Upconversion Properties of Ln³⁺ Doped NaYF₄/Polymer Composite Fibers Prepared by Electrospinning

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Ln³⁺ doped (Yb³⁺,Tm³⁺ codoped and Yb³⁺,Er³⁺,Tm³⁺ tridoped) NaYF₄/poly(vinyl pyrrolidone)(PVP) (M₆ ≈ 1 300 000) composite fibers with an average diameter of 300–800 nm were prepared by electrospinning and characterized by X-ray diffraction, field emission scanning electron micrography, and Fourier transform infrared spectra. Their upconversion (UC) luminescence properties were studied in contrast to the corresponding Ln³⁺ doped NaYF₄ nanoparticles (15–20 nm) under 980-nm excitation. The results demonstrate that in the Yb³⁺,Tm³⁺ codoped composite fibers the blue emission of 1G₄→H₆ is dominantly strong, while in the nanoparticles the red emission of 3F₅/₂→H₆ contributes considerably to the increase of the excitation power. This indicates that the color purity of blue is improved greatly by the modification of PVP. In the tridoped Yb³⁺,Er³⁺,Tm³⁺ composite fibers, white light with more stable color balance (blue 1G₄→H₆ of Tm³⁺, green 3H₁₁/₂→I₃/₂ of Tm³⁺, and red 4F₉/₂→I₅/₂ of Er³⁺) was obtained. The improved UC properties in the composite fibers are attributed to the suppressed local thermal effect. The energy transfer and UC populating processes are discussed.

I. Introduction

In recent years, much attention has been paid to nanostructures with controllable sizes, shapes, and compositions.¹ For a broad range of applications, one-dimensional (1D) nanostructures are of fundamental importance.²⁻⁴ These complex architectures, such as nanowires, nanorods, nanobelts, and nanotubes, are expected to display an important role for both fundamental studies and technological applications.⁵⁻⁷

A large number of synthetic and fabrication methods have already been demonstrated for generating 1D nanostructures, such as using an anodic aluminum oxide template,⁸ homoge-neous precipitation,⁹ hydrothermal or solvothermal treatment,¹⁰⁻¹² and so on. These methods are usually employed to produce inorganic 1D nanostructures; however, they are incapable of preparing 1D organic—inorganic nanomaterials.

Electrostatic fiber formation, so-called electrospinning, is a simple, convenient, and versatile technique for generating long fibers with diameters ranging from tens of nanometers up to micrometers. It has been demonstrated that a variety of materials, such as organic,¹³⁻¹⁵ inorganic,¹⁶⁻¹⁸ and hybrid polymers (organic—inorganic composites)¹⁹,²⁰ can be electrospun to form uniform fibers.²¹ These systems that combine both inorganic and organic characters are found to have the advantage in many fields of application, such as membrane technology,²² tissue engineering,²³ optical sensors, biosensors,²⁴ superhydrophobic surfaces,²⁵ and drug delivery.²⁵

In this paper, we demonstrate the experimental studies on lanthanide doped NaYF₄/PVP composite fibers in contrast to NaYF₄ nanoparticles. It is well known that NaYF₄ is a superior material, and many works have been done to study the structure and UC mechanism.²⁶⁻²⁹ In particular, Yb³⁺,Tm³⁺ and Yb³⁺,Er³⁺ codoped NaYF₄ nanocrystals are known as some of the most efficient UC materials because of the very low phonon energies of their lattices.³⁰⁻³⁴ However, the organic modified UC materials have not been reported, to our knowledge. PVP is an important organic material in optical and electric design. It is expected that the existence of PVP not only can control the structural properties in electrospinning but also can modify the UC luminescence processes of rare earth ions.

In the present work, NaYF₄:Yb³⁺,Tm³⁺/PVP composite fibers were investigated and it was observed that the energy transfer and UC luminescence processes of NaYF₄: Yb³⁺,Tm³⁺ nanocrystals in the composite fibers were modified greatly because of the interaction between PVP and Tm³⁺. Furthermore, white light was designed and generated by doping another lanthanide ion, Er³⁺ (red and green), into the NaYF₄:Yb³⁺,Tm³⁺(blue) system under the excitation of a 980-nm laser diode. More stable white light was observed in the composite fibers in comparison to the nanoparticles. To the best of our knowledge, there was no study on the modification of PVP to lanthanide ions, which makes it of particular interest as a lighting material with great application potential.

