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Solvent-assisted selective synthesis of $NaLaF_4$ and LaF_3 fluorescent nanocrystals *via* a facile solvothermal approach

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ABSTRACT

A facile solvothermal approach was developed to selectively synthesize water-soluble $NaLaF_4$ or LaF_3 nanocrystals (NCs) by tuning the solvent components. In ethonal/H_2O media, high-quality LaF_3 NCs were prepared by using NaF and $LaCl_3$ as the precursors. More interestingly, thermodynamically non-preferred $NaLaF_4$ nanorods could be obtained when ethylenediamide (EN) was introduced to the ethonal/H_2O solvent. All of the products were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM), and the crucial effects of EN on morphology and structure of the NCs were studied. Furthermore, by doping different lanthanide ions, these LaF_3 and $NaLaF_4$ NCs could emit intense upconversion (UC) or downconversion (DC) fluorescence, which showed potential applications in color displays, light-emitting diodes, optical storage and optoelectronics.

1. Introduction

In recent years, the controllable synthesis of rare earth (RE) fluorides nanocrystals (NCs) has attracted considerable interest. With low energy phonons, fluorides NCs can serve as excellent host materials for both upconversion (UC) and downconversion (DC) fluorescence processes, and therefore can be applied in the fields of phosphors, displays, optical amplifiers and biolabeling [1–8].

Among these rare earth fluorides NCs, REF_3 and $NaREF_4$ are two types of important structures which have found extensive applications [9–11]. Although various methods have been developed for the synthesis of REF_3 or $NaREF_4$ NCs, it is still a big challenge to synthesize NCs with predictable structures of REF_3 or $NaREF_4$ for a certain type of RE ion. For example, when the precursors of Na^+, F^- and Y^{3+} all existed in a reaction system either through modified co-precipitation routes or solvothermal methods, $NaYF_4$ could be prepared [6,12,13]. However, when Na^+, F^- and La^{3+} were used as the reactants, only LaF_3 but no $NaLaF_4$ NCs were generally obtained [3,5,9,14].

As we known, the cation radius of the RE ions decreases from 1.06 Å for La^{3+} to 0.85 Å for Lu^{3+} while the lattice constants from the hexagonal phase $NaLaF_4$ to $NaLuF_4$ vary for a_0 from 6.157 to 5.967 Å and for c_0 from 3.822 to 3.528 Å. As a result, cations are difficult to settle into the lattice in compounds with large RE cations such as $NaLaF_4$, which makes the synthesis of these compounds more difficult than that of $NaYF_4$ or $NaLuF_4$ [15]. To the best of our knowledge, it is still lack of powerful and efficient synthetic approaches for the preparation of $NaLaF_4$ NCs.

Additionally, the cation radius of lanthanum is known to be the largest in the lanthanides. Therefore, if an effective method can be established to controllably synthesize $NaLaF_4$ NCs, other $NaREF_4$ with a smaller cation radius can be also prepared using the same technique.

Herein, we developed a facile solvothermal strategy for the controllable synthesis of hexagonal phase $NaLaF_4$ nanorods with the assistance of ethylenediamide (EN). In addition, by merely tuning the components of the solvent, $NaLaF_4$ and LaF_3 NCs can be selectively prepared. Moreover, the as-prepared LaF_3 and $NaLaF_4$ NCs all show intense green UC and DC fluorescence by co-doping Yb^{3+}/Er^{3+} or Ce^{3+}/Tb^{3+} under the 980 nm or 254 nm irradiations respectively, showing potential application in multiple optics-related fields.

2. Material and methods

Ethylenediamide, anhydrous ethanol and hydrochloric acid were obtained from Beijing Chemical Corp. (Beijing, China). SpecPure grade lanthanide oxides were obtained from Grirem Advanced Materials Co., Ltd. (Beijing, China). Lanthanide chlorides were prepared by dissolving the corresponding rare earth oxides in hydrochloric acid at elevated temperature, following with evaporation of the solvent at vacuum.

