Supporting Information

3D Assembly of Upconverting $NaYF_4$ Nanocrystals by AFM Nanoxerography: Creation of Anti-Counterfeiting Microtags

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Synthesis of lanthanide doped, core and core-shell β-$NaYF_4$ nanocrystals

The synthesis of oleate stabilized upconverting core and core-shell β-$NaYF_4$ NCs was achieved by following literature procedures.[1,2] For a typical synthesis of core β-$NaYF_4$ nanocrystals, a suspension of lanthanide acetates (1 mmol) in appropriate ratios (see Table S1) and oleic acid (6.4 ml) in octadecene (17 ml) was heated to 140 °C under vacuum until a clear pale yellow solution was obtained. The resulting solution was cooled to room temperature (RT) and a 10 ml methanolic solution of NaOH (2.5 mmol) and ammonium fluoride (4 mmol) was added dropwise with stirring, to obtain a pale yellow slurry. After stirring this mixture for about 2h, the temperature of the mixture was raised to 70 °C and held there until the entire methanol evaporated. The mixture was then brought under a gentle flow of argon, and the temperature was raised to 300 °C and maintained there for 60 min. An orangish solution is obtained at this stage, which was cooled to RT and 20 ml of ethanol was added to precipitate the NCs as a white solid. This was collected by centrifugation and washed twice with 10–15 ml portions of ethanol, before redispersing in hexane to required concentrations. Transmission electron microscopy (TEM) analysis (Figure S1) of the NCs indicated 21 nm spherical particles (Table S1).

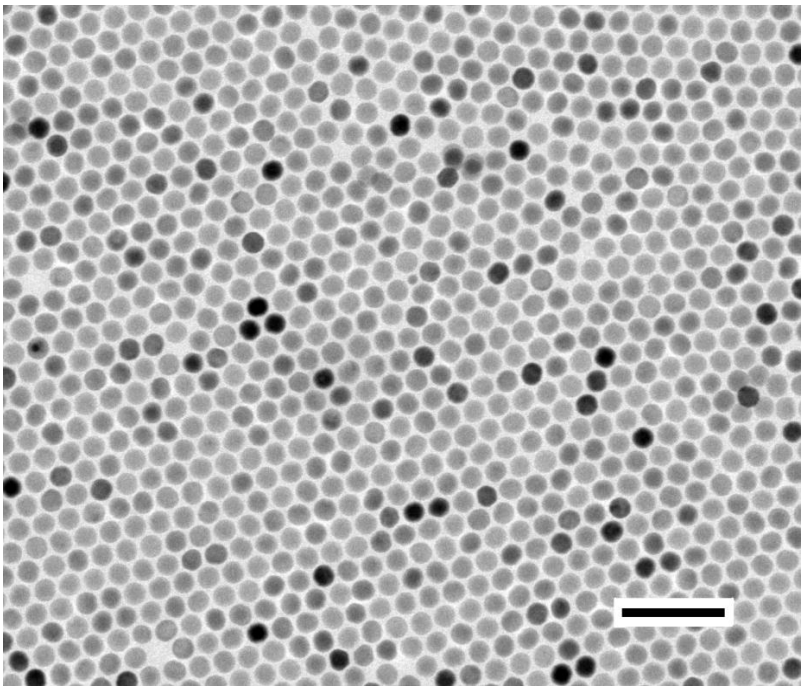

Figure S1. Transmission electron microscopy image of oleate stabilized $NaYF_4:Er^{3+},Yb^{3+}$ nanocrystals. Scale bar: 100 nm.

Table S1. The lanthanide precursor quantities (mmol) used in the synthesis of core $NaYF_4$ nanocrystals

Upconverting core nanocrystals	$Y(OAc)_3$	$Gd(OAc)_3$	$Yb(OAc)_3$	$Er(OAc)_3$	$Tm(OAc)_3$	NC size (nm)
$NaYF_4:Er^{3+},Yb^{3+}$	0.8	----	0.18	0.02	----	22
$NaYF_4:Gd^{3+},Er^{3+},Yb^{3+}$	0.5	0.3	0.18	0.02	----	16
$NaYF_4:Gd^{3+},Tm^{3+},Yb^{3+}$	0.555	0.24	0.20	----	0.005	16

Note: Gd^{3+} was doped in the core NCs to restrict their size[3] (16 nm, samples in the last two rows of the above table), so that the dimension of core-shell NCs matches with the core NC size (22 nm, sample in first row of the above table) used for the fundamental studies.

