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Multicolor tunability and upconversion enhancement of fluoride nanoparticles by oxygen dopant

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The ability of manipulating upconversion luminescence of lanthanide-ion doped fluoride upconversion nanoparticles (UCNPs) is particularly important and highly required due to their widely applications in color displays, multiplexing bioassays and multicolor imaging. Here, we developed a strategy for simultaneously tuning color output and enhancing upconversion emission of Yb/Er doped fluoride UCNPs, based on adjusting oxygen doping level. The synthesis of multicolored multifunctional NaGdF4:Yb, Er UCNPs was used as the model host system to demonstrate this protocol. Ammonium nitrate (NH4NO3) was used as oxygen source and added into reaction system at the beginning stage of nucleation and growth process of fluoride UCNPs, which facilitate the formation of enough oxygen atoms and the diffusion of those into fluoride host matrix. The results revealed the multicolour output and upconversion enhancement mainly resulted from the variation of phonon energy and crystal field symmetry of host lattice, respectively. This strategy can be further expanded to other fluorides host matrices. As an example of the application, multicolored UCNPs were used as color converter in light emitting diodes, which can effectively convert near-infrared light into visible ones. It is expected these multicolored UCNPs are promising for applications in multiplexing biodetection, bioimaging (optical and magnetic resonance imaging) and other optical technologies, and the present method for the control of O2- doping may also be used in other functional nanomaterials.

Introduction

The ability of tuning multicolor emission of upconversion nanomaterials is important for their myriad applications in sensing, display, light emitting technology, in vitro and in vivo bio-imaging and medical sciences.1 As compared to the conventional organic fluorescent dyes and quantum dots, lanthanide-ion doped fluoride upconversion nanoparticles (UCNPs) show great potential technological applications,2,3 because they exhibit low cytotoxicity,4 high resistance to photobleaching and blinking,5 large anti-Stokes shifts,6 narrow-band emissions, high chemical stability,7 deep penetration to biological tissues,8,9 and high signal-to-noise ratio.10-11

Recently, several attempts have been made to tune multicolor upconversion emission. The typical approach is doping multi-activators and adjusting their concentration in upconversion nanomaterials.12-14 Because lanthanide ion exhibit characteristic emission bands with specific wavelengths, the multicolor output of UCNPs can be obtained by adjusting the intensities of different emission peaks of various activators through controlling their40 doping level in nanoparticles. However, the presence of high concentration dopant and multi-activators could result in high cross-relaxation, and thus reduce upconversion intensity.12 Researchers have been attempting to minimize this deleterious cross-relaxation in multiply activators recently.11 Alternatively, multicolor tuning from single lanthanide-ion activator can also greatly enrich the colors of UCNPs by controlling the relative intensities of different emission peaks.10a,13,14 Although we had reported the manipulation of color emissions from single lanthanide-ion activator,10a,13,14 the upconversion emission intensity was still sacrificed, which may limit applications of fluoride UCNPs due to the reduced emission intensity. Therefore, to ensure the application performance of UCNPs, it is important and highly required to develop a method for simultaneously tuning color output and enhancing upconversion emission, however, it is still a substantial challenge.15

Here, we report a strategy for simultaneously tuning color output and enhancing upconversion emission of single lanthanide-ion activator in fluoride UCNPs, based on adjusting oxygen doping level. Er/Yb doped NaGdF4 UCNPs were chosen as the model host system to demonstrate this protocol because of its multifunctional properties.16,17 Ammonium nitrate (NH4NO3) was used as the oxygen source to introduce the oxygen dopant (O2-) into host matrix of fluoride UCNPs. The existence of oxygen dopant in fluoride host lattice enhances phonon energy of fluoride host lattice and increases the transition probability of Er3+ ions, resulting in the variation of Er/Yb doped fluoride emissions from green to red. Moreover, O2- ions doping also induces the great enhancement of upconversion luminescence and the splitting of red-emitting level of Er3+ ions due to the decrease of crystal field symmetry. In the proof-of-concept, the O2- ions...
doped upconversion nanoparticles were incorporated into polymer and employed as color converter in light emitting diodes (LEDs) (Scheme 1).

