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A facile hydrothermal route at designated pH values has been developed to synthesize a series of well-dispersed LaF$_3$ colloidal nanocrystals (NCs) with a rich variety of morphologies, including nanoparticles, hexagonal nanoplates and fullerene-like nanoparticles. X-ray diffraction, scanning electron microscopy, transmission electron microscopy, high-resolution transmission electron microscopy, Fourier transform infrared spectroscopy, and photoluminescence spectra were used to characterize the samples. It is found that the formation of monodispersed fluoride NCs not only closely correlates with the pH values of the mother solutions, but also depends on the basicity of the base employed adjusting pH value. The strong alkaline solution in the absence of any organic additive in this system was found to be a prerequisite for producing hexagonal fullerene-like LaF$_3$ nanodisks. A mechanism for the formation of the fullerene-like LaF$_3$ via the local Ostwald ripening has been proposed based on observations of time-dependent experiments. The multicolor upconversion (UC) emission was successfully realized in a series of Yb$^{3+}$/Er$^{3+}$ doped LaF$_3$ NCs by excitation in the near-infrared region. The UC emission ratios of red to green for a series of LaF$_3$ NCs can be tuned by adjusting the pH values of the mother liquids and an UC mechanism activated by the high energy phonons inherent in the hollow LaF$_3$ nanoplates is proposed. It is expected that these rare-earth fluoride NCs might have potential in applications for photocatalysis, biolabelling and drug-delivery.

**Introduction**

LaF$_3$ nanocrystals (NCs) are one of the most efficient host materials for upconversion (UC) processes, which can be applied in the fields of lighting, display technology and biolabels. So the synthesis of LaF$_3$ nanomaterials has attracted considerable interest and various methods have been developed recently.\(^1\)\(^\text{-}\)\(^3\) To the best of our knowledge, most of the available synthetic approaches involving modified precipitation, polyol, and hydrothermal methods are based on the liquid precipitation reaction between rare-earth (RE) nitrates/chlorides and HF/NaF/NH$_4$F. But the LaF$_3$ NCs obtained by these methods were generally spherical or irregular in shape, because of the rapid nucleation process involved. So it still remains a challenge to find a suitable reaction system for growing high-quality LaF$_3$ NCs in terms of monodisperse, well-shaped, and single-crystalline NCs. Yan and co-workers first reported the synthesis of LaF$_3$ triangular nanoplates via a single source precursor La(CF$_3$COO)$_3$ route, but these nanoplates are inactive in UC luminescence.\(^4\)\(^\text{-}\)\(^5\) Similar methods were then employed by several groups to synthesize NaYF$_4$ crystals.\(^6\)\(^\text{-}\)\(^7\) Unfortunately, these methods were based on the thermo-decomposition of RE trifluoroacetates [RE(TFA)$_3$, RE = La, Y, Yb, Er and Tm] at high temperature in organic solvents, which need severe experimental conditions (300 °C, waterless, oxygen-free and inert gas protection). Therefore, it still remains a challenge to identify a suitable reaction system for growing high-quality RE doped LaF$_3$ NCs with novel structure and UC luminescence. The keys to a successful synthesis are to select suitable precursors, to control the coordinating behavior of the ligand and the growth rates.\(^8\)\(^\text{-}\)\(^13\)

