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Er³⁺ microcrystals

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Geometry modulated upconversion photoluminescence of individual NaYF₄: Yb³⁺, Er³⁺ microcrystals

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Upconversion (UC) photoluminescence (PL) properties of individual β -NaYF₄: Yb³⁺, Er³⁺ microcrystals are investigated on their crystal orientation and size by a confocal micro-photoluminescence (μ -PL) system. The UC PL intensities including red and green bands of individual microcrystals change nearly lineally with their diameter but in different slopes. The ratio of integrated PL intensities between red and green bands (R/G) of individual microcrystals can be modulated by the crystal geometry, which is attributed to the optical propagation path and optical loss coefficient α . PL emission mapping along the crystal surface reveals a typical characteristic of optical waveguide in our UC microcrystals. Importantly, the variation of anisotropy in (100) and (001) crystal plane influences the UC PL spectra in the single microcrystals. Our finding could help the basic understanding of UC luminescence in micro/nanocrystals and hint their optimized fabrication for enhanced light emission. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4977020]

The near infrared (NIR) excited lanthanide-ion doped (Ln^{3+} -doped) upconversion luminescence nanoparticles (UCNPs) have been alternative to organic fluorophosphorus and quantum dots in a wide range of potential applications in biological tagging and imaging,^{1,2} photovoltaics,³ 3D displays,⁴ and barcoding.⁵ Among all the Ln^{3+} -doped compounds, the hexagonal Ln^{3+} -doped β -NaYF₄ appears to be one of the best candidates for UC due to their low phonon energies, high refractive index, and high chemical stability.^{6,7} Uniform UC micro/nanocrystals with tunable emission and morphologies could be achieved by adjusting the molar ratio of starting materials and kinds of dopants.^{8–10} Although the UC luminescence of bulk Ln^{3+} -doped compounds have been investigated for numerous years, the ensemble measurement on bulk powder samples diminishes precise optical feature of individual micro- or nanocrystals due to the random orientation and ambiguous amount of particles. Recently, with the help of confocal micro-photoluminescence (μ -PL) spectroscopy and on-demanded synthesis of UC micro/nanocrystals, the UC PL properties of individual micro-/nanocrystals are becoming interesting and can reveal their light emission features precisely.^{11–14}

The Ln³⁺-doped β -NaYF₄ crystal present separated luminescence center in host matrix.¹⁵ Generally, in this kind of sensitizer-activator luminescence system, there are mainly three kinds of photon actions: exciton-exciton (ex-ex) scattering, exciton-longitudinal optic (ex-LO) phonon scattering, and scattering, reflection and even interference at the crystal-air interface.¹⁶ Previous works on β -NaYF₄ UC single crystals have been theoretically and experimentally investigated on the single crystal imaging,⁵ directional emission,^{17,18} and single crystal polarized emission.^{19,20} However, the hexagonal β -NaYF₄ is an anisotropic uniaxial crystal with an optical axis of *c* axis perpendicular to (001) plane.^{21,22} Therefore, the refraction index and the propagation of the emitted light and the symmetry related dipole transition probabilities should be different in (001) plane and other crystal



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plane. Wang et al. have investigated the UC emission and waveguide effect of individual Ln-doped NaYF₄ microcrystals.¹⁷ Qiu et al. have reported the anisotropy dependent polarization in different crystal plane.^{18,19,23} As one anisotropic uniaxial crystal, the propagation of β -NaYF₄ emission at different wavelength in the Ln³⁺-doped UC PL substances have rarely been reported on the geometry effect.

In this letter, β -NaYF₄: 20 % Yb³⁺, 1 % Er³⁺ microcrystals with various aspect ratios in hexagonal shape are investigated on their UC PL properties. A confocal μ -PL setup with the NIR excitation laser line (980 nm) is used to detect the UC emission spectra (e.g. the energy level transition and geometry-dependent UC PL). The ratio of integrated PL intensity between red and green bands (R/G) are systematically investigated and can be attributed to the geometry-induced propagation loss of emission light in (100) and (001) crystal planes.

