Supporting Information

Core/Shell $NaGdF_4$:Nd^{3+}/$NaGdF_4$ Nanocrystals with Efficient Near-Infrared to Near-Infrared Downconversion Photoluminescence for Bioimaging Applications

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I. Determination of Quantum Yield of Photoluminescence

The quantum yield (QY) of photoluminescence is defined as the ratio of the number of the emitted photons to the number of the absorbed photons. It is an important parameter to characterize photoluminescence, providing information on radiative and nonradiative processes in luminophores (molecules, ions, nanoparticles, *etc*.). QY can be measured either by absolute method or on a relative basis, using standard with known QY as a reference. Here, we determined the QY of our nanocrystals by referencing to the standard: indocynine green dye in DMSO with a known quantum yield of 12%.[56] The quantum yield of the nanoparticles, QY_X, was calculated according to the following equation:[S1]

$$QY_X = QY_R \cdot \frac{E_X}{E_R} \cdot \frac{A_R}{A_X} \cdot \frac{I_R}{I_X} \cdot \frac{N_X^2}{N_R^2} \qquad \text{(S1)}$$

where QY_R and QY_X are the quantum yields of the referenced standard sample and the sample to be determined, respectively; E_R and E_X are the numbers of the emitted photons for referenced standard sample and measured sample, respectively; A_R and A_X are the numbers of the photons absorbed by referenced standard sample and measured sample, respectively; I_R and I_X indicate the relative intensity of the exciting light for referenced standard sample and measured sample, respectively; N_R and N_X are the average refractive index of the solvent used for dissolving referenced standard sample and measured sample, respectively. Subscripts R and X refer to the referenced standard sample and the sample to be measured, respectively.

Determination of Quantum Yield of Photoluminescence in Nanocrystals $NaGdF_4$:Nd^{3+} and Core/Shell Nanocrystals $NaGdF_4$:Nd^{3+}/$NaGdF_4$ Dissolved in Hexane: Exactly the same geometry was used to excite the referenced standard sample (indocynine green DMSO solution) and the measured sample (suspensions of nanocrystals $NaGdF_4$:Nd^{3+} and core/shell nanocrystals $NaGdF_4$:Nd^{3+}/$NaGdF_4$), and to detect their corresponding PL spectra. A calibrated SPEX 270M spectrometer (Jobin Yvon) equipped with an InGaAs TE-cooled photodiode (Electro-Optical Systems, Inc.) was utilized for recording NIR PL. During the QY measurement, the same laser line at 740 nm with a spectrum profile displayed in Figure 3A is employed to perform the excitation; the absorbance of the referenced standard sample and the measured samples has been matched at 740 nm by adjusting the concentration of these two samples. An "optically thin" absorbance of 0.06 at 740 nm is employed for all measurements in order to avoid the effect of reabsorption. The parameter of $A_R I_R / A_X I_X$ in Equation (S1) is a constant, which is evaluated to be about 1.32 for all the measured samples. It should be emphasized that it is very important to take the excitation laser profile into consideration in order to get the correct parameter of $A_R I_R / A_X I_X$, as absorptions of nanocrystals $NaGdF_4:Nd^{3+}$ or core/shell nanocrystals $NaGdF_4:Nd^{3+}/NaGdF_4$ have sharp peaks around 740 nm, in marked contrast to the smooth absorption peak of referenced standard sample of indocynine green. DMSO with a refractive index of 1.48 and hexane with a refractive index of 1.38 were used to dissolve the standard reference of indocynine green and to dissolve nanocrystals $NaGdF_4:Nd^{3+}$ and core/shell nanocrystals $NaGdF_4:Nd^{3+}/NaGdF_4$, respectively. The parameter of N_X^2 / N_R^2 in Equation (S1) was determined to be 0.87, leading the parameter $A_R I_R N_X^2 / A_X I_X N_R^2$ to be a constant parameter, B, of 1.15. The equation (S1) can thus be simplified to,

$$QY_X = QY_R \cdot \frac{E_X}{E_R} \cdot B \qquad \text{(S2)}$$

As illustrated in Figure 3B, the integrated NIR PL intensity in the wavelength range of 800-1400 nm in nanocrystals of $NaGdF_4$ doped with Nd^{3+} of 3, 6, 10, and 15% was estimated to be about 1.61, 0.68, 0.36, and 0.26 times higher than the PL intensity of standard indocynine green, while the integrated NIR PL intensity in ($NaGdF_4$:3% Nd^{3+})/$NaGdF_4$ core/shell nanocrystals was about 2.9 times higher than the PL intensity of standard indocynine green. According to Equation (S2), these intensity ratios correspond to a quantum yield of 22, 9.4, 5.0, and 3.6% for nanocrystals of $NaGdF_4$ doped with Nd^{3+} of 3, 6, 10, and 15%, and a quantum yield of about 40% for ($NaGdF_4$:3% Nd^{3+})/$NaGdF_4$ core/shell nanocrystals, respectively.

The measurement of QYs was repeated using four different concentrations of our sample dissolved in hexane and referenced standard sample of indocynine green. Almost the same values were obtained for nanocrystals of $NaGdF_4$ doped with Nd^{3+} of 3, 6, 10, and 15% and for ($NaGdF_4$:3% Nd^{3+})/$NaGdF_4$ core/shell nanocrystals.