Synthesis of monodispersed hollow spheres is currently attracting continuous interest because these hollow spheres have potential applications in catalysis, photonic crystal, chromatography, protection of biologically active agents, fillers (or pigments, coatings), and dye sensitized solar cells.\(^14\)\(^\text{-}\)\(^18\) In particular, the hollow spheres composed of RE doped nanoparticles are of interest recently not only because of their diverse properties, such as high quantum yield, low photobleaching, narrow emission band, and long luminescent lifetime,\(^19\) as compared with conventional luminescent materials, but also because these luminescent hollow spheres could be used as carrier of targeted drugs for bioapplications.\(^20\) For instance, Shan et al. fabricated hollow NaYF$_4$ NCs via the co-thermalysis of a mixture of trifluoroacetate precursors in trioctylphosphine oxide by Kirkendall effect.\(^21\) Jia et al. prepared well-shaped Y$_2$O$_3$:Eu hollow microspheres via a urea-based homogeneous precipitation technique in the presence of colloidal carbon spheres as hard templates followed by a subsequent heat treatment process.\(^22\) Zhang et al. obtained RE hollow cubic phase NaYF$_4$ nanoparticles by a controlled ion exchange process from cubic phase Y$_2$O$_3$ nanospheres.\(^23\) These preparation processes are
attractive, however, some evident defects, such as cumbersome and time-consuming physical and chemical processes in templates is insurmountable, whereas Kirkendall effect and Ostwald ripening techniques are primarily limited to specific materials such as metals, metal oxides, and chalcogenides (including Au, Ag, platinum cobalt oxides). Recently, Chen et al. described the fabrication of EuF₃ and SmF₃ hollow sub-microcrystals by hydrothermal route in the presence of ethylenediaminetetraacetic acid (EDTA). PrF₃ hollow nanocrystals were synthesized under the microwave-assisted heating hydrothermal conditions by Ma et al.. These nano/micro particles are well characterized as the paper brings some news in the synthetic concept in nanoparticle chemistry. So the discovery and exploitation of a facile and green universal method to prepare high quality hollow RE doped NCs is urgently required. To the best of our knowledge, there have been no reports on uniform RE doped LaF₃ hexagonal hollow nanocrystals (fullerene-like nanoparticles) with bright UC luminescence. Moreover, few studies have focused on how the shapes and structures of RE doped LaF₃ nanomaterials, that is desirable for bio-labelling and drug-delivery applications, affect on luminescence and electronic transition properties.

In this paper, a simple hydrothermal approach in the absence of any organic additive at the designated pH value and reactive temperature, was proposed to synthesize monodispersed RE doped LaF₃ nanoparticles. By controlling pH in solution, LaF₃ spherical nanoparticles, hexagonal nanocrystals and fullerene-like nanocrystals could be selectively synthesized. Furthermore, we systematically discuss the growth process of a series of LaF₃ NCs and UC luminescence properties adjusted by pH values. These RE doped LaF₃ NCs show great potential applications as biosensors and drug-delivery.

Experimental

Chemicals

LaF₃ (99.99%), TiO₂ (99.99%), Eu₂O₃ (99.99%), Er₂O₃ (99.9%), and Yb₂O₃ (99.99%) were purchased from Sinopharm Chemical Reagent Co., Ltd, China, and other chemicals were purchased from Beijing Fine Chemical Company, China. All chemicals are of analytical grade reagents and used as received unless otherwise noted. RE nitrate stock solutions of 0.2 mol/L were prepared by dissolving the corresponding metal oxide in nitric acid at elevated temperature.

Sample preparation

LaF₃-Yb³⁺/Er³⁺ NCs have been fabricated via a facile hydrothermal route. In a typical experiment, to a 100 mL of beaker containing 20 mL water was added to a water solution (1.5 mL) containing La(NO₃)₃, Yb(NO₃)₃ and Er(NO₃)₃ at a 80:18:2 ratio with a total RE amount of 0.3 mmol. The resulting mixture was thoroughly stirred. Subsequently, an aqueous solution (1.2 mL) containing 1.2 mmol NaF was added and stirred for 30 min. The pH value of the solution was titrated with sodium hydroxide or nitric acid solution. Subsequently, the solution was transferred to a 40.0 mL Teflon-lined autoclave, and heated at 200 °C for 24 h, at which time the mixture was cooled down to room temperature.

The resulting nanoparticles were precipitated out through an addition of ethanol, collected by centrifugation, washed with ethanol, and finally dried under 60 °C for 12 h. In addition, Eu³⁺ and Tb³⁺/Yb³⁺/Er³⁺ doped fluoride were prepared with stoichiometric, and other conditions are the same as those mentioned above for synthesizing LaF₃-Yb³⁺/Er³⁺ NCs. It should be stated that all samples were hydrothermally treated at 200 °C for 24 h.

Characterization

Powder X-ray diffraction (XRD) data was recorded on a D/Max2550VB+/PC X-ray diffraction meter at a scanning rate of 15°/min in the 20 range from 15° to 75°, with Cu Ka (40 kV, 40 mA) irradiation (λ=0.15406 nm). Low-resolution and high-resolution transmission electron microscopy (TEM) measurements were carried out on a JEOL 2100 TEM operated at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) micrographs were obtained using a Hitachi S-4800 FE-SEM. Fourier transform infrared spectroscopy (FTIR) was carried out on a Bruker EQUINX55 spectrometer using KBr pellets.

