

Reconstructing the Surface Structure of $NaREF_4$ Upconversion Nanocrystals with a Novel K⁺ Treatment

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ABSTRACT: Property of the nanocrystals' surface structure plays a key role in developing novel nanomaterials with high performance and new functionalities. Conventional methods of nanocrystal surface engineering are commonly based on tuning the synthesis reaction parameters or growing core—shell structures, which usually results in increasing the size of the nanoparticles. Here, we report an approach to tailoring the surface crystalline structure of β -NaYF₄ nanocrystals by reheating the nanocrystals in a K⁺-rich environment of the oleic acid-1-octadecene (OA-ODE) system. We found that the crystal surface stability of nanocrystals was decreased in the K⁺-rich solution, which reconstructs the nanocrystals' surface into a porous surface structure. With a systematic design of experiments, the roles of the cations, such as K⁺, K⁺-Gd³⁺, and Na⁺-Y³⁺, are individually identified, which leads to



a reformation of the surface structure of the hexagonal $NaYF_4$ nanocrystal into different forms, e.g., a mesostructured, spherical, and diamond surface. The technique of tailoring the surface crystalline structures will provide new insight for the shape and surface-dependent property studies and luminescence enhancement without a size increase.

INTRODUCTION

Nanocrystals can display a range of anisotropic surface crystalline features by exposing different facets, which leads to different surface charges, surface defects, compositions, and morphologies. The surface properties are usually closely related to the physical properties of nanocrystals, such as luminescence, electronics, magnetics, and catalysis. Engineering a nanocrystal's surface structure, such as the surface nanostructure, surface layer composition, exposed facets, to study these properties in many nanomaterials, has been found helpful toward in-depth understanding of the nanocrystal growth mechanism and new development of novel nanomaterials for broad applications in health, energy, and the environment.^{1–5}

Lanthanide-doped upconversion nanoparticles (UCNPs),⁶ e.g., Yb³⁺, Tm³⁺, or Er³⁺ co-doped NaYF₄ nanocrystals, emitting visible and ultraviolet light under near infrared excitation, have attracted an increasing amount of attention due to their unique optical properties for a broad range of applications, including security ink,^{7,8} super-resolution nanoscopy,⁹ bioimaging,^{10–13} nanomedicine drug delivery,^{11,14–16} and 3D volumetric display.^{17,18} As the surface feature played more important roles in these applications, the surface structure of UCNPs gradually becomes one of the significant factors for their novel function and property. However, the surface structure study is usually due to the lack of a surface structure tailoring technique. With the growing desire to profoundly understand the role of the nanocrystal surface structure, the research focus is gradually shifting from the size and shape control to the surface structure control. Although recent advances in the synthesis of UCNPs have allowed for the fine-tuning of the nanoparticle's size and shape, there is still much room for improvement in the surface structure tailoring technique. So far, conventional methods for tuning the nanocrystals' surface structure are still based on changing the reaction parameters of nanocrystal synthesis, e.g., surfactants, precursor concentration,¹⁹ pH value,²⁰ temperature,²¹ and dopants.²²⁻²⁵ However, changes in these reaction parameters will also vary the number of nuclei, resulting in the size changes of the nanoparticles. Furthermore, the core-shell structure has been adopted to enhance luminescence and to control the morphology. By tuning the shell thickness and the shell growth direction, UCNPs not only demonstrated enhanced luminescence $^{26-29}$ but also that the shape of nanocrystals can be well controlled to produce varied shapes.³⁰ However, the shell growth method inherently generates changes in size, thus making it not well suited for surface structure tailoring. Therefore, a new surface structure tailoring

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Figure 1. Unit cells of β -NaYF₄ (a) and orthorhombic K₂YF₅ (b) (space group: *Pna*21 (33), *a* = 10.791 Å, *b* = 6.607 Å, *c* = 7.263 Å); the scheme (c) describing the formation process of NaYF₄/K₂YF₅ nanocrystals with a porous surface by reheating the NaYF₄ nanocrystals with excess K⁺ in the OA-ODE system at a reaction temperature of 300 °C; the TEM images of the NaYF₄ nanocrystals before (d) and after (e) the reheating treatment with excess K⁺. The scale bar is 100 nm. The X-ray diffraction (XRD) patterns (f) before and after the treatment, which could be well indexed to orthorhombic K₂YF₅ (JCPDS no. 72-2387) and hexagonal NaYF₄ (JCPDS no. 16-0334).

strategy, that is able to maintain the size of nanocrystals, is required.

