Triple-doped KMnF$_3$:Yb$^{3+}$/Er$^{3+}$/Tm$^{3+}$ nanocubes: four-color upconversion emissions with strong red and near-infrared bands

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Triple-doped (Yb$^{3+}$/Er$^{3+}$/Tm$^{3+}$) KMnF$_3$ nanocubes with uniform sizes of 250 nm were synthesized by a facile hydrothermal route using the oleic acid as the capping agent. It was found that these nanocubes can simultaneously exhibited four-color (blue, green, red and NIR) upconversion emissions under a single 980 nm near-infrared (NIR) laser excitation, which should have potential multicolor in vivo imaging applications. Specifically, the red (660 nm) and NIR (800 nm) peaks, known as two “optical windows” for imaging biological tissues, were strong. The spectral and pump analyses indicated the two-photon processes were responsible for the both red and NIR emissions.

Upconversion nano-particles (UCNPs) have the ability to convert lower energy (near-infrared (NIR) or infrared (IR)) radiation into high-energy radiation (ultraviolet or visible) via multiphoton absorption and energy transfer (ET) processes, which are promising for applications in optical bioimaging, biodetection, clinical diagnosis, three-dimensional display technologies, photocatalysis, as well as solar cells. To date, the rather popular UCNPs systems for biomedical imaging applications are mainly based on Er$^{3+}$ and Tm$^{3+}$ ions sensitized by Yb$^{3+}$ ions with visible and near-infrared emissions. The emissions of UCNPs in the red (660 nm, Er$^{3+}$/Yb$^{3+}$) and NIR regions (800 nm, Tm$^{3+}$/Yb$^{3+}$) are known as the two “optical windows” for imaging biological tissues. The red emission is suitable for in vitro imaging because the images can be observed by naked eyes. In vivo imaging prefers NIR-to-NIR emissions, allowing certain penetration depth for inspection. For the red emissions, Bai et al. showed that varying Yb$^{3+}$ concentration or doping Mn$^{2+}$ ions into the NaYF$_4$ matrix were effective for red luminescence enhancement. For the NIR emissions, Chen et al. reported that the UC NIR emission at 800 nm was increased by 43 times in NaYF$_4$:Yb$^{3+}$/Tm$^{3+}$ nanoparticles by heavily doping with Yb$^{3+}$ ions. Recently, Liu group successfully prepared KMnF$_3$ nanocrystals codoped with Yb$^{3+}$/Er$^{3+}$ or Yb$^{3+}$/Tm$^{3+}$ ions and found them showing substantially higher red and NIR emission intensity than that of the rare-earth doped NaYF$_4$ nanocrystals. In general, most of the conventional imaging methods are monochrome and only able to detect one contrast agent at a time, limiting us to single parametric data. However, the unique properties of multicolor emissions, photostability, high penetration depth, and low photo damaging in principle enable UC materials to act as multi-color imaging probes for biomedical applications. In the pioneer work of multicolor imaging in vivo, Kobayashi et al. employed a polyamidoamine dendrimer platform linked to five dye molecules as different optical probes, permitting five-color optical imaging using a multiple-excitation spectrally resolved fluorescence imaging technique. However, simultaneously providing multicolor excitation lights and guarantee their penetration depths...
which are determined by the nature of light color itself are difficult, and thus it limits the practical applications of multicolor in vivo imaging.

Due to multicolor emission characteristics of UCNPs, simultaneous detection of multiple analytes or optical probes in a complex sample should be feasible if appropriate UCNPs were prepared and used. Ideally, in vivo multicolor tissue characterization relies on: (1) the identification of multiple targets; (2) target-specific optical probes with distinct fluorescent properties; and (3) effective real-time multicolor optical cameras that permit accurate unmixing of different fluorescent probes with a single NIR excitation in vivo. The present rare-earth doped nanocrystals are generally not suitable for multiplexing biodetection, due to their limited number of colors. It is therefore necessary to develop UCNPs with multicolor fluorescence emissions under NIR excitation at the same wavelength. Along this line, several recent studies focused on multicolor UC emission with a more boader spectrum of color output by using different host/activator combinations. Rantanen et al. demonstrated simultaneous detection of two analytes using UC donors with multiplex emission characteristics. Nann et al. reported the preparation of complex colloidal UCNPs systems and observation of the four-color (blue, green, red and NIR) emissions. They synthesized four different types of UCNPs by doping NaYbF₄ with different rare-earth ions, and thus obtain a four-color UC emission system for the potential multiplexing analysis by mixing these UCNPs. Jiang et al. prepared core-shell structured nanoparticles with UCNP core and dye-doped silica shell to enable multi-color emissions for multiplex bioassays.