**Experimental**

**Synthesis of multicolor nanoparticles**

For a typical synthesis of NaGdF$_4$:Yb, Er UCNPs, a mixture of Er$_2$O$_3$ (0.02 mmol), Yb$_2$O$_3$ (0.20 mmol), Y$_2$O$_3$ (0.78 mmol) and Na$_2$CO$_3$ (1.0 mmol) was dissolved in 10 mL of 50% aqueous trifluoroacetic acid at 80 °C. The residual water and acid were slowly evaporated to dryness. Then, octadecylamine (100 mmol) were added. The reaction solution was heated to 120 °C and maintained for 30 min under reduced pressure with magnetic stirring to remove residual water and oxygen, during which time the flask was purged periodically with dry nitrogen. The resulting optically transparent solution was heated to 300 °C and maintained for 1 h under a nitrogen atmosphere. During the heating process, a certain amount of NH$_4$NO$_3$ was added into reaction system at 250 °C, because which facilitate the formation of enough oxygen and the diffusion of formed oxygen dopant into host matrix. The products were isolated by centrifugation. This procedure was repeated at least two times. The resulting nanoparticles were dried under vacuum for 24 h.

NaGdF$_4$:Yb, Er UCNPs with multicolor output were obtained by changing the added amount of NH$_4$NO$_3$ while other conditions were held constant. The procedure for the synthesis of NaYF$_4$:Yb, Er and NaLuF$_4$:Yb, Er UCNPs was similar to the above description.

**Synthesis of methyl methacrylate-butyl acrylate copolymer (P(MMA-co-BA))**

1.0 g of AIBN was added into the flask containing 150 mL of petroleum ether. The solution was heated to 80 °C. Then a mixture solution of methyl methacrylate (15 g) and butyl acrylate (15 g) were dropped into the above solution. The polymerization proceeded for 6 h at 80 °C. The resulting turbid solution was cooled to room temperature. The P(MMA-co-BA) was obtained by precipitation and dried under vacuum for 24 h.

**Preparation of nanocomposite and coating on NIR-LED devices**

Various amounts of NaGdF$_4$:Yb, Er UCNPs with multicolor output (100 mg for 50 wt %, 70 mg for 35 wt %, 40 mg for 20 wt %) were dispersed in 3 mL of chloroform solution. Then 100 mg of P(MMA-co-BA) was added and the mixture was sonicated for 10 min. The chloroform was then slowly evaporated, and the polymer thin film was coated on the lens of LEDs by solvent casting.

**Characterization**

Upconversion fluorescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer under the excitation of a 980 nm diode laser. The transmission electron microscopy (TEM) images were taken with a Tecnai F20 S-TWIN microscope. Powder X-ray diffraction patterns were recorded on a Rigaku D/MAX-2400 diffractometer with Cu-Ka radiation. The scanning-step size was 0.02°. X-ray fluorescent spectra were measured with an XRF-1800 spectrophotometer of SHIMADZU. Raman spectra were collected on a DL-2 Raman spectroscopy equipped with a 244 nm laser (Dalian Institute of Chemical Physics, China).

**Results and discussion**

**Preparation and structure characterization of NaGdF$_4$:Yb, Er UCNPs**

To introduce the oxygen dopant into host matrix of fluoride UCNPs, ammonium nitrate (NH$_4$NO$_3$) was used as the oxygen source and added into reaction system at 250 °C, because which facilitate the formation of enough oxygen and the diffusion of formed oxygen dopant into host matrix (Fig. S1 and S2). The O$^2-$ doping level in fluoride UCNPs was controlled by adjusting

![Scheme 1](image_url)
the amount of NH₄NO₃. TEM in Fig. 1 shows NaGdF₄:Yb, Er UCNPs prepared with varying amounts of NH₄NO₃ are all near-spherical shape. The mean size of nanoparticles increases from 7 nm, to 10, 13 and 14 nm with the amount of NH₄NO₃ increased from 0 mg, to 20, 30 and 40 mg, respectively. This is because the formed oxygen increased the concentration of anion in reaction solution and promoted the growth of NaGdF₄:Yb, Er UCNPs, and thus resulted in the increase of nanoparticles size. This is in agreement to X-ray diffraction patterns (XRD) of UCNPs where the diffraction peak width narrowed with the increase of NH₄NO₃. XRD pattern of those particles shows that there are cubic α-NaGdF₄:Yb, Er (JCPDS No.27-0697) and there were no GdOF and no other phase and impurities were formed. X-ray fluorescent spectroscopy (XRF) was used for the measurement of doped oxygen content in NaGdF₄ UCNPs. It is shown that the oxygen content in NaGdF₄:Yb, Er UCNPs increased gradually from 2.09 wt% to 10.10 wt% with the increase of the amounts of NH₄NO₃ from 20 mg to 50 mg (Table 1). This result was further validated by XRD pattern where the diffraction peak positions shifted to the high-angle direction (e.g. (200), (220) and (311), Fig. S3), indicating that the lattice cell contracted as O²⁻ partially substituted for fluorine ions (F⁻). It is noted that the lattice cell contracted though the radius of O²⁻ (140 pm) was larger than that of F⁻ (133 pm), because one O²⁻ can substitute two F⁻ positions in host lattice due to the electrical neutrality of whole fluoride particle, which further implied the incorporation of oxygen into NaGdF₄ host.

