2O$ was dissolved in 50 ml deionized water to form a solution. Then 4 mmol of ethylenediaminetetraacetic acid disodium (Na_2H_2EDTA) was added to above solution, followed by addition of several drops of ammonia (25 wt.%) under vigorous stirring to form a clear solution. After that, 50 ml 0.16 M KBF_4 suspension was slowly added to the above solution under vigorous stirring. The mixture pH was adjusted to 6.0 with 10% HNO_3 solution. After stirring about 30 min, the mixture 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 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.

2.2. Characterization of disk-like CeF_3 particles

XRD was performed on a D/Max-2550 X-ray diffractometer with monochromatized CuKα radiation (λ=0.1540562 nm). TEM and SAED were recorded on a transmission electron microscopy (TEM, JEOL JEM-200CX). Samples for TEM are 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 FEI SIRION-100 filed-emission scanning electron microscope.

3. Results and discussions

The crystal structure and phase purity of the samples were characterized by XRD. Fig. 1 shows the XRD of the as-synthesized CeF_3 samples. The major detectable diffraction peaks can be readily indexed to the pure hexagonal phase of CeF_3 with calculated lattice constants of a=0.7124 nm, c=0.7267 nm , which are basically

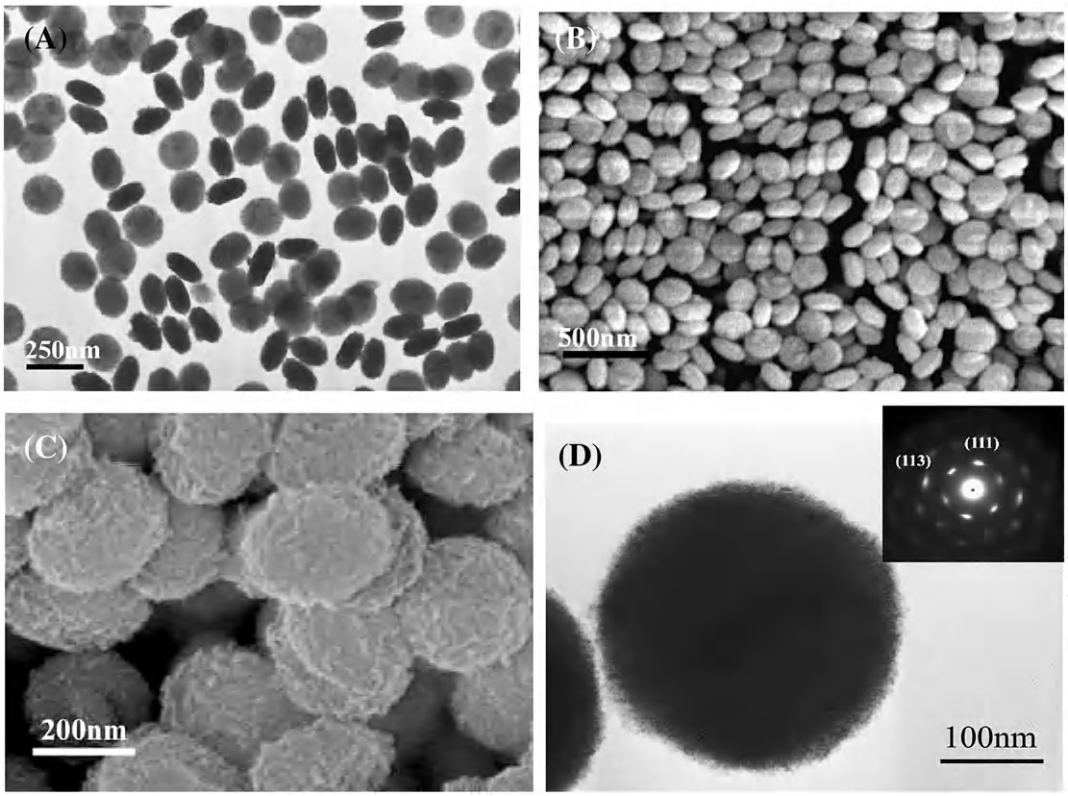

Fig. 2. TEM (A, D) and SEM (B, C) images of CeF_3 products by microwave heating for 26 min.

consistent with the literature values of $a=0.7137$ nm, $c=0.7295$ nm (JCPDS 85-1343). No impurity phase could be found. The high and sharp peaks indicate that the sample is well crystallized. The XRD patterns indicate that the pure well-crystallized CeF_3 crystals can be easily obtained in our occurent synthetic route.