Results and discussion

Structure and morphology

In our current system, via facile hydrothermal route in a closed system the as-prepared LaF₃ products with multiform structures and morphologies have been synthesized. Many experimental parameters can influence the growth and crystal structure of LaF₃ NCs. Of course, the final morphology of a crystal is also the result of the cooperation of many parameters, such as hydrothermal temperature and reactive time. We kept hydrothermal temperature and reactive time the same, and emphasized the pH value of mother solution effects in the growth of NCs. Interestingly, two different crystal phases were observed in the process of synthesizing the NCs. Fig. 1 shows the XRD patterns of Yb³⁺/Er³⁺ co-doped LaF₃ NCs hydrothermally treated 24 h under various pH values tuned by employing NaOH solution. All diffraction peaks shown in Fig. 1 can be indexed easily as pure, hexagonal phase of LaF₃ [space group P₆₃mc (JCPDS No. 32-0483)], synthesized at a pH value of less than 12.

It is worth pointing out that all the peaks have been apparently broadened and weaken with elevating pH values of solutions as shown in Fig. 1(a), indicating the smaller crystal sizes. When pH value up to 14, all of the reflections could be readily indexed to the hexagonal phase of La(OH)₃ [(space group P63/m (JCPDS No. 36-1481)] in Fig. 1(b).

TEM provides further insight into the morphology and microstructural details of the RE based series of LaF₃
nanostructures. Figs. 2(a)-2(f) show typical images of these RE compound nanoparticles, from which it can be seen that the as-obtained LaF$_3$ NCs at low pH value present the irregularly shape [Fig. 2(a)]. However, the morphology and size of LaF$_3$ crystallites obtained varied greatly depending upon the pH value of the mother solution. The size of the LaF$_3$ nanoparticles shrinks from approximately 80 to 20 nm when the pH values of solutions increased from 2 to 12 [Figs. 2(a) and 2(b)], which is in consistent with the analysis of the XRD. Interestingly, when the pH value is adjusted to 12 by employing 5 mol/L NaOH solution, unique and regular hollow-hexagonal shape nanoplates, known as fullerene-like, are yielded in large quantities [Fig. 2(b)]. The high-resolution TEM (HRTEM) image of a single nanosphere provides more detailed structural information on these fullerene-like nanostructures. Fig. 2(c) shows a HRTEM image of LaF$_3$ nanoparticles with an individual close-caged particle and an approximately 25 nm of outer diameters and 15 nm of inner diameters have been provided as further evidence for the formation of RE fluoride fullerene-like nanostructures. As disclosed by the corresponding HRTEM image, cavities of nanoparticles are half-penetrated, which is confirmed by the lattice stripes within the cavity, as shown in Fig. 2(c). The HRTEM image of a single nanosphere [Fig. 2(c)], indicating that the distance between the adjacent lattice planes is 0.32 nm, is ascribed to (111) crystal plane of the hexagonal phase LaF$_3$. The corresponding selected area electron diffraction pattern in Fig. 2(d) indicates that the LaF$_3$ hollow nanospheres are single crystals and the most distinct five concentric diffraction rings can be indexed to (002), (111), (300), (302), (411) and (330) planes from the center, sequentially. When the pH value is further adjusted to 14 by employing NaOH, La(OH)$_3$ microrods with the length and diameter of about 20 µm and 1 µm, respectively, were obtained in Fig. 2(e). No evident modifications on morphology and phase of fluoride products by doping different RE ions are observed. For example, the morphology and phase of Eu$^{3+}$ (2 %) doped fullerene-like LaF$_3$ nanoparticles prepared at the same conditions of pH are similar as Yb$^{3+}$/Er$^{3+}$ (18/2 %) doped fullerene-like LaF$_3$ nanoparticles.

The strong dependence of morphology and phase on basicity is found in the hydrothermal synthesis of LaF$_3$ NCs. The weak base like NH$_3$.H$_2$O gives the different results, and only LaF$_3$ NCs are obtained, while La(OH)$_3$ can not be observed at a pH range from 2 to 12. If pH value is tuned to 12 by employing ammonia water, the final product was found to be unique and regular LaF$_3$. The influence of the pH values on the shapes of LaF$_3$:Yb$^{3+}$/Er$^{3+}$ (18/2 %) NCs at the different pH values adjusted with 5 mol/L NaOH in (a)-e. (a) Irregular structure obtained at pH=4; (b) and (c) hexagonal nanoplates with hollow structure obtained at pH=12; (d) Selected area electron diffraction pattern corresponding to figure 2(b); (e) Microrods of La(OH)$_3$:Yb$^{3+}$/Er$^{3+}$ (18/2 %) at a pH=14; (f) Hexagonal nanoplates of LaF$_3$:Yb$^{3+}$/Er$^{3+}$ (18/2 %) at a pH of 12 adjusted with ammonia solution (25%). These samples were hydrothermally treated at 200 °C for 24 h.