Herein, we developed a facile hydrothermal strategy to obtain multicolor emissions by preparing tri-doped KMnF₃:Yb³⁺/Er³⁺/Tm³⁺. The as-prepared UCNPs exhibit four-color (blue, green, red and NIR) UC emissions upon a single excitation at 980 nm, which should have a potential use in multicolor in vivo imaging for simultaneously providing multi-color excitation lights with deep imaging depth. In addition, UCNPs are a promising candidate to harvest NIR sunlight and improve the power conversion efficiency of solar cells, i.e., dye sensitized solar cell (DSSC). As some DSSC are designed based on the addition, UCNPs are a promising candidate to harvest NIR sunlight and improve the power conversion efficiency of complex colloidal UCNPs systems and observation of the four-color (blue, green, red and NIR) emission bands matching the absorption bands of dyes may have a potential to improve overall absorption efficiency.

**Results and Discussion**

Figure 1a is a typical SEM image of as-prepared KMnF₃:20%Yb³⁺/2%Er³⁺/2%Tm³⁺ UCNPs and Fig. 1b shows the average size distribution of the samples corresponding to those in Fig. 1a. It can be seen that the UCNPs are well dispersed and exhibit uniform nanocube shape with an average size of 250 nm. The crystal structures and the phase purity of the as-prepared tri-doped KMnF₃ nanocubes were examined by the X-ray diffraction (XRD) analysis (see Fig. 1c). All peaks are sharp and match well with the standard JCPDS No.17-0116 of KMnF₃, indicating high phase purity and crystallinity of obtained samples.

Typical UC emission spectra for various samples under diode laser excitation of 980 nm are shown in Fig. 2. KMnF₃:Yb³⁺/Tm³⁺ samples show only one blue emission at 476 nm and one NIR band at 800 nm (Fig. 2a), corresponding to the ⁴G₄ (Tm³⁺) → ³H₄ (Tm³⁺), and ³H₄ (Tm³⁺) → ³H₄ (Tm³⁺) transitions of Tm³⁺ ions, respectively. KMnF₃:20%Yb³⁺/2%Er³⁺ samples show only a single red emission at 660 nm corresponds to the ⁴F₉/₂ → ⁴I₁₁/₂ transitions of Er³⁺ ions (Fig. 2b). Very interestingly, tri-doped KMnF₃:Yb³⁺/Er³⁺/Tm³⁺ nanocubes exhibits four-colored bands (Fig. 2c). Noteworthy that, besides emission bands of 476 nm, 800 nm owing to Tm³⁺ ions and the 660 nm band owing to Er³⁺ ions are all preserved in the spectra, a new green UC emission centered at 540 nm is also observed at the same time.

Firstly, appearance of the new 540 nm green UC emission can be explained as follows. Usually, the single red UC emission (660 nm) is observed for Yb³⁺/Er³⁺ codoped KMnF₃ samples. However, for tri-doped KMnF₃:Yb³⁺/Er³⁺/Tm³⁺ samples, owing to the coexistence of Er³⁺ and Tm³⁺ ions, the cross relaxation ³F₅/₂ (Tm) + ⁴F₉/₂ (Er) → ⁴G₄ (Tm) + ⁴I₁₁/₂ (Er) between Tm³⁺ and Er³⁺ ions in KMnF₃, may cause decreases in population of ⁴I₁₁/₂ state and increases in population of ⁴G₄ state. The green emission is thus generated through the ⁴H₅/₂ → ⁴S₅/₂ → ⁴I₁₁/₂ transition of Er³⁺ ions as explained in detail below.

