Colloidal synthesis and blue based multicolor upconversion emissions of size and composition controlled monodisperse hexagonal NaYF$_4$ : Yb,Tm nanocrystals†

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Monodisperse β-NaYF$_4$ : Yb,Tm nanocrystals with controlled size (25–150 nm), shape (sphere, hexagonal prism, and hexagonal plate), and composition (Yb: 20–40%, Tm: 0.2–5%) were synthesized from the thermolysis of metal trifluoroacetates in hot surfactant solutions. The upconversion (UC) of near-infrared light (980 nm) to ultra-violet (360 nm), blue (450 and 475 nm), red (650 and 695 nm) and infrared (800 nm) light in the β-NaYF$_4$ : Yb,Tm nanocrystals has been studied by UC spectroscopy. Both the total intensity of UC emissions and the relative intensities of emissions at different wavelengths have shown a strong dependence on different particle sizes and different Tm$^{3+}$ and Yb$^{3+}$ concentrations. As a result, different overall output colors of UC emissions can be achieved by altering sizes and Yb$^{3+}$/Tm$^{3+}$ doping concentrations of the β-NaYF$_4$ : Yb,Tm nanocrystals. The intensity-power curves of a series of samples have proved that emissions at 360 and 450 nm can be ascribed to four-photon processes ($^{1}D_{2}$ to $^{1}H_{6}$ and $^{1}D_{2}$ to $^{1}H_{4}$, respectively), while emissions at 475 and 650 nm are three-photon processes ($^{2}G_{4}$ to $^{2}H_{6}$ and $^{2}G_{4}$ to $^{2}H_{4}$, respectively) and emissions at 695 and 800 nm are two-photon ones ($^{1}F_{2}$ to $^{1}H_{6}$ and $^{3}F_{4}$ to $^{3}H_{6}$, respectively). A UC saturation effect would occur under a certain excitation intensity of the 980 nm CW diode laser for the as-obtained β-NaYF$_4$ : Yb,Tm nanocrystals, leading to the decrease of the slopes of the I–P curves. The results of our study also revealed that the successive transfer model instead of the cooperative sensitization model can be applied to explain the UC behaviors of the β-NaYF$_4$ : Yb,Tm nanocrystals, leading to the decrease of the slopes of the I–P curves. The results of our study also revealed that the successive transfer model instead of the cooperative sensitization model can be applied to explain the UC behaviors of the β-NaYF$_4$ : Yb,Tm nanocrystals, leading to the decrease of the slopes of the I–P curves.

Introduction

Upconversion (UC) phosphors, especially rare-earth-based (RE-based) UC phosphors, have been a hotspot of material research for several decades because of their wide and important applications in many realms, such as solid-state lasers, IR imaging and bioimaging.$^{1-2}$ Compared to those traditional biological labels, for example, organic dyes$^{3}$ and semiconductors,$^{4}$ RE-based UC fluorescent (from near-infrared (NIR) to visible) nanoparticles possess several inherent advantages, including weak autofluorescence backgrounds, strong penetration abilities for NIR radiation, resistances to photobleaching, and low toxicity,$^{5-6}$ among those UC materials, β-NaYF$_4$ is considered to be one of the most efficient host materials for green/blue UC phosphors when sensitized by Yb$^{3+}$ and activated by Er$^{3+}$/Ho$^{3+}$/Tm$^{3+}$ ions due to the relatively low lattice phonon energy.$^{1,7}$