Fig. 1 XRD patterns of LaF$_3$:Yb$^{3+}$/Er$^{3+}$ (18/2 %) and La(OH)$_3$:Yb$^{3+}$/Er$^{3+}$ (18/2 %) samples prepared at different pH values adjusted with NaOH after 24 h at 200 °C and the standard data of hexagonal LaF$_3$ (JCPDS No. 16-0334) and La(OH)$_3$ (JCPDS No. 36-1481) as references.
hexagonal plates with an average edge length of about 50 nm and a thickness of 20 nm, as shown in Fig. 2(f). It can be seen from Fig. 2(f) that most of the nanoplates lie flat on the faces, and some stand on their edges. These nanoplates exhibited a relatively narrow size distribution although the edge lengths of the nanoplates shown in the TEM images seemed not very uniform due to the NCs being tilted by different angles on the carbon grid, which is consistent with the previously reported by Chen et al.\textsuperscript{29} Similar size-control phenomena for LaF\textsubscript{3} samples have also been observed by employing ammonia water to tune the pH of mother liquid. These results indicate that the control of size, shape and crystal phase of fluoride crystals not only depend on the pH of the initial solution, but also depend on the basicity of the base. A small hydrolysis constant of the alkali would benefit the combination of F\textsuperscript{−} and RE\textsuperscript{3+} ions to transform RE\textsuperscript{3+} complex into REF\textsubscript{3} lattice. When different pH values are tuned by using the different basicities, OH\textsuperscript{−} ligands can capture or release La\textsuperscript{3+} to form La(OH)\textsubscript{3} or LaF\textsubscript{3} nucleus, and change ion mobility, solubility as well as density of charges on the growing crystal faces to affect the morphology significantly.\textsuperscript{30,31} As far as the La(OH)\textsubscript{3} colloidal precipitates are concerned, the optimal conditions for the formation of La(OH)\textsubscript{3} seeds are a basic environment.\textsuperscript{31} While the rod or tube shape is common for La(OH)\textsubscript{3} crystals with hexagonal layer structures.\textsuperscript{31}

The mechanism of the formation of fullerene-like nanoparticles

The influence of chemical potential on the morphology evolution of NCs has been elucidated by Peng et al. and in the case of nanostructure with preferential growth direction it would be advantageous to have a higher chemical potential,\textsuperscript{32,33} which is mainly determined by the pH value and monomer concentration of the solutions in our reaction system.\textsuperscript{34} While small particle size requires high supersaturation,\textsuperscript{35} it is expected that, in this case, high supersaturation is achieved by high pH value.

To investigate the growth mechanisms of the fullerene-like LaF\textsubscript{3} nanoparticles, detailed time-dependent experiments were carried out at hydrothermal conditions. The XRD patterns and the corresponding SEM of the intermediates of Yb\textsuperscript{3+}/Er\textsuperscript{3+} co-doped LaF\textsubscript{3} NCs prepared under a pH value of 12 using NaOH solution at different reaction time intervals are shown in Fig. 3 and Fig. 4, respectively. It is clear that after 0.5 h the XRD pattern matches the hexagonal phase of La(OH)\textsubscript{3} NCs (space group P6\textsubscript{3}m\textsubscript{2}, JCPDS No. 36-1481), which is a precursor in the production of LaF\textsubscript{3} NCs. As shown in Fig. 4(a), the diameter and the length of La(OH)\textsubscript{3} NCs are about 8 nm and 16 nm, respectively. The hexagonal phase La(OH)\textsubscript{3} NCs present preferred growth direction along the c axis. With reaction time prolonging to 5 h, XRD displays a mixed phase composed of hexagonal phase La(OH)\textsubscript{3} and hexagonal phase LaF\textsubscript{3} [Fig. 3(b)]. This indicated that the samples transformed partially from hexagonal phase La(OH)\textsubscript{3} to hexagonal phase LaF\textsubscript{3}. Evidence can also be seen from the TEM image in Fig. 4(b). Here we can see that the new hexagonal nanoplates with a size of ~20 nm and some nanorods disappeared.