The Yb³⁺ and Er³⁺ doped β -NaYF₄ microcrystals are synthesized by a facile EDTA assisted hydrothermal process,¹¹ where EDTA is applied as a capping agent to hinder the growth of (001) plane of β -NaYF₄. The diameter and length of the single crystals can be directly modulated by tuning the concentration of EDTA. Fig. 1 shows the SEM images of the β -NaYF₄ with different diameters and lengths, which have been dispersed in cyclohexane and spread onto silicon wafers. It can be seen that the bottom-up synthesized β -NaYF₄ microcrystals are in micrometer scale with naturally smooth boundaries. Four samples with various aspect ratio are used to investigate geometry-dependent UC PL properties which are denoted as S1 (length/diameter of 10.6 µm/1.6 µm), S2 (7.5 µm/3.3 µm), S3 (5.4 µm/4.4 µm), and S4 (1.3 µm/5.1 µm). The corresponding selected area electron diffraction (SAED) pattern of the sample S2 indicates that the β -NaYF₄ microcrystals are single crystalline and meet our precise investigation on UC PL properties, which will be studied on the geometry effect (length and diameter) with samples S1-S3, and the facet effect with samples S3 and S4 via our home-made UC µ-PL system.

The schematic diagram of the home-made confocal μ -PL system is shown in Fig. 2(a). A 980 nm semiconductor laser is adopted as the excitation light source and then focused with a numerical aperture microscope objective lens (NA = 0.85, 50×) to a spot diameter of about 1.4 μ m. The UC PL spectra are recorded with a NOVA Laboratory Class spectrometer with a Thorlabs FESH0750 filter placed in front of the entrance of the monochromator. The detection interval space of the spectrometer is 0.8 nm. The microcrystals are spread onto silicon wafers for individual testing. When (100) crystal plane is irradiated by the incident light (the side face of the hexagonal cylinder crystal parallel to wafer), we define it as horizontally settled (V). All μ -PL spectra are excited under unpolarized laser at room temperature. The typical UC PL spectra of individual microcrystal with different diameter (horizontally settled) are shown in Fig. 2(b). Bright green emissions are observed when the microcrystals are excited by 980 nm laser. All the spectra have three main emission bands. Three



FIG. 1. Statistic of the length and diameter of synthesized β -NaYF₄: Yb³⁺, Er³⁺ microcrystals. Scale bar of the insert SEM images is 3 µm. The insert selected area electron diffraction (SAED) pattern (S2) indicate the β -NaYF₄: Yb³⁺, Er³⁺ microcrystal is single crystalline. Scale bar of the SAED pattern is 1/10 nm⁻¹.



FIG. 2. (a) Schematic diagram of the home-made confocal μ -PL system. Scale bar is 3 μ m. (b) UC μ -PL spectra of individual β -NaYF₄: Yb³⁺, Er³⁺ microcrystal with different diameters (S1, S2, and S3) when they are horizontally settled (H). The insert pictures are the corresponding luminescent micrograph when the excitation laser line is located at the center of the measured microcrystals. (c) Energy level diagram of Er³⁺ ion and Yb³⁺ ion and the UC mechanisms for the green and red emissions. (d) The integrated PL intensities of red and green emission and the ratio of integrated PL intensity between red and green bands (R/G) of the samples in (b) as a function of the microcrystal diameter.