More recently, much attention has been focused on the size/shape/phase-controlled synthesis, UC properties and mechanisms, and bio-applications of the NaYF$_4$ : Yb,Er/Tm nanocrystals.$^{8}$ For instance, Haase and co-workers$^{8}$ reported the precipitation-based synthesis of NaYF$_4$ : Yb,Er/Tm nanoparticles with bright UC emissions, revealing the application potential of UC nanocrystals in bio-imaging areas. Li et al.$^{9}$ obtained NaYF$_4$ nanocrystals with controllable size and morphology and high dispersibility by hydrothermal procedures. Yan et al.,$^{9}$ Capobianco et al.$^{9d,e}$ and Chow et al.$^{9f}$ developed the method of thermal decomposition of metal–organic complexes in hydrophobic high-boiling solvents to synthesize monodisperse NaYF$_4$ : Yb,Er/Tm nanocrystals with controllable size, shape and phase. Yan et al.$^{9b,c}$ also studied the nucleation and growth kinetics, and multicolor UC emissions and mechanisms of NaYF$_4$ : Yb,Er nanocrystals, revealing the relationships between the outcome UC emissions and size, shape, phase and composition of the nanocrystals. Liu and coworkers$^{9c,d}$ realized the tuning of the outcome UC light color of NaYF$_4$ : Yb,Er nanocrystals via incorporating Tm$^{3+}$ cations and altering the doping concentrations. Veggel et al.$^{9h}$ obtained transparent UC NPs-polymer composite materials via
dispersing NaYF₄ nanoparticles into PMMA through an in situ polymerization method. Zhang and co-workers employed NaYF₄: Yb,Er@SiO₂ as fluorescent labels in cell imaging. Also, they achieved multicolor UC fluorescence by using NaYF₄: Yb,Er nanocrystals as the energy donor in the FRET process to organic dyes and QDs.

Compared to the massive studies on the NaYF₄: Yb,Er nanocrystals with green UC emissions, researches on the NaYF₄: Yb,Tm nanocrystals with blue emissions are still scarce, though they are important and necessary supplement to the NIR to visible light UC nanomaterials. For example, Nann et al. exploited NaYbF₄: Tm nanocrystals as one of the probes for multiplexing detections. Zhang et al. studied the core–shell effects and the bio-applications of NaYF₄: Yb,Er and NaYF₄: Yb,Tm nanocrystals. Prasad et al. introduced NaYF₄: Yb,Tm nanoparticles as an in vitro and in vivo NIR–NIR UC probes. Further compared to the systematic studies of UC emissions and mechanisms of bulk NaYF₄: Yb,Tm materials, the fundamental understanding of the size/shape/phase modulated UC properties and mechanisms of NaYF₄: Yb,Tm nanocrystals is still rather inadequate.

In this article, we report the controlled synthesis, tuning of the UC emission colors, and the inherent UC mechanisms of monodisperse NaYF₄: Yb,Tm nanocrystals with different dopant ratios (Yb: 20–40%, Tm: 0.2–5%), sizes (25–150 nm), and shapes (sphere, hexagonal prism, and hexagonal plate).

Experimental section

A Schlenk line system and commercially available reagents were used in the synthesis procedure. Rare-earth oxides (RE = Y, Yb, and Tm), oleic acid (OA; 90%, Alpha), oleylamine (OM; >80%, Acros), 1-octadecene (ODE; >90%, Acros), trifluoroacetic acid (99%, Acros), CF₃COONa (>97%, Acros), absolute ethanol, and cyclohexane were used as received. RE(CF₃COO)₃ were prepared via the literature method.

Synthesis of α-NaYF₄: Yb,Tm nanocrystals

1 mmol of CF₃COONa and the appropriate proportion of Y(CF₃COO)₃, Yb(CF₃COO)₃, and Tm(CF₃COO)₃ were added to a mixed solution of OA (10 mmol), OM (10 mmol), and ODE (20 mmol) in a three-necked flask at room temperature. Then, the slurry was degassed and heated to 140 °C with vigorous magnetic stirring for 30 min in a temperature-controlled electromantle to remove water and oxygen, and thus to form an optically transparent, colorless or slightly yellow solution. Next, the solution was heated to 300 °C at a heating rate of 20 °C min⁻¹ under a high purified N₂ atmosphere. The solution became a bit turbid and was maintained at this temperature for 30 min under N₂ atmosphere. The solution was left to be air-cooled with gentle stirring for 5–10 min after it became transparent again. Then, an excess amount of ethanol was poured into the solution at room temperature. The resultant turbid mixture was separated by a centrifuge; and the products were collected. The as-precipitated nanocrystals, without any size-selections, were washed several times with cyclohexane and ethanol, and then dried at 80 °C in air for 24 h.

