

# A Method to Improve the Up-Conversion Fluorescence of Polymer Modified NaYF<sub>4</sub>:Yb,Er(Tm) Nanocomposites

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## ABSTRACT

The modification of NaYF<sub>4</sub>:Yb,Er(Tm) nanoparticles synthesized in the presence of an ionic surfactant is critical to their application in biological fields for better solubility and biocompatibility. In this work, NaYF<sub>4</sub>:Yb,Er(Tm) was transformed from insoluble, inactive to hydrophilic, biocompatible via ligand exchange modification with polyacrylic acid (PAA). Ligand exchange was carried out at room temperature when a colloidal solution of NaYF<sub>4</sub>:Yb,Er(Tm) in tetrahydrofuran (THF) was treated with excess PAA. The PAA modified NaYF<sub>4</sub>:Yb,Er(Tm) nanoparticles got better surface properties but with declined inner up-conversion fluorescence. Generally, coating an analogous layer of material outside the core nanoparticles can improve the optical properties of the core. Accordingly, NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub> nanoparticles were synthesized before PAA modification to avoid the optical intensity decaying. The result of fluorescence test proved that the water soluble NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub>/PAA nanocomposites had a sound up-conversion property compared with that of NaYF<sub>4</sub>:Yb,Er(Tm)/PAA. Furthermore, the up-conversion fluorescence property of the nanocomposite varied with the doping ratio of Er(Tm) to Yb and the possible mechanism for this change was also discussed.

**Keywords:** Doping Ratio; Fluorescence; Ligand Exchange; Polyacrylic Acid; Sodium Yttrium Fluoride; Surface Modification

## 1. Introduction

Up-conversion fluorescence materials are attracting much attention, owing to their unique optical properties and potential applications. Among all the up-conversion fluorescence materials, hexagonal-phase NaYF<sub>4</sub>:Yb,Er(Tm) is one of the most efficient 980 nm near-infrared (NIR) to visible (green and blue) up-conversion phosphors [1,2]. In bulk, the low phonon energy of the host strongly suppresses multiphonon relaxation process in the emission centers, leading to up-conversion emission. Yb<sup>3+</sup> working as a activator with Y<sup>3+</sup> sensitizes Er<sup>3+</sup>(Tm<sup>3+</sup>) to emit green (blue) and red lights. In the recent decade, the research of up-conversion materials was mainly focused on the biological and medical fields such as low-intensity IR imaging and sensitive bioprobes [3,4].

Biological application of the up-conversion fluorescence materials presents new challenges of the development of nano-science and nano-technology, especially the surface modification study of nanoparticles. As well known, ligand exchange is a versatile way to modify the surfaces of nanoparticles for better solubility and bio-

compatibility. Dykstra *et al.* [5] prepared the CdSe/ZnS nanoparticles by an organometallic route in the presence of trioctylphosphine oxide (TOPO) and then used (PEG)-phosphine oxide copolymer to remove the TOPO for obtaining hydrophilic nanoparticles. Zhang *et al.* [6] chose polyacrylic acid and poly-allylamine to replace the original hydrophobic ligand on magnetic nanoparticles at an elevated temperature in a glycol solvent and rendered it high water solubility. Lin *et al.* [7] successfully synthesized at 150°C the OA-capped PbS QDs with emission in the NIR and modified the PbS by ligand exchange with polyelectrolytes for the application of deep-tissue *in vivo* imaging.

Ligand exchange is also suitable for the modification of NaYF<sub>4</sub>. In our work, PAA was chosen as the ligand polymer because of its excellent properties including hydrophilicity, abundant reactant groups (carboxyl) and non-toxicity. In order to eliminate the quenching effect from polymer, the nanoparticles of NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub> core-shell were firstly synthesized before PAA modification [8]. The middle NaYF<sub>4</sub> layer protected the inner core and its crystal structure, thus enhancing the fluorescence property. The final resultant of NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub>/PAA nanocomposites prom-

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ised to have better comprehensive properties, which made it possible to be applied in biological fields.

