Supporting Information

Hard Proof of the NaYF₄/NaGdF₄ Nanocrystal Core/Shell Structure

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Experimental Section

Materials

All chemicals utilized were purchased from Aldrich, unless otherwise noted. The NaYF₄/NaGdF₄ core/shell nanocrystals (NCs) used in this study were synthesized using a modification of a recently reported procedure.¹

Synthesis of β -NaYF₄ Nanocrystals

In a typical synthesis, 0.6374 g (2.00 mmol) of Y(CH₃CO₂)₃ hydrate 99.9 % was added to a 100 mL three-neck round-bottom flask with 30 mL octadecene and 12 mL oleic acid. The solution was heated slowly to 140 °C under vacuum with magnetic stirring for 30 minutes to form Y(oleate)₃ and to remove residual water and oxygen. The temperature

was lowered to 50 °C and the reaction flask placed under a gentle flow of Argon. During this time a solution of 8 mmol (0.2964 g) ammonium fluoride and 5.0 mmol (0.2 g) sodium hydroxide dissolved in 20 mL of methanol was prepared. Once the reaction reached 50 °C the methanol solution was added and the resulting cloudy mixture was stirred for 30 minutes at 50 °C. The reaction temperature was increased and the methanol evaporated from the reaction mixture. After the evaporation of the methanol the reaction temperature was increased to 300 °C as quickly as possible and maintained at this temperature for 60 minutes under the argon gas flow. During this time the reaction would become progressively clearer until a completely clear yellowish solution was obtained. The mixture was allowed to cool to room temperature. The NCs were precipitated by the addition of ethanol and isolated *via* centrifugation at 4500 rpm corresponding to a relative centrifugal field (RCF) of approximately 1000. The resulting pellet was dispersed in a minimal amount of hexanes and precipitated with excess ethanol. The NCs were again isolated *via* centrifugation at 4500 rpm each time. The NCs were then dispersed in 10-15 mL of hexanes.

Synthesis of β -NaYF₄/ β -NaGdF₄ Core/Shell Nanocrystals

0.8083 g (2.00 mmol) of Gd(CH₃CO₂)₃ hydrate 99.9 % was added to a 100 mL three-neck round-bottom flask with 30 mL octadecene and 12 mL oleic acid. The solution was heated slowly to 140 °C under vacuum with magnetic stirring for 30 minutes to form Gd(oleate)₃ and to remove residual water and oxygen. The temperature was lowered to 80 °C and the reaction flask placed under a gentle flow of Argon. A solution of 2 mmol of NaYF₄ NCs in 10-15 mL of hexanes was added to the solution. The solution was maintained at 80 °C until all the hexanes were removed. The reaction mixture was cooled

to 50 °C and a solution of 8 mmol (0.2964 g) ammonium fluoride and 5.0 mmol (0.2 g) sodium hydroxide dissolved in 20 mL of methanol was added. The resulting cloudy mixture was stirred for 30 minutes at 50 °C. The reaction temperature was then increased and the methanol evaporated from the reaction mixture. After the evaporation of the methanol the reaction temperature was increased to 300 °C as quickly as possible and maintained at this temperature for 60 minutes under the argon gas flow. The mixture was allowed to cool to room temperature and the NCs isolated using the same procedure of precipitate and isolation mentioned above. The isolated NCs were then dispersed in ~20 mL of hexanes for subsequent measurements.

Phase Transfer Procedure

Phase transfer of the oleate-coated NaYF₄/NaGdF₄ core/shell NCs into water was performed using a PEG (2000)-phosphate ligand [PEG = poly(ethylene glycol)] recently employed by our group. Details of the procedure can be found in a recent publication.²

Characterization

Powder X-ray diffraction (XRD) data were acquired with a Rigaku Miniflex Diffractometer. Samples were drop-casted onto a zero-background holder and then allowed to dry. Cr radiation was used at 30 kV and 15 mA with a K β filter, a 4.2° scattering slit, and a 0.3 mm receiving slit. XRD data was collected in the 20-140° (2 θ) range.

Energy dispersive X-ray spectroscopy (EDS) was carried out with a Hitachi S-3500N Scanning Electron Microscope (SEM). Samples were directly dried onto conductive carbon tape on an aluminum SEM sample holder.