The size and morphology of the samples were examined by TEM and SEM. Fig. 2A is a typical TEM image, which shows that the as-synthesized CeF_3 products are monodisperse round or spindle-like particles. Fig. 2B further confirms that the obtained CeF_3 products are in fact highly uniform and monodisperse disk-like particles. The yield of the disk-like products is closed to 100%. It could be estimated that these disk-like particles have the average diameter of 230 nm and thickness of 76 nm. A high resolution SEM image is shown in Fig. 2C, which offers a clear view of the surface morphology. It can be seen that the disk-like CeF_3 particles have rather rough surfaces and many small cross-linked sheet-like structures could be seen on these rough surfaces. Fig. 2D is the typical TEM image of a single CeF_3 particle, which shows well-defined round shape. The SAED (the inset of Fig. 2D) indicates that it is a single cystalline and the diffraction spots are indexed to the (111) and (113) planes, respectively.

The effect of microwave heating time on the sizes and morphologies of CeF_3 products was also studied. When the reaction time was reduced to 12 min, the reaction solution just became turbid and the obtained CeF_3 products were small disk-like nanoparticles with blurry outlines and less uniform sizes, with mean diameter about 50 nm and thickness about 16 nm (Fig. 3A). When reaction time was up to 26 min, the obtained CeF_3 products had clear disk-like outlines and uniform sizes as shown in Fig. 2. With reaction time elongated to 1 h, the CeF_3 products were still disk-like particles with larger average diameter and thickness, which were 350 nm and 130 nm, respectively (Fig. 3B).

In order to investigate the effect of the complexing reagent on the formation of the disk-like CeF_3 particles, the CeF_3 products were prepared by microwave heating process without complexing reagent.

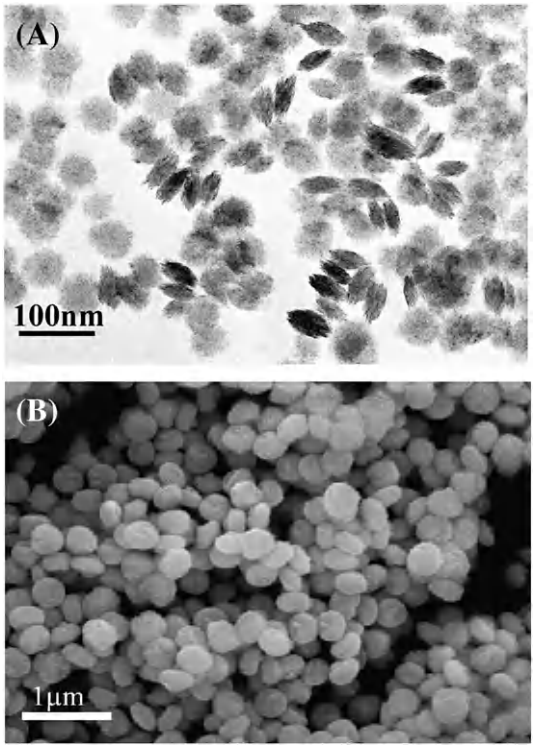

Fig. 3. TEM and SEM images of CeF_3 products by microwave heating for (A) 12 min and (B) 1 h.

