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Branched $NaYF_4$ Nanocrystals with Luminescent Properties

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In this article, branched $NaYF_4$ nanocrystals have been successfully synthesized via a simple hydrothermal method. On the basis of the analysis of HRTEM and TEM images, the growth modes of the branched structure and further branching behavior have been proposed. The up- and down-conversion luminescence of branched $NaYF_4{:}Er^{3+}/Yb^{3+}$ and $NaYF_4{:}Eu^{3+}$ have been characterized. Multiarmed $NaYF_4$ phosphors can be introduced into polystyrene to form composite luminescent polymers because of its special geometrical shape. In conclusion, the luminescent branched particles should be of wide potential application as building blocks in the future nanoscience and nanotechnology.

Introduction

Future nanodevices require a high diversity of building blocks unique in both function and structure.[1,2] Branched structures on the nanometer scale have received much consideration in recent years because of their intrinsic electronic, magnetic, photonic, and catalytic properties and their potential to be crucial building blocks for future nanodevices by a "bottom-up" self-assembly process.[3,4] The appearance of branched structures greatly increases the diversity of building blocks. Branching and further branching of nanocrystals can effectively increase the structural diversity of building blocks and create more complex structural architectures.[5]

Until now, branched nanocrystals of metal, metal oxide, and semiconducting materials have been successfully synthesized.[6−17] Branched semiconducting nanocrystals, such as CdS, CdSe, and ZnO, have been well researched for several years.[9−11] These kinds of branched structures share a typical character "polymorphism". They usually have an isotropic core and anisotropic arms, which require the coexistence of two different kinds of crystal structures in the same nanocrystals. The other kind of branched structure that has been developed is noble metal branched nanocrystals with no polymorphism. For example, branched gold nanocrystals with face-centered cubic structure have been synthesized by using CTAB as a regulating reagent in liquid medium.[6] These different growth modes enabled the controlled growth of nanocrystal building blocks with complex topologies.

$NaYF_4$, an excellent luminescent host material, has many applications in lighting and display devices, optical telecommunications, and solid-state lasers because of its high radiative emission rate, narrow emission bands, and stability and durability under high temperature and intense excitation energy.[18−20] $NaYF_4$ usually adopts face-centered cubic or

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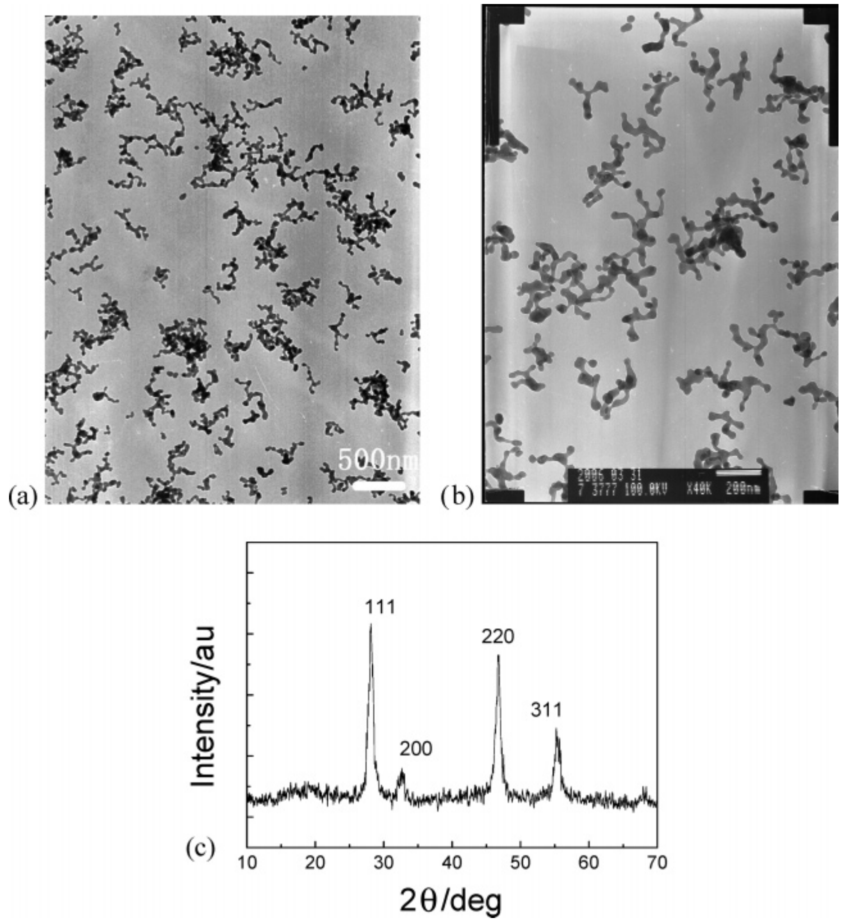