An FEI Tecnai 200 keV Field Emission **Scanning Transmission Electron Microscope** was used to collect transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images. Samples were deposited on thin, carbon-coated copper grids for imaging. Particle sizes were calculated by averaging over the long and short axis of each particle.

X-ray photoelectron spectroscopy (XPS) was carried out at the Canadian Light Source, Inc. in Saskatoon, Saskatchewan, using the spherical grating monochromator (SGM) undulator beamline, 11-ID.1, and a Scienta 100 hemispherical analyser equipped with a channel plate detection system. Particles were drop casted onto Au foil on a sample holder and allowed to dry, followed by immediate mounting into the vacuum sample chamber. No charging effects were observed at low particle concentration. The spectra were measured with a pass energy of 50 eV and an energy step size of 0.05 eV. The beamline exit setting was set to 200 μm .

All photoemission spectra were fitted and subtracted with polynomial background fits using Origin data analysis and graphing software (version 7.5). Three different fits were performed for each peak (Figure S5) and the peaks were integrated after subtraction of the background fit. The areas were averaged and the standard deviation calculated. Because it was clear some fits qualitatively under- or over-estimated the peak area, the standard deviation likely over-estimated the error associated with the area for some peaks. As such, after propagating the error to the final ratio ($\text{Y}^{3+}/\text{Gd}^{3+}$), the % error (standard deviation/ratio) of each point was calculated and then averaged as a whole (over all kinetic energies) to give an average error of ca. 8%. This value was then used as the % error for each point of the Y^{3+} 3d to Gd^{3+} 4d ratio at varying kinetic energies.

Both Y^{3+} 3d and Gd^{3+} 4d peaks were scanned at the same time and had similar kinetic energies (within ca. 15 eV), therefore the peak areas were not corrected for the sensitivity of the electron detector, the intensity of the photon beam or the number of scans, because all of these terms cancel in the ratio calculation (Y^{3+}/Gd^{3+} ratio shown in Figure 2b). The peak areas were however corrected for the photo-ionization cross-sections.

T₁ measurements at 1.5 and 3 T were performed on a clinical MRI scanner (GE Signa, GE Medical Systems, Milwaukee, WI) using a standard inversion recovery spin echo sequence with a repetition time (TR) of 2500 ms, an echo time (TE) of 9 ms and nine inversion recovery times, (TI = 50, 350, 650, 950, 1250, 1550, 1850, 2150 and 2450 ms); the field of view was 12 x 6 cm² and image plane was 128 x 128, slice thickness 5 mm; allowing simultaneous imaging of up to fifty vials containing 1.5 ml of different contrast agent concentrations. The regions of interest, were then drawn for each of the vials at TI = 2450 ms and the signal containing on average 20 voxels for all TI's was then evaluated. The signal to noise ratio was approximately 200.

Supplementary Figures

Figure S1. EDS spectra of core (top) and core/shell (bottom) NCs.

Table S1. EDS data (atomic %)

	<i>F</i>	<i>Na</i>	<i>Y</i>	<i>Gd</i>
Core	61.6	18.7	19.7	0
Core/Shell	71.7	11.2	8.2	8.9

Figure S2. XRD patterns for core/shell (top), core (middle), and standards β -NaYF₄ and β -NaGdF₄ (bottom).

Figure S3. Survey spectrum of NaYF₄/NaGdF₄ NCs. The C 1s peak was used as reference.

Figure S4. XPS spectra of Y^{3+} 3d and Gd^{3+} 4d core levels at different kinetic energies. The X-ray photon energies are only approximate.

Figure S5. Example of the background fitting employed. (a-c) The Y^{3+} 3d peak, measured with a photon energy of ~ 500 eV, is fitted with three different polynomials. (d) The background is then subtracted before the area is integrated (example using 2nd order polynomial). The area of the three (a-c) after subtraction is averaged, $1.15\text{E}6$, and the standard deviation was found to be $2.67\text{E}4$, giving a % error of 2.32% at this kinetic energy. The same is done for Gd^{3+} 4d peaks and then the ratio ($\text{Y}^{3+}/\text{Gd}^{3+}$) and propagated error are calculated at every kinetic energy.

References for Supporting Information

1. Qian, H.-S.; Zhang, Y. *Langmuir* **2008**, *24*, 12123.
2. Boyer, J.-C.; Manseau, M.-P.; Murray, J. I.; van Veggel, F. C. J. M. (*submitted*) **2009**.