Ultraviolet Upconversion Enhancement in Triply Doped NaYF₄:Tm³⁺,Yb³⁺ Particles: the Role of Nd³⁺ or Gd³⁺ Co-doping

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ABSTRACT

Upconversion (UC) particles are currently under intensive investigation, normally for their visible instead of ultraviolet (UV) light luminescence under near-infrared (NIR) irradiation. As a commonly studied host, NaYF₄ in particular is known to have low phonon energy and high UC efficiency. Here, we present our work on enhancing UC luminescence in the UV region by adding a third dopant into a binary-doped NaYF₄:Yb³⁺,Tm³⁺ host. More specifically, neodymium (Nd³⁺) or gadolinium (Gd³⁺) ions was co-doped into parent NaYF₄:20mol%Yb³⁺,0.5mol%Tm³⁺ UC particles to enhance their UV UC luminescence. Experimental results demonstrated that these particles exhibited the highest degree of UV UC enhancements when co-doped with 0.05mol% Nd³⁺ or 2.0mol% Gd³⁺, expanding the potential of this type of materials into many possible applications by directly converting NIR irradiation into UV light. Fundamentally, the UV UC emission dependence of these triply doped NaYF₄:Yb³⁺,Tm³⁺ particles with different Nd³⁺ and Gd³⁺ doping concentrations was investigated in terms of ground state absorption, excited state absorption and energy transfer UC mechanisms.

Keywords: upconversion; ultraviolet; NaYF₄; neodymium (Nd³⁺); gadolinium (Gd³⁺); doping

INTRODUCTION

Ultraviolet (UV) light is only 3% of sunlight at ground level (with the Sun at its zenith) because most of it is fortunately blocked by the atmosphere with its harmful effects on our lives.^[1] However, UV light possesses a wide variety of benefits and broad health and industrial applications.[1, 2] For example, UV light is commonly used for waste and contaminated water sanitation treatment, and to treat certain diseases such as psoriasis etc.[3] Other than presented in sunlight, UV radiation is produced by electric arcs and specialized lights such as mercury-vapor lamps, tanning lamps, and black light, which are not energy sustainable and convenient. Materials that emit UV light under desired conditions would allow more widespread applications. In this regard, upconversion (UC) phosphor materials that sequentially absorb low energy photons and emit higher energy photons with an anti-Stokes' emission process have been studied intensively in the past decades in diverse research fields for both their fundamental scientific importance and their potential applications in compact solid-state lasers, optical data storage, solar energy conversion, biological imaging, medical diagnostics and disinfection of surfaces and water.[4-14] UC solids doped with trivalent lanthanide ions (Ln^{3+}) has emerged as a type of powerful materials to be excited even without coherent excitation sources in contrast to other emission processes based on multiphoton absorption. Many energy transfer mechanisms, such as excited state absorption (ESA), energy transfer upconversion (ETU), photon avalanche (PA), cooperative luminescence, etc., have been proposed. Among many Ln^{3+} ions, Er^{3+} , Tm^{3+} , Pr^{3+} , Ho^{3+} , and Nd^{3+} are excellent UC activators because of their abundant ladder-like energy levels with long-lived excited states, and Yb^{3+} is used as a common sensitizer in ETU systems due to its unique and simple energy

levels with only one excited level of $^2F_{5/2}$. [15-19] However, UC efficiency measured as absolute quantum yield, is far from satisfactory due to the parity forbidden $4f-4f$ transitions and low absorption cross-sections of Ln^{3+} ions in addition to non-radiative processes due to the quenching of high frequency vibrations by surface ligands, such as hydroxyl groups, especially for nanoparticles (NPs). So far, the highest UC efficiency reported for NIR-to-visible conversion was from $LiLuF_4$ host doped Er^{3+} and Tm^{3+} under 127 W/cm^2 laser excitation: absolute quantum yields of 5.0% and 7.6%, respectively, and that from $NaYF_4:Er^{3+},Yb^{3+}$ and $NaYF_4:Er^{3+}$ under laser excitations of 20 and 0.27 W/cm^2 : 4% and 5.1%, respectively. [19, 20] Moreover, other than the reported visible-to-UV UC from $Y_2SiO_5:Pr^{3+},Gd^{3+},Li^{+}$ with poor UC efficacy (0.001% under 0.002 W/cm^2 excitation), [21] no other studies have been reported on adjusting absorption position of sensitizing materials to shorter wavelengths in the visible range. Correspondingly, UC efficiency enhancement often occurs under NIR excitation to visible light emission. [6, 22-27] Considering the broad application potentials of UV light in UV solid-state laser, photocatalysis, and disinfection, etc., in addition to the fact that the majority of sunlight at ground level is visible and infrared light, there is an urgent need to enhance UV UC efficiency under visible and/or NIR excitation.