main emission bands of these Yb³⁺ and Er³⁺-doped β -NaYF₄ microcrystals at 523 nm, 541 nm, and 655 nm are attributed to the energy transitions of ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$, and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$, respectively,²⁴ which are shown in Fig. 2(c). The Er^{3+} ion can be promoted to the ${}^{4}I_{11/2}$ and ${}^{4}F_{7/2}$ state through the ground state absorption (GSA) or excited state absorption (ESA) of laser photons. Alternatively, the transition can be realized by absorbing photons from radiative relax of Yb³⁺ from $2F_{5/2}$ state to ${}^{2}F_{7/2}$ state based on energy transfer UC (ETU) processes. The Er³⁺ ion at ${}^{4}I_{11/2}$ state can nonradiatively relax to the ${}^{4}I_{13/2}$ state, and is further excited to the ${}^{4}F_{9/2}$ state by ESA or ETU process to generate red emission light by radiative relax to ${}^{4}I_{15/2}$ ground state finally. The Er^{3+} ion at ${}^{4}F_{7/2}$ state can be nonradiatively relax to the ${}^{2}I_{11/2}$, ${}^{4}S_{3/2}$, and ${}^{4}F_{9/2}$ state and then transited to ${}^{4}I_{15/2}$ ground state by radiative relax to generate green and red emission light. Fig. 2(d) presents the integrated intensities of green emission bands (535 - 565 nm) and red emission bands (640 - 680 nm) of individual microcrystals with various diameters. The integrated PL intensities of green and red emission bands are increased nearly linearly with the diameter. When the incident light is focused as a spot on the surface of the horizontally settled individual microcrystals, the exposure volume is determined by the spot size and sample diameter. In our test system, the spectrometer collects the signals of the emission light scattered from the excited region along the path opposite to that of the incident light. It can be approximately noted that, the number of the luminescence centers is in proportion to the exposure volume if the Er^{3+} ions and Yb^{3+} ions are uniformly doped. Therefore, more luminescence centers are excited and higher luminescence intensity could be achieved in the samples with larger exposure volume if other effects can be ignored, such as the cross-relaxation induced by defects, and surface ligands, sensitizers, and activators induced concentration quenching. Hence, the exposure areas of the samples are the same, so the intensity of the emission light should be in proportion to the diameter when the single microcrystals are horizontally settled. Interestingly, the intensity ratio between red and green bands (R/G) decreases with the increasing of diameter (Fig. 2(d), blue line). The emission light from the location excited by the incident laser would experience scattering, reabsorbing, and reflection in the microcrystals. The optical loss in this process can be evaluated by the optical loss coefficient α . Therefore, the diameter induced variety in R/G is attributed to the optical path and optical loss coefficient α dependent variation of optical loss of the different emission

bands during the propagation in the microcrystals. The optical loss and wavelength redistribution due to a remote energy relay (RER) process could influence the light emission properties of CdS and organic triphenylimidazole (TPI) microcrystals.^{25,26} According to the Bouguer-Lambert-Beer law, light can be weaken when propagating in the medium.²⁷ The optical loss coefficient α can be expressed by the equation,²⁵ $I = I_0 \cdot e^{-\alpha L}$, where I and I_0 are the intensities of the monochromatic emission light spot at the sample surface and that at the luminescence center, respectively, and L is the propagation distance. In addition, according to the Cauchy dispersion formula, the velocity and the refraction index of the light propagating in the medium various dependent of the wavelength.²⁸ The dispersion relation can be expressed as followed, $n(\lambda) = A + B \cdot \lambda^{-2} + C \cdot \lambda^{-4}$, where n and λ are the refraction index and wavelength of the light propagating in the medium, and A, B, and C are the constants depending on the medium. It can be speculated that the optical loss coefficient α shouled depend on the wavelength of the light. Consequently, the optical loss and hence the R/G should be in dependence of the wavelength-related optical loss coefficient α and the propagating distance L. As shown in Fig. 2(d), the logarithmic value of R/G decreases nearly linearly depend on the diameter. Here, we simply deduce the functional relations between R/G and the wavelength-related optical loss coefficient α and the propagating distance L based on Bouguer-Lambert-Beer law as followed:

$$\frac{R}{G} = \frac{I_{red}}{I_{green}} = \frac{I_{o, red} \cdot exp[-\alpha (red) \cdot L]}{I_{o, green} \cdot exp[-\alpha (green) \cdot L]}$$
$$= \frac{I_{o, red}}{I_{o, green}} \cdot exp[\alpha (green) \cdot L - \alpha (red) \cdot L],$$

where I_{red} and I_{green} are the integrated PL <u>intensities</u> of the red and green emission bands at the surface of the crystal respectively. $I_{o, red}$ and $I_{o, green}$ are the PL intensities of intrinsic red and green emission bands of the luminescence center. To simplify the equation, we set γ is I_{red}/I_{green} , and γ_o is $I_{o, red}/I_{o, green}$. The equation can be transformed as followed:

$$\ln \gamma = \ln \gamma_o \times [\alpha (green) - \alpha (red)] \times L.$$

Therefore, the logarithmic value of R/G (ln γ) would changes linearly with the difference in optical loss coefficient α and the propagating distance L. Consequently, the ln γ will changed nearly linearly as shown in Fig. 2(d).

