Intense ultraviolet upconversion emission from water-dispersed colloidal YF$_3$:Yb$^{3+}$/Tm$^{3+}$ rhombic nanodisks†

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Intense ultraviolet upconversion emission has been observed in water-dispersed uniform rhombic nanodisks (side length of ~14 nm and thickness of ~2.5 nm) of YF$_3$ co-doped with Yb$^{3+}$ sensitizer and Tm$^{3+}$ activator ions, when excited at ~980 nm.

Lanthanide-doped upconversion nanoparticles (UCNPs) possess a unique attribute to convert near infrared light (NIR) into shorter wavelength NIR, visible, and ultraviolet (UV) emissions via the use of real ladder-like energy levels in lanthanides.$^{1-10}$ The efficiency of the UC process is several orders of magnitude higher than for conventional multi-photon absorption that involves virtual intermediate energy levels, enabling them to be excited by a low-cost continuous-wave (CW) diode laser and thus eliminating the necessary use of ultra-short pulsed lasers to implement multi-photon excitation.$^{11-16}$ To date, efficient NIR-to-NIR and NIR-to-visible UC emission from lanthanide-doped nanoparticles has been achieved and utilized for a range of applications such as anti-counterfeiting, photovoltaic solar energy conversion, high contrast 3D bioimaging, and photodynamic therapy.$^{17-23}$ However, the lack of efficient NIR-to-UV UCNPs has limited the development of biophotonics applications.

Efficient NIR-to-UV UCNPs are desired for many biological applications due to the wide range of potential imaging and therapeutic uses of UV light and the ability of NIR excitation to penetrate biological media. It is well known that UV photons can trigger photochemical reactions to manipulate the functions of biomolecules or to mediate the on-demand drug release in live systems.$^{24-27}$ However, traditional means of generating UV excitation via UV lamps or lasers are limited by severe phototoxicity and significantly limited tissue penetrability. In situ generation of UV light through NIR-to-UV in UCNPs can circumvent these drawbacks, as NIR excitation light is not absorbed by tissues, thus providing increased light penetration in tissues.$^{26,27}$ However, the practical use of NIR-to-UV UCNPs in biology remains rather limited due to the lack of water-dispersible UCNPs with intense UV UC emission. Fundamentally, the low efficiency arises from the fact that NIR-to-UV UC emission typically involves higher order multi-photon processes, e.g., four- or five-photon processes.$^{26,27}$ By contrast, the more well-developed NIR-to-NIR or NIR-to-visible UC emission systems generally involve a two-photon process. Thus, the selection of a host lattice with an appropriate crystal phase and low lattice phonon energy is of particular importance to minimize energy loss due to relaxations from intermediate levels in UCNPs.$^3$ In addition, biological systems contain a large pool of water molecules, which promote nonradiative relaxation of the relevant upconversion excited states of lanthanide-doped nanoparticles via coupling to high frequency OH vibrational modes.$^{10}$ This requires the use of appropriate hydrophilic ligands on the NP surface that must allow water miscibility while at the same time isolating the UCNPs from the quenching effect of water.

