Supporting Information

Large-scale dewetting assembly of gold nanoparticles for plasmonic enhanced upconversion nanoparticles

Christian Clarke†, Deming Liu§, Fan Wang†, Yongtao Liu†, Chaohao Chen†, Cuong Ton-That†,*, Xiaoxue Xu†,* and Dayong Jin†,§,*

†Institute for Biomedical Materials and Devices, Faculty of Science, University of Technology Sydney, NSW, 2007, Australia.

§Department of Chemistry and Biochemistry, Concordia University, Montréal, QC H4B 1R6, Canada.

∥ARC Research Hub for Integrated Device for End-user Analysis at Low-levels (IDEAL), Faculty of Science, University of Technology Sydney, NSW, 2007, Australia.

Corresponding Authors

*Email: dayong.jin@uts.edu.au

*Email: xiaoxuehelen.xu@uts.edu.au

*Email: cuong.ton-that@uts.edu.au
General procedures. A modified solvent thermal method was used to prepare the core β-NaYF₄:20%Yb,2%Er UCNPs and a modified one pot hot injection method was used to prepare the β-NaYF₄:20%Yb,2%Er@NaYF₄ UCNPs.¹ β-NaYF₄:20%Yb,2%Er@NaYF₄ UCNPs were diluted and dropcast onto clean glass cover slides and dried in air. The slides were then plasma sputter coated with a 1 nm layer of Au using a Leica EM ACE600 sputtering and carbon thread coater and annealed in a Lindberg Blue Mini-mite tube furnace with a N₂ flow rate of 100 SCCM for 1 hour at 400°C. The size and morphology of the synthesized UCNPs were characterized using a FEI Tecnai T20 TEM with an operating voltage of 100 kV. Samples were prepared by placing a drop of dilute UCNPs onto formvar-coated copper grids (300 mesh) and letting it dry in air. Additional SEM imaging was performed on a Zeiss Supra 55VP SEM at 10kV. UV-Vis measurements were performed on a Cary 7000 universal measurement spectrophotometer calibrated to a single baseline. X-ray photoelectron spectroscopy (XPS) and near edge X-ray adsorption fine structure (NEXAFS) in partial electron yield (PEY) and total fluorescent yield (TFY) modes was performed on the Soft X-ray Spectroscopy beamline at the Australian Synchrotron. Samples were prepared on clean test grade silicon wafer (<1 ohm/cm) and loaded into the analysis chamber at ultrahigh vacuum (~10⁻¹⁰ mbar) for data acquisition. Survey spectra calibrated to a polycrystalline Au reference were collected at Al Kα (1486eV). A scanning confocal microscope system (optical path shown in Figure S5) equipped with a fiber-couple 976 nm single mode polarized diode laser focused through a 100x objective lens (NA 1.4) was used to measure the upconversion emission of single UCNPs at low power (20mW which was measured at the objective back aperture). The emitted light from a sample was collected by the same objective lens, which was refocused into an optical fiber having a core size of 50μm matching the first Airy disk of the system. A single photon counting avalanche diode (SPAD) detector was connected to the collection optical fiber to detect the emission intensity. The scanning was achieved by the
moving of a 3D piezo stage and lifetime was fitted to a double decay exponential function. For each sample more than 10 single UCNPs values were averaged to give mean intensity and lifetime.

**Simulation details.** Applied from previous work\(^2\) to investigate quantum efficiency enhancement due to internal defect reduction in NaYF\(_4\):Yb,Er upconversion nanocrystals a simplified energy level diagram was considered as shown in Figure S4 (A) which involves two energy levels associated with the sensitizer Yb\(^{3+}\) ions (\(^2\)F\(_{7/2}\) and \(^2\)F\(_{5/2}\), represented as S1 and S2, respectively). Assuming: (a) the excitation photons are absorbed by Yb\(^{3+}\) only and (b) energy transfer happens between Yb\(^{3+}\) on the excited level and Er\(^{3+}\) on both the ground and the intermediate levels, the following independent rate equations can be obtained.