Based on the above analysis of XRD, it can be appointed that the hexagonal nanoplates of hexagonal La(OH)\textsubscript{3} phase is formed, as disappears the nanorods of hexagonal La(OH)\textsubscript{3} phase. The changes on the phase, morphology and size from Fig. 4(a) to 4(b) indicate that the products undergo a dissolve-renucleation process. This is different from the course of evolution of hexagonal NaYF\textsubscript{4} NCs obtained from commercial Y\textsubscript{2}O\textsubscript{3} by in-situ ion exchange process without the changes on the size and morphology.\textsuperscript{36} When the time is further increased to 12 h, pure hexagonal phase (JCPDS No. 32-0483) [Fig. 3(c)] and the desired hexagonal solid nanoparticles without hollow structure [Fig. 4(c)] can be obtained. Extending the thermally treating time to 24 h, hexagonal phase hollow LaF\textsubscript{3} plates with diameters of 25 nm can be easily obtained [Fig. 3(d) and Fig. 4(d)].
shape under hydrothermal conditions. The formation of the NCs follows the aggregation growth theory at a pH range from 2 to 10. This mechanism requires that a sufficient amount of ions and primary particles participate in the growth process in order to obtain an aggregation growth. When the pH was adjusted between 11 and 12, it is easier to form mono- and poly-nuclear La(OH)$_3$ species or La(H$_2$O)$_x$ species accompanied with NaF species, serving as the nucleate seeds in precursor solution at room temperature. When the mixture solution was transferred to an autoclave, the nucleate seeds further crystallize and coarsen. However, as heating up to a certain temperature, the La(OH)$_3$ species seem not to be the stable phase. It is reported that the NaF monomer also was the quasi-steady state species and its molar ratios over the other fluorides were the key factors to decide the growth rate and the sizes of final NaYF$_4$ particles.$^6$ With the hydrothermal process evolving, the energy provided by the reaction system becomes higher until a certain moment when it is high enough to overcome the reaction energy barrier. The La(OH)$_3$ solid nanospheres become dissolved through a dissolution-recrystallisation process and the LaF$_3$ nanoflosses are formed which are adsorbed on the larger La(OH)$_3$ solid nanospheres (step 3 in Scheme 1) because the hexagonal phase LaF$_3$ is a thermodynamically more stable structure. The growth modes are different from the tubular hexagonal NaYF$_4$ NCs by fluorinating an RE–OH bond to RE–F bond fluoride.$^{37}$ The transformation process can be described with the following equations.

\[
2\text{La(OH)}_3 + 7\text{NaF} \rightarrow \text{LaF}_3 + 3\text{NaLaF}_4 + 6\text{Na}^+ + 6\text{OH}^-; \\
3\text{NaLaF}_4 + \text{La}^{3+} \rightarrow 4\text{LaF}_3 + 3\text{Na}^+.
\]

During the further growth process of LaF$_3$ crystals, RE(OH)$_3$ monomers in solution fast redissolved under the hydrothermal conditions and RE$^{3+}$ ions diffuse onto the surface of a growing crystal and their subsequent fast incorporation with F$^-$ into the LaF$_3$ lattice. While generated OH-, that is the weak capping ligand, is preferentially bound to the highest-energy {0001} surfaces of LaF$_3$ (Scheme 1), which suppresses the growth of nuclei along {0001} surfaces. The growth of LaF$_3$ along six symmetric directions of {1010} finally results in hexagonal plate particles at a pH of 12.

Scheme 1  Schematic illustration for the possible formation processes of β-LaF$_3$:Yb$^{3+}$/Er$^{3+}$ (18/2 %) and La(OH)$_3$:Yb$^{3+}$/Er$^{3+}$ (18/2 %) NCs with various morphologies using NaF as fluoride at different pH values.

This feeding mode can be regarded as a similar process to the “injection single precursor” technique,$^{38}$ which will ensure a higher monomer concentration of LaF$_3$ by the redissolved La(OH)$_3$ and NaF species. La(OH)$_3$ and NaF species therefore seem to act as a homogeneously dispersed reservoir of monomers.$^{39}$ If La(OH)$_3$ and NaF species as a reservoir releases monomers at a rate sufficient to ensure a moderate to high level of supersaturation during the first stage of the LaF$_3$ particles growth, focusing of sizes by diffusion-control will occur in accord with the observed narrow particle size distribution and regular hexagonal plate of final products.$^{8,40}$ In this stage, the LaF$_3$ particles grow very fast, while the molar fraction of precursor La(OH)$_3$ particles as the provider of monomers rapidly decrease. As long as La(OH)$_3$ molar fraction is not too low, a few of RE(OH)$_3$ crystal seeds inevitably growth at a higher monomer concentration solution due to the phase matching between LaF$_3$ and La(OH)$_3$.