Synthesis of β-NaYF₄: Yb,Tm nanocrystals

The synthesis procedure of β-NaYF₄: Yb,Tm nanocrystals was similar to the synthesis of α-NaYF₄: Yb,Tm nanocrystals except that (a) quantitative CF₃COONa and α-NaYF₄:Yb,Tm nanocrystals were added to a mixed solution of OA (20 mmol), and ODE (20 mmol) and, (b) the reaction temperature was increased to 320–330 °C and maintained for 30–45 min (see Table S1 in the ESIF). These obtained nanocrystals could be easily redispersed in various nonpolar organic solvents (e.g., cyclohexane) and showed good redispersibility even after aging for a long time.

Instrumentation

X-ray diffraction (XRD) patterns of the dried powders were recorded on a Rigaku D/MAX-2000 diffractometer (Japan) with a slit of 1/2° at a scanning rate of 4° min⁻¹ using Cu-Kα radiation (λ = 1.5418 Å). Samples for transmission electron microscopy (TEM) analysis were prepared by drying a drop of colloid solution of NaYF₄: Yb,Tm nanocrystals in cyclohexane on copper grids coated by amorphous carbon. Particle sizes and shapes were examined by a TEM (200CX, JEOL, Japan) operated at 160 kV. High resolution TEM (HRTEM) and EDS analysis was performed on a FEG-TEM (Teeneai F30, Philips, USA) operated at 300 kV. UC emission spectra of all samples (1 wt % NaYF₄: Yb,Tm nanocrystal dispersion in cyclohexane) were measured on a Raman spectrometer (Jobin-Yvon HR800, France) with an external tunable 2 W 980 nm diode laser as the excitation source under the same conditions.

Results and discussion

1. Characteristics of β-NaYF₄: Yb,Tm nanocrystals

High-quality β-NaYF₄: Yb,Tm nanocrystals (nanospheres, hexagonal nanoprisms, and hexagonal nanoplates) in a pure hexagonal structure (space group: P6) with different Yb and Tm

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>Size/nm</th>
<th>Structure</th>
<th>Space group</th>
<th>Morphology</th>
</tr>
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<tbody>
<tr>
<td>Yb (%)</td>
<td>Tm (%)</td>
<td>24.4 ± 1.2</td>
<td>Hexagonal</td>
<td>P6</td>
</tr>
<tr>
<td>0.2</td>
<td>0.5</td>
<td>23.9 ± 0.8</td>
<td>Hexagonal</td>
<td>P6</td>
</tr>
<tr>
<td>150 × 70</td>
<td>Hexagonal plates</td>
<td>24.1 ± 0.8</td>
<td>Hexagonal</td>
<td>P6</td>
</tr>
<tr>
<td>24.2 ± 0.8</td>
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<td>24.5 ± 0.8</td>
<td>Hexagonal</td>
<td>P6</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
<td>23.7 ± 0.7</td>
<td>Hexagonal</td>
<td>P6</td>
</tr>
<tr>
<td>0.5</td>
<td>25.4 ± 1.0</td>
<td>Hexagonal</td>
<td>P6</td>
<td>Sphere</td>
</tr>
<tr>
<td>24.6 ± 0.8</td>
<td>Hexagonal</td>
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<td>Hexagonal</td>
<td>P6</td>
</tr>
<tr>
<td>40</td>
<td>0.2</td>
<td>23.9 ± 0.8</td>
<td>Hexagonal</td>
<td>P6</td>
</tr>
<tr>
<td>0.5</td>
<td>23.1 ± 0.9</td>
<td>Hexagonal</td>
<td>P6</td>
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</tr>
<tr>
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<td>Hexagonal</td>
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<tr>
<td>24.4 ± 1.0</td>
<td>Hexagonal</td>
<td>24.4 ± 1.0</td>
<td>Hexagonal</td>
<td>P6</td>
</tr>
</tbody>
</table>

* Molar ratio of reactants. ** The standard deviation statistic from at least 50 particles.
NaYF₄ : Yb,Tm nanocrystals showed high size- and shape-revealed by TEM measurements. All the obtained RE cations in the final nanocrystalline products agree well with the original molar ratios of the metal precursors (see Table 2), indicating that quantitative doping of Yb³⁺ and Tm³⁺ ions into NaYF₄ lattice was achieved by the present synthesis method.