\[
\frac{dn_1}{dt} = -c_1 n_1 n_{S2} + (A_2+W_2)n_2 + (1-b)A_3 n_3
\]

\[
\frac{dn_2}{dt} = c_1 n_1 n_{S2} - c_2 n_2 n_{S2} - (A_2+W_2)n_2 + (bA_3+W_3)n_3
\]

\[
\frac{dn_3}{dt} = c_2 n_2 n_{S2} - (bA_3+W_3)n_3
\]

\[
\frac{dn_{S2}}{dt} = P_{980} n_{S1} - A_3 n_{S2} - (c_1 n_1 + c_2 n_2)n_{S2}
\]

where \(P_{980}\) is the absorption rate of Yb\(^{3+}\), \(W_S\) is the intrinsic decay rate of excited Yb\(^{3+}\), \(c_i\) is the upconversion coefficient between excited Yb\(^{3+}\) and Er\(^{3+}\) on level i, \(A_i\) is the radiative decay rate of Er\(^{3+}\) on level i, \(W_i\) is the non-radiative decay rate of Er\(^{3+}\) on level i (this parameter will be affected by the internal defect density), \(b\) is the branching ratio for Er\(^{3+}\) decaying from level 3 to level 2 and n is the population of ions on an energy level satisfying

\[n_1 + n_2 + n_2 = 1\]
\[ n_{s1} + n_{s2} = 1 \]

A MATLAB program solves the system of equations from \( t = 0 \) to \( t = t_f \), where \( t_f \) depends on the longest lifetime in the system. The numerical solution of the total system of equations is the population of each energy level as a function of time. The quantum efficiency can then be achieved from the emission ratio and absorption ratio.

Table S1. Comparison of plasmonic metal decorated UCNPs

<table>
<thead>
<tr>
<th>Core UCNP</th>
<th>Spacer</th>
<th>Plasmonic Metal</th>
<th>UCL Enhancement Factor</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaYF(_4):Yb/Tm</td>
<td>PAA/PAH</td>
<td>Au</td>
<td>~2.5</td>
<td>3</td>
</tr>
<tr>
<td>NaYF(_4):Yb/Er/Gd</td>
<td>-</td>
<td>Au</td>
<td>~3.9</td>
<td>4</td>
</tr>
<tr>
<td>NaYF(_4):Yb/Er</td>
<td>SiO(_2)</td>
<td>Ag</td>
<td>~4</td>
<td>5</td>
</tr>
<tr>
<td>NaYF(_4):Yb/Er/Tm</td>
<td>Al(_2)O(_3)</td>
<td>Au</td>
<td>~5.2/3.5</td>
<td>6</td>
</tr>
<tr>
<td>NaYF(_4):Yb/Er</td>
<td>NaYF(_4)</td>
<td>Au</td>
<td>~5.5</td>
<td>This work</td>
</tr>
</tbody>
</table>
Figure S1. (A) TEM image of 35 nm diameter CS β-NaYF₄:20%Yb,2%Er@NaYF₄ UCNPs, (B) SEM image of 15 nm dewetted Au nanoparticles, (C) TEM image of 45 nm diameter CS β- NaYF₄:20%Yb,2%Er@NaYF₄ UCNPs and (D) SEM image of 55 nm diameter Au-CS β- NaYF₄:20%Yb,2%Er@NaYF₄@Au UCNPs.
Figure S2. NEXAFS spectra of CS UCNPs with 15 nm shell before (CS-UCNP) and after annealing (Au-CS UCNP) in (A) TFY and (B) PEY modes for Yb M edge. (C) XRD of CS UCNPs with 15 nm shell before and after annealing at 400 °C for 1 hour.
Figure S3. The scanning confocal images of the Core UCNPs (A), CS UCNPs with 5 nm, 10 nm and 15 nm inert shell (B-D) after annealing at 400 °C for 1 hour with no Au. Each scanned image is $3\mu$m $\times$ $3\mu$m and the colour bar indicates the emission intensity range of the single UCNPs.
Figure S4. (A) Simplified energy level diagram used for simulation and (B) Simulation of quantum efficiency attenuation vs internal defect density.
**Figure S5.** Experimental set-up of the confocal scanning microscope. SMF, single-mode fiber; L1, collimation lens; HWP, half-wave plate; PBS, polarized beam splitter; QWP, quarter-wave plate; M, mirror; DM, dichroic mirror; OL, objective lens; L2, collection lens; BPF, band pass filter; SPAD, single-photon avalanche diode; CCD, charge coupled device.

**References**