For the core-shell synthesis, yttrium acetate hydrate (1 mmol), oleic acid (6.4 ml) and octadecene (17 ml) were mixed together and heated to 140 °C under vacuum until a clear solution formed. The solution was then cooled to 80 °C, and cyclohexane dispersion of core NCs was injected and maintained at the same temperature until all the cyclohexane evaporated. Subsequently, the solution was cooled to 50 °C and a methanolic solution of NaOH (2.5 mmol) and ammonium fluoride (4 mmol) was added dropwise and stirred for 2 h. The temperature of the mixture was raised to 70 °C to remove methanol and a gentle flow of argon was applied before raising the temperature further to 300 °C. After maintaining at this temperature for 75 min, the solution was cooled to RT and the NCs recovered by following the same procedure as described for the core $NaYF_4$ NCs and redispersed in hexane to desired concentration. TEM analysis (Figure S2) of the obtained core-shell NCs indicated that they had rod shapes with the short axis being 18 nm for both and the long axis being 22 nm and 25 nm, respectively for $NaYF_4:Gd^{3+},Er^{3+},Yb^{3+}/NaYF_4$ and $NaYF_4:Gd^{3+},Tm^{3+},Yb^{3+}/NaYF_4$.

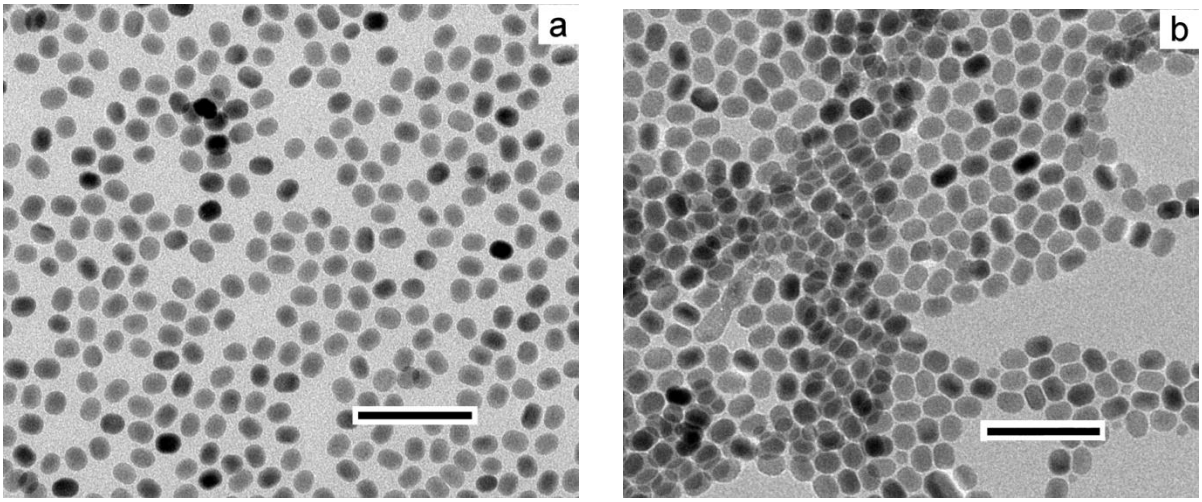

Figure S2. Transmission electron microscopy images of oleate stabilized core-shell nanocrystals: (a) $NaYF_4:Gd^{3+},Er^{3+},Yb^{3+}/NaYF_4$ and (b) $NaYF_4:Gd^{3+},Tm^{3+},Yb^{3+}/NaYF_4$. Scale bar: 100 nm.

Phase transfer of the hydrophobic oleate stabilized $NaYF_4$ nanocrystals to water

A procedure adapted from literature was utilized for achieving this. Typically, 0.2 ml of 0.1 M HCl was added to 3 mg of the solid core-shell NCs suspended in 3 ml water, and the mixture was sonicated at RT for 2–3 h. A turbid suspension was obtained, indicating the transfer of particles to the water. This solution was stirred overnight at RT and then diluted to 6–7 ml and extracted with 5 ml portions of diethyl ether to remove organic impurities. The extraction was repeated twice to obtain a clearer solution. This solution was finally centrifuged at 4500 rpm to remove the large aggregates and the clear supernatant of water dispersed $NaYF_4$ nanocrystals was collected.

Directed assembly of positively charged β-$NaYF_4$:Er^{3+},Yb^{3+} nanocrystals from water dispersions by AFM nanoxerography

A two-step protocol published earlier by our group,[4] was used to assemble positively charged β-$NaYF_4$:Er^{3+},Yb^{3+} nanocrystals from water dispersions on rectangular charge patterns of both polarities written on PMMA films.

A monolayer of β-$NaYF_4$:Er^{3+},Yb^{3+} nanocrystals is formed on the negative charge patterns irrespective of their surface potentials, thanks to the Coulomb force. No nanocrystal deposition occurs on the positive charge patterns, due to Coulomb repulsion. Figure S3 shows typical results obtained with charge patterns of maximum surface potentials written on a 100 nm PMMA film.