Figure 1. (a and b) TEM images of obtained product. (c) XRD pattern of obtained product.

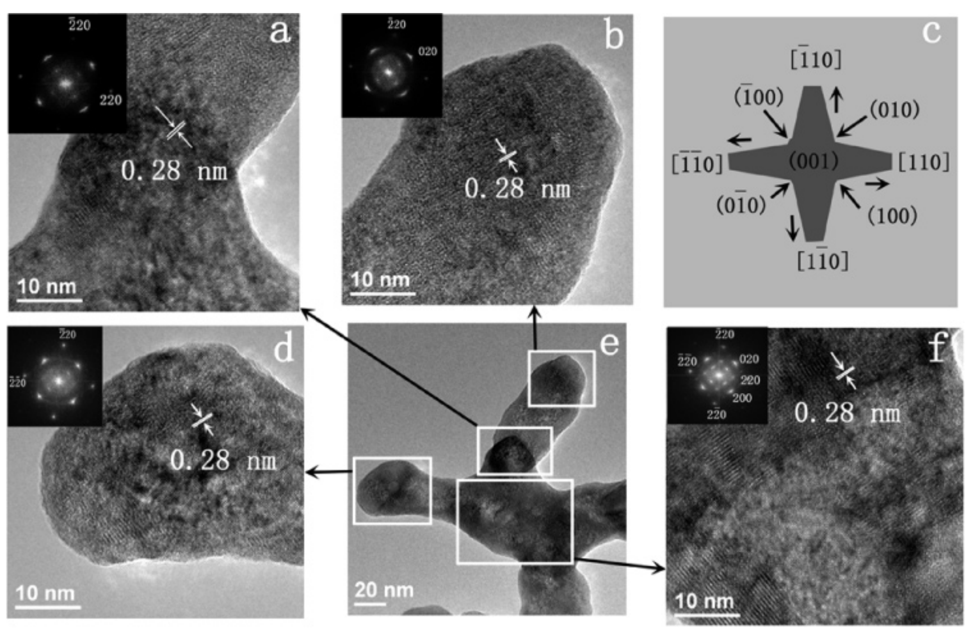

Figure 2. HRTEM images of (e) a single tetrapod, (a, b, d, and f) different parts of the single tetrapod (insert, corresponding Fuorier transform electron diffraction pattern) and (c) a diagram illustrating the growth mode of the tetrapod.

hexagonal crystal structures, which indicate that these luminescent materials may grow into branched morphologies following either polymorphism or no polymorphism modes.

Since the luminescent properties of lanthanide-doped phosphors are host sensitive and can be tuned by adjusting the crystal fields of the phosphors, synthesis of lanthanide-doped NaYF$_4$ phosphors with novel morphology, such as branched structures, may lead to the discovery of novel size-depended