In our previously reported work,³¹ we found that, in the ripening stage of nanocrystals, the crystal surface of β -NaYF₄ nanocrystals will be less stable with excess Nd³⁺ in the reaction solution. This suggests that reheating nanocrystals in a cationrich solution could be a new route for nanocrystal surface structure engineering. With this knowledge, we conducted a detailed study to ascertain the change(s) and found a way to tailor the surface structure of the β -NaYF₄ nanocrystal. This method is based on the interactions between crystal surface stability and the ion environment changes at the ripening stage of nanocrystals. We systemically studied the surface structure changes of NaYF₄ nanocrystals in a different cation-rich environment. Different alkali metal cations (Na⁺ and K⁺) and rare-earth cations $(Y^{3+} and Gd^{3+})$ were applied to generate the cation-rich environment. By applying K⁺-rich solution, the surface structure of the original β -NaYF₄ nanocrystals was transformed into a mesostructured surface, while by applying K⁺- and Gd³⁺-rich solution, new facets exposing the surface were obtained, forming a diamond shape. Although the surface nanostructure changed, the treated nanocrystals maintained the original size. This surface structure control method not only offers a new route for nanocrystal surface structure engineering and more options for surface-dependent property studies but also provides a novel technique for designing and synthesizing multifunctional heterogeneous nanocrystals.

RESULTS AND DISCUSSION

To systemically investigate the role of different cation-rich environments and avoid interference from original shape differences, we designed the experiment as follows: (i) hexagonal prism β -NaYF₄ nanocrystals were selected to undertake the study (Table S1), which were prepared via our reported high-temperature coprecipitation method (see the Materials and Methods section); (ii) the cations (in excess) selected for treating these β -NaYF₄ prism nanocrystals included (1) K⁺, (2) K⁺ and Gd³⁺, and (3) Na⁺ and Y³⁺; (iii) the reheating treatment involved the mixture of nanocrystals and the selected cations in excess in a solution of oleic acid-1octadecene (OA-ODE); the reaction temperature was varied from 280 to 310 °C, and the reaction time varied from 15 to 60 min (for details, see the Materials and Methods section). (iv) The roles of the different cations (excess) were studied by comparing the shape and surface structure changes of the nanocrystals before and after the treatment.

Reheating Treatment with Excess K⁺. Figure 1 shows the reconstructed surface structure of β -NaYF₄ nanoparticles after a heating treatment with excess K⁺. An average size of circa 45 nm \times 85 nm, as evidenced by the TEM image (Figure 1d), was employed to study the effect of reheating treatment with excess \overline{K}^+ . The TEM image presented in Figure 1e reveals the distinct difference between the original β -NaYF₄ nanoparticles and the resulting nanoparticles after the treatment. The most obvious difference lies in the appearance of a mesostructured architecture. X-ray diffraction analysis was carried out to determine the crystal phases present after the treatment, and the results are shown in Figure 1f. The XRD patterns were in accordance with the reference patterns of the bulk phase orthorhombic K_2YF_5 and β -NaYF₄ nanocrystals, suggesting that the mesostructured nanocrystals are composed of the newly formed orthorhombic K₂YF₅ nanocrystals on the surface and original β -NaYF₄ as the core nanocrystals. The formation of the mesostructured surface should be driven by a unique ion environment of excess K⁺ ions and inherent crystal stability of β -NaYF₄ and K₂YF₅. In the K⁺-rich environment, β -NaYF₄ shows susceptibility to etching as the monomer from crystal dissolution was expensed by K⁺ to form K₂YF₅. The unit cells of β -NaYF₄ and K₂YF₅ in Figure 1a and Figure 1b show their big crystal structure differences, respectively. To further understand the formation process of the mesostructured surface, we monitored the surface reforming process by recording TEM images of the nanocrystals at different treatment times.