A commonly studied UC host is $NaYF_4$, known for its lower phonon energy and consequently enhancement in the luminescent quantum yield. Among the two most frequently studied host lattices of $NaYF_4$, i.e. α -cubic and β -hexagonal phases, the latter has been proven to yield emissions with higher intensity. [28-30] Therefore, the β -phase $NaYF_4$ has been used here as a host to engineer and enhance UV UC doped with suitable lanthanide ions. Known for their unique optical properties with defined wavelength

emissions, lanthanide dopants have been used at optimal concentrations to fine-tune output color emissions and intensities with the β -phase NaYF₄. The mechanism by which excitation and emission occur is through energy transfer between some lanthanide ions behaving as sensitizers and the others as activators which are responsible for observed light emission. For example, NaYF₄:20mol%Yb³⁺,0.5mol%Tm³⁺ is widely known for its blue and UV UC emissions, however enhancement of their emissions has not been adequately explored.[28-30]

In this study, by using well studied NaYF₄:20mol%Yb³⁺,0.5mol%Tm³⁺ (NYT) particles with well-established syntheses as the parent host, we report their UV UC enhancement by further introducing Nd³⁺ or Gd³⁺ ions under 980 nm excitation. Apart from dopant modification, the effects of different excitation sources for UV UC were also investigated using both laser and Xenon (Xe) lamp. Results indicated that certain UV emissions, even deep UV at 242 nm, were emerged once excited at 980 nm from laser while the UV emissions under Xe lamp ensure that sunlight could be an optional excitation source.

EXPERIMENTAL SECTION

Chemicals: The starting materials including sodium hydroxide [NaOH], yttrium nitrate hexahydrate [Y(NO₃)₃·6H₂O], ytterbium nitrate pentahydrate [Yb(NO₃)₃·5H₂O], thulium nitrate pentahydrate [Tm(NO₃)₃·5H₂O], neodymium nitrate hexahydrate [Nd(NO₃)₃·6H₂O], gadolinium nitrate hexahydrate [Gd(NO₃)₃·6H₂O], butanoic acid (CH₃CH₂CH₂COOH), ethanol (CH₃CH₂OH), sodium fluoride (NaF), and hexanes (C₆H₁₄) were purchased from Sigma Aldrich. All chemicals are of analytical grade reagents and used directly without further purification.

Synthesis of Triply Doped UC Particles of NYT:Nd³⁺/Gd³⁺: Preparation of the parental NYT particles was done with 1 mmol of rare earth nitrates, i.e. 79.5% Y(NO₃)₃·6H₂O, 20.0% Yb(NO₃)₃·5H₂O, and 0.5% Tm(NO₃)₃·5H₂O. For triply doped samples, Nd³⁺ ions (0.05-2mol%) or Gd³⁺ ions (0.5-79.5mol%) with different doping concentrations were added into the solution for preparing the parental NYT particles by keeping the Yb³⁺ and Tm³⁺ concentrations constant while varying the Nd³⁺ and Gd³⁺ concentrations with respect to the Y³⁺ concentration. These solid rare earth nitrates were mixed in a liquid mixture of 25 ml ethanol and 5 ml water with constant stirring. To this solution 7 ml of butanoic acid were added along with 0.7 g of NaOH.[31] After stirring for 30 minutes at room temperature, this first solution was mixed with a second solution containing 0.504 g of NaF in 20 ml of water which was added drop-wise. The final mixture was transferred to a 48 ml Teflon container held in a stainless steel autoclave followed with 30 min of additional stirring and then treated at 200 °C for 5 h. Once the autoclave apparatus naturally cooled to room temperature, the products were washed with ethanol, n-hexane and deionized water, followed by drying at 120 °C in an oven. The synthesized samples were labeled schematically as shown in Fig. 1.

Figure 1. Schematic labeling of the synthesized samples: NYT for the parental NaYF₄:20mol%Yb³⁺,0.5mol%Tm³⁺ particles; NYT:xmol%Nd³⁺ for the triply doped

NaYF₄:20mol%Yb³⁺,0.5mol%Tm³⁺,xNd³⁺ particles with different Nd³⁺ doping levels x = 0.05, 0.1, 0.2, 0.5 and 2; and NYT:ymol%Gd³⁺ for the triply doped NaYF₄:20mol%Yb³⁺,0.5mol%Tm³⁺,yGd³⁺ particles with different Gd³⁺ doping levels y = 0.5, 2, 10 and 79.5. Samples with compositions NYT,0.05mol%Nd³⁺ and NYT,2mol%Gd³⁺ are labeled as NYTN and NYTG, respectively.

Materials Characterization: Powder x-ray diffraction (XRD) of the prepared samples was measured by a Rigaku-MiniflexTM II x-ray diffractometer with CuKα₁ radiation (λ = 0.15406 nm). The morphologies of the samples were observed by means of a field emission scanning electron microscopy (Carl Zeiss Sigma VP FESEM) equipped with a field emission gun operated at 5 kV. Energy Dispersive x-ray (EDX) spectral analysis was performed under 20 kV. Digital micrograph software GATAN was used to analyze the collected SEM images.