### Multicolor tunability and enhancement of upconversion emission

Fig. 2a shows NaGdF₄:Yb,Er UCNPs prepared with no oxygen doping show the strong green emission peaks around 520 and 540 nm, which can be assigned to the H₁₁/₂, S₅/₂ → I₇/₂ transitions, and the relative weak red emission peaks of F₉/₂ → I₅/₂ transition of Er³⁺ ion. The doping of O²⁻ ions in UCNPs led to a fast increase in red emission of Er³⁺ ions, resulting that the intensities ratio of green to red emissions gradually decreases from 2.60 to 0.02 (Fig. S4), and therefore the color output of NaGdF₄:Yb,Er could be finely tuned from green to red. When the added amount of NH₄NO₃ was increased to 40 mg, the red emission increased significantly and pure red emission was observed (Fig. 2b and S4). To investigate the multicolor output mechanism, we further tested the upconversion mechanism of NaGdF₄:Yb,Er UCNPs. The number of photons involved in the upconversion process was calculated by the power dependent luminescence intensities in log-log plots. The experimental data for 550 and 650 nm emission bands of NaGdF₄:Yb, Er were fitted with a straight line with a slope of ~2 (Fig. 2c and S5), indicating a two-photon emission process. According to the two-photon involved energy transfer upconversion process (Fig. 2d), the nonradiative absorption of...
The weighted average phonon energies of NaGdF$_4$:Yb, Er enhanced gradually with the increase of oxygen contents. This in turn has increased the multiphonon-nonradiative relaxation probabilities of excited Er$^{3+}$ ion from $^2$H$_{11/2}$, $^4$S$_{3/2}$ to $^4$F$_{9/2}$ level and $^1$I$_{11/2}$ to $^1$I$_{13/2}$ level, and reduced the intensities ratio of green to red emissions, and therefore resulted in multicolor emission.

It is noted that doping of O$_2^-$ ions not only facilitates the output of red emission but also greatly enhances the intensity of upconversion emission (Fig. 2b). The introduction of sufficient O$_2^-$ ions into NaGdF$_4$:Yb,Er led to a strong and enhanced red emission (Fig. 2b) due to the increase of particle size,$^{25}$ the multiphonon-nonradiative relaxation process and the change of crystal field symmetry of light-emitting lanthanide-ion. The increase of nanoparticle size enhanced the upconversion emission by reducing the surface quenching.$^{25}$ And the O$_2^-$ doping resulted in the red-emitting level to the red-emitting ones, and then also enhance the red emission (Fig. 2d). Furthermore, the doping O$_2^-$ ions dopant decreases the crystal field symmetry, which increases the transition probability of forbidden-transitional 4f electrons of lanthanide ions, thus further enhancing emission.$^{13b,13e}$ This phenomena are in consistent with the recent reports on Mn$^{2+}$ ions doped nanoparticles.$^{13e,26}$ It is also observed the great splitting of red-emitting level of Er$^{3+}$ ion when O$_2^-$ dopant content was higher than 7.13 wt%, indicating the decrease of crystal field symmetry of fcc NaGdF$_4$, further suggesting the doping of O$_2^-$ ions into NaGdF$_4$ crystal.$^{13e,27}$

**Oxygen ions doping mechanism**

To elucidate the doping mechanism of O$_2^-$ ions, we added NH$_4$NO$_3$ into reaction solution at different temperatures and investigated the effect of that on the upconversion luminescent properties. It is observed that the relative intensities of red emission ($^4$F$_{9/2}$$\rightarrow$$^1$I$_{15/2}$ transition) of Er$^{3+}$ ions increased with increasing the addition temperature from 120 to 250 °C (Fig.S2).