II. Experimental Section

In a typical experiment, NaYF₄/PVP composite fibers were prepared by electrospinning from a solution containing NaYF₄ nanoparticles and PVP with different ratios. The schematic
The diagram of the electrospinning setup was shown in Figure 1. It consisted of three major components: a high-voltage power supply, a spinneret (a needle), and a collector plate (a grounded conductor). As a nonmechanical fiber drawing method, electrospinning involved the stretching of inorganic nanomaterials and polymer hybrid solution (or melt) with electrostatic forces. The voltage used for electrospinning was 13 kV.

For the synthesis of the lanthanide doped NaYF₄ colloids, polyol method was employed in this work. In the preparation of NaYF₄:Yb³⁺,Tm³⁺ nanoparticles, stoichiometric amounts of NaF (99.99%), Y(NO₃)₃·6H₂O, Yb(NO₃)₃·6H₂O, Tm(NO₃)₃·6H₂O were mixed together with a desirable amount of diethylene glycol (DEG, 98%, A. R.) to make the metal ion concentration 0.02 mol/L and then transferred to a round-bottomed flask. The mixture was heated to 180 °C in a silicon oil bath under vigorous stirring for 2 h. When the suspension was cooled to room temperature, the colloids were separated by centrifugation and washed with ethanol several times. The preparation procedure of NaYF₄:Yb³⁺,Er³⁺,Tm³⁺ nanoparticles was same as that of NaYF₄:Yb³⁺,Tm³⁺ nanoparticles.

It is well known that the homogenization of the composite fibers is one of the most important factors of its optical and mechanical properties. Note that the aggregation of nanoparticles always happens in the drying and annealing process. So, in this work we avoided the nanoparticle drying step and added an appropriate amount of PVP directly to NaYF₄ colloids according to the weight ratio of PVP to NaYF₄ colloids of 1:1, 2:1, 3:1, and 4:1. A long time of stirring and ultrasonic was then carried out to obtain a homogeneous hybrid solution. Successful electrospinning requires the use of an appropriate solvent and hybrid-polymer system to prepare solutions exhibiting the desired viscoelastic behavior. The viscous solution of NaYF₄/PVP composites was controlled by adding enough ethanol to make the weight ratio of PVP to ethanol 12 wt %. After stirring, the final solution was then electrospun to form composite fibers.

The X-ray diffraction (XRD) data of the fibers was collected on Rigaku D/max-RA X-ray diffractometer using a Cu target radiation source. The morphology of the fibers was inspected using a Hitachi S-4800 field emission scanning electron micrograph (FE-SEM). Fourier transform infrared spectroscopy (FTIR) was recorded in the range of 700–4000 cm⁻¹ on a Fourier transform spectrometer (Perkin-Elmer, Spectrum 1) with a resolution of 1 cm⁻¹. The emission spectra were recorded at room temperature using a Hitachi F-4500 fluorescence spectrometer equipped with a 980-nm laser diode. UC fluorescence dynamics were measured under the excitation of a 980-nm optical parameter oscillator (OPO) laser pumped by a pulsed Nd:YAG laser, which had a pulse duration of 10 nm and a repetition frequency of 10 Hz.

III. Results and Discussion

A. Structure and Morphology. Figure 2 shows the XRD patterns of NaYF₄ nanoparticles and the composite fibers with different ratios of PVP to NaYF₄. The powder sample was well-crystallized, and all of the peaks could be readily indexed to the cubic NaYF₄ phase. Also, peaks of the cubic NaYF₄ phase appeared in all of the composite fiber samples, implying the existence of NaYF₄ nanoparticles in the composite fibers.

Figure 3 depicts SEM images of the samples. Figure 3a shows that the NaYF₄ nanoparticles are dispersed uniformly and the average size of them is 15–20 nm. The general overview SEM image in Figure 3b shows that the fibers are oriented randomly and the lengths of them are several 10 mm. Figure 3c–f shows the enlarged images of single fibers of the samples with ratios of 1:1 to 4:1. The diameters of the samples are ~300, 400, 500,
and 800 nm, respectively, corresponding to the 1:1, 2:1, 3:1, and 4:1 samples. In the sample with a ratio of 1:1, it can be seen that some nanoparticles aggregate together. As for the other samples, the NaYF₄ nanoparticles are dispersed homogeneously in the composite fibers.

