Supporting Information

Size-Tunable, Ultra-Small NaGdF₄ Nanoparticles: Insights into their T₁ MRI Contrast Enhancement

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Supplementary Figures

Figure S1. Low resolution TEM images of (A) monodisperse NaYF₄ NPs, and (B) polydisperse NaGdF₄ NPs grown at the same conditions

Figure S2. Low resolution TEM images of as synthesized oleate-coated NaGdF₄ NPs (A) 2.5 nm, (B) 4.0 nm, (C) 6.5 nm, and (D) 8.0 nm, *Scale bar = 100 nm*

Figure S3. Low resolution TEM images of ligand exchanged hydrophilic PVP-coated NaGdF₄ NPs, (A) 2.5 nm, (B) 4.0 nm, (C) 6.5 nm, and (D) 8.0 nm, *Scale bar = 100 nm*

Figure S4. T_2 relaxivity plot of 2.5 nm PVP-coated NaGdF₄ NPs measured at 1.5 T

Figure S5. Powder X-Ray Diffraction spectra of A) NaGdF₄/Yb³⁺/Tm³⁺ core, and B) NaGdF₄/Yb³⁺/Tm³⁺/NaGdF₄ core/shell NPs matched with β -NaGdF₄ reference pattern

Relaxivity Calculations*

The concentration of Gd^{3+} ions determined by ICP-MS in the stock solution was used to calculate the molecular mass of NaGdF_4 in the specimen using the ratio

$$m(\text{Gd}) / m(\text{NaGdF}_4) = 0.6137$$

This was used to calculate the r_1/M (**Mass relaxivity**) values.

The NaGdF_4 NPs synthesized have Hexagonal closed pack (HCP)- crystal structure and the density of HCP NaGdF_4 5.65 g/cc was used to determine the mass of a NP, considering that the NPs are perfect spheres and their volume determined using

$$V = 4/3 \pi R^3 \text{ (where R is the radius of the NP)}$$

Comparing the mass of the single NP and the total mass determined from ICP-MS the total number of NPs (N) in the stock solution was determined and used to calculate the r_1/NP (**Nanoparticle or per probe relaxivity**) values

The surface area (SA) of the NP was then calculated using

$$\text{SA} = 4\pi R^2 \text{ (where R is the radius of the NP)}$$

Using that the total surface area of the NP in the stock solution was calculated

$$\text{Total surface area (TSA)} = N * \text{SA}$$

TSA value was used to determine the r_1/SA (**relaxivity per m^2 of nanoparticle surface**) values.

* Average ionic relaxivity values were used to calculate the r_1/M , r_1/NP , r_1/SA .

Tumbling time of the NPs (τ_R)

$$\tau_R = 4\pi\eta a^3/3k_B T$$

Where, η dynamic viscosity = 10^{-3} pa.s, $k_B T = 4 \times 10^{-21}$ J, a = hydrodynamic radius of the NP, $T = 298$ K.