When NH$_4$NO$_3$ was added into reaction solution at 300 °C, the relative intensity of red emission decreased again. Usually, the thermal decomposition mechanism of NH$_4$NO$_3$ was as follows lower than 150 °C:$^{17}$

$$\text{NH}_4\text{NO}_3 \rightarrow \text{HNO}_3 + \text{NH}_3$$

$$4\text{HNO}_3 \rightarrow 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2$$

$$\text{NH}_4\text{NO}_3 + 2\text{NO}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} + 2\text{HNO}_3$$

When the temperature was higher than 230 °C, NH$_4$NO$_3$ was decomposed as follows:

$$2\text{NH}_4\text{NO}_3 \rightarrow 2\text{N}_2 + \text{O}_2 + 4\text{H}_2\text{O}$$

Generally, oxygen atoms were first formed after decomposition of NH$_4$NO$_3$. Two formed oxygen atoms combined to form O$_2$. The formed oxygen atoms can be partially reduced to oxygen ions in the presence of octadecylamine molecule due to the reduction capability of amine group.$^{28}$ It is observed that more oxygen atoms were formed for a certain amount of NH$_4$NO$_3$. 

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**References**

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**Fig. 3** Raman spectra of NaGdF$_4$ nanoparticles prepared with various amount of NH$_4$NO$_3$, 2 mmol. Due to the strong luminescence of Er$^{3+}$ ion under ultra-violet laser excitation, the ratio of signal-to-noise of Raman spectra could be declined. Thus, the corresponding Yb and Er undoped NaGdF$_4$ nanoparticles were synthesized in the same way for the test of phonon energy by Raman spectroscopy.

Lanthanide ion can be affected by the surrounding crystal field environment after doping into the host lattice according to the crystal field theory. The phonon energy of host lattice (or host lattice vibration) could affect the multiphonon-relaxation of the excited lanthanide ion. The nonradiative relaxation of excited 4f electron from a high-energy emitting level to a low-energy one can increase the populations of a low-energy emitting level, and thus enhance the light output in that level. According to Miyakawa-Dexter theory,$^{23}$ the multiphonon-nonradiative relaxation probability among various excited levels of lanthanide ion is expressed the following:

$$W_n(T) = W_n(0)[1 - \exp(-h\nu/kT)]^n$$

where $W_n(T)$ is the rate at temperature $T$, $W_n(0)$ is the rate at 0 K, $n = \Delta E/h\nu$, $\Delta E$ is the energy gap to the next level, and $h\nu$ is the phonon energy involved. The equation indicates the higher the phonon energy, the higher the nonradiative relaxation probability of excited lanthanide ion. The phonon energy of upconversion nanoparticles with different O$_2^-$ content were measured by Raman spectroscopy (Fig. 3). It is revealed that NaGdF$_4$ nanoparticles prepared with 0, 20, 30, and 50 mg of NH$_4$NO$_3$ exhibit the peak 1 positions at 323, 328, 332 and 335 cm$^{-1}$, respectively. The results show the red shift with increasing oxygen content. In addition, the relative intensities of peaks 2 (410 cm$^{-1}$) and 3 (538 cm$^{-1}$) increase gradually. These results indicated that the weighted average phonon energies of NaGdF$_4$:Yb, Er enhanced gradually with the increase of oxygen contents. This in turn has increased the multiphonon-nonradiative relaxation probabilities of excited Er$^{3+}$ ion from $^2$H$_{11/2}$, $^4$S$_{3/2}$ to $^4$F$_{9/2}$ level and $^1$I$_{11/2}$ to $^1$I$_{13/2}$ level, and reduced the intensities ratio of green to red emissions, and therefore resulted in multicolor emission.$^{24}$

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when the temperature was higher than 230 °C. Correspondingly, more oxygen dopant would diffuse into the host lattice of fluoride nanoparticles, which facilitates the improvement of O$_2^-$ doping level in fluoride UCNPs and the enhancement of phonon energy, resulting in the increase of red emission. In addition, UCNPs were in large size when the temperature rises to 300 °C, because fluoride UCNPs began to nucleate and grow after decomposition of metal trifluoroacetate precursors at around 250 °C.  