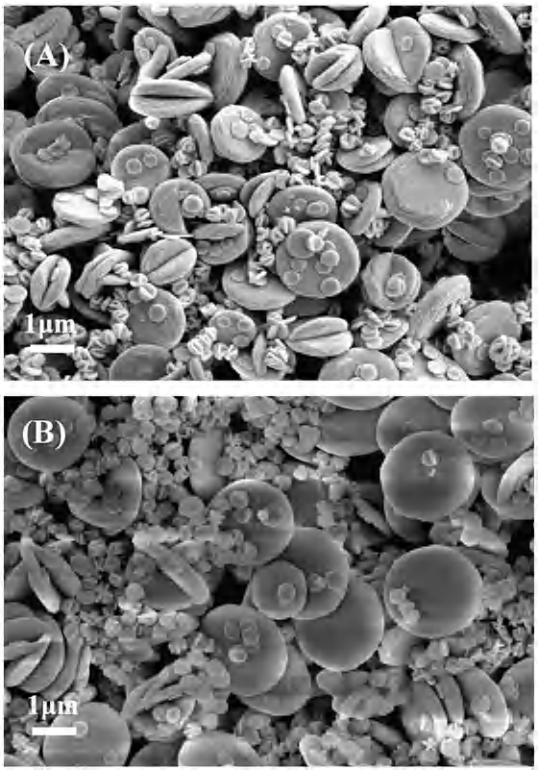

Fig. 4. SEM images of CeF_3 products prepared by microwave heating for (A) 26 min and (B) 1 h without complexing reagent.

Fig. 4 shows SEM images of the samples prepared by microwave heating for different time without complexing reagent. It can be seen from Fig. 4 that the CeF_3 products obtained at 26 min without complexing reagent showed an ununiform disk-like morphology, which was similar to that of the CeF_3 products obtained at 1 h. The diameter of the CeF_3 products prepared at 1 h was ranged from 360 nm to 2 μm, larger than that of the products obtained at 26 min. Moreover, many disk-like CeF_3 particles were often intercrossed together. Therefore, the complexing reagent played a crucial role on the formation of uniform disk-like CeF_3 nanocrystals.

Based on our experimental results, the formation mechanism of the uniform and monodisperse disk-like CeF_3 nanocrystals under microwave conditions is probably related to the coordination of Ce^{3+} and Na_2H_2EDTA to form Ce^{3+}-EDTA complex. According to Liu's report [20], the probable reaction process in our current experiment can be summarized as following expressions:

$$Ce^{3+} - EDTA \rightarrow Ce^{3+} + EDTA \quad (1)$$

$$Ce^{3+} + 3BF_4^{-} \rightarrow CeF_3 + 3BF3 \quad (2)$$

$$BF_3 + 3H_2O \rightarrow 3H^+ + 3F^{-} + H_3BO_3 \quad (3)$$

$$Ce^{3+} + 3F^{-} \rightarrow CeF_3 \quad (4)$$

When no complexing reagent was used, the reaction solution became turbid after microwave irradiation for 2–3 min. The reaction between Ce^{3+} and F^- produced by hydrolysis of KBF_4 was so fast that nucleation occurs at an outburst speed which led to ununiform disk-like morphologies. However, when the Ce^{3+} was treated with Na_2H_2EDTA before microwave irradiation, the Ce^{3+}-EDTA complex was formed and the reaction solution became turbid after microwave irradiation for 11–12 min. Under microwave irradiation conditions, Ce^{3+} ions were

continuously supplied at a convenient rate by gradual dissociation of the Ce^{3+}-EDTA complex, which served as a Ce^{3+} reservoir. This kind of Ce^{3+} feeding mode might lead to uniform and monodisperse disk-like CeF_3 particles. The exact mechanism of complexing reagent on the formation of uniform disk-like CeF_3 particles needs to be further investigated.

4. Conclusions

In summary, highly uniform and monodisperse disk-like CeF_3 particles with diameter about 230 nm and thickness about 76 nm were successfully synthesized via a mild and facile microwave route assisted by a complexing reagent, ethylenediamine tetraacetic acid disodium salt (Na_2H_2EDTA). The obtained CeF_3 particles has good crystallinity and high purity. It was found that the reaction time and the complexing reagent played crucial roles on the formation of uniform and monodisperse disk-like CeF_3 particles. The strategy presented in this work is expected to prepare other rare earth compound nano or microcrystals.

Acknowledgements

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