Upconversion Emission, Quantum Yield and Lifetime Measurements: The excitation and emission spectra of the as-prepared samples NYT, NYT,xmol%Nd³⁺ (x = 0.05, 0.1, 0.2, 0.5 and 2) and NYT,ymol%Gd³⁺ (y = 0.5, 2, 10 and 79.5) were measured using an Edinburgh Instruments FLS980 fluorometer system equipped with a Xenon lamp as a continuous excitation source and a TE-cooled photo-multiplier tube (Hamamatsu, Model R928P) for emission detection. All the excitation and emission spectra were corrected for the spectral sensitivity of the system and detector, as well as intensity variation in the Xe light-source using a reference diode. In addition, the temporal evolutions (photoluminescence decay) of the emission intensity as a function of time were measured utilizing a pulsed Xenon flash-lamp and a pulsed LED laser source at 980 nm as excitation sources. The pulsed Xenon flash-lamp has a pulse width of approximately 2 μs and its wavelength is controlled by the excitation monochromator. The entire system was controlled through Edinburgh Instruments F980 data acquisition software. The collected

decay curve was analyzed using Exponential Fit Analysis software F980 provided by Edinburg Instruments. All the emission and excitation spectral measurements were performed at room temperature. For absolute quantum yield (QY) measurements and emission intensity comparisons, a 150 mm BenFlect coated integrating sphere was employed in the Edinburgh Instruments FLS980 fluorometer. Details about QY setup and measurements can be found on supplementary information (see ESI-1).

RESULTS AND DISCUSSION

Summary of structural properties and morphology:

To confirm the crystallinity of the synthesized $\text{NYT}_{x\text{mol}\%}\text{Nd}^{3+}$ ($x = 0.05, 0.1, 0.2, 0.5$ and 2) and $\text{NYT}_{y\text{mol}\%}\text{Gd}^{3+}$ ($y = 0.5, 2, 10$ and 79.5) particles, their XRD patterns were collected (Fig. 2). The position and intensity of all diffraction peaks were in good agreement with those of the pure β -hexagonal NaYF_4 (JCPDS card No. 16-0334) indicating the pure phase of the synthesized NYT particles with varying concentrations of Nd^{3+} or Gd^{3+} . Doping levels of 0.05-2.0mol% of Nd^{3+} ions or 0.5-79.5mol% of Gd^{3+} ions did not cause any phase change in the crystalline structure of the parental NYT particles containing a hexagonal β -phase throughout all tested samples. But, replacing Y^{3+} ions ($r = 1.159 \text{ \AA}$) with large Nd^{3+} ($r = 1.249 \text{ \AA}$) or Gd^{3+} ($r = 1.193 \text{ \AA}$) ions exhibits an increase in crystallinity at low doping levels ($\text{Nd}^{3+} \leq 0.05\text{mol}\%$ or $\text{Gd}^{3+} \leq 2\text{mol}\%$), and follows with lower crystallinity at higher doping level ($\text{Nd}^{3+} > 0.05\text{mol}\%$ or $\text{Gd}^{3+} > 2\text{mol}\%$). The broadening of XRD peaks with increasing Gd^{3+} or Nd^{3+} dopant levels indicates a reduction of the average crystallite size or crystallinity. In addition, the XRD peaks shift towards lower diffraction angles by comparing the NYT and $\text{NYT}_{79.5\text{mol}\%}\text{Gd}^{3+}$

samples could cause by a significant increase in lattice parameter owing to the complete substitution of smaller Y^{3+} ions by Gd^{3+} ions in the host lattice. By simply judging from the XRD peak height and width, the highest crystallinity was observed from sample NYT:2mol% Gd^{3+} (i.e. NYTG) among all the samples studied in this work.

Figure 2. XRD patterns of the parental NYT particles co-doped with varying concentrations of (a) Nd^{3+} : 0%, 0.05%, 1% and 2% in the as-prepared NYT: $x\%Nd^{3+}$ with respect to x , and (b) Gd^{3+} : 0.5%, 2.0%, 10%, and 79.5% in the as-prepared NYT: $y\%Gd^{3+}$ with respect to y .

SEM images in Fig. 3 show the morphology of the synthesized samples under this investigation. The introduction of Nd^{3+} or Gd^{3+} ions alters the morphology or size of the parental NYT, consistent with XRD data (Fig. 2). Parental NYT particles are rod-shaped with an average length of ~ 400 nm and a width of ~ 200 nm. The average size of the particles were found to be ~ 100 nm for the NYT:79.5mol% Gd^{3+} sample which is smaller than the parental NYT, NYT,0.05-2.0mol% Nd^{3+} and NYT,2-10mol% Gd^{3+} samples. The decrease in size of NYT,0.05-2mol% Nd^{3+} and NYT,0.5-79.5mol% Gd^{3+} nanocrystals as a function of Nd^{3+} or Gd^{3+} concentration could be attributed to the strong effect of the Nd^{3+} or Gd^{3+} doping ions on the crystal growth rate of the parental NYT through surface

charge modification.[32] When the Gd^{3+} concentration was increased to 79.5mol%, there was a slight morphology change from prominent rod-like to nearly spherical particles.

Figure 3. SEM images of the parental NYT particles co-doped with varying concentrations of Nd: (a) 0%, (b) 0.05% and (c) 2%; and Gd: (d) 2.0%, (e) 10% and (f) 79.5%.