To the best of our knowledge, fluorescence properties of the NaYF<sub>4</sub> with a size of several nanometers after modification are barely discussed, although the research about the up-converting fluorescence of NaYF<sub>4</sub> core material has been widely carried out. However, in our work, fluorescence properties of the NaYF<sub>4</sub>:Yb,Er(Tm)/PAA core-shell nanoparticles and the NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub>/PAA core-shell-shell nanocomposites were mainly explored. It is more significant to study the fluorescence of polymer modified NaYF<sub>4</sub>, as the existence of polymer often causes the quenching effect which is one of the most important influence factors for a bio-labeling material. Besides that, the color changing rules of NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub>/PAA nanocomposites were also revealed in this article. It is the first time to explore the relationship in details between lanthanide doping ratio and fluorescence property of the nanoparticles after modification with PAA.

## 2. Experimental

### 2.1. Synthesis of the Host Material: Hexagonal NaYF<sub>4</sub> Nanoparticles

The synthesis basically followed the routes below. Briefly, the yttrium perchlorate (Y(ClO<sub>4</sub>)<sub>3</sub>) was prepared at the beginning by dissolving the rare earth oxide in perchlorate acid. Ten mL of 0.4 M Y(ClO<sub>4</sub>)<sub>3</sub> was dispersed in 60 mL cyclohexane. Under vigorous stirring in a three-neck flask, the mixture was heated to 40°C and maintained for 20 min after the addition of some amount of the surfactant sodium oleate of 0.4 M. Then, 20 mL of 0.8 M sodium fluoride was added into this reaction system and maintained at the same temperature for 60 min. The final mixture was standing for 15 min to gain an obvious interface between oil and water phases. The product was dispersed homogeneously in 60 mL of cyclohexane (oil layer). NaYF<sub>4</sub> nanoparticles were precipitated by centrifugation and ultrasonication treatments for the cyclohexane solution and washed by ethanol and hydroxide sodium for at least 3 times.

### 2.2. Synthesis of NaYF<sub>4</sub>:Yb,Er(Tm) Nanoparticles and NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub> Core/Shell Nanoparticles

The synthesis of NaYF<sub>4</sub>:Yb,Er(Tm) is similar to that of NaYF<sub>4</sub> nanoparticles. The lanthanides were put into the reaction system in the form of rare earth perchlorate including Y(ClO<sub>4</sub>)<sub>3</sub>, Yb(ClO<sub>4</sub>)<sub>3</sub>, Er(ClO<sub>4</sub>)<sub>3</sub> and Tm(ClO<sub>4</sub>)<sub>3</sub>. Ten mL mixture of a designated molar ratio of Y to Ln (0.4M Y(ClO<sub>4</sub>)<sub>3</sub> and Ln(ClO<sub>4</sub>)<sub>3</sub> (Ln = Yb, Er(Tm))) was dispersed in 60 mL cyclohexane. The reaction condition and other procedures are the same as those of NaYF<sub>4</sub>

mentioned above. NaYF<sub>4</sub>:Yb,Er(Tm) nanoparticles were precipitated by centrifugating half of the cyclohexane (oil layer) suspension.

Recently, several similar methods have been reported in the literature for synthesizing NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub> core/shell nanoparticles [9-11]. In this paper, we also take this way to produce NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub> core/shell nanoparticles. In a typical process, five mL 0.4 M Y(ClO<sub>4</sub>)<sub>3</sub> and 5 mL of sodium oleate solution (0.4 M) were then put into another half of the cyclohexane suspension and stirred for 20 min. Ten mL of 0.8 M sodium fluoride was added and vigorously stirred for 60 min. All the reactions were carried out at 40°C. After centrifugation, the resulting nanoparticles of NaYF<sub>4</sub>:Yb,Er(Tm) and NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub> core/shell composites were dried in vacuum at 60°C for at least 12 h.

### 2.3. PAA Surface Modification of NaYF<sub>4</sub>:Yb,Er(Tm) and NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub> Core/Shell Nanoparticles via Ligand Exchange

The NaYF<sub>4</sub>:Yb,Er(Tm)/PAA and NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub>/PAA were prepared by mixing a solution of excess PAA with that of NaYF<sub>4</sub> nanoparticles in tetrahydrofuran (THF) and then stirred overnight. Herein, THF is good solvent for hydrophilic PAA and hydrophobic NaYF<sub>4</sub> nanoparticles, and the other organic solvents don't reach the same effects as THF does. Taking the synthesis of NaYF<sub>4</sub>:Yb,Er/PAA as an example, PAA (84.7 mg) was mixed with NaYF<sub>4</sub>:Yb,Er(20.8 mg) in THF(15.0 mL) in a 50 mL conical flask and this mixture was stirred at 30°C overnight. The resultant was homogeneous and ivory white in color. This conical flask was then placed into a boiling water bath to evaporate the THF. After the solvent evaporation, a white solid was obtained. This white solid was then washed by sodium hydroxide and alcohol for 3 times. NaYF<sub>4</sub>:Yb,Er/PAA was not soluble in cyclohexane but can readily be transferred to methanol or water to form robust colloidal solutions.

