



Supporting Information

for

Effect of different silica coatings on the toxicity of upconversion nanoparticles on RAW 264.7 macrophage cells

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Experimental details, additional UC luminescence spectra, XRD data, STEM images, ICP-OES, and cell cycle data

X-ray diffraction (XRD)

For XRD measurements, a minimum amount of 10 mg dried samples were used. The XRD device was a STOE Stadi P from STOE. A Cu K α_1 radiation source with a radiation wavelength of 0.15405 nm was used. The measurement angle was between 10-90° and with a measurement time of 120 s/0.2°.

Measurements of the upconversion luminescence

The upconversion luminescence (UCL) was measured at 25°C with a *FluoroMax-4* spectrometer from *Horiba Jobin Yvon* equipped with a 2 W 980 nm laser diode from *Insaneware-Robert Nowak*. The concentration of the samples was 1-2 g/L in cyclohexane for oleate-capped UCNPs or ethanol for silica-coated UCNPs, and quartz glass cuvettes (*QS Suprasil*, 5 mm, *Hellma* or *VWR*) were used.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

The elemental composition of the UCNP cores was determined by ICP-OES. For this purpose, 1 mL ($c = 5$ g/L) of their dispersion in cyclohexane was dried. The dried UCNPs were subsequently dissolved in 1 mL of aqua regia for 30 minutes and diluted with 5 mL of ultrapure water. The measurements were performed with an iCAP 6000 Series ICP Spectrometer from Thermo Scientific with a radial optical approach. For calibration, series of solutions with different concentrations were prepared separately from an erbium standard for ICP ($c(\text{Er}^{3+}) = 1, 5, 10$ ppm), ytterbium standard for ICP ($c(\text{Yb}^{3+}) = 10, 20, 40$ ppm), and an yttrium standard for ICP ($c(\text{Y}^{3+}) = 10, 20$ and 40 ppm).

X-ray diffraction measurements

The XRD diffractogram (Figure S1) shows a predominantly hexagonal crystal structure for example at 18°, 29°, 44° and 54° (ICDD no. 28-1192), with two minor peaks from the α -phase at 47° for [220] reflex and 55° for [311] reflex (ICDD no. 06-0334; see Figure S1).

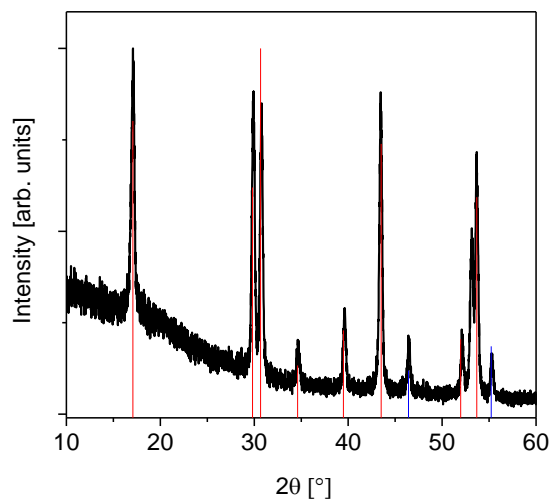


Figure S1: XRD diffractogram of the NaYF₄: Yb, Er cores (red lines: hexagonal phase peaks (ICDD no. 28-1192); blue lines: cubic phase peaks (ICDD no. 06-0334)).

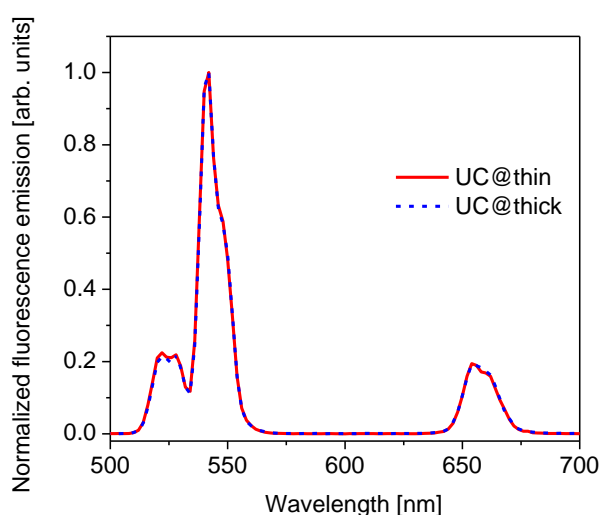


Figure S2: Upconversion luminescence spectra of UC@thin_NH₂ ($r_{\text{SiO}_2} = 8 \pm 2$ nm) and UC@thick_NH₂ ($r_{\text{SiO}_2} = 21 \pm 2$ nm) in ethanol. The cores of both particles are NaYF₄: 18% Yb, 2% Er nanoparticles. The spectra are normalized at 655 nm for better comparison. The excitation power density was 2 W/cm² at 980 nm.