Secondly, UC emission intensity (I) was further measured as a function of laser power (P) (Fig. 3) to explore the UC mechanism of Yb³⁺, Tm³⁺, and Er³⁺ ions in KMnF₃ matrix. Because Iᵢ ≈ Pⁿ holds for the unsaturated UC process, where n is the number of pump photons absorbed per upconverted photons emitted, the value of n can be determined to be the slope after linearly fitting the I-P data in a double logarithmic plot. For the tri-doped KMnF₃:Yb³⁺/Er³⁺/Tm³⁺ sample, the obtained n values are 2.94, 1.95, 1.92, and 1.99 respectively for the UC emission peaks at 476 nm (blue), 540 nm (green), 660 nm (red), and 800 nm (NIR). Therefore, it can be deduced that the three-photon process is responsible for blue UC emission, two-photon process is responsible for green red and 800 nm UC emissions.

At last, the overall UC emission mechanism and population process in rare-earth doped KMnF₃ is schematically illustrated in Fig. 4. Upon excitation at 980 nm, the red UC emission (660 nm) can be ascribed to nonradiative energy transfer from the ⁴S₅/₂ levels of Er³⁺ to the ⁴T₁ level of Mn³⁺, followed by the falling-back transition to the ⁴F₉/₂ level of Er³⁺ and the ⁴F₉/₂ to ⁴I₁₁/₂ transition.

It would be interesting to have a closer look at the role of Mn³⁺ played in the multi-photon excited mechanism, based on the literature findings, for both double-doped KMnF₃:Yb/Er system and triple-doped KMnF₃:Yb/Er/Tm system. For the simpler double-doped KMnF₃:Yb/Er system, it is accepted that Mn³⁺ ions play the important role in the single-band UC emission (the complete disappearance of 540 nm green emission and appearance of only 660 nm red emission). According to the literature, close proximity...
and excellent overlap of energy levels of the Mn$^{2+}$ and Er$^{3+}$ ions in the host lattices cause very efficient nonradiative energy transfer from the $^2$H$_{11/2}$ and $^4$S$_{3/2}$ levels of Er$^{3+}$ to the $^4$T$_{1}$ level of Mn$^{2+}$, and this nonradiative energy transfer process is followed by the back-energy transfer to the $^4$F$_{9/2}$ level of Er$^{3+}$, thus leading to only 660 nm red emission. The mechanism is illustrated in the right part of Fig. 4 where only three Yb$^{3+}$, Mn$^{2+}$ and Er$^{3+}$ ions are involved. On the other hand, for the more complex triple-doped KMnF$_3$:Yb/Er/Tm system, as illustrated in Fig. 4 where all four Yb$^{3+}$, Mn$^{2+}$, Er$^{3+}$ and Tm$^{3+}$...
ions are involved, reappearance of 540 nm green emission is due to the additional resonant cross relaxation process between Er$^{3+}$ and Tm$^{3+}$ ions: \(3F_4 (\text{Tm}^{3+}) + 4F_{9/2} (\text{Er}^{3+}) \rightarrow 1G_4 (\text{Tm}^{3+}) + 4I_{15/2} (\text{Er}^{3+})\). This process causes the population of 1G4 state of Tm$^{3+}$ ions and depopulation of 4F9/2 state of Er$^{3+}$ ions. Because the energy level of 1G4 state (Tm$^{3+}$) equals to that of 4F7/2, photons lose fraction of energy in 4F7/2 (Er$^{3+}$) and drop to 2H11/2/4S3/2 (Er$^{3+}$) state through the multiphonon assisted relaxations, and finally leading to 540 nm green emission.

