Synthesis of triple-doped core/shell/shell upconversion nanoparticles

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Abstract. A novel triple-doped core/shell/shell NaGdF4/NaGdF4:Yb,Tm,Nd/NaGdF4 upconversion nanoparticles (UCNPs) has been designed and synthesized by thermal decomposition. Yb3+ and Nd3+ were used as sensitizers and Tm3+ with multi-level was activators. Three-layout nanoparticles exhibits 1.5 times strong emission than two-layout structure. The UC spectrum exhibits two bands centered at 525–535 and 578–585 nm from Nd3+, corresponding to 5G7/2→4I9/2 and 5G7/2→4I11/2 transitions after excitation at 800 nm. These nanocrystals are promising an attractive luminescent biomarkers for biological and magnetic resonance imaging.

1. Introduction
Over the past few years, rare earth doped upconversion nanocrystals have been extensively studied[1-5]. In photoluminescence, upconversion luminescence is an anti-stokes phenomenon that long-wave radiation with low energy absorption is converted into short-wave radiation with high energy[6-7]. Rare earth ions are widely used in upconversion luminescent materials due to their abundant energy level structure, usually composed of activators, sensitizers and matrix materials. Activators provide luminescent centers with abundant energy levels. The commonly used rare earth ions are Er3+, Ho3+ and Tm3+ which have multi-level. Sensitizers absorb energy and transfer it to the activator ions, sensitize the luminescence of other rare earth ions, and improve the luminescence properties. Commonly used sensitizers are Yb3+ and Nd3+[8]. The rare earth-converted nanocrystals have the advantages of high sensitivity, low toxicity, high chemical stability, etc., but the fluorescence intensity is low, which greatly limits its development[9-10]. Core/shell upconversion nanomaterials can suppress the fluorescence quenching on the surface of the materials, fill the lattice defects of incomplete coordination of rare earth ions, and thus improve the fluorescence intensity of rare earth upconversion nanomaterials[11-12].

In the present study, we successfully prepared the triple-doped core/shell/shell structure of NaGdF4/NaGdF4:Yb,Tm,Nd/NaGdF4 nanocrystals by thermal decomposition in the presence of oleic acid and 1-octadecene[13]. We chose NaGdF4 as the host material because of its high upconversion efficiency. In the middle layer, Yb3+ ions can play the part of energy-transfer bridging ions between sensitizer Nd3+ ions and energy acceptor Tm3+ ions[11]. Nd3+ has two NIR excitation bands at 525 and 590 nm, and transitions from 5G7/2 to 4I9/2 and 5G7/2 to 4I11/2, respectively[14-15]. It was worth noting

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that we found that UCNPs of the three-layer core/shell/shell structure had 1.5 times the fluorescence intensity of the two-layer structure.

2. **Experiment**

2.1 The experimental materials:
Gd$_2$O$_3$, Yb$_2$O$_3$, Tm$_2$O$_3$, Nd$_2$O$_3$ (99.9%, Sigma), oleic acid (OA; 90%, Sigma), 1-octadecene (ODE; >90%, Sigma), cyclohexane (>90%, Sigma), Anhydrous ethanol (>99.5%, Sigma), Anhydrous methanol (>99.5%, Sigma), Hydrochloric acid (AR), rare-earth chlorides are prepared by our group.

2.2 Synthesis of rare-earth chlorides:
At first, the molar ratio of Gd$_2$O$_3$, Yb$_2$O$_3$, Tm$_2$O$_3$, Nd$_2$O$_3$ is 80.5%:18%:0.5%:1%, which are stirred in hydrochloric acid solution from turbid to a clear solution. The solution is evaporated and crystallized under 100 degrees Celsius to obtain dried rare-earth chlorides.

2.3 Synthesis of NaGdF$_4$:
At room temperature, 1mmol GdCl$_3$, 6mL OA, 15mL ODE were put into a 100mL three-necked flask. The flask was put in the heating mantle and the solution was heated for 30 min at 160 °C. Close the heating button and allow the solution to cool down to room temperature. Then pipette 10mL NaOH(2.5mmol, 0.1g)-NH$_4$F(4mmol, 0.148g)-methanol solution into the three-necked flask, and keep the reaction at room temperature for 30 min. Increase the temperature to 110 °C for 15min under the condition of vacuum, then raise the temperature to 330 °C for 60min under nitrogen atmosphere. Shut off the heating button and allow the solution to cool down to room temperature while stirring.