Take the synthesis of $NaLaF_4$ nanorods for an example, in a typical procedure, 2 mmol lanthanum chlorides was dissolved in 10 mL of DI H_2O under sonication and transferred to a 50 mL Teflon-linked autoclave. Then 20 mL EN was added under vigorous stirring to form a white mixture. 8 mmol NaF dissolved in 10 mL ethanol was then injected into the autoclave, and the final mixture was agitated thoroughly for about 5 min. Finally the autoclave was sealed and solvothermally treated at 190 °C for 24 h. The product was collected by centrifugation, washed with anhydrous ethanol for several times, and dried at 60 °C. LaF_3 NCs were prepared following the similar procedures except that the solvent components were changed.

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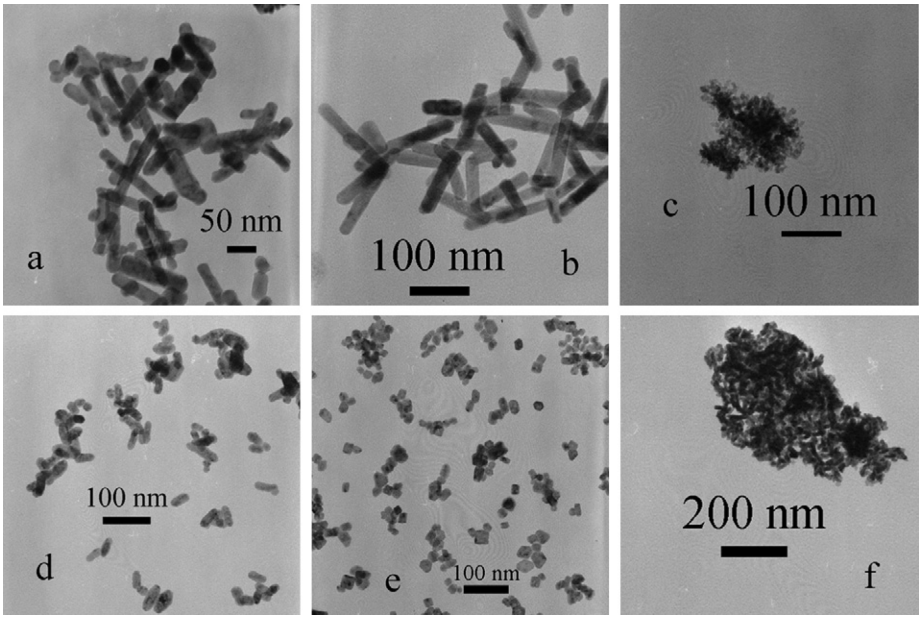

Fig. 1. TEM images of the as-synthesized NCs solvothermally treated at 190 °C for 24 h under different solvent conditions. Solvent components: (a) 20 mL H_2O/20 mL EN; (b) 10 mL H_2O/10 mL ethanol/20 mL EN; (c) 20 mL ethanol/20 mL EN; (d) 40 mL H_2O; (e) 20 mL H_2O/20 mL ethanol; (f) 40 mL ethanol. Other experimental conditions were the same as described in Section 2.

A JEM-1200EX transmission electron microscope (TEM) (JEOL, Japan) was used to investigate the size and morphology of the NCs. Powder X-ray diffraction (XRD) patterns were obtained on a D/max-2500 X-Ray Diffractometer (Rigaku, Japan) with Cu Kα radiation at 1.5406 Å. Fluorescence spectra of the NCs were measured on an F-4500 fluorescence spectrophotometer (Hitachi, Japan).

3. Results and discussion

3.1. Solvent-assisted selective synthesis of $NaLaF_4$ nanorods and LaF_3 nanoparticles

Following the standard synthesis procedures stated above, the products synthesized in various solvents consisting of H_2O, ethanol, EN or their mixtures were characterized by TEM, and the images were shown in Fig. 1. The corresponding XRD patterns were shown in Fig. 2. As can be seen, when other experimental conditions were fixed, the morphology and structure of the final products were greatly influenced by the solvent compositions.