As shown in Figure S1, at first, the prism β -NaYF₄ nanocrystals show slight etching at the edge-corner area after 5 min of the reheating treatment. This is due to the higher chemical potential of the ions at the edge-corner area than the other part of the crystal surface. After 15 min of treatment, a "rough" surface layer was observed. We attribute this to the dissolution of NaYF₄ and the formation of K₂YF₅ clusters on the surface of the NaYF₄ nanocrystal. As the reaction time was increased from 15 to 45 min, K₂YF₅ clusters induce the formation of the mesostructured surface at the outer area of the β -NaYF₄ nanocrystal. We further studied the formation of the mesostructured surface at the presented of the mesostructured surface at different reaction temperatures.



Figure 2. Scheme of synthesizing core-shell UCNPs with a hollow surface structure. TEM images of the core NaYF₄:Yb³⁺,Er³⁺ nanocrystals (a), the core-shell NaYF₄:Yb³⁺,Er³⁺/NaYbF₄ nanocrystals (b), the core-shell after 5 min of reheating treatment with excess K⁺ (c), and the core-shell after 20 min of reheating treatment with excess K⁺ (d). XRD patterns of the core NaYF₄:Yb³⁺,Er³⁺ nanocrystals, the core-shell NaYF₄:Yb³⁺,Er³⁺/NaYbF₄ nanocrystals, the core-shell NaYF₄:Yb³⁺,Er³⁺/NaYbF₄ nanocrystals, and the core-shell UCNPs after 20 min of reheating treatment with excess K⁺ (e). The PL spectrum of these UCNP nanocrystals with the same concentration (1 mg/mL) under 980 nm laser excitation at the same power density (10 W/cm²) (f).



Figure 3. (a) Scheme of Gd^{3+} doping concentration of $NaYF_4$ nanocrystals influencing the reheating treatment in excess K⁺ solution. TEM images of different percentages of Gd^{3+} -doped β -NaYF₄ nanocrystals before (b: 0, c: 10, d: 20, and e: 100% NaGdF₄ shell) and after the surface treatment in the conditions of excess K⁺ (0.272 mmol/mL) under 310 °C for 20 min (f: 0, g: 10, h: 20, and i: 100% NaGdF₄ shell). Scale bars are100 nm.

 β -NaYF₄ nanocrystals were treated in a K⁺ ion-rich (0.272 mmol/mL) OA-ODE solution at different temperatures, 300, 310, and 320 °C for 15 min. Figure S2 shows that the formation of K₂YF₅ is accelerated at higher temperature. However, high temperature and long reaction time induce damage to the crystalline structure of the nanocrystals due to over dissolution. Thus, the control of temperature and reaction time is important for engineering the mesostructured surface, especially for smaller particles, since the dissolution rate of the β -NaYF₄ nanocrystal increases as the particle size reduces due to the lower surface stability or higher chemical potential as the particle size reduces.

Hollow Surface Shell Treatment. To demonstrate that the porous surface structure treatment not only works for NaYF₄ nanocrystals, we also apply this method for generating the porous surface for NaYF₄/NaYbF₄ core—shell nanocrystals, as shown in Figure 2. β -NaYF₄:Yb³⁺,Er³⁺ nanocrystals with an average size of 50 nm (as shown in Figure 2a) were synthesized. These core nanocrystals were covered with a NaYbF₄ shell of approximately 10 nm in thickness (as shown in Figure 2b). The contrast between the NaYbF₄ shell and NaYF₄:Yb³⁺,Er³⁺ core was observed in the TEM image. The NaYF₄:Yb³⁺,Er³⁺/NaYbF₄ core—shell nanocrystals were applied for the reheating treatment with excess K⁺ at 300 °C for 20 min. We observed that the morphology of the core—shell