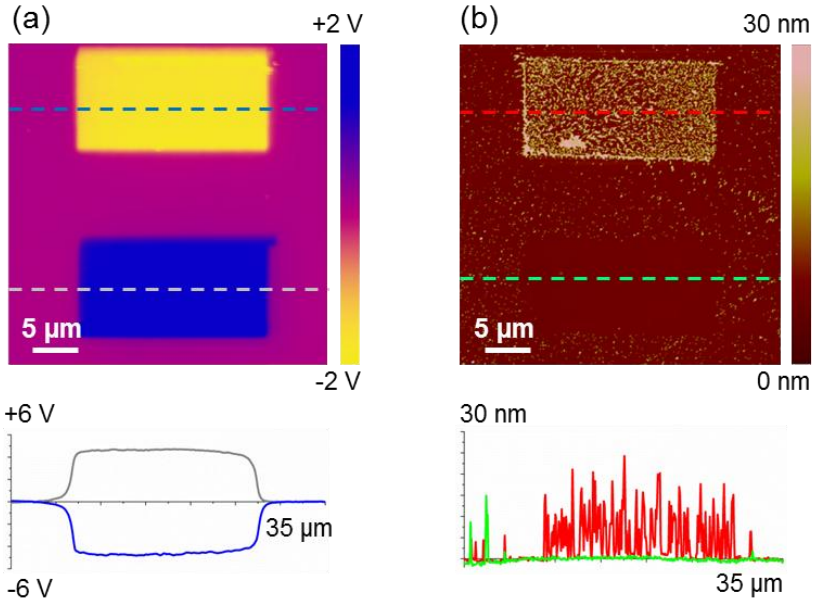

Figure S3. (a) KFM surface potential image of rectangular (20 µm × 10 µm) charge patterns with surface potentials of +4.7V and -4.7V; (b) AFM topographical image of the nanocrystal assembly obtained after developing these charge patterns using positively charged β-$NaYF_4$:Er^{3+},Yb^{3+} nanocrystals (~1.0×10^{13} NCs/mL) dispersed in water.

Comparison of the photoluminescence of β-$NaYF_4$:Er^{3+},Yb^{3+} nanocrystals: assemblies on charge patterns *versus* hexane suspension

The upconversion photoluminescence from the nanocrystal assemblies on 5 µm square charge patterns under 980 nm continuous wave (cw) laser diode excitation corresponds very well with that obtained from their hexane suspensions (Figure S4).

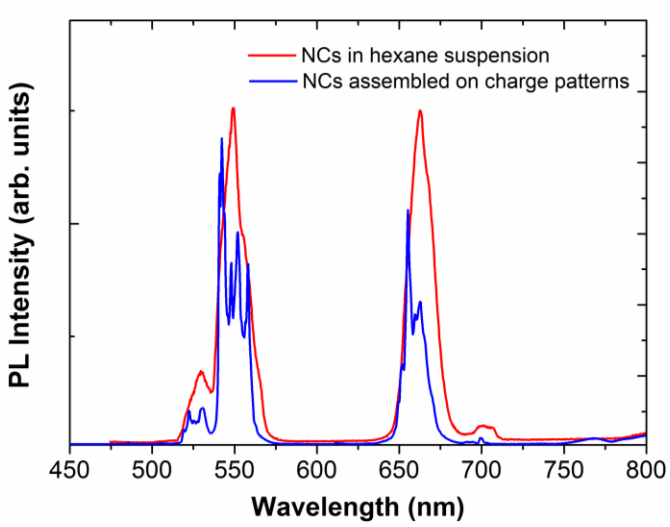

Figure S4. Photoluminescence (PL) spectra of β-NaYF4:Er^{3+},Yb^{3+} nanocrystals in hexane suspension (red curve) and β-$NaYF_4$:Er^{3+},Yb^{3+} nanocrystals assembled on 5 µm square charge patterns (blue curve) by AFM nanoxerography, upon excitation with 980 nm cw laser diode.

References

[1] Li, Z.; Zhang, Y. An Efficient and User-Friendly Method for the Synthesis of Hexagonal-Phase $NaYF_4$:Yb,Er/Tm Nanocrystals with Controllable Shape and Upconversion Fluorescence. *Nanotechnology* **2008**, *19*, 345606–345610.

[2] Qian, H.-S. ; Zhang, Y. Synthesis of Hexagonal-Phase Core−Shell $NaYF_4$ Nanocrystals with Tunable Upconversion Fluorescence. *Langmuir* **2008**, *24*, 12123–12125.

[3] Wang, F.; Deng, R.; Wang, J.; Wang, Q.; Han, Y.; Zhu, H.; Chen, X.; Liu, X. Tuning Upconversion Through Energy Migration in Core–Shell Nanoparticles. *Nat. Mater.* **2011**, *10*, 968–973.

[4] Palleau, E.; Sangeetha, N. M.;Viau, G.; Marty, J.-D.; Ressier, L. Coulomb Force Directed Single and Binary Assembly of Nanoparticles from Aqueous Dispersions by AFM Nanoxerography. *ACS Nano* **2011**, *5*, 4228–4235.