In the literature, the observation of NIR-to-UV UC emission in colloidal nanoparticles has been limited to Yb$^{3+}$/Tm$^{3+}$-doped LiYF$_4$ and NaY(Gd)F$_4$ nanocrystals, generally dispersed in an organic solvent, with an optimized Yb$^{3+}$ concentration of...
25–30% and Tm$^{3+}$ concentration of 0.5–2%.\textsuperscript{31–35} Though aqueous dispersions of these nanoparticles have been utilized for proof-of-concept demonstrations of photoactivation, the luminescence is quenched by factors of 3–5 times upon transfer from the organic to the aqueous phase.\textsuperscript{28,38} Yttrium fluoride (YF$_3$) has been found to be a good host lattice for efficient UC emission owing to its crystal field and its low lattice phonon energy;\textsuperscript{39} the largest UC efficiency of bulk YF$_3$ materials doped with Yb$^{3+}$/Er$^{3+}$ or Yb$^{3+}$/Tm$^{3+}$ has been reported to be greater than that of hexagonal NaYF$_4$ materials doped with Yb$^{3+}$/Er$^{3+}$ or Yb$^{3+}$/Tm$^{3+}$, which are presently considered to be the most efficient.\textsuperscript{1} This suggests the use of YF$_3$ as a matrix for UV UC generation. Wang et al. reported strong UV UC emission from 700 nm sized YF$_3$:20% Yb$^{3+}$/1% Tm$^{3+}$ powders synthesized in a quaternary reverse microemulsion system.\textsuperscript{37} However, these particles are too large and are not dispersible in an aqueous phase. Recently, intense UV UC emission was observed in a nano-glass–ceramic comprising YF$_3$:Yb$^{3+}$/Tm$^{3+}$ nanoparticles of about 10 and 20 nm embedded in a glass matrix,\textsuperscript{29,31} demonstrating the appropriateness of the YF$_3$ matrix for UV UC generation. However, at this point there is no prior report on intense UV UC emission from water-dispersed colloidal YF$_3$:Yb$^{3+}$/Tm$^{3+}$ nanoparticles.

Here, we present a simple thermolysis approach to synthesize uniform YF$_3$:Yb$^{3+}$/Tm$^{3+}$ rhombic nanodisks with an average side length of 14 nm and a thickness of 2.5 nm. Utilization of the hydrophilic ligand poly(acrylic acid) (PAA, molecular weight 1800) imparts good aqueous solubility to the rhombic nanodisks while retaining the intensity of UV UC emission. In addition, we show that the efficiency of UV UC emission in these aqueous rhombic nanodisks can be enhanced by increasing the sensitizer concentration to decrease the sensitizer–activator distance for improved energy transfer from Yb$^{3+}$ to Tm$^{3+}$ ions. The maximum UV UC output is determined for water-dispersed YF$_3$:90% Yb$^{3+}$, 2% Tm$^{3+}$ nanodisks, which is about 6 times larger than that for the water-dispersed YF$_3$:10% Yb$^{3+}$, 2% Tm$^{3+}$ nanodisks.

YF$_3$ nanocrystals doped with 2 mol% Tm$^{3+}$ and 10, 30, 50, 70, 90 and 98 mol% Yb$^{3+}$ were synthesized using the thermolysis method adapted from our recent work.\textsuperscript{34} The synthetic details are described in the Experimental section of the ESI.\textsuperscript{†} Fig. 1 displays transmission electron microscopy (TEM) images of YF$_3$:10 mol% Yb$^{3+}$/2 mol% Tm$^{3+}$ nanocrystals dispersed in hexane (prior to ligand exchange, Fig. 1a) and water (after ligand exchange, Fig. 1b). Both Fig. 1a and b show that the NPs are uniform in size, with rhombic shapes. The average side length of these NPs is determined to be 14.3 nm in the histogram of the side length distribution (see ESI, Fig. S1†). Moreover, it should be noted from Fig. 1b that the aqueous YF$_3$:10% Yb$^{3+}$/2% Tm$^{3+}$ NPs (after ligand exchange) retain their size, shape, and monodispersability after phase transfer, and no aggregates are formed. Fig. 1c displays a high resolution TEM (HRTEM) image of several NPs; the rhombic area defined by the white line is composed of 10 × 10 atoms, with an area of 3.763 nm × 3.820 nm, indicating the orthorhombic crystal phase.\textsuperscript{38,39} The orthorhombic crystal phase is also verified by X-ray diffraction (see ESI, Fig. S4†). Fig. 1d shows a side view of several rhombic nanodisks, showing that the thickness of the rhombic nanodisk is 2.5 nm. Two-dimensional fast Fourier transform (FFT) patterns of Fig. 1c and d, depicted in the insets of Fig. 1c and d, indicate the high crystallinity of these rhombic nanodisks. A schematic illustration of the growth mechanism of YF$_3$ rhombic nanodisks is displayed in Fig. 1e. As one can see, the thermal decomposition of lanthanide trifluoroacetate salts at high temperature is utilized to produce the YF$_3$ nuclei in the mixed solvents of oleic acid and 1-octadecene. The non-coordinating octadecene is used as the primary solvent due to its high boiling point (∼315 °C), while oleic acid is chosen as a surface capping ligand, as its carboxylic group can coordinate with the metallic elements, and its long hydrocarbon chain can be used to prevent nanoparticle aggregation and control chemical reactions at the nanoscale.\textsuperscript{40–43} Subsequently, the nuclei grow up, crystallize, and form rhombic nanodisks. The formation of nanodisks might arise from a two-dimensional growth of homogeneous rhombic nuclei due to the preferred attachment of oleic acid to the side (101) facets rather than to the top or bottom (020) facets. The rhombic geometry of the nanodisks is
The synthesized rhombic nanodisks are capped by an oleic acid ligand, making them soluble in the organic phase, but not dispersible in water. In order to utilize these rhombic nanodisks for biomedical applications, we replaced the original oleic acid capping group with a hydrophilic ligand, PAA. The detailed procedure for ligand exchange is described in the ESI. The accomplishment of ligand exchange was confirmed by Fourier transform infrared (FTIR) spectroscopy (see ESI, Fig. S2†). The PAA surface coating allows these rhombic nanodisks to be readily dispersed in water, forming a transparent and stable colloidal suspension that showed no sediments for a period of 4 weeks.