Figure 4. Scheme of applying shell growth and surface structure treatment for fabricating complex nanostructured UCNP nanocrystals. NaYF₄@ NaY_{0.7}Gd_{0.3}F₄ nanocrystals were treated with excess K⁺ (0.272 mmol/mL) under 310 °C for 15 min. TEM images of NaYF₄ core nanocrystals (a), NaYF₄@NaY_{0.7}Gd_{0.3}F₄ core-shell nanocrystals (b), the final product of NaYF₄@NaY_{0.7}Gd_{0.3}F₄@K₂Gd_xY_{1-x}F₅ flower-shape nanocrystals (c, d), and STEM image and elemental mapping images of NaYF₄@NaY_{0.7}Gd_{0.3}F₄@K₂Gd_xY_{1-x}F₅ nanocrystals (e-i). The scale bar in panel (d) is 5 nm, and other scale bars are 50 nm.

UCNPs has an obvious change at 5 min. A thin layer of a more "rougher" surface was formed on the NaYbF4 shell layer of core-shell nanocrystals (Figure 2c), compared with the original smooth surface of the NaYF₄:Yb³⁺,Er³⁺/NaYbF₄ nanocrystals (Figure 2b). After the reheating treatment for 20 min, the rough surface was further transformed into a hollow surface structure, as the TEM image shown in Figure 2d. The big contrast between the solid core and hollow shell was clearly characterized by the TEM image. The XRD patterns of the sample after 20 min of reheating treatment (Figure 2e) were in accordance with the reference patterns of the bulk phase orthorhombic K_2 YbF₅ and β -NaYF₄ nanocrystals, suggesting that the hollow surfaced core-shell nanocrystals are composed of the newly formed orthorhombic K₂YbF₅ nanocrystal on the surface and the original NaYF₄ nanocrystal. Further, we characterized the luminescence property of the hollow surface-structured core-shell nanocrystals under 980 nm laser excitation. Figure 2f shows that the emission intensity of the hollow surface-structured core-shell nanocrystals is slightly lower than the NaYF₄:Yb³⁺,Er³⁺/NaYbF₄ core-shell nanocrystals, but it is above 2 times higher than the emission intensity of the core nanocrystals. It suggests that, through this hollow surface shell treatment, the UCNPs show both a hollow surface structure and enhanced upconversion luminescence. These UCNPs may have a potential value in several applications, for example, as nanoprobes for a biosensor and as luminescent drug carriers for biomedical application.

Tailoring Surface Treatment by Doping Gd³⁺. To tailor the surface nanostructure, we further studied the reheating treatment process with changing the nanocrystals' surface stability. According to Liu et al.'s report,¹⁷ the crystal stability of NaGdF₄ is higher than NaYF₄, which means that the surface stability of the NaYF₄ nanocrystal will increase with more doping percentages of Gd³⁺. Therefore, we synthesized NaYF₄ nanocrystals with different Gd³⁺ doping concentrations to tune the surface stability (Figure 3a). Considering that Gd³⁺ doping will decrease the size of NaYF₄ nanocrystals, we choose a small doping concentration range, doping Gd³⁺ with 0, 10, and 20%, (see Figure 3b-d, respectively) to maintain these samples with the same size. Also, a 100% Gd³⁺ doping sample was prepared by synthesizing NaYF₄/NaGdF₄ core-shell nanocrystals with a similar size, 40-50 nm (see Figure 3e). These samples were treated with excess K⁺ (0.272 mmol/mL) at 310 °C for 20 min. As shown in Figure 3, for 0% Gd³⁺, the β -NaYF₄ nanocrystals (Figure 3f) dissolved very quickly and resulted in the fragmentation of the nanocrystals; 10% Gd³⁺ ion-doped β -NaYF₄ nanocrystals (Figure 3g) were dissolved at a relatively slower rate in comparison to the 0% Gd³⁺-doped sample, but they showed extensive damage with only the inner part of the nanocrystal not showing any extensive damage. Gd³⁺ iondoped β -NaYF₄ (20%) prism nanocrystals (Figure 3h) maintained their initial size; however, the crystal surface changed from the initially smooth to a mesostructured surface. For the 100% Gd³⁺ doping sample, (Figure 3i) the NaYF₄/ NaGdF₄ core-shell nanocrystals mostly maintain the coreshell structure, and only a small amount of nanocrystals appears partly damage at the edge, at which may lack the NaGdF₄ shell protection. These results fully demonstrate that selecting rational doping concentration of Gd³⁺ ions would have β -NaYF₄ nanocrystals owning proper crystal surface stability to achieve the relevant surface structure in a K⁺ ionrich environment and to allow more complex surface structures to be designed and tailored for new functionalities.