To further explore the PL emission light distribution of different position in individual microcrystals, the PL mapping test is performed by fixing the laser at the edge and moving the detection position in the tested microcrystal (sample S1) along the transverse axis of (100) crystal plane. Fig. 3 shows the typical mapping graph result of red band (645 - 675 nm) and green band (535 - 565 nm) of an individual microcrystal. The brightness denotes the luminescent intensity. The UC PL spectra at different positions along the same crystal plane have similar profile but their intensities changes. The intensity at the laser position is the highest and decreases when the detection position is shifted away from the laser excitation position. A dark area appears when the detection position is about 6 µm away from the laser point. When the detection position moves to the edge of the microcrystal, bright emission appears again. This phenomenon can be attributed to the optical waveguide effect and remote propagation of the emission light in the microcrystal. The light can reach (001) plane by propagating along a straight line or continuously refection at the (001) plane. The dark arear between the laser excitation point and the sample edge is due to the total internal reflection at the crystal-air interface.

As an anisotropic uniaxial crystal, the UC PL, the refractive index and the optical loss of individual β -NaYF₄: Yb³⁺, Er³⁺ microcrystals should vary in (100) plane and (001) plane. Therefore, the UC PL spectra of the single microcrystals (sample S3 and S4) when they are horizontally (H) and vertical (V) settled are investigated and shown in Fig. 4(a). The UC PL intensities of individual microcrystals with various lengths differ when they are vertical settled. This phenomenon can be attributed to the discrepancy in exposure volume as discussed above. It's worth noting that the R/G changes dramatically when the incident light exciting different crystal plane (100) plane (horizontally settled, H) and (001) plane (vertical settled, V), as shown in Fig. 4(b). The large discrepancy in R/G cannot



FIG. 3. Light emission mapping of red (645 - 675 nm) and green emission bands (535 - 565 nm) of an individual microcrystal (S1) when it is horizontally settled (H). The detection position is along the middle line of the upper surface of the microcrystal with space of every around 700 nm. The focal length keeps constant in the test. Scale bar of the SEM image the corresponding luminescent micrograph is 3 μ m.

be explained just by difference of optical length. As an anisotropic dielectric crystal, β -NaYF₄ has one optical axis parallel to (100) plane and across the center of (001) plane. The refraction index and thus the optical loss coefficient α are different along the (100) plane and the (001) plane. Therefore the R/G ratio can also be modulated by the anisotropy. Notebly, when (100) plane is excited, the UC PL spectra at 659.6 nm is slightly enhanced and shifts to 662.73 nm when (001) plane is excited (Fig. 4(a)). This phenomena can be attributed to the anisotropic crystal field induced discrepancy of electric dipole strength around the Er³⁺ ion in crystal structure.^{18,19} Qiu et al. have also report the slight difference in spectrum when using polarized incident lingt to excite different crystal plane of Er³⁺ doped NaYF₄.¹⁹ For Er³⁺ doped β -NaYF₄, Er³⁺ takes the Y³⁺ site with the C_{3h} symmetry. The energy level structure of the Er³⁺ will split into hyperfine arrangement due to the crystal-field (CF) splitting.^{18,19} Due to the anisotropy, the oscillator strength of Er³⁺ differs along different directions for single crystalline particles, which results in different dipole transition probabilities at different wavelength and hence the anisotropic local emission bands discrepancy of UC luminescence.²¹

In summary, unique UC PL phenomena of β -NaYF₄: 20 % Yb³⁺, 1 % Er³⁺ single microcrystals at room temperature have been observed under excitation of 980 nm laser. Bright UC PL of individual crystals have been observed. The PL intensities are depended on the geometry (diameter when horizontally settled and length vertically settled) determined exposure volume. The R/G can be modulated by the optical propagation path and optical loss coefficient α which can also be adjusted by the geometry. The distribution of the PL emission light of the crystal is mapped by detecting various positions along the crystal surface and presents a typical characteristic of optical waveguide. In addition, the anisotropic crystal field induced variation of electric dipole strength around the Er³⁺ ion in (100) and (001) plane leads to change of the UC PL spectra near 659.6 nm. These findings could provide help to understand the UC PL of individual microcrystals. It has important implications for the advancement of the application of the UC micro/nanocrystals in the fields of single particle-based bioimaging and optical display.



FIG. 4. (a) UC μ -PL spectra of individual β -NaYF₄: Yb³⁺, Er³⁺ microcrystal of different sizes when they are horizontally settled (H) and vertical settled (V). The insert pictures are the corresponding luminescent micrographs when the surrounding is dark. (b) Integrated PL intensity of the green and red emission bands and R/G of the samples in (a).

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