Although NH$_4$NO$_3$ can effectively decompose into oxygen atoms at 300 °C, it is difficult to further diffuse formed O$_2^-$ ions into host lattice of fluoride UCNPs with large size (See Supporting Information Fig. S6). Together, NH$_4$NO$_3$ was added into reaction system at the beginning stage of nucleation and growth process of fluoride UCNPs (at around 250 °C) facilitated the formation of enough oxygen atoms and the diffusion of that into fluoride host lattice (Scheme 2). Therefore, the improvement of red emission of Er$^{3+}$ ions and the manipulation of the color output of fluoride UCNPs were easily achieved by adjusting the amount of NH$_4$NO$_3$.

**Multicolor output of other fluoride UCNPs**

To extend the generality of the control of oxygen doping in fluoride nanomaterials for color tuning and upconversion enhancement, we also synthesized NaYF$_4$:Yb, Er and NaLuF$_4$:Yb, Er UCNPs based on the above method. Similarly, we can also achieve the multicolor output of Yb/Er in other fluoride host lattices in the same way (Fig. 4). The red emission (4F$_{9/2}$$\rightarrow$4I$_{15/2}$) of Er$^{3+}$ ions increased strongly with the increase the addition amounts of NH$_4$NO$_3$ (Fig. 4, S7 and S8). The relative intensities of green emission bands decreased rapidly. We can observe that the green emissions almost disappeared and only red emissions were exhibited for NaYF$_4$:Yb, Er and NaLuF$_4$:Yb, Er UCNPs after addition of 20 and 16 mg of NH$_4$NO$_3$, respectively. Correspondingly, the yellow-green, yellow, orange and red were shown. And upconversion emission intensities were also enhanced greatly. These results indicate that the multicolor tuning and upconversion enhancement of Er ion in other fluoride host lattices (e.g. NaYF$_4$ and NaLuF$_4$) can also be achieved based on controlling oxygen doping by adjusting the amount of NH$_4$NO$_3$.

**Application of multicolored UCNPs as color converter materials for LED devices**

In a proof-of-concept, the oxygen doped fluoride UCNPs with multicolor emission and high photostability were used as color converter material in light emitting devices. The multicolored NaGdF$_4$:Yb, Er UCNPs were mixed with methyl methacrylate-butyl acrylate copolymer (P(MMA-co-BA)) to prepare nanocomposites. The nanocomposite with various amount of NaGdF$_4$:Yb, Er nanoparticles was fabricated and their upconversion spectra were measured. The upconversion intensities of nanocomposites were enhanced with the increasing of upconversion nanoparticles content (Fig. 5a). The color-converted LEDs exhibited bright near green, yellow-green, yellow and red output (Fig. 5b), which corresponded to the

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**Scheme 2** Schematic illustration of O$_2^-$ ions doping mechanism.

**Fig. 4** Upconversion spectra of NaYF$_4$:Yb,Er (a) and NaLuF$_4$:Yb,Er (b) UCNPs prepared with various amount of NH$_4$NO$_3$ per 2 mmol (normalized to Er$^{3+}$ 655 nm emission). All of the UCNPs were excited at 980 nm with a 260 mW diode laser.
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Notes and references

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† Electronic Supplementary Information (ESI) available: upconversion spectra of NaYF₄:Yb, Er UCNP's prepared with various oxygen sources (trimethylamine N-oxide and ammonium carbonate, Fig. S1) and different addition temperatures of NH₄NO₃ (Fig. S2), enlarged XRD patterns (Fig. S3), the intensity ratios of green to red emissions of NaGdF₄:Yb, Er UCNP's prepared with various amounts of NH₄NO₃ (Fig. S4), power dependence of upconversion spectra of NaGdF₄:Yb, Er UCNP's prepared at 300 °C for 1 h (Figure S5), upconversion spectra of the product after further reaction between as-prepared NaYF₄:Yb, Er and 50 mg of NH₄NO₃ at 300 °C for 1 h (Fig. S6), XRD patterns of NaYF₄:Yb, Er and NaLuF₄:Yb, Er UCNP's prepared with various amounts of NH₄NO₃ (Fig. S7 and S8), the corresponding magnetization curves of NaGdF₄:Yb, Er UCNP's (Fig. S9). See DOI: 10.1039/b000000x/c.