However, LaF$_3$ solid solution particles containing impurities phase such as La(OH)$_3$ and NaLaF$_4$ are weak crystalline due to a rapid grow rate in the first region. In the subsequent stage, most of the La(OH)$_3$ particles have already been consumed and the growth rate of the LaF$_3$ particles controlled by the diffusion rate of monomers will present downward trend. Since La(OH)$_3$ crystals is thermodynamically less stable than LaF$_3$, La(OH)$_3$ particles finally are depleted. The inner crystallites of this LaF$_3$ hexagonal plate might be weaker than that of outer owing to the decline in grow rate, which make the inner weak crystallites dissolve and transfer out by a localized Ostwald ripening and the...
cation exchange between La\(^{3+}\) and Na\(^{+}\). Faster ionic motion usually ensures a reversible pathway between the fluid phase and the solid phase, which allows atoms, ions, or molecules to adopt correct positions. Matter relocation during prolonged processes, which is indispensable in the ripening, may also result in unexpected hollow structure if starting solid precursors become compositionally complicated.

When the pH up to 14 employing NaOH, a higher pH implies a higher OH\(^{-}\) ion concentration and a higher chemical potential in solution. A higher chemical potential is preferable for the growth of nanowires. However, higher OH\(^{-}\) ion concentrations result in a higher concentration of La(OH)\(_3\) monomers and thus reduce the rate of ionic motion. Finally, few LaF\(_3\) seeds were obtained due to exhaustion of La\(^{3+}\) ions. In following hydrothermal process, dissolution of La(OH)\(_3\) monomers is restricted by the value of K\(_{sp}\) for La(OH)\(_3\). Therefore, La(OH)\(_3\) microrods, instead of LaF\(_3\) particles, is formed similar to previous reports by Wang et al.\(^{34}\)

When ammonia water is employed to adjust pH value of solution, LaF\(_3\) precipitate is prior to form due to the low value of dissociation constant for NH\(_3\).H\(_2\)O, which leads to form LaF\(_3\) crystals. When further elevating pH, unique and regular hexagonal plates are obtained because OH\(^{-}\) ligand preferentially bound to the highest-energy \{0001\} surfaces of growing crystal.\(^{12}\) So these results proved employing strong base to adjust the pH value of solutions was necessary to form the hollow hexagonal plates, which will allow the formation of intermediate RE(OH)\(_3\) and result in a complicated primary particles. Scheme 1 depicts a proposed schematic illustration of the nucleation and growth processes of the NCs. The irregular sphere formation can be attributed by the aggregated particles accompanied, while the formation of a hexagonal hollow nanodisc crystal can be ascribed to the localized Ostwald ripening and a cation exchange mechanism.\(^{25,26,42}\) In our experiments, OH\(^{-}\) ions play an important role in the process. OH\(^{-}\) not only can promote the growth along six symmetric directions by adsorbing on \{0001\} planes, but also promote the localized Ostwald ripening by introduction of impurity phase of La(OH)\(_2\).

The photoluminescence properties of doped fullerene-like LaF\(_3\) nanoparticles

The UC luminescence of RE ions has been investigated extensively because of their potential application in various fields, i.e. lighting or display, IR detection and medical imaging.\(^{43-46}\) RE fluorides with a high refractive index and low phonon energy, have become a research focus on the materials field owing to their unique applications based on optical characteristics arising from the 4f electrons. To examine the feasibility of the as-obtained NCs as efficient UC host materials, the most frequently used UC ion Er\(^{3+}\) and the sensitizer ion Yb\(^{3+}\) were co-doped into a series of LaF\(_3\) samples synthesized under different pH value conditions. Fig. 5 shows UC emission spectra of a series of Yb\(^{3+/Er^{3+}}\) co-doped LaF\(_3\) samples in the range of 500–700 nm under 980 nm excitation. All transitions are assigned to the Er\(^{3+}\) ion. Green luminescence corresponding to the \(^{2}H_{11/2}\)\(^{4}S_{3/2}\)\(^{2}H_{11/2}\) transitions locates in the wavelength region of 500–575 nm, and the \(^{4}F_{9/2}\)\(^{4}I_{15/2}\) transition derived red luminescence ranges from 625 to 700 nm. The weak emission at about 410 nm is attributed to \(^{2}H_{15/2}\)\(^{4}I_{15/2}\) transition. These UC peaks in Fig. 5 is in agreement with what have been reported for Yb\(^{3+/Er^{3+}}\) UC in NaYF\(_4\) NCs.\(^{47-50}\) It is noticed that the luminescence emission intensity and the ratio of red to green emission bands in Yb\(^{3+/Er^{3+}}\) doped LaF\(_3\) can be tuned by adjusting the pH values of mother liquors. Obviously, the Er\(^{3+}\) and Yb\(^{3+}\) double-doped LaF\(_3\) NCs display the strong UC emission, and even the white light can be observed by naked eye when Yb\(^{3+/Tm^{3+/Er^{3+}}}\) are co-doped in LaF\(_3\) NCs. These spectra measurements indicate LaF\(_3\) host synthesized by hydrothermal route is a kind of efficient UC host materials.