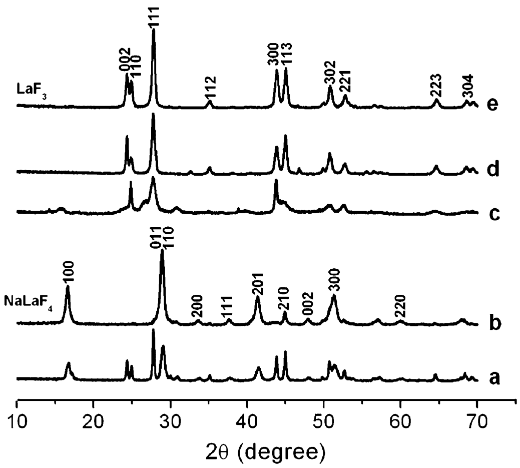

Fig. 2. XRD patterns of the as-prepared NCs corresponding to the samples (a–e) shown in the TEM images of Fig. 1.

Fig. 1a showed the TEM images of the NCs prepared in the solvent of 20 mL H_2O/20 mL EN. It can be seen that the products were mainly short nanorods with diameters about 20–30 nm and lengths up to 200 nm, and also accompanied with a portion of elongated spherical nanoparticles. XRD patterns (Fig. 2a) demonstrated that the products were the mixture of hexagonal phase LaF_3 (JCPDS PDF 72-1435) and hexagonal phase $NaLaF_4$ (JCPDS PDF 75-1923). It can be deduced that the nanorods were $NaLaF_4$ and the elongated particles were LaF_3 NCs (Compared with image b and d). However, when the mixture of 10 mL H_2O/10 mL ethanol/20 mL EN was used as the solvent, the elongated LaF_3 nanoparticles were disappeared and all of the products were short nanorods. Rod-shaped $NaLaF_4$ NCs showed very uniform diameters of 25–30 nm and the lengths were ranged from 75 to 200 nm. The XRD pattern of the nanorods (Fig. 2b) showed that the peak positions and intensities agreed well with the data reported in the JCPDS standard card (75-1923) of pure hexagonal $NaLaF_4$ crystals.

From the TEM and XRD results of sample a and b shown in Fig. 1 and Fig. 2, it seemed that the addition of ethanol to the EN/H_2O was beneficial for the formation of $NaLaF_4$ nanorods. So we speculated at the beginning that ethanol in the solvent might play crucial roles in the formation of pure $NaLaF_4$ nanorods. However, this possibility was weakened, because when we employed the solvent of 20 mL ethanol/20 mL EN, only very tiny and agglomerated LaF_3 nanoparticles, instead of $NaLaF_4$, were obtained (Figs. 1c and 2c). These results indicated that for the proposed method, although appropriate volume of ethanol in the solvent could promote the formation and crystallization of $NaLaF_4$ nanorods, it was not the dominant influence factor in this study. Then we performed a series of experiments to further study the effects of solvents on the NCs growth.

In order to investigate the effect of EN on the formation of $NaLaF_4$ nanorods, the solvents without the addition of EN were used to prepare samples while other parameters were not changed.

When using H_2O, ethanol or their mixture as the solvents without EN, the products were all pure hexagonal phase LaF_3 NCs, which could be deduced from the XRD results shown in Fig. 2. In pure H_2O, monodisperse, elongated spherical LaF_3 nanoparticles were obtained with the diameters of 30–60 nm (Fig. 1d). When the mix-

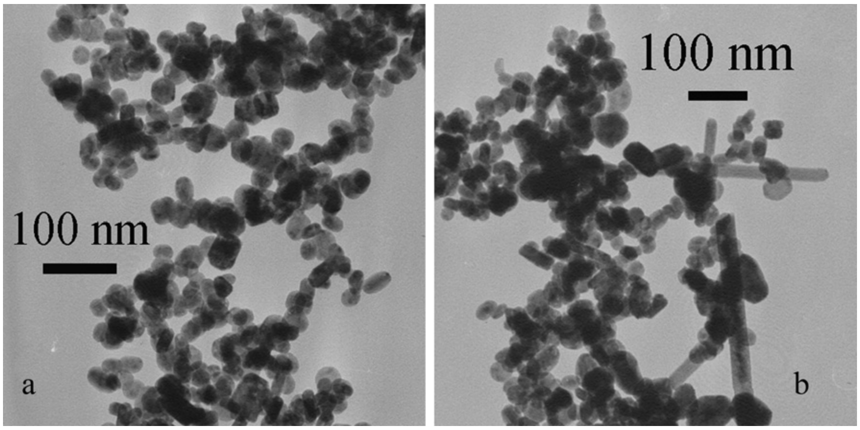

Fig. 3. TEM images of samples prepared in the solvent of (a) 1 mL EN/39 mL H_2O and (b) 5 mL EN/35 mL H_2O. Other experimental conditions were the same as in Fig. 1.