2. UC properties of β-NaYF₄ : Yb,Tm nanocrystals

2.1. UC emissions of β-NaYF₄ : Yb,Tm nanocrystals. As shown in Fig. 3a, in the case of β-NaYF₄ : 30%Yb,0.5%Tm nanocrystals, the near-ultra-violet to visible emission bands of the UC spectra of Yb³⁺/Tm³⁺ transitions include 360 (1D₂ – 3H₆), 450 (1D₂ – 3H₄), 475 (1G₄ – 3H₆), 650 (1G₄ – 3H₄) and 695 nm (F₂ – 3H₄). The infrared emission at around 800 nm is much stronger than those of ultra-violet and visible light, which enables the as-obtained β-NaYF₄ : Yb,Tm nanocrystals to be excellent candidates for NIR-NIR bioprobes (Fig. 3b and Fig. S2 of the ESI†).

2.2. UC emissions of β-NaYF₄ : Yb,Tm nanocrystals with different doping ratios of Yb³⁺ and Tm³⁺. In the research work of bulk GdF₃ : Yb,Tm³⁺ and YF₃ : Yb,Tm³⁺ materials, Hewes et al.¹¹ and Ostermayer et al.¹² studied the UC luminescence mechanism of Yb³⁺ and Tm³⁺ system, pointing out the four-, three- and two-photon processes involved in the UC light and the effects of different doping ratios of Yb and Tm cations on the UC emissions.

The UC excitation and emission behavior of as-synthesized β-NaYF₄ : Yb,Tm nanocrystals are similar to those of bulk materials, and can be also artificially altered by changing different doping ratios. As seen from Fig. 4a, the UC intensities vary as a function of the doping ratio of Yb³⁺ and Tm³⁺. The UC emissions reached the maximum value at the molar ratio of 2:1 for Yb³⁺/Tm³⁺.
for the β-NaYF₄: 20%Yb,0.5%Tm sample is rather weak. With the concentration of Yb³⁺ fixed at 20%, as the molar ratio of Tm³⁺ decreases from 5% to 0.2%, the intensities of the emissions at around 360 and 450 nm increase more quickly than those at 475 and 650 nm. This result shows that the increase of Tm³⁺ concentration from 0.2% to 5% tends to quench the blue UC emissions. The same effects of different doping ratios of Tm³⁺ also take place when the molar ratio of Yb³⁺ is fixed at 30% and 40% (see Fig. S4 of the ESI†). As a result, by increasing the doping ratio of Tm³⁺, the color of the overall emission light can be tuned from bright blue to purple, and to dark red for the β-NaYF₄: 20%Yb,0.2–5%Tm nanocrystals (see Fig. 4b–f). As shown in Fig. 4b to f, after mild sonication, those colloid solutions which have been aged for more than half a year can be easily redispersed in cyclohexane showing relatively low scattering effects under the laser beam. The effect of different doping ratios of Yb³⁺ cations is shown in Fig. 5 and Fig S5.† With the molar ratio of Tm³⁺ ions fixed at 0.5% or 1%, the relative intensities of emissions at around 360, 450 and 475 nm gradually increase as the molar ratio of Yb³⁺ increases from 20% to 30% and to 40%, while that at around 650 nm is slightly changed.

2.3. UC emissions of β-NaYF₄: Yb,Tm nanocrystals with different sizes. Different particle sizes also result in the differences of relative intensities of each UC emission peak and thus the different overall color of the total UC emissions for the as-obtained β-NaYF₄: Yb,Tm nanocrystals. As shown in Fig. 6, when the particle sizes increase from 25 to 50 nm, the relative intensities of UV and blue emission (360 and 450 nm) increase dramatically, while the relative intensities of emissions at 475, 650 and 700 nm would not change so much, and thus the total color would become bluer as a result. When the size of β-NaYF₄: 30%Yb,0.5%Tm nanocrystals further increases to about 150 nm with the shape evolution from hexagonal prism to hexagonal plate, the relative intensity of two-photon process (695 nm) decreases significantly, while intensities of the four-photon processes (360 and 450 nm) also drop unexpectedly.

