Facile synthesis of intense green-emitting LiGdF₄:Yb,Er-based upconversion bipyramidal nanocrystals and their polymer composites

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Figure S1. Photographs of Li(Gd$_{1-x}$Y$_x$)F:Yb,Er UCNP solutions under (a) ambient light and (b) IR light illumination (980 nm, 2W cw laser). The UCNPs in each solution correspond to the UCNPs shown in Figure 1 [i: Y = 0 mol%, ii: Y = 20 mol%, iii: Y = 40 mol%, iv: Y = 60 mol%, v: Y = 80 mol%].
Figure S2. Absorption spectrum of LGY$_{0.4}$F:Yb,Er UCNPs.
Figure S3. UC PL intensity at green and red spectral regions as a function of incident laser power density. The double-logarithmic plot gives rise to linear plots in which slopes are $1.66 \pm 0.04$ and $1.94 \pm 0.03$ for green and red emissions, respectively, suggesting that the green and red emissions from LGY$_{0.4}$F:Yb,Er UCNPs are dominated by two photon upconversion process.
Upconversion (UC) quantum yield (QY) of LGY$_{0.4}$F:Yb,Er upconversion tetragonal bipyramids (UCTBs) was calculated using the QE of β-NaYF$_4$:Yb,Er upconversion nanoparticles (UCNPs) according to following equation, \(^{(S1)}\)

\[
UCQY_S = \left( \frac{PL_S}{PL_R} \right) \left( \frac{Abs_R}{Abs_S} \right) \left( \frac{n_S}{n_R} \right)^2 UCQY_R
\]

Where $UCQ$, $PL$, $Abs$, and $n$ indicate the upconversion quantum yield, integrated PL intensity, optical absorption at excitation wavelength, and refractive index of solvent, respectively, and subscripts $S$ and $R$ represent sample and reference, respectively. Boyer et al. reported absolute QY of β-NaYF$_4$:Yb,Er UCNPs under 150 W/cm$^2$, thus the UCQY of the LGY$_{0.4}$F:Yb,Er UCTBs can be determined by measuring the UC PL spectra and the absorption values at the excitation wavelength for the LGY$_{0.4}$F:Yb,Er and β-NaYF$_4$:Yb,Er UCNPs.

According to Boyer et al., absolute UCQE of the β-NaYF$_4$:Yb,Er UCNPs with 30 nm size under ~980 nm excitation (power density = 150 W/cm$^2$) is 0.1% \(^{(S2)}\). The 30 nm β-NaYF$_4$:Yb,Er UCNPs were synthesized by using the synthetic procedure described in the following publications:


No changes were made to the reported procedures.
Figure S4. (a, b) TEM and HR-TEM images and (c) XRD pattern of $\beta$-NaYF$_4$:Yb,Er UCNPs. The size of the $\beta$-NaYF$_4$:Yb,Er UCNPs is about 30 nm. The spacing between two adjacent lattices are 0.52 nm which is in good agreement with interplanar $d$-spacing between \{10\} planes. XRD pattern of the $\beta$-NaYF$_4$:Yb,Er UCNPs is well matched with literature value (JCPDS 28-1192). These results indicate as-synthesized NaYF$_4$:Yb,Er has single hexagonal phase.
Figure S5. PL spectra of LGY\textsubscript{0.4}F:Yb,Er and β-NaYF\textsubscript{4}:Yb,Er under 971 nm excitation with 150 W/cm\textsuperscript{2} power density. The PL spectra of LGY\textsubscript{0.4}F:Yb,Er and β-NaYF\textsubscript{4}:Yb,Er were normalized with the absorbance value at 971 nm. According to Eq. S1, UCQY of the LGY\textsubscript{0.4}F:Yb,Er was calculated to be 0.16% which is higher than β-NaYF\textsubscript{4}:Yb,Er (~ 30 nm) UCNPs.
Figure S6. Intensity ratio of green to red emission of Li(Gd,Y)F₄:Yb,Er UCNPs with varying Y³⁺ concentration from 0 mol% to 80 mol%.
Figure S7. XRD patterns of Li(Gd,Y)F₄:Yb,Er UCNPs with varying Y concentrations. When the concentration of Y was 0 and 20 mol%, tetragonal LiGdF₄ phase was not observed. Instead, orthorhombic GdF₃ phase was observed. Thus, in this manuscript, although we describe Li(Gd,Y)F₄:Yb,Er as nominal composition, LiGdF₄:Yb,Er and Li(Gd₀.6,Y₀.2)F₄:Yb,Er means GdF₃:Yb,Er, and (Gd,Y)F₃:Yb,Er, respectively.
Figure S8. HR-TEM images of Li(Gd,Y)F$_4$:Yb,Er UCNPs with varying Y concentration. (a) 0 mol%, (b) 20 mol%, (c) 40 mol%, (d) 60 mol%, and (e) 80 mol%. Inset of (c) shows FFT diffractogram for the HR TEM image.
Figure S9. TEM image of Li(Gd,Y)F₄:Yb,Er rhombic plates with no Y³⁺ doping.
Table S1. Particle sizes of Li(Gd,Y)F$_4$:Yb,Er with various Y$^{3+}$ doping concentrations.