This study focused on triply doped $NaYF_4$ samples with UV UC emission as bright as possible, so only the NYTN and NYTG samples with high crystallinity were analyzed. In this way, changes in UV UC emission intensity among all three investigated samples (i.e. NYT, NYTN and NYTG) can be basically attributed to changes in energy transfer processes among the dopants and not due to the crystallinity or particle size of the as-prepared samples.

Upconversion analysis under 980 nm excitation:

Different co-doping concentrations of Nd^{3+} (0.05-2.0mol%) or Gd^{3+} (0.5-79.5mol%) into the parental NYT particles were studied for their role in enhancing UV UC photoluminescence (PL) while keeping Yb^{3+} and Tm^{3+} concentrations in $NaYF_4$ constant.

First emission spectra (Fig. 4) of the NYT,xmol%Nd³⁺ (x = 0.05, 0.1, 0.2, 0.5 and 2) and NYT,ymol%Gd³⁺ (y = 0.5, 2, 10 and 79.5) were collected under 980 nm excitation. By the first glance, the doping levels of Nd³⁺ and Gd³⁺ ions had different effects on the UV UC emission and PL intensity. Here, the role of Nd³⁺ dopant in enhancing the UV UC emission of the parental NYT particles will be discussed first, followed by that of Gd³⁺ dopant.

Figure 4. Upconversion emission spectra under 980 nm excitation: the as-prepared NYT:xmol%Nd³⁺ (x = 0.05, 0.1, 0.2, 0.5 and 2) particles in the wavelength ranges of (a) 250 to 850 nm, (b) 250 to 500 nm and (c) 230 to 320 nm, and (d) UC spectra for the as-prepared NYT:y mol%Gd³⁺ (y = 0.5, 2, 10 and 79.5) particles in the ranges of 280 to 500 nm, (e) emission from Gd³⁺ at 311 nm at different Gd³⁺ doping concentrations for NYT:y mol%Gd³⁺ (y = 0.5, 2, 10 and 79.5) particles, (f) the UC intensity comparison among samples NYT, NYTN and NYTG within the range of 250-500 nm.

The UV UC PL spectra (Fig. 4a-c) from the as-prepared NYT:xmol%Nd³⁺ (x = 0.05-2) particles exhibit four enhanced bands centered at 242, 289, 345 and 362 nm from Tm³⁺,

corresponding to $^3P_{1,2} \rightarrow ^3H_6$, $^1I_6 \rightarrow ^3H_6$, and $^1D_2 \rightarrow ^3H_6$ transitions, respectively.[33, 34] Low phonon energy in NYT might be responsible for 242 and 289 nm emissions by helping decrease the nonradiative transitions and increase the radiative transitions resulting the $^3P_{1,2} \rightarrow ^3H_6$ and $^1I_6 \rightarrow ^3H_6$ emissions.[34] The other two visible bands centered at 450 and 475 nm in the UC emission spectra can be attributed to $^1G_4 \rightarrow ^3H_6$ radiative transitions of Tm^{3+} . In addition, four more enhanced UC emission peaks at 242, 250, 261 and 272 nm were observed at deep UV region compared to that of the parental NYT sample as shown in Fig. 3c. Based on intensity analysis, a three-fold intensity enhancement was observed for the NYTN sample in all bands below 400 nm, compared to that of the parental NYT sample. Moreover, intensity enhancement was also observed for the blue (440 to 500 nm) and visible light emissions from the as-prepared NYT:xmol%Nd³⁺ (x = 0.05-2) when compared to that of the parental NYT particles (Figure 3a&b), which is originating from the transition of Tm^{3+} and simultaneous reduction of the emission at 800 nm arising from the $^3G_4 \rightarrow ^3H_6$ transition of Tm^{3+} .

To understand these observations, it is reasonable to expect that the high absorption cross-section of Nd³⁺ at 800 nm will ultimately reduce the Tm^{3+} emission at 800 nm as shown in Fig. 3a. Together with the Nd³⁺ $\rightarrow$ Tm^{3+} back energy transfer, UV emission from the Nd³⁺-sensitized UC emission of Tm^{3+} was fine-tuned in the UV region by varying the co-doped Nd³⁺ concentration as shown in Fig. 3b. The optimal concentration of Nd³⁺ ions was 0.05mol%, yielding the highest UV UC emission enhancement. The increase of PL intensity at the low co-doping concentration of Nd³⁺ (Figure 3a-c) can be attributed to the fact that the NYT:xmol%Nd³⁺ (x = 0.05-2) samples with low concentration of Nd³⁺ (0 < x < 0.1) have efficient energy transfer processes between Nd³⁺ and Tm^{3+} ions. When the

Nd^{3+} doping level was increased above 0.2mol%, suppression of UV UC emission intensity (rather than enhancement) from these triply doped UC particles was observed. This is believed that the added Nd^{3+} dopants quench energy that is being transferred above the optimal Nd^{3+} doping concentration. So it is observed that the addition of Nd^{3+} ions to the parental NYT in the triply doped samples at low doping concentrations produces UC PL enhancement in the emission peaks below 500 nm. In this UC process, Nd^{3+} ions act as a sensitizer, resulting in the enhancement of UV UC emission of the parental NYT particles under 980 nm excitation. This has been verified with experiments shown in the supplementary information (ESI-2), and the circulation of energy among the three doping ions (i.e. Yb^{3+} , Tm^{3+} and Nd^{3+}) and finally back to Tm^{3+} has been further discussed with proposed energy level diagram in the later section.