### 2.4. Characterization

TEM images of the NaYF<sub>4</sub>:Yb,Er(Tm) nanoparticles and NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub> core/shell nanocomposites were collected on a JEOL JEM 3010 transmission electron microscope. Powder X-ray diffraction spectra were acquired with a D8 advance X-ray diffractometer, with Cu K $\alpha$  radiation at 1.5406 Å. Fourier transform infrared spectroscopy (FTIR) was performed to further characterize the composition and structure of the nanocomposites. Samples of the modified nanoparticles were ground with KBr and then compressed into slices. The spectrum was taken from 500 to 3500 cm<sup>-1</sup>.

## 2.5. Fluorescence Property

Up-conversion fluorescence spectra were obtained on a LS-55 luminescence spectrometer (Perkin-Elmer) with an external 980 nm laser diode (1 W, continuous wave with 1 m fiber, Beijing Viasho Technology Co.) as the excitation source in place of the Xe-lamp in the spectrometer. For comparison, all the nanoparticles were milled to powder and compressed into the groove.

## 3. Results and Discussion

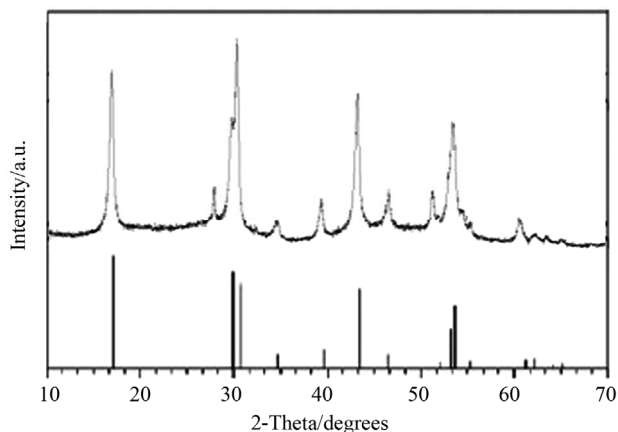
### 3.1. Size Analysis of the Core Nanoparticles by XRD and TEM

**Figure 1** shows the X-ray diffraction (XRD) result of the host material NaYF<sub>4</sub>. The well-defined peaks indicated the high crystallinity of the nanoparticles. The peak positions and intensities of XRD patterns matched closely with those of hexagonal  $\beta$ -NaYF<sub>4</sub> in JCPDF (28 - 1192) [9]. From the line breadth of the diffraction peaks, the crystallite size of the samples was estimated to be approximately 6.9 nm for NaYF<sub>4</sub> nanoparticles based on the Debye-Scherrer formula.

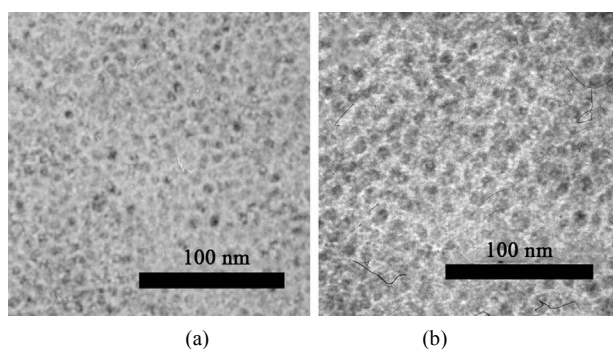
**Figures 2(a)** and **(b)** show the transmission electron microscopy (TEM) images of NaYF<sub>4</sub>:Yb,Er(Tm) core and NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub> core/shell nanoparticles, respectively. It was calculated that the average sizes of them were 8.2 nm and 12.0 nm, respectively. The doping ratio of Lanthanide Yb,Er (Tm) is so tiny compared with yttrium that **Figure 2(a)** also can represent the TEM image of NaYF<sub>4</sub> host materials. So the size of NaYF<sub>4</sub> (8.2 nm) from TEM is basically consistent with the result (6.9 nm) from Debye-Scherrer formula.