ture of 20 mL H_2O and 20 mL ethanol was used, the addition of ethanol to H_2O could further improve the crystallinity of LaF_3, thus more regular spherical-shaped NCs with narrower size distributions (25–35 nm) and good monodispersity were obtained (Fig. 1e). These well-crystallized LaF_3 NCs were prepared without adding any size-controlling reagents as usually used in conventional preparation approaches, and they could be easily dispersed in H_2O or ethanol to form stable colloids under sonication. However, similar to the preparation of $NaLaF_4$ nanorods, when pure ethanol was used, only irregular and aggregated LaF_3 NCs were synthesized (Fig. 1f).

3.2. Reaction mechanism

In this work, products with various morphology and structures were obtained by using the same reaction precursors but different solvent compositions, which meant that the solvent played key roles in the NCs synthesis.

For NCs preparation, it was general to add ethanol as low dielectric medium to the aqueous solution to alter the dielectric property of the solvent as well as the resulting particle properties, and addition of appropriate volume of ethanol to H_2O could improve the NCs quality [16,17], which was consistent with our results. However, it had been demonstrated above that ethanol was not the dominant influence factor in this study because high-quality products could not be obtained when pure ethanol (or ethanol/EN) was used as the solvent.

Since the possibility of ethanol had been excluded, all of the experimental results shown above suggested that EN might play a crucial role for the formation of $NaLaF_4$ nanorods in the presence of H_2O. Based on these phenomena, the roles of EN in the formation of $NaLaF_4$ nanorods can be postulated as follows.

As we known, the synthesis of $NaREF_4$ NCs is easy for small-radius RE cations (e.g., Y^{3+}, Lu^{3+}). However, cations are somewhat difficult to settle into the lattice in compounds with large RE cations such as $NaLaF_4$ [15]. The cation radius of lanthanum is the largest in the lanthanides due to the lanthanide contraction, which makes the solution synthesis of $NaLaF_4$ more difficult than that of $NaYF_4$. As a result, for most reported wet chemical NCs preparation routes, LaF_3 instead of $NaLaF_4$ were generally obtained although abundant Na^+ ions existed [3,5,9,14].

In the absence of EN for this proposed method, the NCs were formed through a co-precipitation reaction-based solvothermal route and the nucleation and growth rate of the NCs was rapid. As a result, only LaF_3 NCs could be prepared although a large amount of Na^+ existed in the system, which was consistent with the literature results.

However, when EN was added into the solvent, the situation was quite different. First, it served as the solvent and efficient chelator for RE ions. In addition, EN was a strong base when dissolved in H_2O. Therefore, in the solvents containing EN and H_2O, La^{3+} cations would hydrolyze to produce a white precipitate of $La(OH)_3$. Under the solvothermal conditions, $La(OH)_3$ would slowly re-dissolve to release La^{3+}, and La–EN complexes would be formed due to the strong coordination effect of La^{3+} and EN. Because of the strong chelation of the EN with the released La^{3+}, F^- had to compete with EN during the nucleation and growth process of the NCs. Therefore, compared with the solvothermal synthetic routes without using EN, the hydrolysis of La^{3+}, dissolution of the $La(OH)_3$, as well as the strong coordination of La^{3+} and EN made the nucleation and growth rate of the NCs slow enough to allow the cations settle into the $NaLaF_4$ lattice, which facilitated the formation of $NaLaF_4$ nanorods. Furthermore, the decomplexed EN would attach to the surface of the nanorods to render the products water-soluble. The results of this contribution also agreed well with our previous work which had demonstrated that slow nucleation and growth processes could provide sufficient crystallization time to produce high-quality NCs [5,18].

