Supporting Information

Thermo-Enhanced Upconversion Luminescence in Inert-Core/Active-Shell UCNPs: Inert-Core Matters

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Fig. S1 The size distributions of (a) NaGdF$_4$ inert-core and (b) NaGdF$_4$@NaGdF$_4$: Yb/Tm inert-core/active-shell UCNPs.

Fig. S2 (a$_1$-c$_1$) TEM micrographs of the NaGdF$_4$ inert-core with different sizes about 17 nm, 27
nm, 43 nm, respectively. (a$_2$-c$_2$) The corresponding TEM micrographs after coating active-shell (about 1.5 nm thickness). (a$_3$-c$_3$) The integrated UCL intensities of NaGdF$_4$@NaGdF$_4$: Yb/Tm (20/1 mol%) UCNPs with different inert-core size.

**Fig. S3** Temperature-dependent integrated UCL intensities for NaGdF$_4$: Yb/Tm (20/1 mol%, ~12 nm) and NaGdF$_4$@NaGdF$_4$: Yb/Tm (20/1 mol%, ~9@3 nm) UCNPs.
Fig. S4 Temperature-dependent integrated UCL intensities including 475 nm and 802 nm for NaGdF₄@NaGdF₄: Yb/Tm (20/1 mol%) UCNPs with different sizes of (a) ~9@3 nm, (b) ~17@3 nm, (c) ~27@3 nm (d) ~43@3 nm.
Fig. S5 Temperature-dependent UCL emission spectra ($\lambda_{\text{ex}} = 980$ nm) of NaGdF$_4$@NaGdF$_4$: Yb/Er (20/2 mol%) inert-core/active shell UCNPs with different sizes of (a) ~9@3 nm, (b) ~17@3 nm, (c) ~27@3 nm (d) ~43@3 nm. (e) Temperature-dependent integrated UCL intensities for NaGdF$_4$@NaGdF$_4$: Yb/Er (20/2 mol%) UCNPs with different inert-core sizes.
Fig. S6 Temperature-dependent decay lifetimes for $^1G_4$ excited state of Tm$^{3+}$ in NaGdF$_4$@NaGdF$_4$: Yb/Tm (20/1 mol%) UCNPs with different sizes of (a) ~9@3 nm, (b) ~17@3 nm and (c) ~43@3 nm.

Fig. S7 Temperature-dependence DCL emission spectra of NaGdF$_4$@NaGdF$_4$: Yb/Tm (20/1 mol%) UCNPs with different sizes of (a) ~9@3 nm, (b) ~17@3 nm and (c) ~43@3 nm.
**Fig. S8** The lifetime ratio for $^2F_{5/2}$ excited state of Yb$^{3+}$ in NaGdF$_4$@NaGdF$_4$: Yb/Tm (20/1 mol%) UCNPs of different sizes.

**Fig. S9** Simulation distribution diagram of rare earth ion in the inert-core/active-shell structure with a certain thickness of shell.
Fig. S10 Plots of the temperature-dependence of the interplanar spacing expansion factor $I_T$ for the (110) and (201) planes of the samples.