Figure 4 shows the FTIR of pure PVP and composite fibers. The FTIR spectra of the composite fibers were similar to that of the pure PVP fiber in the studied range. A broad band at 3400 cm⁻¹ was observed in the pure and composite fibers, which was generated by vibrations of associated hydroxyl groups. The contamination of trace hydroxyl groups in the fibers was due to the electrospun solution. The absorption peak of the C=O group in the PVP located at 1660 cm⁻¹, whereas in the composite fibers it shifted to 1669 cm⁻¹ (see the inset of Figure 4), which indicated that NaYF₄ nanoparticles were stabilized through chemical interactions with the oxygen atoms of the polypyrrolidone units of PVP. This interaction might come from the donation of a pair of electron transfers from the carbonyl oxygen to lanthanide ions.

B. UC Luminescence of NaYF₄:Yb³⁺,Tm³⁺/PVP Composite Fibers. Figure 5a shows the normalized UC luminescence spectra in the NaYF₄:Yb³⁺,Tm³⁺ nanoparticles under different excitation powers. The blue emission centers at ~476 nm, corresponding to the ¹G₄ ⁴- ³H₆ transition of Tm³⁺. A weak shoulder corresponding to the ¹D₂ ⁰- ³F₄ transition appears at 451 nm. The emission at 649 nm corresponds to the transition of ¹G₄ ⁴- ³H₄ of Tm³⁺. The emissions from 660 to 740 nm are attributed to ³F₂,₃ ⁴- ³H₄ transitions of Tm³⁺, as labeled in the figure. Because the excitation power is lower, the ¹G₄ ⁴- ³H₄ blue emission is dominantly strong. As the excitation power increases to 1450 mW, the ³F₂,₃ ⁴- ³H₄ red emissions increase more intensively relative to the blue and the sample displays mixed color of blue and red. In addition, it can be also observed that the intensity ratio of ³F₂,₃ ⁴- ³H₄ to ³F₂,₃ ⁴- ³H₄ varies greatly with the increase of excitation power. This intensity ratio as a function of excitation power is drawn as Figure 9a. The ratio increases originally with excitation power, then approaches at a maximum, and then decreases with excitation power. The origin of the intensity ratio variation is caused by the thermal effect caused by laser irradiation, which will be discussed later. A similar result was also observed and discussed in Y₂O₃:Er³⁺,Yb³⁺ nanocrystals.

Figure 5b depicts the normalized UC luminescence spectra in the 1:1 composite fibers. It can be seen that as the excitation power varies, the ¹G₄ ⁴- ³H₄ blue emission is dominant all the time, which differs from the nanoparticles. In addition, because the excitation power is high enough, the blue emission at 451 nm originating from the ¹D₂ ⁰- ³F₄ transition becomes stronger and the red emissions from 660 to 740 nm become weaker in comparison to the nanoparticles. The intensity ratio of ³F₂,₃ ⁴- ³H₄ to ³F₁ ⁴- ³H₄ in the composite fibers has only a little variation in contrast to that in the pure nanoparticles (see Figure 9a).

Figure 6 shows the normalized UC emission spectra of the nanoparticles and the composite fibers with different concentrations of PVP. It is obvious that the intensity of ¹D₂ ⁰- ³F₄ relative to ¹G₄ ⁴- ³H₄ increases gradually with the increase of PVP concentration. As the PVP concentration varies, the intensity of ³F₂,₃ ⁴- ³H₄ relative to ³G₂ ⁴- ³H₄ has little variation.

