

Formation mechanism and luminescence properties of nanostructured sodium yttrium fluoride corn sticks synthesized by precipitation transformation method

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Abstract: Monodisperse sodium yttrium fluoride corn sticks with hexagonal nanostructure were successfully prepared by a facile and repeatable precipitation transformation method. The phase and morphology of the products were characterized with X-ray diffraction (XRD) and scanning electron microscopy (SEM). The growth mechanism was studied, indicating that the initial generated $Y(OH)_3$ gradually translated into YF_3 and then transformed into corn stick-like $H-NaYF_4$ nanoparticles owing to the crucial role of fluorine ions in the solution. The up-conversion (UC) luminescence properties of $H-NaYF_4:20\%Yb^{3+},2\%Er^{3+}$ nanocrystals were discussed. The intensive green emission in the range of 510–570 nm was attributed to the ($^2H_{11/2}, ^4S_{3/2}$) \rightarrow $^4I_{15/2}$ transition and the weaker red emission between 640 and 680 nm was originating from the $^4F_{9/2}\rightarrow^4I_{15/2}$ transition.

Keywords: precipitation transformation; nanomaterials; photoluminescence; rare earths

Due to their excellent optical performances such as low toxicity, narrow emission peaks, high photostability and long fluorescence lifetime, rare earth ion-doped up-conversion (UC) nanomaterials have achieved extensive attention from researchers. These materials exhibited considerable potential applications in the fields of optical probe, telecommunication, biological detection, solar cells, and so on^[1–6]. Especially, rare earth ion-doped up-conversion fluorescence nanocrystals displayed their superiority in biological applications^[7–9] compared with organic fluorescent dyes and quantum dots.

Among these up-conversion luminescent materials, $NaLnF_4$ and LnF_3 nanocrystals have been considered as superior host matrixes for UC phosphors. Ln^{3+} -doped $NaYF_4$ nanomaterials are the most ordinary up-conversion fluorescence materials, thus many studies have been focused on the synthetic strategies to realize their potential biological applications^[10–15]. By far, highly-pure Ln^{3+} -doped $NaYF_4$ nanocrystals have been obtained via hydro/solvo-thermal reactions and thermal decomposition^[16–20]. However, there are respective limitations for

these synthesis methods to prepare inorganic functional nanomaterials, for example, complicated process, low output and high energy consumption, and so forth.

Herein, we demonstrated a simple and economical strategy for the large-scale synthesis of monodisperse ion-doped $H-NaYF_4$ nanocrystals via liquid phase precipitation transformation method with $Y(NO_3)_3$ and NaF as raw materials. The structure, formation mechanism and photoluminescence (PL) properties of the products also were investigated in detail.

1 Experimental

1.1 Preparation

All of the chemical reagents, including sodium fluoride (NaF), yttrium oxide (Y_2O_3 , 99.99%), ytterbium oxide (Yb_2O_3 , 99.99%), erbium oxide (Er_2O_3 , 99.99%), polyethyleneglycol (PEG-6000), sodium hydroxide ($NaOH$), propanetriol and ethanol, were of analytical grade and used without further purification. 0.5 mol/L of rare earth nitrate aqueous solution was obtained by dis-

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solving corresponding rare earth oxide in nitric acid solution. 1 mL of yttrium nitrate aqueous solution (0.5 mol/L) was put into a 50 mL beaker with 0.4 g of PEG-6000, followed by adding 6 mL of distilled water and 5 mL of propanetriol. The mixture was stirred vigorously with the pH value tuned by 1.0 mL of sodium hydroxide solution (4.0 mol/L). 6 mL of sodium fluoride (0.5 mol/L) was added in succession. The resulting solution was kept stirring at room temperature for 2 h. At the end of the reaction, a white precipitate was obtained by centrifugation. The products were washed with EtOH and distilled water several times, then dried at 80 °C oven for further characterization. For the synthesis of hexagonal NaYF₄: 20%Yb,2%Er nanocrystals, a mixture of Y₂O₃ (0.78 mmol), Yb₂O₃ (0.20 mmol), and Er₂O₃ (0.02 mmol) was dissolved in concentrated nitric acid to make up 0.5 mol/L of Ln(NO₃)₃ aqueous solution. Other experimental procedure kept changeless.

1.2 Characterization

The morphologies of the samples were characterized by thermal field environment scanning electron microscopy (SEM, FEI Quanta 400) with gold coating. The samples for SEM examination were prepared by suspending solid samples in alcohol and dripped on a slide, which was stucked on specimen stage. The crystallinity and crystal structure of the samples were examined by an X-ray diffractometer (XRD, Rigaku D/max 2200 VPC, graphite monochromator, 48 kV and 24 mA) with Cu K α radiation ($\lambda=0.15418$ nm). Up-conversion fluorescence spectra were obtained on a Jobin Yvon Horiba Fluorolog-3 luminescence spectrometer with an external 980 nm laser diode as the excitation source in place of the xenon lamp in the spectrometer.