More complex nanostructured nanocrystals can be synthesized by combining the epitaxial shell growth technique and the surface structure tailoring method presented here. As an example, we show here that the synthesis of the flowerstructured heterogeneous nanocrystals, β -NaYF₄@ NaY_{0.7}Gd_{0.3}F₄@K₂Gd_xY_{1-x}F₅, were produced by adopting both the epitaxial shell growth and treatment in a K⁺ ionrich environment. First, β -NaYF₄ prism nanocrystals with an average particle size of 40 nm (Figure 4a) were prepared. The



Figure 5. Scheme of tailoring the NaYF₄ nanocrystal's surface structure via reheating treatment with excess K⁺ and Gd³⁺. TEM images of different sized NaYF₄ nanocrystals, 20 (a), 30 (b), 40 (c), and 80 nm (d) before and after (e: 20, f: 30, g: 40, and h: 80 nm) the reheating treatment with excess K⁺ (0.272 mmol/mL) and Gd³⁺ (0.036 mmol/mL) at 300 °C for 60 min (scale bar: 100 nm). STEM image (i) and an elemental mapping image of 30 nm NaYF₄ nanocrystals after the reheating treatment with excess K⁺ and Gd³⁺, (j) the element of Y, (k) the element of Gd, and (l) the element of Na (the scale bars are 25 nm).

nanoparticles were covered with a thin shell whose composition was 30% Gd³⁺-doped β -NaYF₄. The 30% Gd³⁺doped β -NaYF₄ shell is more stable than the β -NaYF₄ core in the K⁺ ion-rich environment. Then, the β -NaYF₄@ NaY_{0.7}Gd_{0.3}F₄ core-shell nanoparticles (Figure 4b) were treated in the K⁺ ion-rich environment at 310 °C for 15 min. As shown in Figure 4c, the core-shell nanoparticles underwent a change in their morphology from a prism to flower shape. The high-resolution TEM image (Figure 4d) shows that the flower shape is formed by cutting off the six edge-corner areas from the original prism nanoparticles. This is in agreement with the result in Figure S1, which shows that the dissolution of β -NaYF₄ nanoparticles starts at the edge-corner area of the prism nanoparticles. The elemental mapping results (Figure 4e-i) clearly show that Na⁺ ions are found in the core, whereas K⁺ and Gd³⁺ ions are found in the shell. This provides the evidence supporting the nanostructure morphology observed in the TEM images. The flower nanostructure possesses a hollow surface; thus, the Gd³⁺ ions will distribute in the outer layer of the nanocrystals, which will endow the nanostructure with both magnetic and fluorescence properties that may be used for drug delivery and bioimaging applications.

Mechanism of the Surface Structure Tailoring. The crystal stability of nanoparticles changes with the varied cationrich environment. To reveal the mechanism of the surface structure tailoring by the reheating treatment, we further systemically studied the reheating treatment with different cation-rich solutions, such as excess K⁺ and Gd³⁺, excess Na⁺ and Y³⁺ (Figure S3), and excess K⁺ and Y³⁺ (Figure S4). Figure S3 shows three typical surface structures obtained, a spherical surface, mesostructured surface, and passive facet tuning, which were realized from the reheating treatment with excess Na $^{\rm +}$ and Y $^{3+}$, excess K $^{\rm +}$, and excess K $^{\rm +}$ and Gd $^{3+}$, respectively.