In contrast, when the parental NYT particles were co-doped with Gd^{3+} (0.5, 2, 10 and 79.5mol%), the integrated PL intensity below 400 nm from transitions of Tm^{3+} increases remarkably (Fig. 3d). There are two exciting points to be pointed out: (1) the very intense UV emissions at 289, 353 and 368 nm and (2) the new emission band at 311 nm. Apparently, in triply doped $\text{NYT:y mol\%Gd}^{3+}$ ($y = 0.5, 2, 10$ and 79.5), the co-doped Gd^{3+} ions introduced a new UC emission band at 311 nm, which indicates that the Gd^{3+} ions significantly contribute to the emission of the $\text{NYT:y mol\%Gd}^{3+}$ ($y = 0.5, 2, 10$ and 79.5) particles in the UV region under 980 nm excitation. To verify the new emission bands from Gd^{3+} , we further compared the emission spectrum of the parental NYT sample to those of $\text{NYT:y mol\%Gd}^{3+}$ ($y = 0.5, 2, 10$ and 79.5) particles under the identical conditions (Fig. 3d). The intensities of the UV emissions at 353 and 368 nm are quite intense and comparable to the blue emissions at 450 and 475 nm. The Gd^{3+} doping

concentration was varied in a wide range to replace the Y^{3+} ions to fine-tune the UC PL emission intensity of 311 nm. Based on the UC PL intensity analysis, the optimal concentration of Gd^{3+} dopants was 2.0mol%, yielding the highest UV UC emission enhancement below 400 nm. In addition, the change in the fluorescence intensity depending on the Gd^{3+} concentration implies that there is concentration quenching occurring between Gd^{3+} ions under high concentrations, similar to Nd^{3+} ions. Finally, from Fig. 3f, it is clearly seen that sample NYTG possesses highest UC intensity compared to that of NYT and NYTN under the same excitation and measurement conditions. The larger UC emission intensity for sample NYTG can be associated with the increase of hexagonal phase and crystallinity in the triply doped samples at the Gd^{3+} doping level of 2.0mol%, which is fully consistent with XRD analysis (Fig. 2b). The subsequent decrease in UC emission intensity at higher Gd^{3+} doping is primarily attributed to the reduction in crystal size and crystallinity. Smaller nanocrystals and lower crystallinity tend to have increased surface quenching sites and thus suppress UC luminescence by enhanced nonradiative energy transfer processes of the luminescent Yb/Tm/Gd ions in the NaYF_4 host.[32]

UV UC quantum yield under 980 nm excitation:

Apart from comparing UC emission intensity among samples NYT, NYTN and NYTG in the integrating setup, UV UC PL QYs were also measured to monitor the enhancement effect by co-doping Nd^{3+} or Gd^{3+} ions from the most efficient samples (detailed in ESI-1). Measurements were done under 980 nm excitation at the excitation power density of $25.5 \pm 2.6 \text{ W/cm}^2$. UV UC QYs were measured by integrating the emission spectra corresponding to each individual manifold spanned over the range of 230 to 850 nm. As

shown in Fig. 5, sample NYTG possesses highest UV UC QY compared to the parental NYT and sample NYTN. Individually, UV (230-320 nm) UC QY of sample NYTG was measured to be $0.02 \pm 0.002\%$, which is two times of that of the sample NYTN ($0.01 \pm 0.001\%$) and more than six times higher than that of the parental sample NYT ($0.0031 \pm 0.0003\%$). Similarly, UV (320-400 nm) UC QY of NYTG was measured to be $0.18 \pm 0.016\%$, which is two times of that of NYTN ($0.09 \pm 0.009\%$) and nine times of that of NYT ($0.02 \pm 0.003\%$). The UC QY for blue (425-500 nm) emission was found to be ($0.32 \pm 0.03\%$) from NYTG, $\sim 40\%$ higher than NYGN ($0.23 \pm 0.03\%$) and four times of NYT ($0.08 \pm 0.008\%$). Finally, the NIR (740-850 nm) UC QY was also measured from NYTG ($2.2 \pm 0.20\%$), NYTN ($0.52 \pm 0.050\%$) and NYT ($0.75 \pm 0.070\%$). Compared to the parental sample NYT under 980 nm excitation, the increase in UV UC QYs but simultaneous decrease in NIR QY from sample NYTN ensures that Nd^{3+} ions act as a sensitizer for the doubly doped sample NYT. Higher UV QYs from samples NYTN and NYTG indicate that both Nd^{3+} and Gd^{3+} ions can act as efficient co-dopants into the parental NYT to enhance UV UC while Gd^{3+} ions significantly contribute to the new emission band at 311 nm with a QY of ($0.001 \pm 0.0001\%$) in addition to strong UV emission enhancement at 353 and 368 nm under 980 nm excitation.