Determination of Quantum Yield of Photoluminescence in Core/Shell Nanocrystals $NaGdF_4$:Nd^{3+}/$NaGdF_4$ Dispersed in Water: The QY of NIR PL in water-dispersed core/shell nanocrystals $NaGdF_4$:Nd^{3+}/$NaGdF_4$ was determined using hexane-dispersed core/shell nanocrystals $NaGdF_4$:Nd^{3+}/$NaGdF_4$ as a standard reference with a quantum yield of 40%. The QY value for nanocrystals of $NaGdF_4$:Nd^{3+}/$NaGdF_4$ dispersed in water was estimated to be about 20%; its determination procedure was similar to the measurement of the quantum yield of nanocrystals $NaGdF_4$:Nd^{3+} dispersed in hexane.

II. Supporting Figures

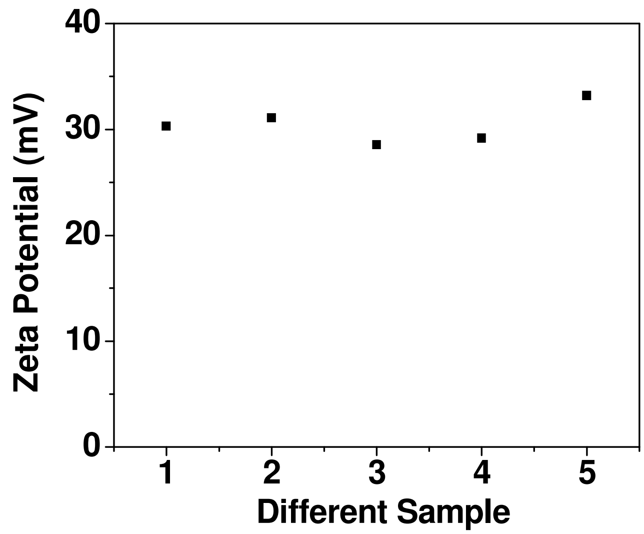

Figure S1. Zeta potential measurements of five different samples of suspensions of ligand-free ($NaGdF_4$:3% Nd^{3+})/$NaGdF_4$ core/shell nanocrystals dissolved in water.

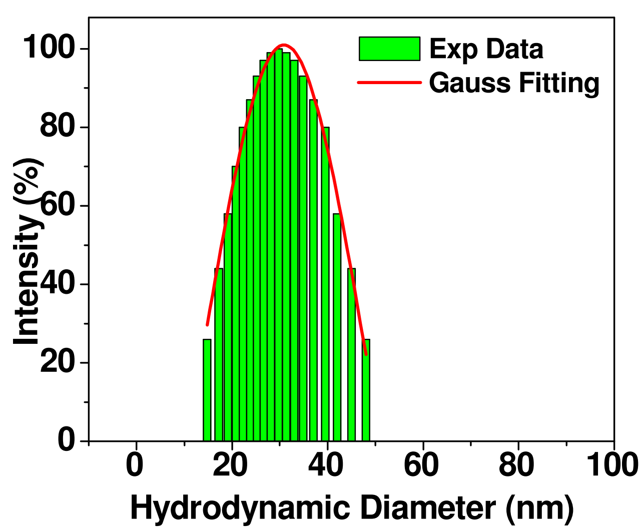

Figure S2. Hydrodynamic diameter of ligand-free ($NaGdF_4$:3% Nd^{3+})/$NaGdF_4$ core/shell nanocrystals.

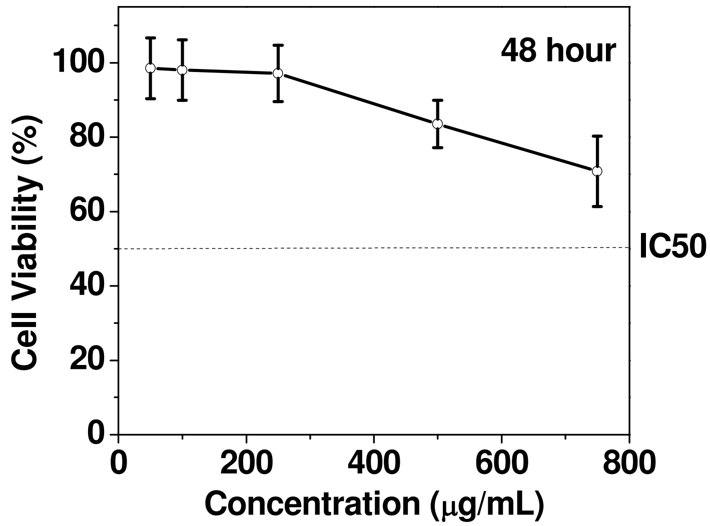

Figure S3. Cell viability assay with Hela cell treated with different concentration of ligand-free core/shell $NaGdF_4$:Nd^{3+}/$NaGdF_4$ nanoparticles. After incubating these nanoparticles with HeLa cells for 48 hours, the cell viability was then assessed utilizing MTS method via Cell Titer-Glo™ luminescent cell viability S-3 assay (Promega Corporation, Madison, WI). The viability of the untreated cells was assumed to be 100% as a control. As shown in the figure, no overt toxicity was observed for the concentration of nanoparticles as high as 300 μg/mL; however, the cell viability decreases gradually for higher concentration.

Supporting References

S1. Rhys Williams, A. T.; Winfield, S. A.; Miller, J. N. *Analyst*, **1983**, *108*, 1067-1071.