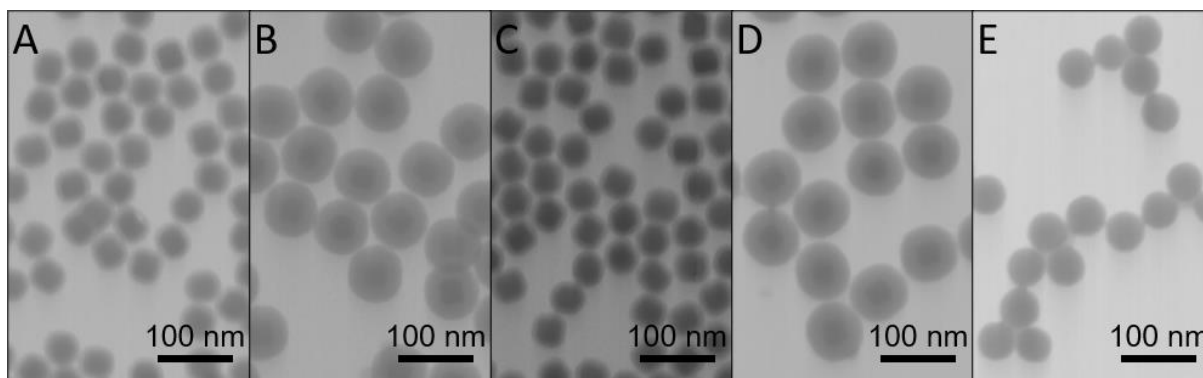


Figure S3: STEM images of A: UC@thin_NH₂ ($r_{\text{SiO}_2} = 8 \pm 2$ nm); B: UC@thick_NH₂ ($r_{\text{SiO}_2} = 21 \pm 2$ nm); C: UC@thin_RBITC_NH₂ ($r_{\text{SiO}_2} = 9 \pm 2$ nm); D: UC@thick_RBITC_NH₂ ($r_{\text{SiO}_2} = 22 \pm 2$ nm) and E: functionalized SiO₂-nanoparticles SiO₂@RBITC_NH₂ (average STEM-diameter = 52 ± 3 nm). The cores of all particles are NaYF₄: 18% Yb, 2% Er nanoparticles

Table S1: Filtered lanthanide ions value from the corresponding chlorides obtained from ICP-OES measurement.

Initial ions concentration	Y		Yb		Er	
[ppm]	Concentration [mmol/L]	Ions filtered [%]	Concentration [mmol/L]	Ions filtered [%]	Concentration [mmol/L]	Ions filtered [%]
1	$[4.30 \pm 0.05] \cdot 10^{-3}$	38 ± 3	$[1.00 \pm 0.01] \cdot 10^{-3}$	17 ± 2	$[3.32 \pm 0.05] \cdot 10^{-4}$	6.0 ± 0.6
2	$[1.00 \pm 0.01] \cdot 10^{-2}$	45 ± 4	$[2.40 \pm 0.01] \cdot 10^{-3}$	21 ± 2	$[7.48 \pm 0.05] \cdot 10^{-4}$	6.4 ± 0.6

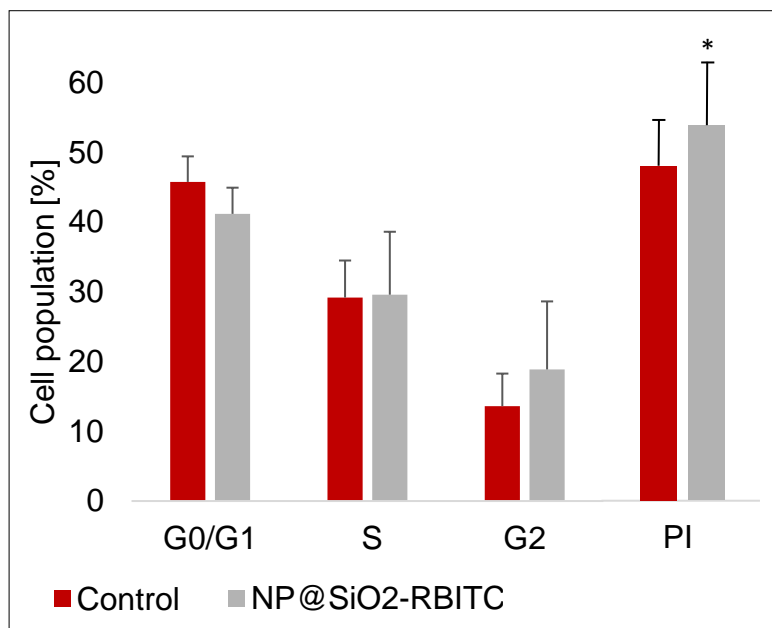


Figure S4: Effect of silica particles without a UCNP core (NP@SiO₂-RBITC-NH₂) on the cell cycle dynamics of RAW 264.7 macrophages after 24 h of exposure. The concentration was 200 µg/mL.