Figure 5. UC QYs at various emission wavelengths of samples NYT, NYTN and NYTG under 980 nm excitation.

Power dependence under 980 nm excitation:

To further understand the number of photons involved in populating the 3P_2 , 1I_6 , 1D_2 , and 1G_4 states of Tm^{3+} including $^6P_{7/2}$ for Gd^{3+} ions, the power dependence, i.e. the relationship between the UV UC emission intensity versus the excitation power density, of the samples NYTN and NYTG were analyzed because these emission bands exhibited the highest degree of UV UC enhancement (Fig. 6). The slopes of the double logarithmic plots of UV emission intensity ($\ln I$) as a function of excitation power density ($\ln W$) from sample NYTN (centered at 242, 289, 345 and 362 nm) and sample NYTG (289, 311, 362, and 475 nm) was determined using the linear section of the plots shown in Fig. 6. The fitted slopes were determined to be three and four, indicating three photon UC processes for bands of 362 and 475 nm and four photon UC processes for bands of 242, 311, 289

and 345 nm, respectively. Since the UC emissions at 242, 289, 311 and 345 nm are more sensitive to excitation power density than those at 362 and 475 nm, these emissions were possibly generated differently from the five photons process as we proposed in the energy level diagram below (Figure 8). This discrepancy could be due to the involvement of Nd^{3+} in the circulation of energy transfer from $\text{Yb}^{3+} \rightarrow \text{Tm}^{3+} \rightarrow \text{Nd}^{3+}$ and back to Tm^{3+} as we would explain later. The schematic of the possible energy-transfer mechanisms leading to the above upconversion emissions are explained through the energy level diagram below. It was also noted that the intensities of all these UV UC emission bands increased with increasing excitation power (ESI-3). Within our experimental capability, i.e. at approximately excitation power density $< 25.5 \text{ W/cm}^2$, none of the UV UC emission bands corresponding to Tm^{3+} and Gd^{3+} ions reached saturation. Therefore, it is expected that the UV UC emission intensity of these UC particles would continue to increase until saturation is reached at excitation power density greater than 25.5 W/cm^2 .

Figure 6. Dependence of UV UC luminescence intensity ($\ln I$) versus excitation power density (I_{W} , W/cm^2): (a) NYTN and (b) NYTG under 980 nm excitation at room temperature.

Emission and decay properties under DC and UC excitations:

Measured excitation spectra of samples NYT, NYTN and NYTG with fixed emissions at 650 and 800 nm show strong excitation bands at 357 nm and 470 nm corresponding to Tm^{3+} ($f-f$) manifolds with weak Tm^{3+} ($f-f$) excitations at ~ 250 and 510 corresponding to $^3\text{H}_6$ to $^3\text{P}_{0,1,2}$ and $^1\text{G}_4$ (Fig. S4a). Therefore, upon excitation at strong excitation bands at 357 and 470 nm, wide-range downconversion emission spectra (300 to 850 nm) for these samples (Fig. S4b) show almost all relevant emission transitions of Tm^{3+} , corresponding to the manifolds $^1\text{G}_4 \rightarrow ^3\text{H}_6$, $^1\text{G}_4 \rightarrow ^3\text{F}_4$ and $^3\text{H}_4 \rightarrow ^3\text{H}_6$ emission transitions in the spectral region of 440-500, 640-680 and 700-850 nm, respectively. Furthermore, their intrinsic lifetimes were measured under pulsed excitations at 357 and 470 nm (Figures 7a, S5 and S6) and tabulated in Table 1 with the corresponding fitting.

Figure 7. Temporal evolution of Tm^{3+} emission intensity (a) after pulse downconversion (Stokes) excitation at 357 nm from NYT, and after pulse upconversion excitation at 980 nm from: (b) NYT, (c) NYTN and (d) NYTG.

Similarly, the temporal evolution of the UC PL intensity at 242, 289, 345, 362, 450, 475, 650 and 800 nm as a function of time for these three samples, including an additional emission bands at 311 nm for NYTG, after the microsecond excitation pulse at 980 nm was obtained (Fig. 7b-d). These decay curves were fitted by the exponential function as shown in eq. 1:

$$I(t) = I_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right), \quad (1)$$

where A is the fitting parameters and τ_1 is the fluorescence decay times. All the fitted decay times are tabulated in Tables 1 and 2, and the corresponding fitting examples are represented in Figure S6.

TABLE 1. Effective lifetimes of Tm^{3+} excited states from the NYT, NYTN and NYTG particles measured after pulsed excitation at 357 nm and 470 nm.