For the blue (476 nm) and NIR (800 nm) emissions, the energy transfer from the first Yb$^{3+} \rightarrow$ Tm$^{3+}$ excites the $^3H_6 \rightarrow ^3H_4$ transition, at the same time the redundant energy dissipated by phonons. Then, the Tm$^{3+}$ ion is firstly relaxes to the lower $^3F_4$ state and further promoted to the $^3F_{2+3}$ state through a continuous Yb$^{3+} \rightarrow$ Tm$^{3+}$ energy transfer process. The $^3H_4$ state can be populated by the efficient non-radiative relaxation from the $^3H_6$ state. The strong NIR UC (800 nm) is due to the $^3H_4 \rightarrow ^3H_6$ transition. In addition, the blue emission (476 nm) corresponds to the of $^1G_4 \rightarrow ^3H_6$ transition, where the $^1G_4$ level is populated by the efficient energy transfer from the $^3H_6$ state. The unexpected green emission (540 nm) is attributed to the co-doping of Tm$^{3+}$/Er$^{3+}$ ions in KMnF$_3$ matrix. The resonant cross relaxation process $^3F_4 (\text{Tm}^{3+}) + ^4F_{9/2} (\text{Er}^{3+}) \rightarrow ^1G_4 (\text{Tm}^{3+}) + ^4I_{15/2} (\text{Er}^{3+})$ between Er$^{3+}$ and Tm$^{3+}$ ions leads to the population of $^1G_{4}$ state of Tm$^{3+}$ ions and depopulation of $^4I_{15/2}$ state of Er$^{3+}$ ions, and then to $^2H_{11/2}/^4S_{3/2}$ state through the multiphonon assisted relaxations.

Conclusions

In summary, we have developed a facile hydrothermal method for preparation of tri-doped KMnF$_3$ nanocubes with simultaneous four-color (blue, green, red and NIR) UC emissions. Of particular interests, the red and NIR bands, known as so-called “optical window” for imaging biological tissues, are strong.
spectral and pump dependence analyses indicate that two-photon process is responsible for the red and NIR emissions. We believe that this proof-of-concept demonstration of a multicolor emission across a broader spectra (blue to NIR) using tri-doped single KMnF3 host system may have potential applications for multiplexing analysis and/or multi-optical window imaging of biological tissues.

Methods

Materials. MnCl2, KF, KOH, ethanol, oleic acid (OA) at AR grade were obtained from Sinopharm Chemical Reagent Company, China. YbCl3·6H2O, ErCl3·6H2O, TmCl3·6H2O were obtained from Conghua City JianFeng Rare Earth Company, China. All other chemical agents obtained from commercial routes were of analytical grade and were used without further purification.

Preparation of tri-doped KMnF3 nanocubes. The rare-earth tri-doped KMnF3 nanocubes were hydrothermally prepared by using MnCl2 and KF as precursors at 180 °C. Typically, 1.5 g (27 mmol) KOH, 2 mL H2O, 4 mL ethanol (48 mmol) and 9 mL of (24 mmol) OA (90 wt%) were well mixed at the room temperature for 10 min. A white viscous solution was obtained. The 10 mL (0.2 mol/L) MnCl2 solution, 15.5 mg (0.4 mmol) YbCl3·6H2O, 1.5 mg (0.04 mmol) ErCl3·6H2O and 1.5 mg (0.04 mmol) TmCl3·6H2O was subsequently added and vigorously stirred for 20 min. Then 8 mL (1.25 mol/L) KF was added into the above solution. After incubation for 1 h, the mixture was transferred to a 50 mL Teflon-lined autoclave, and then heated at 180 °C for 24 h. After cooling down, the products were removed by centrifugation, then washed with ethanol, and dried under vacuum at room temperature for 24 h.

Characterization. X-Ray powder diffraction (XRD) characterization were carried out on a Rigaku D/max-γ/B diffractometer equipped with a rotating anode and a Cu Kα source (λ = 0.15418 nm). SEM micrograph was obtained using a field emission scanning electron microscope (FESEM, MX2600FE). Upconversion luminescence spectra were measured by a regeneratively amplified 980 nm diode laser (Hi-Tech Optoelectronics Co. Ltd., Beijing). The emitted UC fluorescence signal was collected by a lens-coupled monochromator (Zolix Instruments Co. Ltd., Beijing) at 3 nm spectral resolution with an attached photomultiplier tube (Hamamatsu CR131). All measurements were performed at room temperature.

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Author Contributions
H.W. designed and performed the experiments and wrote the manuscript together with Y.W. and X.D.H. R.L.H. synthetized the KMnF3 NPs and provided the SEM images. J.H.S. and Z.J.L. designed and managed the upconversion luminescence spectra. S.J.L. and Y.G. reviewed the discussed the results. All the authors reviewed the manuscript.

Additional Information
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