Compared to those smaller nanospheres or nanoprisms, UC properties of large hexagonal plates seem to be more similar to
those of $\beta$-NaYF$_4$ : Yb,Tm crystals in micro-scale$^{12}$ and macro-scale. In addition, as the particle size increases, the overall intensity of all UC emissions also increases for the as-obtained $\beta$-NaYF$_4$ : Yb,Tm nanocrystals, resulting in much brighter outcome light which can be seen by naked eyes. The reason for the variation in both relative and total emission intensities observed for the as-obtained $\beta$-NaYF$_4$ : Yb,Tm nanocrystals was considered to be mainly ascribed to different surface states of nanocrystals with different sizes and shapes, as also revealed in the studies of the UC properties of $\beta$-NaYF$_4$ : Yb,Er nanocrystals synthesized by similar methods.$^{68}$ On the one hand, larger particle size, i.e. smaller surface-to-volume ratio, means the existence of lower density of surface quenching centers and thus leads to the enhanced total UC emissions for the bigger $\beta$-NaYF$_4$ : Yb,Tm nanocrystals than those for the bigger ($\sim$150 nm) nanocrystals is interesting. The unexpected stronger four-photon process emissions in smaller $\beta$-NaYF$_4$ : Yb,Tm nanocrystals is rather interesting. Herein, we assumed that the unexpected UC spectra were caused by different local structures around the photoactive sites with the reduction of crystalline size, the increase of surface-to-volume ratio and the inhomogeneity of dopant ions in relatively small nanocrystals.$^{79}$ As mentioned above, in smaller particles, larger surface-to-volume ratio ($s/v$) would decrease the total intensity, as well as the relative intensity of emissions from higher energy levels ($^1D_2$ of Tm$^{3+}$, for example); however, in smaller particles the variation of doped Tm$^{3+}$ concentration in different nanocrystals (see EDS results in Table S2 of the ESi$^+$) would also be more significant than in larger ones and thus there would be some nanocrystals with much lower Tm$^{3+}$ concentrations which could give much stronger emissions from $^1D_2$ to $^3H_6$ as the self quenching of Tm$^{3+}$ ions decreased dramatically,$^{146}$ leading to the bluer emission. In our experiment, we further assumed that, when the particle size increased from about 25 nm ($s/v = 0.24$ nm$^{-1}$, sphere) to 50 nm ($s/v = 0.12$ nm$^{-1}$, hexagonal prism), the decreasing of surface-to-volume ratio would play a dominant role in affecting the UC emissions, and the intensity of four-photon process emission would become much stronger. However, when the nanocrystals grew further to $\sim$150 nm hexagonal plates ($s/v = 0.06$ nm$^{-1}$, $150 \times 70$ nm, hexagonal plates), the decreasing of surface-to-volume ratio would not have obvious influence on the UC spectra as before. While the enhanced doping homogeneity in large nanocrystals would lead to fewer nanocrystals in which the Tm$^{3+}$ doping concentrations were much lower than expected (see EDS results in Table S2 in the ESi$^+$), and then resulted in the decrease of the relative intensity of four photon emissions. In addition, we supposed that as the particle size increased to hundreds of nanometres, the scattering effects of those particles in the colloidal solutions would become much stronger, which may also have strong effects on the acquired UC spectra.

### 3. UC mechanism of $\beta$-NaYF$_4$ : Yb,Tm nanocrystals

To confirm the multi-photon processes involved in the UC behaviors of our $\beta$-NaYF$_4$ : Yb,Tm nanocrystals, we carried out the power density dependent UC measurements. As shown in Fig. 6 and Fig. S3, we can easily assign the emission bands to different multi-photon transition processes. The ultra-violet emission at about 360 nm and blue emission at about 450 nm are of four-photon processes, that is, the transition from $^1D_2$ to $^3H_6$ and $^1H_6$, respectively. The blue emission at about 475 nm and red emission at about 650 nm are of three-photon processes, $^1G_4$ to $^1H_6$ and $^1G_4$ to $^1H_6$, respectively. And the two-photon UC processes include the emission band of about 695 nm (red, $^3F_3$ to $^3H_6$).