Emission States	Fitted lifetime τ_D (ms)					
	Sample NYT		Sample NYTN		Sample NYTG	
	$\lambda_{\text{ex}} = 357$ nm	$\lambda_{\text{ex}} = 470$ nm	$\lambda_{\text{ex}} = 357$ nm	$\lambda_{\text{ex}} = 470$ nm	$\lambda_{\text{ex}} = 357$ nm	$\lambda_{\text{ex}} = 470$ nm
800 nm	0.72±0.070	1.024±0.080	0.85±0.080	1.39±0.120	0.74±0.072	1.29±0.120
650 nm	0.059±0.005	0.24±0.020	0.070±0.006	0.50±0.042	0.080±0.006	0.050±0.042
450 nm			0.11±0.010		0.07±0.008	

TABLE 2. Effective lifetimes of Tm^{3+} excited states from the NYT, NYTN and NYTG particles measured after pulsed excitation at 980 nm into the $^2\text{F}_{5/2}$ energy level of Yb^{3+} ions.

Emission States	Fitted lifetime τ_D (ms)		
	Sample NYT	Sample NYTN	Sample NYTG
800 nm	1.56 ± 0.003	1.42 ± 0.004	1.38 ± 0.001
650 nm	0.87 ± 0.003	1.07 ± 0.001	0.89 ± 0.096
475 nm	0.94 ± 0.003	1.09 ± 0.003	0.982 ± 0.002
450 nm	0.40 ± 0.003	0.56 ± 0.001	0.428 ± 0.002
362 nm	0.40 ± 0.003	0.57 ± 0.072	0.449 ± 0.003

345 nm	0.23 ± 0.003	0.48 ± 0.0034	0.49 ± 0.003
311 nm			2.730 ± 0.002
289 nm	0.24 ± 0.003	0.44 ± 0.002	0.420 ± 0.002
264 nm			0.97 ± 0.002
242 nm	1.21 ± 0.001	1.12 ± 0.001	

Proposed UV UC Mechanisms:

Although these emission spectra (Figure 3) are consistent with ETU mechanism inducing UV, blue, red and NIR emissions under excitation at 980 nm, pulsed excitation was used in order to distinguish the ETU and GSA/ESA mechanisms by comparing the decays measured upon UC and DC excitations (Figures 7a & S5 & S6 vs 7b-d). The decay times measured under DC and UC conditions should be similar if UC occurs within pulse width by GSA/ESA process.[6, 35] However, as tabulated in Tables 1 and 2, the measured UC decays under 980 nm excitation from these three samples were longer than the corresponding DC decays excited at 357 and 470 nm. This experimental observation confirms that ETU mechanism dominates in these samples. In addition, the lifetime decays including the one at 311 nm corresponding to the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition of the NYTG particles was also observed under 980 nm pulse excitation (Table 2). The decay time for the 311 nm emission was measured to be 2.730 ± 0.002 ms, longer than any other UV emissions, which suggests that the level $Gd^{3+} ({}^6P_{7/2} \rightarrow {}^8S_{7/2})$ can be excited to the higher excitation power density under 980 nm excitation, making $Gd^{3+} ({}^6P_{7/2})$ suitable for UV lasers applications.

Based on the measured data presented above, the possible UV UC luminescence mechanism of the triply doped NYTn and NYTg samples has been proposed in Fig. 8. First Yb^{3+} ions are excited from ${}^2F_{7/2}$ to ${}^2F_{5/2}$ level through ground state absorption (GSA) process under 980 nm excitation. This in turn leads to ETUs between Yb^{3+} to Tm^{3+} and

then Tm^{3+} to Nd^{3+} . Several processes could lead to the population of higher excited states of Tm^{3+} ions from the absorption of a 980 nm photon. First the $^3\text{H}_5$ state of Tm^{3+} populates after dissipating the energy by phonon transferred from Yb^{3+} ions to Tm^{3+} ions. Subsequently, Tm^{3+} ions relax nonradiatively to the lower $^3\text{F}_4$ state and further populate the $^3\text{F}_{2,3}$ states through an ETU from Yb^{3+} ions to Tm^{3+} ions. This indicates that intermediate levels of Tm^{3+} ions are involved in the UC mechanisms to populate their NIR ($^3\text{G}_4$) and red ($^1\text{G}_4$) emitting levels. Since $^1\text{D}_2$ level cannot be directly populated through ETU by $^1\text{G}_4$ owing to the largest energy mismatch (3500 cm^{-1}) between them, the $^1\text{D}_2$ level may be alternatively populated through cross-relaxation (CR) as represented in the energy level diagram. However, the Yb^{3+} to Tm^{3+} ETU populates the $^1\text{G}_4$, $^3\text{P}_{0,1,2}$, and $^1\text{I}_6$ levels of Tm^{3+} , necessarily involving the $^3\text{H}_4$ and $^1\text{D}_2$ levels of Tm^{3+} through ETU. This is also consistent with the high UC emission intensity of NIR emission at 800 nm compared to UC emission intensity for blue and UV emissions observed when excited at 980 nm. In addition, the longer decay time of the $^3\text{H}_4$ level of Tm^{3+} relative to other Tm^{3+} emission states under UC excitation suggest that ETU processes must feed the $^1\text{G}_4$ level of Tm^{3+} .