Figure S3a,b shows the TEM image results of treating the 45 nm \times 60 nm hexagonal prism NaYF₄ nanocrystals with excess Na⁺ (0.091 mmol/mL) and Y^{3+} (0.036 mmol/mL). After the reheating treatment, the original flat surface of the β -NaYF₄ prism nanocrystal, presenting (100) planes and (001) planes, was converted to spherical surfaces. This notable change in the surface morphology suggests an intraparticle ripening process as a consequence of the reheating treatment. It is worth to mention that intraparticle ripening that transfers the ions from one region to other regions of the same particle is different from the typical interparticle Ostwald ripening that is responsible for the growth of larger nanoparticles at the expense of small nanoparticles. For the synthesis of CdSe NPs, Peng et al., found that intraparticle ripening occurs preferentially at a relatively higher monomer concentration, while interparticle ripening is more likely to transpire at lower monomer concentration.³² With regard to the Na⁺- and Y³⁺rich environment, although there is no direct addition of F⁻ ions into the reaction mixture, a relatively higher concentration of the monomer (NaYF₄) is presented at the nanocrystal surface resulting from the dissolution of the nanocrystal. The increase in concentration of the NaYF₄ monomer is due to the diffusion of the F⁻ ions from the surface of the crystal to the solvent mixture that contains the cations, Y3+ and Na+, providing excellent conditions for the formation of the monomer. In the other case, Rinkel et al. reported that β -NaYF₄ NPs with a narrow size distribution upon reheating in an OA-ODE mixture without any precursors resulted in a broad size distribution of nanoparticles. This is because the interparticle Ostwald ripening process occurs when the

concentration of monomers is low.^{33–35} We observed a similar result of interparticle Oswald ripening in the case of reheating β -NaYF₄ in a solution containing an excess of K⁺ and Y³⁺ ions (Figure S4). We also observed that the size of prism β -NaYF₄ NPs decreased gradually, and the size distribution of the nanoparticles increased as a function of reaction time in a K⁺- and Y³⁺-rich environment. Due to the absence of Na⁺ and F⁻ ions, which results in the presence of a lower monomer concentration, interparticle ripening is favored. It is worth noting that, following a 30 min treatment, the overall size of the nanocrystals and a number of clusters can be observed (see Figure S4d). This suggest that NaYF₄ is less stable in the excess K⁺ and Y³⁺ ion environment.

Figure 5 shows that the different sized NaYF₄ nanocrystals, 20, 30, 40, and 80 nm, were treated in the excess K^+ (0.272 mmol/mL) and Gd³⁺ (0.036 mmol/mL) ion environment at 300 °C for 40 min. Their TEM results reveal that all these samples maintain the uniformity in size and shape (see Figure S6), which demonstrates that the excess K^+ and Gd^{3+} ion environment induced an intraparticle ripening process. After the reheating treatment with excess K⁺ and Gd³⁺ ions, 80 nm β -NaYF₄ prism nanocrystals basically maintained their initial shape and size (Figure S61), which is in contrast to the treatment with excess K^+ - Y^{3+} or excess K^+ ions. From the side view of the treated β -NaYF₄ nanocrystals (see Figure S3g), we found that the nearly round surface presenting (001) and (100) planes of original β -NaYF₄ was transformed into a sharp corner-edge surface. It suggests that β -NaYF₄ shows higher stability in an excess K⁺ and Gd³⁺ ion environment than in an excess K⁺ ion environment. This may be attributed to the fact that a more stable NaGdF₄ layer formed via cation exchange between Gd³⁺ and Y³⁺ on the crystal surface, which efficiently inhibited the crystal dissolution. The nanocrystals with smaller sizes (40, 30, and 20 nm) have a different behavior in the treatment than the larger-size nanocrystals (45 nm \times 80 nm). Figure 5e–g shows that these smaller-size β -NaYF₄ nanocrystals were transformed into a diamond-like shape, and the exposed facets tuned from (100) and (001) planes to other planes, which are more stable. From the elemental mapping image of the β -NaYF₄ nanocrystals after the treatment, as shown in Figure 5i–l, we observed that Gd³⁺ ions distribute at the outer layer of the diamond-shape β -NaYF₄ nanocrystals, which suggests that a more stable NaGdF₄ shell formed in the excessive K⁺ and Gd³⁺ ion environment. The transformation process of 30 nm prism β -NaYF₄ nanocrystals was recorded by taking TEM images at different reaction times (see Figure S5). From Figure S5a,b, we observe that the shape transformation from prism to diamond is terminated within 10 min and then the β -NaYF₄ nanocrystals do not change neither with respect to size or shape for a time period of 20-50 min (see Figure S5c-f). It suggest that β -NaYF₄ nanocrystals own a much stable surface after being treated in an excess K⁺ and Gd³⁺ ion environment, which may bring a positive effect to the upconverting luminescence property.