### 3.2. FTIR Spectra of NaYF<sub>4</sub>:Yb,Er(Tm) Nanoparticles before and after PAA Modification

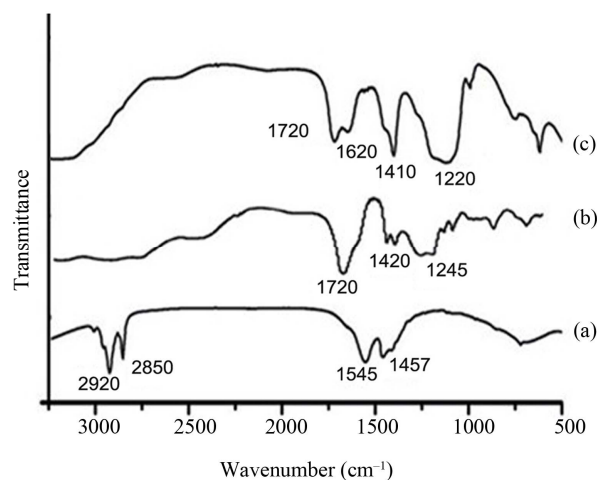
To demonstrate the capping of PAA on the nanoparticles, FTIR spectra of the NaYF<sub>4</sub>:Yb,Er(Tm)/PAA (**Figure 3(c)**) were compared with those of NaYF<sub>4</sub>:Yb,Er(Tm) without surface modification (**Figure 3(a)**) and pure PAA (**Figure 3(b)**). In **Figure 3(a)**, the intense bands in the vicinity of 2920 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> are due to the antisymmetric and symmetric vibration of the -CH<sub>2</sub>, and the bands in 1545 cm<sup>-1</sup> and 1457 cm<sup>-1</sup> are contributed to C = O antisymmetric and symmetric stretching vibrations of carboxylate groups. The band position and shape are the same as the FTIR spectra of sodium oleate [12], so it is concluded that the nanoparticles are capped with sodium oleate before modification. It is obvious that the nanoparticles after ligand exchange (**Figure 3(c)**) have no absorption band of -CH<sub>2</sub> and two new bands appear near 1600 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> corresponding to the R-COO<sup>-</sup> antisymmetric and symmetric stretching vibrations. The



**Figure 1.** XRD pattern of NaYF<sub>4</sub> nanocrystals synthesized with sodium oleate.



**Figure 2.** TEM images of (a) NaYF<sub>4</sub>:Yb,Er(Tm) and (b) NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub>.



**Figure 3.** FTIR spectra of (a) NaYF<sub>4</sub>:Yb,Er(Tm); (b) Pure PAA; and (c) NaYF<sub>4</sub>:Yb,Er(Tm)/PAA.

appearance of R-COO<sup>-</sup> stretching vibration can also be found in the other nanocomposites, such as polyacrylic acid modified aluminum oxide and ferroferric oxide [13,14]. This observation clearly indicates that the sodium oleate on the surface of nanoparticles has been successfully replaced by PAA.

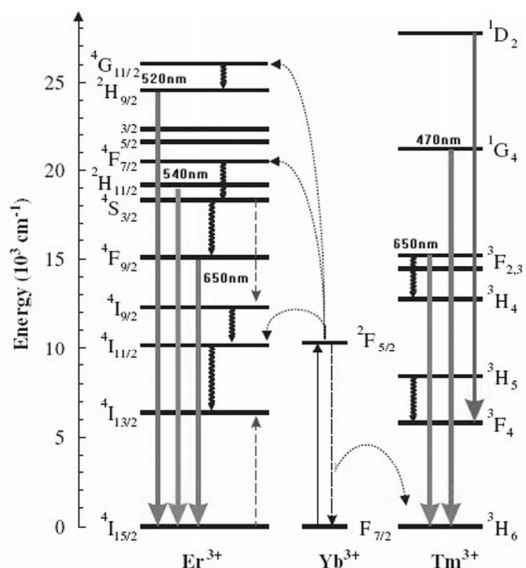
### 3.3. Fluorescence Properties of NaYF<sub>4</sub>:Yb,Er (Tm), NaYF<sub>4</sub>:Yb,Er(Tm)/PAA, and NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub>/PAA

**Figure 4** shows the up-conversion luminescence mechanism of NaYF<sub>4</sub>:Yb,Er(Tm). Up-conversion is an effective avenue for the generation of visible emission with near-infrared (NIR) excitation, which is based on sequential photon absorption and energy transfer steps [15].