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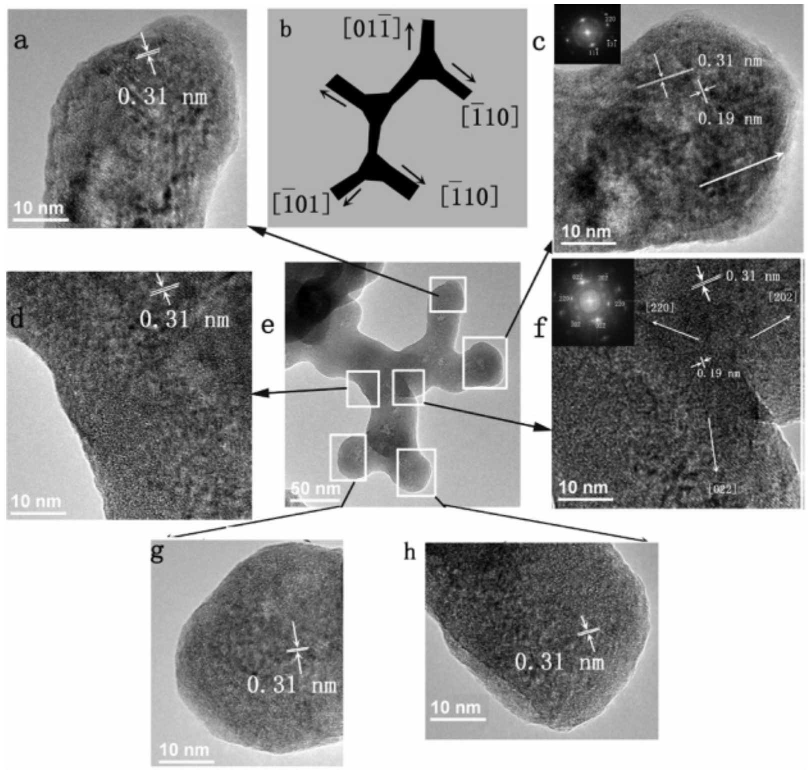

Figure 3. HRTEM images of (e) a single tripodlike nanocrystal, (a, c, d, f, g, and i) different parts of the tripodlike nanocrystal and a (b) digram illustrating the growth mode of the tripodlike nanocrystal.

luminescent properties.[21−25] In addition, branched nanostructures can be mixed with other materials to form multifunctional complex materials[26,27] because of its special geometrical shape. For example, multiarmed $NaYF_4$ phosphors can be introduced into polystyrene to form composite luminescent polymers. Therefore, the synthesis of branched $NaYF_4$ nanocrystals should be of great significance for both research and applications.

Experimental Section

In a typical synthesis, 3.0 g of CTAB, 20 mL of methanol, and 10 mL of water were mixed together; then, 1 mL of 0.5 M $Y(NO_3)_3$ and 3 mL of 1 M NaF were added. Finally, the mixture was transferred to a 40 mL autoclave, which was sealed and heated at 150 °C for about 24 h.

The sample obtained was characterized on a Bruker D8-Advance X-ray powder diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The size and morphology of the nanocrystals were determined by a JEOL JEM-1200EX transmission electron microscope (TEM) at 100 kV and a Tecnai G2 F20 S-Twin high-resolution transmission electron microscope (HRTEM) at 200 kV. Fluorescent spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer. Up-conversion fluorescent spectra were obtained with the LS-50B fluorescence spectrophotometer (Perkin-Elmer Corp., Forster City, CA) with an external 0−800 mW adjustable laser (980 nm, Beijing Hi-Tech Optoelectronic Co., China) as the excitation source, instead of the Xenon source in the spectrophotometer, and with an optic fiber accessory.

Results and Discussion

Branched $NaYF_4$ nanocrystals have been fabricated by using CTAB as regulating agents to facilitate branched growth in a methanol/water system. XRD analysis of obtained products revealed that the product crystallized in a cubic structure of $NaYF_4$. The XRD pattern shown in Figure 1c could be indexed as arising from the cubic phase (JCPDS no. 77-2042) with lattice constant $a = 5.470$ Å. TEM images shown in Figure 1a and b displayed the branched structure of the obtained nanocrystals. Careful observation revealed that the morphologies of nanocrystals were diversity. It could be seen that the nanocrystals were composed of some simple multiarmed morphologies, such as tripod and tetrapod, and other more complicated multibranched structures.