<table>
<thead>
<tr>
<th>Y$^{3+}$ concentration</th>
<th>Crystal structure</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mol%</td>
<td>Orthorhombic</td>
<td>12.1±1.0 nm × 11.4±1.0 nm, thickness = 4.0±0.5 nm</td>
</tr>
<tr>
<td>20 mol%</td>
<td>Orthorhombic</td>
<td>13.4±2.1 nm × 12.3±1.9 nm, thickness = 4.6±0.3 nm</td>
</tr>
<tr>
<td>40 mol%</td>
<td>Tetragonal</td>
<td>60.5±1.6 nm × 55.3±1.4 nm</td>
</tr>
<tr>
<td>60 mol%</td>
<td>Tetragonal</td>
<td>9.9±0.7 nm × 8.8±0.7 nm</td>
</tr>
<tr>
<td>80 mol%</td>
<td>Tetragonal</td>
<td>9.3±0.6 nm × 8.5±0.6 nm</td>
</tr>
</tbody>
</table>

Figure S10. Particle size distribution of Li(Gd,Y)F$_4$:Yb,Er UCNP with varying Y$^{3+}$ doping concentration.
Table S2. Average Bader charge of comprising elements of studied systems.

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Gd</th>
<th>Y</th>
<th>F</th>
</tr>
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<tbody>
<tr>
<td>LiGdF₄</td>
<td>1</td>
<td>2.39</td>
<td>n/a</td>
<td>-0.85</td>
</tr>
<tr>
<td>LiYF₄</td>
<td>1</td>
<td>n/a</td>
<td>2.33</td>
<td>-0.83</td>
</tr>
<tr>
<td>LiGdYF₄</td>
<td>1</td>
<td>2.37</td>
<td>2.33</td>
<td>-0.84</td>
</tr>
<tr>
<td>LiGdYF₄(101)</td>
<td>1</td>
<td>2.37</td>
<td>2.33</td>
<td>-0.85 (-0.78)*</td>
</tr>
</tbody>
</table>

*Four F⁻ ions adjacent to Y³⁺ dopants are less negatively charged.
Figure S11. STEM images of LGY$_{0.4}$F:Yb,Er UCTBs (a) without and (b) with short range ordered arrangement.
Figure S12. (a) Low and (b) high magnification SEM images of LGY$_{0.4}$F:Yb,Er UCTBs.
Figure S13. (a) HAADF, (b) bright-field HR-STEM images of a single LGY$_{0.4}$F:Yb,Er UCTB. (c) colored image of (a). Inset shows Z-contrast variation along line XY. In addition to the overall variation of Z-contrast across the particle, there are also some peaks in the intensity profile indicating existence of heavy dopants in the atomic columns.
Figure S14. (a) HAADF HR-STEM image of a single LGY$_{0.4}$F:Yb,Er UCTB and (b) Z-contrast variation along the line shown in (a). Red arrows indicate low and high intensities for light element (Y) and heavy element (Yb, Er) doping for Gd sites, respectively.
Figure S15. HAADF HR-STEM images of a single LGY$_{0.4}$F:Yb,Er UCTB (a) before and (b) after damage by electron beam. (c) Z-contrast variation along the line shown in (a) and (b). A few STEM image acquisitions do not change overall intensity variation while overall intensity decreases and the difference between peak and valley also decreases (~90% in this image). After certain threshold, some regions in the sample start to be damaged quickly as indicated by the arrows in (b).
Figure S16. EELS spectra of (a) Li, (b) F, (c) Gd, (d) Y, (e) Yb, and (f) Er in an LGY_{0.4}F:Yb,Er UCTBs.
Figure S17. (a) HR-TEM image and (b) XRD pattern of LGY$_{0.45}$F:Yb,Er UCTBs. Inset indicates FFT diffractogram which can be indexed to the tetragonal structure of LiGdF$_4$ with the zone axes along the [010] direction.
Supporting References


S4 Z. Li and Y. Zhang, Nanotechnol., 2008, 19, 345606.