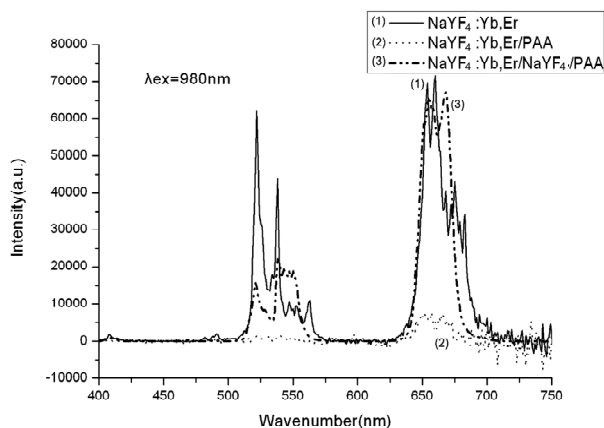
In the case of NaYF<sub>4</sub>:Yb,Er, under the excitation of 980 nm light, which can be absorbed by Yb<sup>3+</sup>, the electrons of Er<sup>3+</sup> are first excited from the <sup>4</sup>I<sub>15/2</sub> to higher level via excitation energy transfer from Yb<sup>3+</sup> to Er<sup>3+</sup> and then to the <sup>4</sup>F<sub>7/2</sub> level by absorbing the energy of another electron from Yb<sup>3+</sup> (<sup>2</sup>F<sub>5/2</sub>). The excited electrons of the <sup>4</sup>F<sub>7/2</sub> (Er<sup>3+</sup>) level then decay to the emitting <sup>2</sup>H<sub>11/2</sub> (the line at 540 nm), and <sup>4</sup>F<sub>9/2</sub> levels (the line at 650 nm), mainly through nonradioactive process. Meanwhile, as for NaYF<sub>4</sub>:Yb,Tm, the emission process is a little different. An Yb<sup>3+</sup> ion in the <sup>2</sup>F<sub>7/2</sub> ground state absorbs a 980 nm photon and transits to excited state <sup>2</sup>F<sub>5/2</sub>. When it drops back to the ground state (<sup>2</sup>F<sub>5/2</sub>-<sup>2</sup>F<sub>7/2</sub>), energy is transferred to an adjacent ground state (<sup>3</sup>H<sub>6</sub>) Tm<sup>3+</sup> ion. After the multistep excitation energy transfer, the Tm<sup>3+</sup> is promoted to the <sup>1</sup>D<sub>2</sub> and <sup>1</sup>G<sub>4</sub> emission levels. These excited electrons on the emitting levels (<sup>1</sup>D<sub>2</sub> and <sup>1</sup>G<sub>4</sub>) then drop back to the low-energy levels (<sup>3</sup>F<sub>4</sub> and <sup>3</sup>H<sub>6</sub>) via fluorescence emission [16,17]. But the <sup>1</sup>D<sub>2</sub> level of Tm<sup>3+</sup> commonly cannot be populated by the photon from Yb<sup>3+</sup> via energy transfer to the <sup>1</sup>G<sub>4</sub> due to the large energy mismatch between them [18].

**Figures 5 and 6** show the up-conversion fluorescence spectra of NaYF<sub>4</sub>:Yb 10%, Er (Tm) 3% before and after surface modification with a 0 - 1500 mw adjustable 980 nm laser. In **Figure 5**, the straight line represents the NaYF<sub>4</sub>:Yb,Er core material, where the green emission around 540 nm and the red emission around 650 nm are attributed to the transitions of <sup>2</sup>H<sub>11/2</sub>-<sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>F<sub>9/2</sub>-<sup>4</sup>I<sub>15/2</sub> for the Er<sup>3+</sup> ions. It is obvious that the emission band of dash line representing NaYF<sub>4</sub>:Yb,Er/PAA is very weak due to the quenching effect from organic PAA. Nevertheless, the emission intensity of NaYF<sub>4</sub>:Yb,Er/NaYF<sub>4</sub>/PAA showed as the dot dash line is dramatically increased by the protection of middle NaYF<sub>4</sub> layer. Especially the red emission band at 650 nm is almost as high as that of the NaYF<sub>4</sub>:Yb,Er nanoparticles before modification.