C. Energy Transfer and UC Luminescence Processes of NaYF₄:Yb³⁺,Tm³⁺. To better understand the UC mechanism in NaYF₄:Yb³⁺,Tm³⁺, the energy transfer and UC luminescence processes under 980-nm excitation are drawn as Figure 7. First, the electrons on ground states ³H₄ are excited to ³H₄ through the first-step energy transfer of Yb³⁺ → Tm³⁺ and then the electrons on ³H₄ relax to ³F₁. Second, the electrons on ³F₂ are excited to ³F₂ through the second-step energy transfer, which
can generate red emission of \( ^3F_2,3-H_6 \) or relax to \( ^3H_4 \). Third, the electrons on \( ^3H_4 \) are excited to \( ^1G_4 \) through the third-step energy transfer, generating blue \( ^1G_4-^3H_6 \) or red \( ^1G_4-^3F_4 \) emission.\(^{38}\) The electrons on \( ^1G_4 \) could also be excited to \( ^1D_2 \) through the fourth-step energy transfer, generating blue \( ^1D_2-^3F_4 \) emission.

In the NaYF\(_4\):\( ^{3+}\)Yb,\( ^{3+}\)Tm system, because the doping concentration of Tm\(^{3+}\) is as high as 0.5\%, the following cross relaxation processes probably happen because the excitation power is high enough, as marked in Figure 7:

\[
\text{Tm(A)}\ ^1G_4 + \text{Tm(B)}\ ^3H_6 \rightarrow \text{Tm(A)}\ ^3F_2,3 + \text{Tm(B)}\ ^3F_4 \tag{1}
\]

\[
\text{Tm(A)}\ ^3F_3 + \text{Tm(B)}\ ^3F_3 \rightarrow \text{Tm(A)}\ ^1D_2 + \text{Tm(B)}\ ^3H_6 \tag{2}
\]

In the nanoparticles, because the excitation power is high enough, the local thermal effect caused by laser irradiation is evident, which leads the temperature at the irradiated spot to increase largely.\(^{1,2}\) This can be concluded from the fact that the intensity ratio of \( ^3F_2-^3H_6 \) to \( ^3F_3-^3H_6 \) varies greatly with the increase of excitation power. The energy gap between \( ^3F_2 \) and \( ^3F_3 \) states is only about 500 cm\(^{-1}\). The population distribution between the two states is dominated by Boltzmann’s distribution, and thus the intensity ratio is a critical parameter in detecting the local temperature. The increased local temperature leads the population of \( ^3F_3 \) to decrease considerably because of thermal activation, while the population of \( ^3F_2 \) relative to \( ^3F_3 \) increases.
TABLE 1: Rise and Decay Time Constants of Er³⁺ and Tm³⁺ in the Presence and Absence of PVP

<table>
<thead>
<tr>
<th>Energy levels</th>
<th>474 nm (1G₄-4H₆)</th>
<th>550 nm (3S₂-4I₁₅/₂)</th>
<th>650 nm (4F₉/₂-4I₁₅/₂)</th>
<th>Energy levels</th>
<th>474 nm (1G₄-4H₆)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb³⁺,Er³⁺,Tm³⁺</td>
<td>τ₁(µs)</td>
<td>41</td>
<td>17</td>
<td>Yb³⁺,Tm³⁺</td>
<td>τ₁(µs)</td>
</tr>
<tr>
<td>nanoparticles</td>
<td>τ₂(µs)</td>
<td>199</td>
<td>126</td>
<td>nanoparticles</td>
<td>τ₂(µs)</td>
</tr>
<tr>
<td>Yb³⁺,Er³⁺,Tm³⁺</td>
<td>τ₁(µs)</td>
<td>40</td>
<td>16</td>
<td>Yb³⁺,Tm³⁺</td>
<td>τ₁(µs)</td>
</tr>
<tr>
<td>fibers</td>
<td>τ₂(µs)</td>
<td>186</td>
<td>118</td>
<td>fibers</td>
<td>τ₂(µs)</td>
</tr>
</tbody>
</table>

As a consequence, the cross relaxation process (2) is not effective. However, the cross relaxation process (1) is effective in the nanoparticles, which leads to the population increase of ³F₂ relative to the ¹G₄ and the intensity increase of ³F₂-⁴H₆ relative to ¹G₄-⁴H₆.

The emission changes for the composite fibers can be attributed to the interaction between the NaYF₄:Yb³⁺,Tm³⁺ nanoparticles and PVP. Some vibration transitions of the PVP may match the energy separations between the two neighboring excited levels exactly and change the populating channels. For example, the excited levels exactly change the populating channels may match the energy separations between the two neighboring levels ³F₂ relative to ¹G₄ and the intensity increase of ³F₂-⁴H₆ effectively. However, the cross relaxation process (1) is effective as a consequence, the cross relaxation process (2) is not effective.