In addition to, it is noticed that the luminescence emission intensity and the ratio of red to green emission bands in Yb\(^{3+/Er^{3+}}\) doped LaF\(_3\) NCs can be tuned by adjusting the pH values of mother liquors. As shown in Fig. 5, the UC luminescence emission of Yb\(^{3+/Er^{3+}}\) co-doped LaF\(_3\) synthesized under acid condition present the stronger luminescence intensity and the lower ratio of red to green emission bands than that of Yb\(^{3+/Er^{3+}}\) double-doped LaF\(_3\) synthesized under basic environment.

Our recent reports show that the luminescence intensity depends on quality of crystallization, particle size, crystallographic phase, composition of host matrix and even local symmetry of matrix.\(^{51,52}\) In order to verify the influence of local environment symmetry on luminescence intensity, the photoluminescence spectra of a series of Eu\(^{3+}\) doped LaF\(_3\) prepared under different pH values are carried out shown in Fig. 6. The spectra are characteristic of the \(^{5}D_{0}\)\(^{7}F_{0}\) line (J=0, 1, 2, 3, 4) of the Eu\(^{3+}\) ion.\(^{53,54}\) Interestingly, we noted that the total intensity of luminescence became weaker (Fig. 6), while the relative intensity ratio of \(^{5}D_{0}\)\(^{7}F_{2}\) to \(^{5}D_{0}\)\(^{7}F_{1}\) transition became stronger with an increase of the value of pH (Fig. 6), and the ratio of I\(_{755}/I_{590}\) for (a)-(d) in Fig. 6 are 0.71, 0.72, 0.90 and 1.29, respectively. It is well-known that the \(^{5}D_{0}\)\(^{7}F_{1}\) transition is electric-dipole transition, and its intensity is significantly affected by the symmetry in local environments around Eu\(^{3+}\) ions. When the symmetry around the Eu\(^{3+}\) ions is lowered, the transition probability of the \(^{5}D_{0}\)\(^{7}F_{1}\) is increased. However, the \(^{5}D_{0}\)\(^{7}F_{1}\) transition is magnetic-dipole allowed and
is relatively insensitive to the local symmetry.\textsuperscript{55} Thus, the symmetry around the Eu\textsuperscript{3+} ions decreased when increasing the value of the pH, which indicates that the crystal field surrounding the Eu\textsuperscript{3+} ions is affected by the decrease of size and hollow fullerene-like structure. But the symmetry around the Eu\textsuperscript{3+} ions induced by the small size of particles with the fullerene structure can not result in a decrease on luminescence. The reduction in emission intensity in the fullerence nanoplates with the hollow structure is caused by the adsorption of a great amount of OH\textsuperscript{-}, on the surface and the hollow structure. Stretching from OH\textsuperscript{-} groups and CO\textsubscript{3}\textsuperscript{2-} yields high energy vibrations (3350 and 1550 cm\textsuperscript{-1}, respectively) that can increase the multi-phonon relaxation rate of the metastable states and thus reduce the overall visible emission intensity and lower ratio of the green-to-red emission.\textsuperscript{56,57} This is supported by FTIR of LaF\textsubscript{3}:Eu\textsuperscript{3+} samples prepared at different pH conditions as shown in Fig. 7, in which the FTIR spectra intensity of OH\textsuperscript{-} and CO\textsubscript{3}\textsuperscript{2-} sharply increase with pH elevating.