The UC emission of YF$_3$:10% Yb$^{3+}$/2% Tm$^{3+}$ nanodisks dispersed in cyclohexane (prior to ligand exchange) and in water (after ligand exchange) under a CW laser diode excitation at 980 nm of 200 W cm$^{-2}$ is shown in Fig. 2. Six distinct UC emission bands are clearly resolved, and centered at 290, 345, 360, 450, 475 and 800 nm, which correspond to the $^1$I$_6$ → $^3$H$_6$, $^1$I$_6$ → $^3$F$_4$, $^1$D$_2$ → $^3$H$_6$, $^1$I$_6$ → $^3$F$_4$, $^1$G$_4$ → $^3$H$_6$, and $^3$H$_4$ → $^3$H$_6$ transitions of Tm$^{3+}$ ions, respectively. It is striking that the four-photon UV UC emission at 360 nm is comparable to the three-photon emission at 475 nm and two-photon emission at 800 nm, illustrating the high UC efficiency of these rhombic nanodisks dispersed in water. Fig. 3 displays a log-log plot of dependence of the intensities of the various emissions on the excitation density, with the slope providing information on the number of photons absorbed for upconversion. More importantly, the intense UV UC emissions of Tm$^{3+}$ remain nearly unchanged before and after ligand exchange, suggesting the uniqueness of the hydrophilic PAA ligand to impart water solubility while negating the effect of vibrational quenching by OH. The result of surface engineering of UCNPs with the PAA ligand differs from the previous surface treatment results by silica coating where a significant quenching of UC emission in water was observed. The nearly unchanged UV UC intensity after PAA ligand exchange should enable applications of these water-dispersed rhombic nanodisks in biophotonics.