The effective thermal exchange between Tm³⁺ ions and PVP also induces the temperature surrounding Tm³⁺ to have only a slight increase in contrast to that in the pure nanoparticles. Thus, a large number of electrons still distribute on the ³F₂ state after two-step energy transfers. The cross relaxation process (2) happens effectively, resulting in the intensity increase of ³D₂-³H₆ relative to ¹G₄-⁴H₆.

D. NaYF₄:Yb³⁺, Er³⁺,Tm³⁺ White Light-Emitting Fibers.

For a variety of purposes, generation of efficient and stable UC white light sources is important. UC white light-emitting fibers with simultaneous blue, green, and red emissions were designed and generated in the NaYF₄:Yb³⁺,Er³⁺,Tm³⁺ composite fibers. Tricolor emissions were generated by Er³⁺ (red and green) and Tm³⁺ (blue). Codoping of Yb³⁺ can greatly increase the sensitivity of photoluminescence of Er³⁺ and Tm³⁺ through energy transfer because of its efficient absorption at 980 nm. Controlling the doping content of the lanthanide ions is significant for the color balance of white light. In NaYF₄ nanoparticles, as the concentrations of Er³⁺, Tm³⁺, Yb³⁺ were adjusted, respectively, to 1.0, 0.5, and 20% in molar ratio, bright white emission was obtained.

Figure 8a shows the normalized spectra of the NaYF₄:Yb³⁺,-Er³⁺,Tm³⁺ nanoparticles under excitation with different powers. It can be seen that all of the tricolor emission lines appear in the visible range. Besides the blue emissions centered at 478 nm of Tm³⁺, the green emissions of ³H₁₁/₂-⁴S₃/₂,⁴I₁₅/₂ of Er³⁺ also appear. The peaks in the red region of 641-725 nm correspond to the stronger ³F₂-⁴I₁₅/₂ transition of Er³⁺ as well as weaker ³F₂,³H₆ transition of Tm³⁺, as labeled in the figure. Note that in the tridoped system as the excitation power varied, a similar tendency for the ³F₂,³H₆ transition of Tm³⁺ was observed, like that in the NaYF₄: Yb³⁺,Tm³⁺,Er³⁺ codoped system. In addition, when the excitation power increases, the intensity ratio of ³H₁₁/₂-⁴I₁₅/₂ to ³S₄/₂-⁴I₁₅/₂ also increases, which can also be attributed to local thermal effect induced by the exposure of the laser diode. In the nanoparticles, the white color balance changes unexpectedly with excitation power because of the variation of the intensity ratio of the green ³H₁₁/₂-⁴S₃/₂-⁴I₁₅/₂ (Er³⁺) to the blue ¹G₄-⁴H₆ (Tm³⁺) as well as the red ³F₂-⁴I₁₅/₂ (Er³⁺).

Normalized UC spectra in the composite fibers with ratio of 1:1 at various pump powers are shown in Figure 8b. It can be seen that the intensity ratio of ³H₁₁/₂-⁴I₁₅/₂ to ³S₄/₂-⁴I₁₅/₂ had only a little variation, implying that the temperature at the irradiated spot changed a little. The relative intensity for the emissions in different visible regions, blue, green, and red, had a smaller variation with excitation power, implying that the color balance is more stable as the excitation power varies. The luminescence spot on the sample with a ratio of 1:1 is inserted in Figure 8b.

The dependence of the intensity ratio of ³H₁₁/₂-⁴I₁₅/₂ to ³S₄/₂-⁴I₁₅/₂ of the nanoparticles and the composite fibers on the excitation power is plotted in Figure 9b. It can be seen that the intensity ratio increases with the excitation power for both samples. In the nanoparticles the intensity increases significantly, whereas in the composite fibers it increases slightly. The energy separation between ³H₁₁/₂ and ³S₄/₂ is ~730 cm⁻¹. The population distribution between them is dominated by thermal activation, which depends strongly on temperature, similar to the ³F₂ and ³F₃ states of Tm³⁺. The result in Figure 9a indicates that in the tridoped composite fibers the thermal effect caused by laser exposure at the irradiated spot was suppressed, which was attributed to the modification of PVP in the composite fibers. The distorted vibration absorption of C=H peaking at 734 cm⁻¹ matches the energy separation between the two green levels of Er³⁺, ³H₁₁/₂, and ³S₄/₂ exactly, bridging the nonradiative relaxation of ³H₁₁/₂-³S₄/₂ through nonradiative energy transfer from Er³⁺ to PVP and quenching the ³H₁₁/₂-³I₁₅/₂ transitions. It is the energy transfer between Er³⁺ and PVP in the composite fibers that suppressed the thermal effect.