As is well-known, the UC intensity and the ratio of red to green depend on the population of the intermediate states. The UC mechanism in Er\textsuperscript{3+} and Yb\textsuperscript{3+} codoped systems is well known and occurs via two successive transfers of energy from the Yb\textsuperscript{3+} ion to the Er\textsuperscript{3+} ion. Following 980 nm irradiation, firstly, Er\textsuperscript{3+} ions in the \(^{4}\text{I}_{15/2}\) state are excited to \(^{4}\text{I}_{11/2}\) state via energy transfer between Yb\textsuperscript{3+} and Er\textsuperscript{3+}. Subsequent, the \(^{4}\text{I}_{13/2}\) levels are populated by radiative or noradiative relaxations of \(^{4}\text{I}_{11/2}\) to \(^{4}\text{F}_{15/2}\) levels via energy transfer or from \(^{4}\text{I}_{13/2}\) to \(^{4}\text{F}_{9/2}\) states via phonon-assisted energy transfer. Subsequent, the \(^{4}\text{S}_{3/2}\) state may be populated by nonradiative relaxations of \(^{4}\text{F}_{9/2}\)\textsuperscript{→}\(^{4}\text{S}_{3/2}\) in LaF\textsubscript{3}:Yb\textsuperscript{3+}/Er\textsuperscript{3+} NCs with low phonon obtained at low pH. In LaF\textsubscript{3}:Yb\textsuperscript{3+}/Er\textsuperscript{3+} fullerence nanoplates, with high energy phonon groups including OH\textsuperscript{-} and CO\textsubscript{3}\textsuperscript{2-}, \(^{4}\text{F}_{5/2}\) state can effectively relax to red luminescent \(^{4}\text{F}_{9/2}\)\textsuperscript{→}\(^{4}\text{S}_{3/2}\) in LaF\textsubscript{3}:Yb\textsuperscript{3+}/Er\textsuperscript{3+} fullerence nanoplates.\textsuperscript{58,59} The proposed conversion mechanism of LaF\textsubscript{3}:Yb\textsuperscript{3+}/Er\textsuperscript{3+} fullerence nanoplates is shown in Fig. 8. Therefore, LaF\textsubscript{3}:Yb\textsuperscript{3+}/Er\textsuperscript{3+} fullerence nanoplates had stronger red emission following near-infrared excitation, which could be used as carrier of targeted drugs for bioapplications. These results indicate that the synthetic method is ideal since it allows tailoring of the UC emission properties of the material simply by varying the pH of mother liquid.

In summary, LaF\textsubscript{3}:Yb\textsuperscript{3+}/Er\textsuperscript{3+} NCs including nanoparticles, hexagonal nanoplates as well as fullerene-like nanoplates and La(OH)\textsubscript{3}:Yb\textsuperscript{3+}/Er\textsuperscript{3+} microrods have been successfully synthesized via a simple and mild hydrothermal route at designated pH values. It is interesting to observe that the hexagonal nanoplates are hollow structure, known as inorganic fullerene-like nanoparticles. XRD, SEM, TEM, HRTEM and
photoluminescence spectra were used to characterize the samples. It is found that the formation of monodispersed fullerene-like LaF$_3$ NCs not only closely correlates with the pH values of the mother solutions, but also depends on the basicity of the base employed adjusting pH value. The formation mechanism of this system was found to be a prerequisite for producing hexagonal fullerene-like LaF$_3$ nanostructures. The strong alkaline solution in the absence of any organic additive in this system was found to be a prerequisite for producing hexagonal fullerene-like LaF$_3$ nanoparticles. The interesting luminescence properties are discussed in detail. It is noticed that the luminescence emission intensity and the ratio of red to green emission bands in of Yb$^{3+}$/Er$^{3+}$ co-doped LaF$_3$ can be tuned by adjusting pH value of mother liquid, which indicates that the synthetic methods is ideal since it allows tailoring of the UC emission properties of the material simply by varying the pH of mother liquid. The regular fullerene-like hexagon nanoplates with tunable luminescence emission are conducive to serve as novel building blocks for new nanodevice applications.

Acknowledgements
The authors acknowledge the financial support of the Natural Science Foundation of Shaanxi Province of China (Grant No. 2014JQ1008), the Special Foundation of Shaanxi Educational Commission of China (Grant No. 12JK0453), the Talent Fund of Shaanxi Province of China (Grant No. QN1237) of Xi’an University of Architecture and Technology.

Notes and references


The formation of fluoride NCs closely correlates with the pH and the basicity of the base employed adjusting pH.