2 Results and discussion

2.1 Phase analysis

Fig. 1 presents the XRD patterns of the samples synthesized by changing the reactant molar ratio of Y(NO₃)₃ and NaF. When the Y:F molar ratio is 1:1, Y(OH)_{2.14}F_{0.86} obtained after 2 h reaction and all the diffraction peaks were in agreement with the standard diffraction patterns (JCPDS 80-2003), as shown in Fig. 1(1). Decreasing the Y:F molar ratio to 1:3, as shown in Fig. 1(2), YF₃ was achieved with the characteristic peaks corresponding to the JCPDS standard of No. 32-1431. It is indicated that fluoride ions (F⁻) replaced gradually the hydroxyl ions (OH⁻) in Y(OH)_{2.14}F_{0.86}. If the Y:F molar ratio is further reduced to 1:6, every diffraction peak is in accord with the JCPDS standard (No. 16-0334) for hexagonal sodium yttrium fluoride (H-NaYF₄). And with the reaction time increased from 2 to 6 h, highly phase-pure H-NaYF₄ is gained, as shown in Fig. 1(3–5).

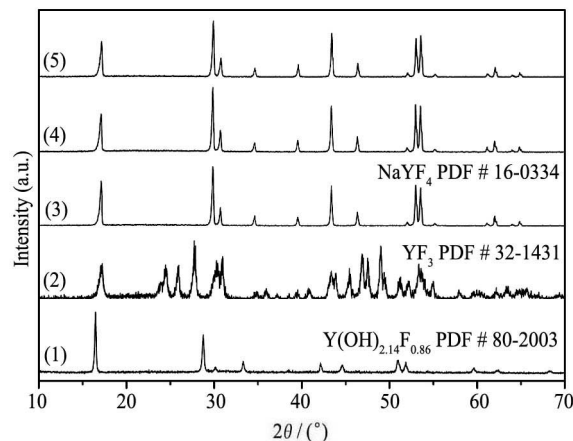


Fig. 1 XRD patterns of Y(OH)_{2.14}F_{0.86} (1) and YF₃ (2) synthesized with the Y:F molar ratio of 1:1 and 1:3 for 2 h; hexagonal NaYF₄ (3, 4, 5) prepared with the Y:F molar ratio of 1:6 for 2, 4 and 6 h, respectively

2.2 Morphology characterization

Fig. 2 shows the typical SEM images of the samples synthesized at different conditions. It could be seen that Y(OH)₃ nanorods were synthesized without the adding of NaF solution, as shown as the XRD pattern in Fig. 2(a) and the SEM image in Fig. 2(b). And Y(OH)_{2.14}F_{0.86} nanotubes were prepared (Fig. 2(c)) with the adding of NaF solution, keeping the Y:F molar ratio of 1:1 reaction. The hollowing from Y(OH)₃ nanorods to Y(OH)_{2.14}F_{0.86} nanotubes was attributed to Ostwald ripening during the replacing of F⁻ ions to OH⁻ ions, which matched well with the XRD data. When the Y:F molar ratio decreased to 1:3, out-of-order YF₃ nanocrystals formed as shown in Fig. 2(d). If the Y:F molar ratio reduced to 1:6, monodisperse NaYF₄ nanoparticles with uniform corn stick morphology were found after 2 h reaction. The even length and diameter of these monodisperse nanoparticles are 170 and 80 nm, respectively. With the reaction time increased to 4 h, it is shown in Fig. 3 that nanostructured NaYF₄ corn sticks became longer with the length of 170–200 nm. When the reaction time further increased to 6 h, the length of NaYF₄ corn sticks is about 210 nm as shown in Fig. 2(f).

2.3 Formation mechanism

Based on the above analysis, it is suggested that the formation of corn stick-like H-NaYF₄ nanoparticles undergoes four stages as follows. (1) At the primary reaction stage or without adding NaF solution, Y(OH)₃ nanorods were yielded. (2) With the adding of NaF solution with the Y:F molar ratio of 1:1, yttrium hydroxide fluoride expressed as Y(OH)_{2.14}F_{0.86} was obtained due to the exchanging between hydroxyl and fluoride ions. And Y(OH)₃ nanorods became hollow owing to ion exchange and Ostwald ripening. (3) With the Y:F molar ratio decreased to 1:3, the hydroxyl ions of Y(OH)₃ were replaced completely by fluoride ions, and YF₃ formed. (4)

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