A typical tetrapodlike nanocrystal is shown in Figure 2e. HRTEM images (Figure 2a, b, d, and f) of different parts of the nanocrystal provided more detailed information about the branched structure. The lattice planes continuously extending in each part of the nanocrystal showed the good crystallinity of the nanocrystal. The distance of the lattice planes extending on the same direction in each part of the nanocrystal had been calculated to be the same (0.28 nm), which could be assigned to the {200} planes of cubic phase $NaYF_4$. It also revealed the branched nanocrystal was a single

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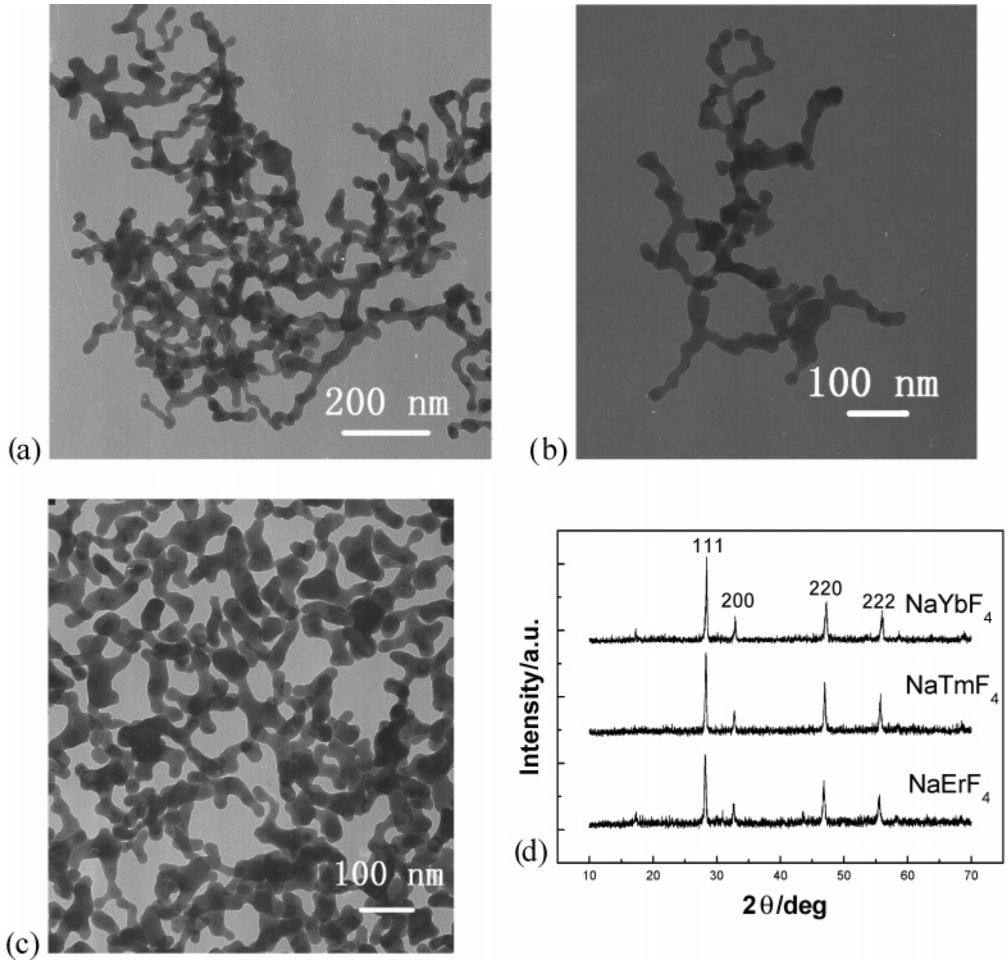

Figure 4. TEM images and XRD patterns of Branched structures of $NaLnF_4$ (Ln = Er, Tm, Yb) synthesized via the same synthetic route for branched $NaYF_4$ nanocrystals. (a) TEM image of branched $NaErF_4$ nanocrystals. (b) TEM image of branched $NaTmF_4$ nanocrystals. (c) TEM image of branched $NaYbF_4$ nanocrystals. (d) XRD patterns of branched structures of $NaLnF_4$ (Ln = Er, Tm, Yb).