During the characterization of UC emissions of $\beta$-NaYF$_4$ : 30%Yb,0.5%Tm nanocrystals (23.9 ± 0.8 nm), we found that slopes of intensity-power ($I/P$) curves of near-UV and visible emission bands would decrease, meaning that a UC saturation effect would take place when the excitation power density of the 980 nm laser increased up to a certain value (see Fig. S6 in the ESi$^+$). We considered the decrease of the $I/P$ curve slopes to be the result of saturation effects of the intermediate levels of Yb$^{3+}$ and Tm$^{3+}$ (esp. $^2F_{5/2}$ of Yb$^{3+}$, $^1D_2$, $^1G_4$ and $^3F_4$ of Tm$^{3+}$), which, as pointed out by Hewes et al.,$^{114}$ can be easily affected by heating effects of the NIR laser beam and some other factors.

Our analyzed experiment results (see Fig. 6 and Fig. S2, S3 and S6 in the ESi$^+$) indicate that the transitions from energy level $^1D_2$ to $^3H_6$ (ground state), $^1H_4$ and $^1H_6$ are four-photon processes, transitions from $^3G_4$ to $^3H_6$ and $^1H_4$ are three-photon processes,
NaYF₄ : Yb,Tm nanocrystals would result in brighter UC light and emissions at 450 and 475 nm (especially the one at 450 nm) (see Fig. 5 and Fig. S5†). However, as the ratio of Yb³⁺ increases further, the quenching of Tm³⁺ manifolds by Yb³⁺ would become more significant and the blue emissions would become weaker instead of becoming stronger any more.³⁹ Our experiments have proved that β-NaYF₄ : 40%Yb,0.5%Tm nanocrystals are much better UC materials with blue emissions than β-NaYF₄ : 20%Yb,0.5%Tm nanocrystals (see Fig. 5). In addition, it is observed with naked eyes that relatively larger β-NaYF₄ : Yb,Tm nanocrystals would result in brighter UC light due to the less surface defects as well as less influence of surface ligands.⁹

As discovered above, a relatively low ratio of Tm³⁺ and about 40% or more of Yb³⁺ may result in the brighter and bluer emissions. Maybe a much lower percentage of Tm³⁺ would also lead to the enhancement of UC transitions of Yb³⁺/Tm³⁺; however, the segregations of Tm³⁺ cations in different particles would be a big problem in the nano-scale if only trace amount of Tm³⁺ was used in the synthesis procedure. And if for bio-imaging applications, a proper size of the nanocrystals should be chosen in order to balance the intensity of emissions and the colloidal dispersibility of the nanocrystals. Also, we noticed that when the concentration of Yb³⁺ raises to even higher stage, the UC emission process, as well as the mechanism beyond, would be significantly different from those discussed above, which would be one of the issues of our further studies.

Conclusions

Differently-sized, monodisperse, and single-crystalline β-NaYF₄ : Yb,Tm nanocrystals were obtained by the thermolysis of metal trifluoroacetates in hot surfactant solutions under a controllable and reproducible way. Multicolor UC emissions (blue, purple and red) can be observed for the as-synthesized β-NaYF₄ : Yb,Tm nanocrystals when excited by a 980 nm CW laser. Through investigating the effects of different concentrations of Tm³⁺ and Yb³⁺ cations and different particle sizes on the UC behaviors of the as-obtained nanocrystals, we found out that relatively low concentrations of Tm³⁺ (i.e. 0.2%) and high doping ratios of Yb³⁺ (i.e. 40%) were more favored to get purer and brighter blue emissions. We have also deduced the four-, three-, and two-photon processes of the UC excitation and emissions for our β-NaYF₄ : Yb,Tm nanocrystals, and proved that the successive transfer model instead of the cooperative sensitization model would be applied to account for the UC mechanism of the present nanocrystals. The unexpected stronger emissions of a four-photon process at 360 and 450 nm for ~50 nm β-NaYF₄ : Yb,Tm nanocrystals than those for the bigger (~150 nm) nanocrystals was observed and explained in terms of the effects of crystal size, surface-volume ratio and homogeneity of the doping cations. In prospect, this work has provided new scientific insights in understanding the fundamental aspects of the size, composition-dependent UC properties and mechanisms of NaYF₄ : Yb,Tm nanocrystals with blue emissions in the nanometric regime, and promises various nanodevice applications (particularly for bio-imaging and bio-labeling) with the as-synthesized nanocrystalline UC phosphors.

Acknowledgements

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Notes and references