E. Upconversion Luminescent Dynamics.

Dynamics of Yb³⁺,Tm³⁺-codoped and Yb³⁺,Er³⁺,Tm³⁺ tridoped systems with the presence and absence of PVP were measured and compared, as shown in Figure 10 (¹G₄-⁴H₆ transition at 474 nm). It should be noted that the output power of the OPO pulsed laser (250 mW) is much lower than that of near-infrared laser diodes (≥360 mW) and the lifetimes obtained from OPO only reflect the dynamics at low excitation power. It can be observed that the dynamics contains a faster rise process and a slower decay process. The rise process corresponds to the energy-transfer-induced population increase as the laser pulse is terminated originally, which depends strongly on the energy transfer rate. The luminescent dynamics are fitted with a universal function

\[ I(t) = I(t) \left( e^{-\frac{t}{\tau_1}} - e^{-\frac{t}{\tau_2}} \right) \]  

where \(\tau_1\) and \(\tau_2\) are the rise and decay time constants, respectively. \(\tau_1\) depends mainly on the energy transfer rate from Yb³⁺ to Tm³⁺ or Er³⁺, whereas \(\tau_2\) depends on the electronic transition rate of the related excited level. The luminescent dynamics of the other transitions were also measured, and the deduced rise and decay time constants were listed in Table 1. The results in Table 1 can be concluded as follows: (1) The
rise and decay time constants in the composite fibers have only a little variation in comparison to those in the pure nanoparticles, indicating that because the excitation power is lower the energy transfer rate from Yb$^{3+}$ to Tm$^{3+}$ (Er$^{3+}$) and the electronic transition rate of the related excited levels rarely vary. This implies that the UC efficiency in the composite fibers should also have little variation relative to the nanoparticles. (2) In the tridoped systems, the rise and decay time constants of the $^1G_4 - ^3H_6$ transition become shorter compared to those in the codoped systems. The decrease of the rise and decay time constants in the composite fibers have only little variation in comparison to those in the pure nanoparticles. In conclusion, this suggests that in the composite fibers, because the excitation power was low, the electronic transition rate, the energy transfer rate from Yb$^{3+}$ to Tm$^{3+}$ (Er$^{3+}$) and the 3 F$^2$ to 3 H$^6$ transitions of Tm$^{3+}$ (Er$^{3+}$) contributes considerably because the excitation power is high, indicating that the color purity of blue is improved greatly by the excitation power of PVP composite fibers, the blue emission of $^1G_4 - ^3H_6$ is dominantly strong all the time, whereas in the nanoparticles the red emission of $^3F_2 - ^3H_6$ greatly increases with the increasing ratio of $^3F_2 - ^3H_6$ to $^3F_3 - ^3H_6$.

IV. Conclusions

Structural and UC luminescence properties of Ln$^{3+}$ doped NaYF$_4$/PVP composite fibers prepared by electrospinning were studied in contrast to the corresponding Ln$^{3+}$ doped NaYF$_4$ nanoparticles under 980-nm excitation. It is interesting to observe that the properties of UC luminescence are improved in the composite fibers. In the NaYF$_4$: Yb$^{3+}$,Tm$^{3+}$/PVP composite fibers, the blue emission of $^1G_4 - ^3H_6$ has a small variation in comparison to those in the codoped systems. As a consequence, the thermal effect in the composite fibers is suppressed. As a consequence, the thermal effect in the composite fibers is suppressed. As a consequence, the thermal effect in the composite fibers is suppressed. As a consequence, the thermal effect in the composite fibers is suppressed. As a consequence, the thermal effect in the composite fibers is suppressed.

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References and Notes