crystal. The observation and analysis of the lattice planes also reveal the epitaxial growth direction is along <110> (see Supporting Information). The inserts showed that the corresponding Fuorier transform electron diffraction patterns of the nanocrystal with spots indexed as face-centered cubic structure. From the SAED, it can be seen that the growth directions of the four arms are consistent with the directions of some diffractional dots, whose orientation index can be appointed to $[\bar{2}\bar{2}0]$, $[\bar{2}20]$, $[2\bar{2}0]$, and [220], respectively. Therefore, it could be concluded that the epitaxial growth direction of the four arms is along $[\bar{1}\bar{1}0]$, $[\bar{1}10]$, $[1\bar{1}0]$, and [110] planes, respectively. The nanocrystal could be viewed like as being flat on its (001) plan with four arms stretching in the direction of $[\bar{1}\bar{1}0]$, $[1\bar{1}0]$, $[\bar{1}10]$, and [110]. The result was in agreement with with the geometry of the tetrapod.

A similar analysis had been carried out on a tripodlike nanocrystal. As shown in Figure 3, the lattice planes extending in each part of the nanocrystal were continuous, and the distance of the exposed lattice planes of nanocrystal extending on the same direction had been calculated to be the same (0.31 nm, {111} crystal planes). The Fourier transform electron diffraction pattern of Figure 3c indicated the longitudinal axis of the arm was $[\bar{1}10]$ (the growth direction of this arm is parallel to the direction of diffractional dot $[\bar{1}10]$). The analysis on the electron diffraction patterns of different parts of the multiarmed nanocrystal and HRTEM of arms of the branched nanocrystal also revealed the preferential growth direction of other arms was along the $[\bar{1}01]$ and $[01\bar{1}]$ planes (Supporting Information S5). The (111) plane was found to be perpendicular, by calculation, to the plane defined by $[\bar{1}10]$, $[\bar{1}01]$, and $[01\bar{1}]$. Therefore, the tripodlike nanocrystal was flat on its (111) plan with three arms stretching in the direction of $[\bar{1}10]$, $[\bar{1}01]$, and $[01\bar{1}]$.

It is worth noting that multibranching behavior was quite common in our system. As shown in Figure 3e, the tripodlike nanocrystal had obviously further branching at the end of each arm. For the polymorphism-branched structure, such as CdS and CdSe, the precondition of further branching was nucleation of a cubic phase after initial arm growth to lead another period of arm growth, which was hard to control in both kinetics and thermodynamics. For $NaYF_4$ branched structures, both the core and arms belonged to the cubic phase; therefore, further branching could be easily initiated by the outer environment, such as the surfactant, micelles, regulating reagents, the concentration of reactants, and so on.

The formation of branched structure was believed to have close relationship with the high concentration of CTAB in the reaction system. When the other experimental parameters were kept unchanged, only spheres or rods of $NaYF_4$ were formed in absence of CTAB. The mixture of a few