On the other hand, EN also had been widely applied as the capping reagent to synthesize various rod-like nanomaterials [19–21]. According to these literatures, it was reasonable to speculate that EN also acted as a structure-directing reagent binding to the surface of crystals, directly affecting the growth of different crystal facets by adjusting the growth rate of different facets, and resulted in the formation of anisotropically regular rod-shaped $NaLaF_4$ in this work.

To sum up, in the solvent of H_2O, ethanol or their mixture, only LaF_3 but no $NaLaF_4$ NCs can be obtained in this work. Upon the addition of appropriate volume of EN, the resulted slow nucleation and crystal growth rate, and the structure-directing effect of EN can stimulate the formation of well-crystallized $NaLaF_4$ nanorods. Based on the proposed mechanism, all the experimental results in this work can be well explained.

To further prove our proposed reaction mechanism and the crucial role of EN on the formation of $NaLaF_4$ nanorods, two additional verification experiments were carried out by employing the solvents of 1 mL EN/39 mL H_2O and 5 mL EN/35 mL H_2O. It can be seen from Fig. 3 that when only 1 mL EN was added into the solvent, the products were all spherical or elongated spherical LaF_3 NCs. However, when the amount of EN increased to 5 mL, some rod-like crystals appeared along with the dominating spherical LaF_3 NCs (Fig. 3b), and some weak characteristic peaks of hexagonal phase $NaLaF_4$ emerged in the XRD pattern (data not shown). These

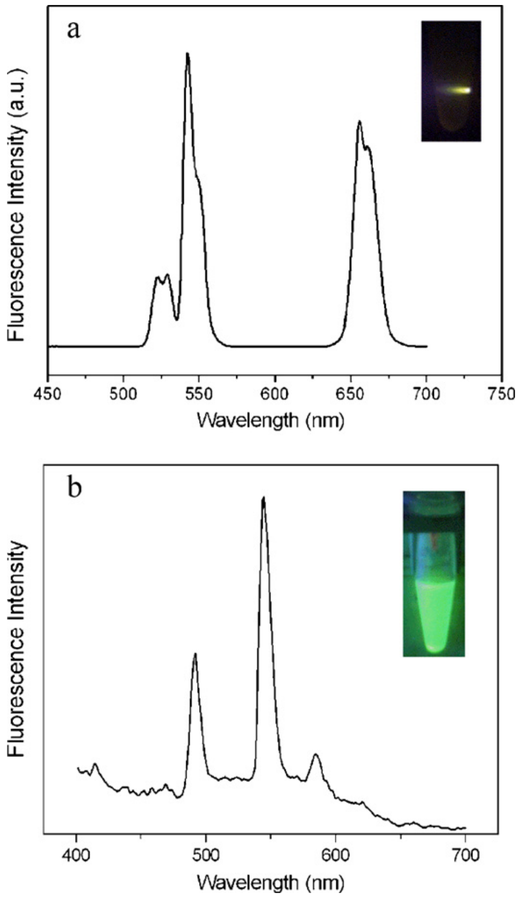

Fig. 4. (a) Room-temperature upconversion fluorescence emission spectrum of 0.2 wt% LaF_3:12%Yb^{3+}, 3%Er^{3+} NCs under irradiation of a 980 nm laser. (b) Room-temperature fluorescence spectrum of 0.2 wt% $NaLaF_4$:5%Ce^{3+}, 5%Tb^{3+} nanorods excited at 254 nm. Insets: Corresponding luminescence photographs of colloid NCs.

results further revealed that the proposed reaction mechanism was reasonable.

In addition, although EN was crucial for the formation of $NaLaF_4$ nanorods, H_2O was also indispensable because the strong basicity of EN, hydrolysis of La^{3+} ions, strong chelating effect of La^{3+}–EN all depended on the presence of H_2O. It can be seen from Fig. 1c that when the solvent of ethanol/EN was used without H_2O, no $NaLaF_4$ crystal could be formed. This also supported our speculation.

3.3. Fluorescence properties

Both LaF_3 and $NaLaF_4$ NCs are good host matrixes for lanthanide-based fluorescence processes. To test the luminescence capabilities of the products in this work, the synthesis of Yb^{3+}/Er^{3+} ion-pair or Ce^{3+}/Tb^{3+} ion-pair co-doped LaF_3 and $NaLaF_4$ NCs were carried out.

