Electronic Supplementary Information

Modifying the Size and Uniformity of Upconversion Yb/Er: NaGdF₄ Nanocrystals through Alkaline-Earth Doping

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**Table S1-S2**

Table S1 Lattice parameters, cell volume and mean size of xCa/20Yb/2Er: NaGdF₄ NCs

<table>
<thead>
<tr>
<th>xCa/20Yb/2Er: NaGdF₄</th>
<th>Lattice parameters (Å)</th>
<th>Cell volume (Å³)</th>
<th>Mean size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0</td>
<td>6.0131 3.6059</td>
<td>112.91</td>
<td>8</td>
</tr>
<tr>
<td>x=10</td>
<td>6.0093 3.6079</td>
<td>112.83</td>
<td>8</td>
</tr>
<tr>
<td>x=20</td>
<td>6.0061 3.6095</td>
<td>112.76</td>
<td>10</td>
</tr>
<tr>
<td>x=25</td>
<td>6.0125 3.6072</td>
<td>112.93</td>
<td>12</td>
</tr>
<tr>
<td>x=30</td>
<td>6.0102 3.6086</td>
<td>112.87</td>
<td>18</td>
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<tr>
<td>x=40</td>
<td>6.0109 3.6076</td>
<td>112.88</td>
<td>22</td>
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</table>

Table S2 UC efficiencies of xCa/20Yb/2Er: NaGdF₄ core NCs and xCa/20Yb/2Er: NaGdF₄@NaYF₄ core-shell NCs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean size (nm)</th>
<th>Power density (W/cm²)</th>
<th>UC efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb/Er: NaGdF₄</td>
<td>8</td>
<td>2.5</td>
<td>0.015</td>
</tr>
<tr>
<td>Yb/Er: NaGdF₄@NaYF₄</td>
<td>11</td>
<td>2.5</td>
<td>0.051</td>
</tr>
<tr>
<td>Ca/Yb/Er: NaGdF₄</td>
<td>18</td>
<td>2.5</td>
<td>0.072</td>
</tr>
<tr>
<td>Ca/Yb/Er: NaGdF₄@NaYF₄</td>
<td>24</td>
<td>2.5</td>
<td>2.300</td>
</tr>
</tbody>
</table>
Figure S1-S24

Figure S1 XRD patterns of \( x \text{Ca}/20\text{Yb}/2\text{Er}: \text{NaGdF}_4 \) NCs: (x=0, 50 mol%).

Figure S2 TEM micrograph of 50Ca/20Yb/2Er: NaGdF_4 NCs.

Figure S3 EDS spectra of \( x \text{Ca}/20\text{Yb}/2\text{Er}: \text{NaGdF}_4 \) (x=0, 10, 20, 25, 30, 40 mol%) NCs, all the signals are normalized to Gd one, and Cu signals come from copper grid.
Figure S4 TEM images of 30Ca/20Yb/2Er: NaGdF$_4$ NCs with (a) low-, and (b) high-magnifications.
Figure S5 XRD patterns of xCa/20Yb/2Er: NaGdF$_4$ NCs synthesized under 280 °C for 30 min: (a) x=0, (b) 30 mol%; Bars in (a) and (b) represent standard cubic NaGdF$_4$ (JCPDS 27-0697) and hexagonal NaGdF$_4$ (JCPDS 27-0699) crystal data, respectively.

Figure S6 TEM micrographs of (a) Yb/Er: NaGdF$_4$ and Ca$^{2+}$-doped Yb/Er: NaGdF$_4$ NCs synthesized at 280 °C for 30 min; (c) HRTEM image of sample (b).
Figure S7 TEM micrographs of 30 mol% Ca$^{2+}$-doped Yb/Er:NaGdF$_4$ NCs prepared at 280 °C for different durations: (a) 15 min, (b) 20 min, (c) 25 min, (d) 30 min, (e) 40 min, (f) 60 min, and (g) 90 min; inset of (e) is the corresponding SAED pattern; (h) XRD patterns of 30Ca/20Yb/2Er:NaGdF$_4$ NCs prepared at 280 °C for different durations.
Figure S8 TEM micrograph of Yb/Er: NaGdF₄ NCs synthesized at 300 ºC for 90 min.

Figure S9 TEM micrographs of 30 mol% Ca²⁺-doped Yb/Er: NaGdF₄ NCs synthesized at 300 ºC for different durations: (a) 90 min, (b) 3h, (c) 6h, and (d) 12h.
Figure S10 XRD patterns of xSr/20Yb/2Er: NaGdF₄ NCs: (x=0, 10, and 20 mol%).

Figure S11 XRD patterns of xBa/20Yb/2Er: NaGdF₄ NCs: (x=0, 10 mol%).
Figure S12 TEM micrographs of xBa/20Yb/2Er: NaGdF₄ NCs: (a) x=0, (b) x=10.

Figure S13 TEM micrographs of xSr/20Yb/2Er: NaGdF₄ NCs: (a) x=0, (b) x=10 and (c) x=20; inset of (c) is the corresponding SAED pattern.
Figure S14 (a) UC emission spectra of xCa/20Yb/2Er: NaGdF₄ NCs (x=0, 30 mol%) under 976 nm excitation; (b) UC emission intensity versus Ca²⁺ doping content.

Figure S15 (a) Photoluminescence spectra of xCa/5Eu: NaGdF₄ (x=0, 10, 20, 30, 40 mol%) NCs under 395 nm excitation, (b) dependence of emission intensity ratio (5D₀ → 7F₂/5D₀ → 7F₁) on Ca²⁺ doping content.

Figure S16 UC luminescent decay curves of xCa/20Yb/2Er: NaGdF₄ (x=0, 10, 20, 30, 40 mol%) NCs: (a) the ⁴S₃/₂ → ⁴I₅/₂ and (b) ⁴F₉/₂ → ⁴I₅/₂ transitions of Er³⁺.
Figure S17 TEM micrograph of 30Ca/20Yb/2Er: NaGdF₄@NaYF₄ core-shell particles with low-magnification.
Figure S18 STEM-HAADF image of 30Ca/20Yb/2Er: NaGdF$_4$@NaYF$_4$ core-shell particles with low-magnification.
Figure S19 High-contrast STEM-HAADF image of Ca/Yb/Er: NaGdF$_4$@NaYF$_4$ core-shell particles.

Figure S20 Low- and high-magnification STEM-HAADF images of Ca/Yb/Er: NaGdF$_4$@NaYF$_4$ core-shell particles fabricated by using high ratio of shell precursors to core NCs in solution.
Figure S21 STEM-HAADF images of (a) 10Ca/20Yb/2Er: NaGdF₄@NaYF₄ and (b) 40Ca/20Yb/2Er: NaGdF₄@NaYF₄ Core-shell NCs.

Figure S22 TEM micrographs of (a) Yb/Er: NaGdF₄ cores and (b) Yb/Er: NaGdF₄@NaYF₄ core-shell particles.

Figure S23 Energy level diagrams of Er³⁺ and Yb³⁺ ions, showing possible energy transfer mechanisms for red and green UC emissions of Er³⁺ activators in the hosts; GSA and ETU represent ground state absorption and energy transfer upconversion, respectively.
Figure S24 Log-log plots of UC emission intensity versus pumping power of the products: (a) Ca/Yb/Er: NaGdF$_4$ core and Ca/Yb/Er: NaGdF$_4$@NaYF$_4$ core-shell particles; (b) Yb/Er: NaGdF$_4$ core and Yb/Er: NaGdF$_4$@NaYF$_4$ core-shell particles.