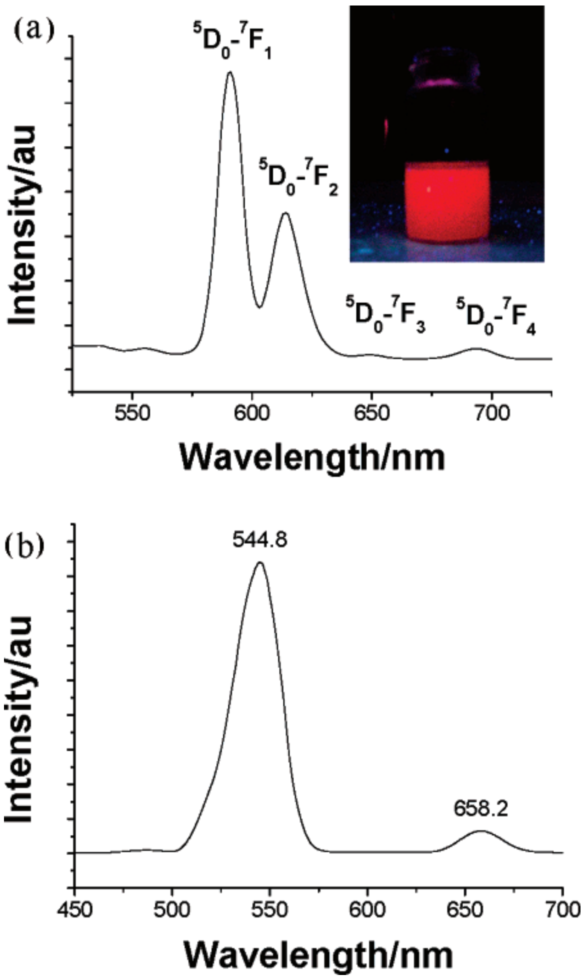

Figure 5. (a) Emission spectra of branched $NaYF_4:Eu^{3+}$ phosphor; excited wavelength = 375 nm. Inset: Digital camera image of $NaYF_4:Eu^{3+}$ phosphor under ultraviolet radiation. (b) Emission spectra of branched $NaYF_4:Er^{3+}/Yb^{3+}$ phosphor under 980 nm laser source.

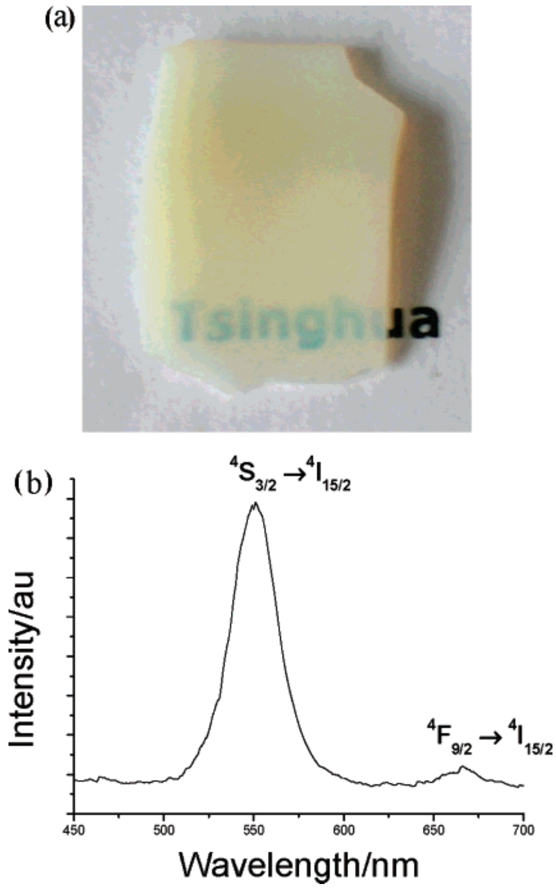

Figure 6. (a) Digital camera image of $NaYF_4$ and polystyrene composite. (b) Emission spectra of $NaYF_4:Er^{3+}/Yb^{3+}$ phosphor and polystyrene composite under a 980 nm laser source.

multiarmed nanocrystals and a majority nanorods formed at the low concentration of CTAB. The adsorption effect of CTAB and methanol on different crystal planes and the influence of micelles formed by CTAB were believed to be main factors to influence the formation of the branched structures. When ethanol was used to replace methanol, a mixture of only multiarmed and rodlike nanocrystals was obtained. This phenomenon revealed that MeOH can favor the formation of multiarmed nanocrystals. Similar phenomena have been observed by Chen et al. in the synthesis of a face-centered cubic Au branched structure in CTAB system.[6]

In addition, a mixture of multiarmed nanocrystals and nanorods can be obtained by adjusting the synthetic conditions (protracting the reaction time or increasing the input of NaF). SAED patterns and XRD pattern analysis revealed that the rods belonged to hexagonal phase of $NaYF_4$, while the multiarmed nanocrystals adopted a cubic phase. (Figure S1) This phenomenon further indicated that the growth of branched cubic-phase $NaYF_4$ nanocrystals should follow the no polymorphism mode, similar to that of the multiarmed Au nanocrystals.