Slope values of 4.99, 5.11, 4.02, 4.13, 3.03, and 2.13 were observed for UC emissions peaked at 290, 345, 360, 450, 475, and 800 nm, respectively. This result illustrates that five-, four-, three-, and two-photon processes are involved to generate the UC emission at 290, 345, 360, 450, 475, and 800 nm, respectively. These observations agree well with previous results of nano-glass-ceramics comprising YF$_3$:Yb$^{3+}$/Tm$^{3+}$ nanoparticles of about 10 and 20 nm. Note that the UC UC emission at 360 nm and the blue emission at 450 nm have the same slope value of ~4, as they arise from the upper level of the $^1$D$_2$ state (see ESI, Fig. S3†). The same five-photon processes for the UV UC emissions at 345 nm and at 290 nm confirm that emissions at these wavelengths arise from the same upper level of the $^1$I$_6$ state of Tm$^{3+}$ ions (see ESI, Fig. S3†). The higher intensity of UV UC emission at 345 nm than that of the UV UC band at 290 nm (see Fig. 2) is attributed to the greater branching ratio of the $^1$I$_6$ → $^3$F$_4$ transition relative to the $^1$I$_6$ → $^3$H$_6$ transition. The slightly larger value of slope = 2.13 than 2 for NIR emission at 800 nm arises from the involvement of the higher energy $^3$G$_4$ state due to the cross-relaxation process of $^3$G$_4$ + $^3$F$_4$ → $^3$H$_6$ + $^3$F$_2$. Mechanisms for UV, visible, and NIR UC generation are presented in the ESI,† which conclude that these emissions arise from multi-step energy transfers from the Yb$^{3+}$ to the Tm$^{3+}$ ions, consistent with prior reports. This work has utilized the nanoscale control of the energy transfer efficiency from the sensitizer Yb$^{3+}$ to the activator Tm$^{3+}$ to enhance the UC efficiency in these water-dispersed nanodisks. We note that unlike the Tm$^{3+}$ activator ion, the Yb$^{3+}$ sensitizer ion has one exclusive excited energy level in the $^3$F$_{5/2}$ state, excluding the possibility of cross-relaxation quenching when increasing its concentration (see ESI, Fig. S3†). Thus, we reason that elevation of the Yb$^{3+}$ concentration within one nanoparticle reduces the distance between the Yb$^{3+}$ and Tm$^{3+}$, leading to an enhancement of energy transfer.

![Fig. 2](image_url) Upconversion emission spectrum of YF$_3$:10% Yb$^{3+}$/2% Tm$^{3+}$ nanocrystals dispersed in cyclohexane (dashed blue line) and in water (solid red line) upon NIR laser diode excitation at 980 nm. The excitation density is ~200 W cm$^{-2}$ and the nanoparticle concentration is 5 mg mL$^{-1}$ for both samples.

![Fig. 3](image_url) Logarithmic plots of the dependence of the intensity of each upconversion band in Fig. 2 on the excitation density in water-dispersed YF$_3$ rhombic nanodisks codoped with 10 mol% Yb$^{3+}$ and 2 mol% Tm$^{3+}$. The slope values of the linear fits (solid line) are presented in the inset together with the peak wavelength of each UC band.
enhancing the efficiency of energy transfer from Yb\(^{3+}\) to Tm\(^{3+}\), which finally leads to an increase of the UV UC emission.