To observe the effect to the upconverting luminescence property, we compared the emission spectrum of 40 nm NaYF₄:20% Yb³⁺, 4% Er³⁺ nanocrystals before and after the reheating treatment with excess Gd³⁺ and K⁺ (Figure 6). The data shows that a luminescence enhancement of about 1.7 times was obtained from this treatment. Also, the luminescence lifetime at the green light emission band of the UCNPs was increased after the reheating treatment with excess Gd³⁺ and



Figure 6. Upconversion luminescence enhanced by facet tuning treatment with excess K^+ and Gd^{3+} . TEM images (a, b), emission spectra (c), and luminescence decay curve at 524 (d) and 545 nm (e) NaYF₄:20%Yb³⁺, 4% Er²⁺ nanocrystals before and after the reheating treatment with excess K^+ and Gd^{3+} . Both samples are tested in 1 mg/ mL of cyclohexane solution under a 980 nm laser with the same power density of ~10 W/cm².

K⁺. The value of lifetime at the 524 nm emission band increased from the original 150.15 \pm 0.18 to 186.87 \pm 0.24 μ s, and the value of lifetime at the 545 nm emission band increased from the original 178.71 \pm 0.25 to 197.13 \pm 0.16 μ s after the reheating treatment. A possible explanation of the luminescence property changes is that a thin inert shell formed on the nanocrystal surface during the intraparticle ripening process, which contributes to the passivation of the crystal surface resulting in decreasing the number of surface defects and protecting the nanocrystals from surface quenching. This explanation is supported by the elemental mapping image (Figure 5k), showing that Gd existed in the outer layer of the treated NaYF₄ nanocrystals. It is worth noting that the reheating treatment maintained the original average size of nanocrystals, although the luminescence enhancement via this reheating treatment is not extreme compared with other methods, like shell coating.

CONCLUSIONS

In summary, we studied the effects of different cation-rich environments containing excess K⁺ and K⁺-RE³⁺ on the surface structure variations of the β -NaYF₄ nanoparticles. The excess cations in the reheating solution of β -NaYF₄ nanoparticles can create a monomer-rich environment together with the dissolved F⁻ ions; thus, intraparticle ripening occurs to change the morphology of the β -NaYF₄ nanoparticles as well as the composition. We observed a significant change on the shape, surface structure, and exposed facet of nanoparticles by applying different cation-rich environments in the reheating treatment. This versatile approach for β -NaYF₄ nanoparticles enables tailor surface structures to enrich the complexity of nanoparticles and unravel the surface-dependent optical properties for further achieving luminescence enhancement. Also, this work offers a method of generating a mesostructured surface of UCNPs, which can be used for the purpose of multimodal bioimaging and drug delivery. Coordinating with the epitaxial shell growth technique, this method may be a useful tool for designing and fabricating a novel hybrid or heterogeneous nanostructure.

MATERIALS AND METHODS

Yttrium chloride hexahydrate (YCl₃· $6H_2O$, 99.99%), ytterbium chloride hexahydrate (YbCl₃· $6H_2O$, 99.998%), gadolinium chloride hexahydrate (ErCl₃· $6H_2O$, 99.9%), potassium hydroxide (KOH, 99%), sodium hydroxide (NaOH, 98%), ammonium fluoride (NH₄F, 99.99%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), and all reagents were used as received without further purification.