For the similarity of lanthanide elements on the ion radii, the crystal structure of $NaLnF_4$, especially for the heavy rare earth elements, such as Er, Tm, and Yb, have great analogy with the crystal structure of $NaYF_4$. Branched structures of $NaLnF_4$ (Ln = Er, Tm, Yb) have been successfully synthesized by using the same synthetic route for branched $NaYF_4$ nanocrystals. (Figure 4) However, for the larger lanthanide ions (La, Pr, Sm), only LnF_3 was obtained in our synthetic condition. And TEM observation of the products shows that there were no branched structures formed. (Figure S2) The results further confirmed the crystal structure of cubic $NaYF_4$ is important for the formation of branched structure.

As an outstanding host material, $NaYF_4$ nanocrystals doped with lanthanide ions can bring various luminescent properties. The most frequently used down-conversion ion Eu^{3+} and up-conversion ion Er^{3+}/Yb^{3+} were selected to dope into the branched $NaYF_4$ nanocrystals to study the luminescent behavior of branched $NaYF_4$ phosphor. Doped samples were prepared by the same synthetic procedure, except for adding 10% (total molar ration) Yb^{3+} and Er^{3+} or Eu^{3+}, in Y^{3+} at the beginning stage. The morphology of doped $NaYF_4$ had no obvious difference with undoped $NaYF_4$ branched nanocrystals. Red light could be observed by naked eyes when the NaYF4:Eu^{3+} nanocrystals were excited by ultraviolet radiation. Digital camera image of luminescence from NaYF4:Eu^{3+} was shown in the inset image of Figure 5a. The emission spectra of NaYF4:Eu^{3+} phosphor was recorded from 500 to 750 nm. The emission peaks could be assigned to the typical ${}^5D_0-{}^7F_J$ ($J = 1, 2, 3, 4$) transition of Eu^{3+} ion.

The peak located at 590 nm (corresponding to $^5D_0-^7F_1$ magnetic dipole transition) is stronger than the peak located at 614 nm (corresponding to $^5D_0-^7F_2$ electric dipole transition). As the relative strength of these two typical peaks of Eu^{3+} ion was strongly depended on the crystal field, it could be figured out the high symmetry of the crystal field Eu^{3+} ion located, which was according with the crystal structure of the branched $NaYF_4$ nanocrystals.

Figure 5b showed the up-conversion emission spectra of $NaYF_4$:Yb^{3+}/Er^{3+} under a 980 nm laser source. The peaks at 545 and 648 nm could be assigned to the typical $^4S_{3/2}-^4I_{15/2}$ and $^4F_{9/2}-^4I_{15/2}$ transitions, respectively. The peak at 545 nm was much stronger than the 648 nm emission, indicating good monochromaticity of the NaYF4:Er^{3+}/Yb^{3+} phosphor.

The branched nanocrystals with luminescence properties were good candidates to be compounded with other materials to form multifunctional complex materials for its unique structure. Here, branched $NaYF_4$:Er^{3+}/Yb^{3+} phosphors have been introduced into polystyrene to develop a novel luminescence lanthanide-doped polymer. Figure 6a showed a digital camera image of $NaYF_4$ and polystyrene composite. The up-conversion luminescent of $NaYF_4$ is maintained in the composite. Under a 980 laser source, the composite can emit green lights (Figure 6b) which can be observed by the naked eye. (Detailed information provided in Figure S3.)

Conclusion

In conclusion, branched nanocrystals of cubic $NaYF_4$ have been successfully synthesized via a simple hydrothermal method. The growth modes of the branched structure and further branching behavior have been discussed. The luminescence of lanthanide ion-doped branched $NaYF_4$ have been characterized. An example of branched $NaYF_4$ applied in the polymer composite was depicted. The branched particles should be of wide potential application as building blocks in future nanoscience and nanotechnology.

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Supporting Information Available: TEM images and XRD patterns of multiarmed nanocrystals, nanorods, and products with larger lanthanide ions, SEM image of the composite, HRTEM images of a single tetrapod, and discussions. This material is available free of charge via the Internet at http://pubs.acs.org.

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