Figure 8. Energy level diagram of the triply doped $\text{Yb}^{3+}, \text{Tm}^{3+}, \text{Nd}^{3+}$ and $\text{Yb}^{3+}, \text{Tm}^{3+}, \text{Gd}^{3+}$ systems to show possible UV UC PL mechanisms at 980 nm excitation for the NYT, NYTN and NYTG samples.

We further proposed that a cross-relaxation process takes place between Nd^{3+} and Tm^{3+} . Based on the emission profile shown in Fig. 4, it can be inferred that the UV emissions below 500 nm has no profile change between the fluorescence spectra of the NYTN or NYTG particles and those of the parental NYT sample, while the UV emissions below 500 nm have enhanced. This phenomenon could be due to the fact that the $^4\text{F}_{3/2}$ level of Nd^{3+} probably feeds the higher excited $^3\text{P}_{0,1,2}$, $^1\text{D}_2$, and $^1\text{G}_4$ states of Tm^{3+} by cross relaxation between Nd^{3+} and Tm^{3+} ions. The reduction of the emission intensity at 800 nm from the NYTN particles compared to that of the parental NYT sample arising from the $^3\text{G}_4 \rightarrow ^3\text{H}_6$ transition of Tm^{3+} . This phenomenon ensures that Nd^{3+} ions act as a

sensitizer to absorb emission light from Tm^{3+} at 800 nm and subsequently transfer energy back to the neighboring Tm^{3+} ions, resulting in the enhancement of UV UC emission under 980 nm excitation. Furthermore, low phonon energy in NYT helped to reduce the nonradiative transition of $^3\text{P}_{0,1,2}$, resulting in the $^3\text{P}_{1,2} \rightarrow ^3\text{H}_6$ and $^1\text{I}_6 \rightarrow ^3\text{H}_6$ emissions at 242 and 289 nm, respectively. However, the low phonon energy of the host was unfavorable to phonon-assisted energy transfer from Yb^{3+} to Tm^{3+} , leading to the population of the $^3\text{P}_{0,1,2}$, $^1\text{I}_6$ and $^1\text{D}_2$ levels. Therefore, enhanced UV emissions below 400 nm could only be realized when there was a circulation of energy transfer from $\text{Yb}^{3+} \rightarrow \text{Tm}^{3+} \rightarrow \text{Nd}^{3+}$ and back to Tm^{3+} . The emission from Nd^{3+} under 980 nm excitation ensured that there existed a circulation of energy transfer from Yb^{3+} to Nd^{3+} and back to Tm^{3+} (Fig. S2).

Fig. 8 also shows the proposed energy level diagram of the NYTG particles. In a $\text{Yb}^{3+}, \text{Tm}^{3+}, \text{Gd}^{3+}$ triply co-doped system, the excited state $^6\text{I}_J$ and $^6\text{P}_{3/2,5/2,7/2}$ of Gd^{3+} ions can be populated through the ET from $^3\text{P}_{2,1,0}$ state of Tm^{3+} . Gd^{3+} concentration dependent UC emission spectra (Fig. 4d) of the NYTG particles also supports the proposed mechanisms of ET from Tm^{3+} to Gd^{3+} . This clearly indicates the importance of populating the $^3\text{P}_{2,1,0}$ efficiently in order to obtain intense UV UC emission at 311 and 306 nm.

CONCLUSION

Here we presented that UV upconversion PL of $\text{NaYF}_4:20\text{mol}\%\text{Yb}^{3+}, 0.5\text{mol}\%\text{Tm}^{3+}$ can be significantly enhanced by further introduction of another rare-earth dopant, i.e. neodymium (Nd^{3+}) or gadolinium (Gd^{3+}). The NYT UC particles exhibited the highest luminescence enhancement in the UV region after co-doping with 0.05mol% Nd^{3+} or

2.0mol% Gd^{3+} . This makes NYTN and NYTG particles as potential candidates for broad UV applications. Through investigation on the dependence of UV UC emissions at different concentrations of the Nd^{3+} and Gd^{3+} dopants in terms of ground state absorption, excited state absorption and energy transfer UC mechanisms, we believe that this previously unexplored area can receive new insights between the sensitizers and activators concentration in this regime. The experimental data indicate that multiple factors, including crystallinity, complex excitation, multiphoton process, and the ETU in the succession from Yb^{3+} to Tm^{3+} and Tm^{3+} to $\text{Nd}^{3+}/\text{Gd}^{3+}$ and back to Tm^{3+} , play key role in these triply doped $\text{Yb}^{3+}, \text{Tm}^{3+}, \text{Nd}^{3+}/\text{Gd}^{3+}$ systems. Therefore, the present work demonstrated higher UV UC performance in addition to a better fundamental understanding of this type of materials, which can be used for a broader range of applications, including photocatalysis, short wavelength solid-state lasers, optical data storage, solar energy conversion in addition to biological and medical applications.

Supporting Information. QY measurement details, Nd^{3+} emission spectra under 980 excitation of NYTN, excitation power dependence upconversion emission, excitation and emission properties under UV excitation, and decay analysis under UV excitations. This material is available free of charge via the Internet.

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