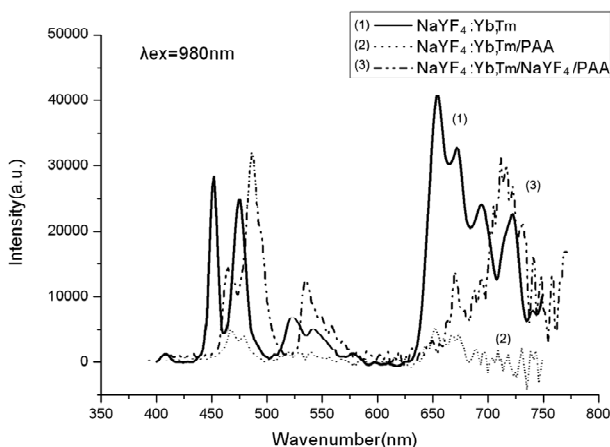
In the case of NaYF<sub>4</sub>:Yb,Tm (shown in **Figure 6**), the red emission appears at the same position and the blue emission is shifted to 470 nm arising from the <sup>1</sup>G<sub>4</sub> to <sup>3</sup>H<sub>6</sub> energy transition. Likewise, the emission intensity of NaYF<sub>4</sub>:Yb,Tm/NaYF<sub>4</sub>/PAA is higher than that of NaYF<sub>4</sub>:Yb,Tm/PAA. So it is concluded that the middle NaYF<sub>4</sub> layer works as a protecting layer which can reduce the influence on fluorescent intensity probably caused from the organic modification.



**Figure 4. Schematic energy level diagrams: upconversion excitation and visible emission schemes for the Er<sup>3+</sup>, Tm<sup>3+</sup> and Yb<sup>3+</sup> ions.**



**Figure 5. Fluorescent spectra of nanoparticles doped with Yb<sup>3+</sup>, Er<sup>3+</sup> before and after PAA modification.**



**Figure 6. Fluorescent spectra of nanoparticles doped with Yb<sup>3+</sup>, Tm<sup>3+</sup> before and after PAA modification.**

### 3.4. Influence of Yb/Er(Tm) Doping Ratio on the Up-Conversion Property

Figures 7 and 8 show the up-conversion fluorescence spectra of NaYF<sub>4</sub>:Yb,Er/NaYF<sub>4</sub>/PAA and NaYF<sub>4</sub>:Yb,Tm/NaYF<sub>4</sub>/PAA under 980 nm excitation, respectively. It is clear that all samples show strong emissions in the visible region. Upon addition of more Er<sup>3+</sup> to Yb<sup>3+</sup>, there is a marked increase in the emission ratio of red to green, as can be seen by comparison among Figures 7(a)-(c). This effect is probably related to the increased possibility of the two-ion Er<sup>3+</sup> cross-relaxation process (<sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>S<sub>3/2</sub>-<sup>4</sup>I<sub>13/2</sub>, <sup>4</sup>I<sub>9/2</sub>) that occurs at higher Er<sup>3+</sup> concentrations. This process depopulates the green-emitting <sup>4</sup>S<sub>3/2</sub> state, thereby increasing the red to green ratio [19]. But in the case of NaYF<sub>4</sub>:Yb,Tm/NaYF<sub>4</sub>/PAA, the result is just contrary (Figures 8(a)-(c)). With the increase of Tm<sup>3+</sup> to Yb<sup>3+</sup> ratio, the red to blue emission is reduced. It shows that at higher Tm<sup>3+</sup> concentration, the Tm<sup>3+</sup> cross-relaxation process of <sup>3</sup>F<sub>2</sub>, <sup>3</sup>H<sub>4</sub>-<sup>3</sup>H<sub>5</sub>, <sup>1</sup>G<sub>4</sub> increases, which plays an important role in populating <sup>1</sup>G<sub>4</sub> Level, thus enhancing the blue emission [17]. It is very significant to find out the color changing rules versus lanthanide doping ratio for fulfilling the different practical requirements. For example, in the fields of *in vivo* imaging and labeling, the variety of color emission can provide more than one binding site to image several bi-molecules at the same time. The fluorescence property is the key for the material to be successfully applied and then further arduous work should be done in the future.