2.4 Synthesis of NaGdF$_4$/NaGdF$_4$:Yb,Tm,Nd:
Transfer the solution of the flask into a beaker, settle of the supernatant, and then transfer the contents to the centrifuge tube. Spin down the product at 4,000 r.p.m., disperse NaGdF$_4$ nanoparticle with cyclohexane.

Repeat step of Synthesis of NaGdF$_4$, weigh 0.8mmol GdCl$_3$:Yb,Tm,Nd instead of GdCl$_3$, and adjust the dosage of NaOH-NH$_4$F-methanol solution.

2.5 Synthesis of NaGdF$_4$/NaGdF$_4$:Yb,Tm,Nd/NaGdF$_4$:
Handling the sample of NaGdF$_4$/NaGdF$_4$:Yb,Tm,Nd nanoparticle in the same way with NaGdF$_4$. Repeat step of Synthesis of NaGdF$_4$, weigh 0.5mmol GdCl$_3$ and 10mL NaOH(1.25mmol, 0.05g)-NH$_4$F(2mmol, 0.074g) -methanol solution instead of 1mmol GdCl$_3$ and 10mL NaOH(2.5mmol, 0.1g)-NH$_4$F(4mmol, 0.148g) -methanol solution.

3. **Results and discussion**

3.1 The high-resolution images:
As shown in the high-resolution (HRTEM) images from Figure 1a, the NaGdF$_4$ core nanoparticles are nearly uniform nanosphere morphology with an average diameter of about 12×15 nm without aggregation. We successively compounded two shells of NaGdF$_4$/NaGdF$_4$:Yb,Tm,Nd with an average diameter of 16×40 nm through an epitaxial growth process. The HRTEM images of Figure 1b reveal that the nanospheres have a rod-like structure. The core/shell/shell UCNPs have an average diameter of 22×45 nm and figure 1c shows the HRTEM images.
3.2 The X-ray diffraction patterns

The crystallinity and the composition of the synthesized nanoparticles patterns of the samples were obtained. The X-ray diffraction (XRD) patterns of NaGdF$_4$ confirm the presence of a pure β phase structure, the XRD image in Fig.2a. Figure 2b shows the XRD pattern of NaGdF$_4$/NaGdF$_4$: Yb,Tm,Nd. The core/shell UCNPs show slightly narrower peak bandwidths. The XRD patterns of core/shell/shell UCNPs are similar to that of core UCNPs. The diffraction peak positions and intensities are in good agreement with the data for the reference (JCPDS card No. 27-0699)[14].

3.3 Fluorescence analysis

Upconversion spectra of UCNPs are characterized under 800nm irradiation with the nearly same concentrations. By comparison, the experiment shows that fluorescence intensity of core/shell/shell nanoparticles exhibits 1.5 times strong emission than two-layout structure as shown in Figure 3. The UC spectrum exhibits two bands centered at 525–535 and 578–585 nm from Nd$^{3+}$, corresponding to $^4G_{7/2}$$-^4I_{9/2}$ and $^4G_{7/2}$$-^4I_{11/2}$ transitions[14-15]. These data demonstrate that core/shell/shell UCNPs can effectively improve the luminous efficiency.
4. Conclusion
In short, we have developed a new class of triple-doped core/shell/shell UCNPs. NaGdF₄, the host matrix was doped with Yb³⁺, Nd³⁺ and Tm³⁺ as sensitizers and activator. HRTEM and XRD were employed to probe the morphology and structures of nanoparticles. It has been proved that the synthesized UCNPs were rod-like structures having high crystallinity. Under near 800 nm excitation, the three-layer core/shell/shell structure exhibited more efficient activator emission. The application in biotechnology is limited by overexposure and tissue penetration depth because of the influence of 980 nm irradiation as well as high absorption and scattering that occurs in biological tissues [16]. To reduce the impacts of penetration depth, absorption and scatter in bio-tissues, we can choose 800 nm laser excitation. This study represents an important advance in the development of luminescent markers suitable for biolabeling applications, enabling in situ imaging of biological and chemical events without overheating issues.

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