It was found that by co-doping Yb^{3+}/Er^{3+}, well-crystallized LaF_3 NCs and $NaLaF_4$ nanorods both exhibited bright yellowish-green upconversion fluorescence under the irradiation of a 980 nm laser. Fig. 4a showed the emission spectrum of the LaF_3: 12%Yb^{3+}, 3%Er^{3+} NCs (synthesized in 20 mL H_2O/20 mL ethanol). There were three main emission peaks at around 525, 545 and 658 nm, which were assigned to the $^2H_{11/2}$ to $^4I_{15/2}$, $^4S_{3/2}$ to $^4I_{15/2}$ and $^4F_{9/2}$ to $^4I_{15/2}$ transitions of erbium, respectively. All of these emissions mentioned above were based on a two-photon process. The UC mechanisms for the Yb^{3+}/Er^{3+} co-doped nanomaterials had been demonstrated in detail in previous works [5,14,18]. Briefly, under 980 nm excitation, an electron of Yb^{3+} (sensitizer) could be excited from the $^2F_{7/2}$ to the $^2F_{5/2}$ level. The energy could be transferred to Er^{3+} (activator ion) nonradiatively to excite it to the corresponding excited level through two-photon processes and then the visible upconversion luminescence could be observed. It was worth noting that the Yb^{3+}/Er^{3+} ion-pair co-doped $NaLaF_4$ nanorods also demonstrated the similar optical properties as that of LaF_3:Yb^{3+}, Er^{3+} NCs and was not shown here for the sake of conciseness.

Fig. 4b showed the fluorescence spectrum of the $NaLaF_4$ nanorods with a doping concentration of 5% Ce^{3+} and 5% Tb^{3+} under the excitation of 254 nm. Ce^{3+} ion served as sensitizer and Tb^{3+} as the activator in the fluorescence processes. Ce^{3+} ion has a relatively broad absorption band centered at ~250 nm with an allowed 4f–5d transition. After being excited, Ce^{3+} can transfer their energy to the Tb^{3+} ions which emit green fluorescence. The typical emission peaks of terbium were observed around 486, 543, and 587 nm assigned to the transitions of $^5D_4$–^7F_J ($J = 6, 5, 4$), respectively.

Furthermore, the novel yellowish-green UC fluorescence photo of the LaF_3:Yb^{3+}, Er^{3+} colloid and the bright green DC luminescence photo of $NaLaF_4$:Ce^{3+}, Tb^{3+} colloid were respectively presented in Fig. 4. The naked eye-visible luminescence again confirmed the unique optical property of the as-synthesized fluoride NCs in this work.

4. Conclusions

High-quality $NaLaF_4$ and LaF_3 NCs were selectively prepared by controlling the solvent compositions. Generally, $NaLaF_4$ NCs are difficult to be synthesized through conventional hydrothermal route by using NaF and La^{3+} as the precursors. In this contribution, it was found that the addition of appropriate amount of EN to the aqueous solvent could finely slow down the NCs nucleation and growth rate, and thus facilitate the formation of hexagonal phase $NaLaF_4$ nanorods. Since the cation radius of La^{3+} is the largest in the lanthanides, if $NaLaF_4$ NCs can be effectively synthesized, other $NaREF_4$ with a smaller cation radius can be also prepared using the same technique. Then we believe that the proposed method may be extended as a general approach to synthesis well-crystallized $NaREF_4$ NCs especially for the RE cations with large radius. In addition, in the solvents without EN, well-crystallized LaF_3 NCs can be prepared without using any additional capping reagents. Effect of the solvent components on the NCs formation was investigated and a reasonable reaction mechanism was proposed.

Furthermore, the as-synthesized $NaLaF_4$ and LaF_3 NCs all exhibited strong UC and DC fluorescence by co-doping Yb^{3+}/Er^{3+} or Ce^{3+}/Tb^{3+} ion-pairs, which showed potential applications as color displays, light-emitting diodes, optical storage and optoelectronics.

Acknowledgments

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