Synthesis of β -NaYF₄ Cores. The β -NaREF₄ core nanocrystals with varied sizes and dopants were synthesized by a modified reported method.³⁶ In a typical procedure, methanol solution (2 mL) of YCl₃ (1.0 mmol) was mixed with OA (6 mL) and ODE (15 mL) in a 100 mL three-neck round-bottom flask. The mixture solution was degassed under Ar flow during the heating up to 150 °C followed by 30 min of isothermal reaction to form a clear solution and then cooled down to room temperature. Methanol (10 mL) containing NH₄F (4 mmol) and NaOH (2.5 mmol) was added into the flask and then stirred for 60 min. The solution was slowly heated up to 110 °C and kept at 110 °C for 30 min to completely remove methanol and any residual water. Then, the reaction solution was quickly heated up to 310 °C and kept isothermally for 1.5 h before being cooled down to room temperature. Ethanol was added to precipitate the nanocrystals, which were washed four times with cyclohexane, ethanol, and methanol. The obtained pure NaYF4 nanocrystals were redispersed in cyclohexane (8.5 mg/mL) for further reheating treatments.

The Reheating Treatment with Excess K⁺ for Porous Surface Structure. In a typical protocol, methanol solution (3 mL) of KOH (3 mmol) was mixed with 3 mL of OA and 8 mL of ODE in a 50 mL three-neck round-bottom flask. The mixture solution was degassed under Ar flow during the heating up to 80 °C followed by 20 min to remove methanol. Then, 2 mL of $NaYF_4$ core nanocrystals in cyclohexane (8.5 mg/mL) was added into the flask and stayed for 10 min to remove cyclohexane. The temperature was further increased to 120 $^\circ \mathrm{C}$ and kept for another 10 min. Then, the reaction solution was heated up to 310 °C with a rate of 10 °C/min and kept isothermally for 15 min. The reaction solution was naturally cooled to 100 °C, and 4 mL of OA was added into the flask for dissolving the excess oleates in the solution. Then, the reaction solution was further cooled to room temperature. Centrifugal precipitation of the product was performed at 9000 rpm for 10 min, and then, the precipitate was washed with cyclohexane, ethanol, and methanol three times.

The Reheating Treatment with Excess Gd³⁺ and K⁺ for Diamond Shape. In a typical protocol, methanol solution (1 mL) of GdCl₃ (0.4 mmol) was mixed with 3 mL of OA and 8 mL of ODE in a 50 mL three-neck round-bottom flask. The mixture solution was degassed under Ar flow during the heating up to 150 °C followed by 30 min of isothermal reaction to form a clear solution and then cooled down to 70 °C temperature. Methanol solution (3 mL) of KOH (3 mmol) was injected into the flask. After staying for 10 min, 2 mL of NaYF₄ core nanocrystals in cyclohexane (8.5 mg/mL) was added into the flask, stayed for 10 min to remove cyclohexane, and heated up to 120 °C for another 10 min. Then, the reaction solution was quickly heated up to 310 °C and kept isothermally for 1 h. The reaction solution was naturally cooled to 100 °C, 4 mL of OA was added into the flask, and then, the reaction solution was cooled to room temperature. Centrifugal precipitation of the product was performed at 9000 rpm for 10 min, and then, the precipitate was washed with cyclohexane, ethanol, and methanol three times.

Characterizations. Standard transmission electron microscopy (TEM) measurements were performed using Philips CM10 TEM with an Olympus Sis Megaview G2 digital camera. The samples were prepared for TEM analysis by placing a drop of a dilute suspension of nanocrystals onto carbon-coated copper grids (300 meshes), and

high-resolution transmission electron microscopy (TEM) measurements were performed with aberration-corrected analytical transmission electron microscopy (TEM; JEOL ARM-200F) operated at 80 kV. High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images and their corresponding elemental mapping images were collected with the same TEM images equipped with a Centurio SSD energy-dispersive X-ray spectroscopy (EDS) detector set at 77 K. Powder X-ray diffraction (XRD) patterns were obtained on a PANalytical X'Pert Pro MPD X-ray diffractometer using Cu K α 1 radiation (40 kV, 40 mA, λ = 0.15418 nm). The XRD samples were prepared by repeatedly drying drops of nanocrystal dispersions in cyclohexane cast on a zero-background silicon wafer.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c04956.

Morphology information table of all nanocrystals used (Table S1) and additional TEM figures, as described in the text (Figures S1-S6) (PDF)

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Notes

The authors declare no competing financial interest.

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