Fig. 4 displays photographic images (top panel) as well as UC spectra (bottom panel) of water-dispersed rhombic nanodisks of YF\(_3\) codoped with 2 mol% Tm\(^{3+}\) ions and various concentrations of Yb\(^{3+}\) ions (10, 30, 50, 70, 90, and 98 mol%). The TEM and XRD results for the rhombic nanodisks of YF\(_3\) co-doped with 2 mol% Tm\(^{3+}\) ions and 10–98 mol% Yb\(^{3+}\) ions confirm that they are all of orthorhombic crystal phase and have similar size distributions (see ESI, Fig. S5–10†). The content of each dopant in these nanodisks is in good agreement with the indicated atomic ratio of precursors (see ESI, Table S1†). Although UV UC is invisible to the naked eye, the visible blue UC emission in combination with the upconversion spectra illustrates the UV UC emission efficiency. As expected, the intensities of UV UC emissions as well as visible and NIR emissions display a gradual increase with an increment of Yb\(^{3+}\) concentration from 10 to 90 mol%, but show a decrease when the Yb\(^{3+}\) concentration reaches 98 mol%. The intensity ratios of the upconversion emissions from the \(^1\text{D}_2\) state and the \(^3\text{G}_4\) state, to the upconversion emission from the \(^3\text{H}_4\) state display a similar trend as the UV UC intensity does when increasing the Yb\(^{3+}\) ion concentration (see the inset of Fig. 4). The enhancement of UV UC intensity as well the increase of the emission intensity ratios clearly illustrate the enhanced energy transfer effects from the sensitizer Yb\(^{3+}\) to the activator Tm\(^{3+}\) due to the decreased distance between them. In particular, when increasing the concentration of sensitizer Yb\(^{3+}\) ions, it is seen that UV UC emissions, assigned to transitions \(^1\text{I}_6\) \(\rightarrow\) \(^3\text{H}_4\), \(^1\text{I}_6\) \(\rightarrow\) \(^3\text{F}_4\), \(^1\text{D}_2\) \(\rightarrow\) \(^3\text{H}_4\), and \(^1\text{D}_2\) \(\rightarrow\) \(^3\text{F}_4\) of Tm\(^{3+}\) ions, increase more rapidly than the blue emission at 475 nm (\(^3\text{G}_4\) \(\rightarrow\) \(^3\text{H}_6\)) and the NIR emission at 800 nm (\(^3\text{H}_4\) \(\rightarrow\) \(^3\text{H}_6\)). This is consistent with the hypothesis that UV UC emissions involve four- or five-photon processes, which are of higher order than the visible blue (three-photon) and NIR (two-photon) emissions. The UV UC output at 360 nm from water-dispersed YF\(_3\):90 mol% Yb\(^{3+}\), 2 mol% Tm\(^{3+}\) nanodisks was determined to be \(\sim\)6 times greater than that from water-dispersed YF\(_3\):10 mol% Yb\(^{3+}\), 2 mol% Tm\(^{3+}\) nanodisks. A similar UC emission enhancement fold at 360 nm is observed for water-dispersed (YF\(_3\):90 mol% Yb\(^{3+}\), 2 mol% Tm\(^{3+}\))/YF\(_3\) core/shell nanoparticles when compared to (YF\(_3\):10 mol% Yb\(^{3+}\), 2 mol% Tm\(^{3+}\))/YF\(_3\) core/shell nanoparticles (Fig. S11†). Since the core/shell structure can effectively suppress surface-related quenching mechanisms, the quenching effects produced by Yb\(^{3+}\) sublattice-mediated energy migrations to nanoparticle surface quenching sites are eliminated in these core/shell nanoparticles. As a consequence, investigations in core/shell nanoparticles substantiate that the enhancement result for Yb\(^{3+}\) 10–90 mol% in Fig. 4 indeed arises from the proposed enhancement mechanism, i.e., the enhanced energy transfers from the sensitizer Yb\(^{3+}\) to the activator Tm\(^{3+}\). Furthermore, the reason for the simultaneous decrease in intensity of the UV, visible, and NIR UC emissions upon increasing the concentration of Yb\(^{3+}\) from 90 to 98 mol% has been investigated in detail by comparing upconversion emission spectra of nanodisks YF\(_3\) doped with Tm\(^{3+}\) of 2 mol% and Yb\(^{3+}\) concentrations of 90, 92, 94, 96, and 98 mol%. A gradual decrease of UV UC emissions is observed for increased Yb\(^{3+}\) concentration in the range of 90–98% (data not shown). This result suggests that, when the concentration of Yb\(^{3+}\) is above 90 mol%, Yb\(^{3+}\) sublattice-mediated energy dissipation processes become more pronounced in comparison with the enhancement effect produced by increased Yb\(^{3+}\) ions, thus quenching the UV UC emissions.

To conclude, we report a simple thermolysis approach to synthesize uniform YF\(_3\):Yb\(^{3+}\)/Tm\(^{3+}\) rhombic nanodisks with an average side length of 14 nm and a thickness of 2.5 nm. The hydrophilic ligand, poly(acrylic acid), imparts water solubility while preserving the intensity of UV UC emissions. The efficiency of the UV UC emission can be significantly enhanced by elevation of the sensitizer concentration, which serves to decrease the sensitizer–activator distance to allow improved energy transfer from the Yb\(^{3+}\) to the Tm\(^{3+}\) ions in the nanoparticles. The observation of intense UV UC emission in the water-dispersed rhombic nanodisks suggests that this formulation may find utility in UV-mediated biophotonic applications.

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Notes and references