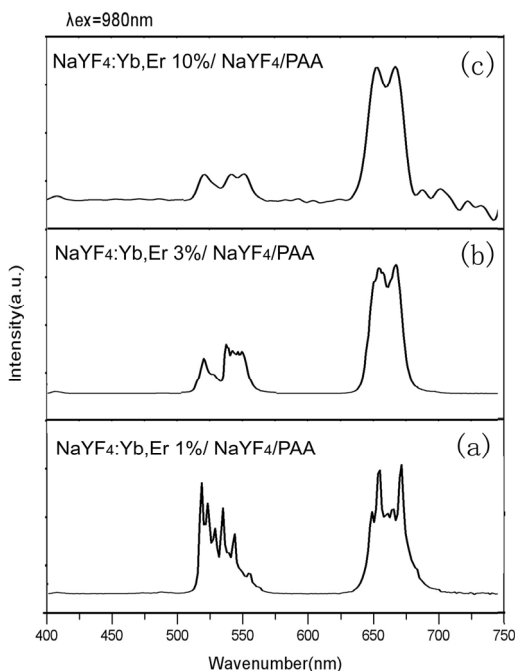


Figure 7. Fluorescent spectra of NaYF<sub>4</sub>:Yb,Er/NaYF<sub>4</sub>/PAA of different Er<sup>3+</sup> doping ratios: (a) 1.0% Er<sup>3+</sup>; (b) 3.0% Er<sup>3+</sup>; (c) 10.0% Er<sup>3+</sup>.

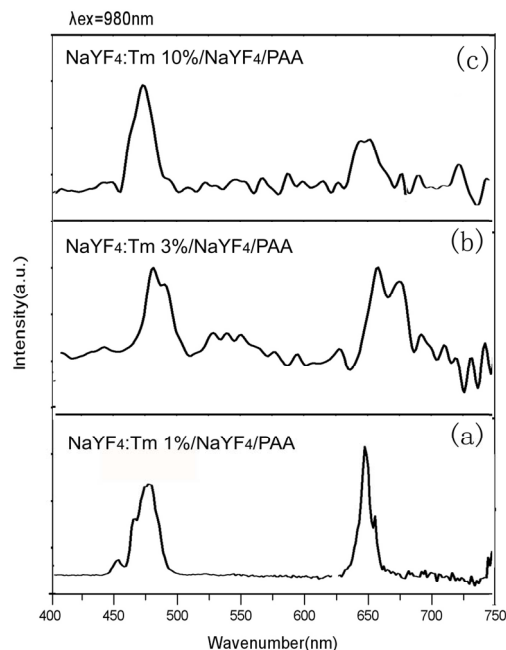


Figure 8. Fluorescent spectra of NaYF<sub>4</sub>:Yb,Tm/NaYF<sub>4</sub>/PAA of different Tm<sup>3+</sup> doping ratio: (a) 1.0% Tm<sup>3+</sup>; (b) 3.0% Tm<sup>3+</sup>; (c) 10.0% Tm<sup>3+</sup>.

### 4. Conclusion

Polymer modification of NaYF<sub>4</sub>:Yb,Er(Tm) can improve the surface property of nanoparticles but decrease the fluorescent intensity of the inner material because of quenching effect. In this study, we described a method to alleviate the quenching effect by coating another NaYF<sub>4</sub> layer outside NaYF<sub>4</sub>:Yb,Er(Tm) inner core to resist the influence from PAA (polyacrylic acid). Photoluminescence checking showed that the up-converting fluorescent intensity of NaYF<sub>4</sub>:Yb,Er(Tm)/NaYF<sub>4</sub>/PAA was obviously higher than that of NaYF<sub>4</sub>:Yb,Er(Tm)/PAA, thus proving the efficiency of this method. Another focus of this paper here was mainly on the relationship between the specific red/green (blue) emission value and Yb/Er (Tm) doping ratio. In summary, when doping the Yb and Er ions, the higher Er<sup>3+</sup> concentrations increased the red to green emission ratio. In contrary, the higher Tm<sup>3+</sup> concentrations just weaken the red emission but enhanced the blue one. The controllable fluorescence efficiency and hydrophilicity with desirable carboxylic functional groups provided by PAA give the core/shell/shell nanocomposites a great potential to be bio-probes.

### 5. Acknowledgements

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