Supporting Information for

Effect of Different Silica Coatings on the Toxicity of upconversion nanoparticles on RAW 264.7 macrophage cells

Cynthia Kembuan,[1] Helena Oliveira,[2] and Christina Graf*[3]

Address: [1]Institut für Chemie und Biochemie, Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustraße 3, D-14195 Berlin, Germany, [2]University of Aveiro, Department of Biology & CESAM, Pt-3810-193 Aveiro, Portugal, and [3]Hochschule Darmstadt - University of Applied Sciences, Fachbereich Chemie- und Biotechnologie, Stephanstr. 7, D-64295 Darmstadt, Germany

Email: Christina Graf - christina.graf@h-da.de

* Corresponding author

Supporting Information:

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 $K_{\alpha 1}$ 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 UCNP or ethanol for silica-coated UCNP, 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 UCNP 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 ($c(Er^{3+})$ = 1, 5, 10 ppm).), ytterbium standard for ICP ($c(Yb^{3+})$ = 10, 20, 40 ppm), and an yttrium standard for ICP ($c(Y^{3+})$ = 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).

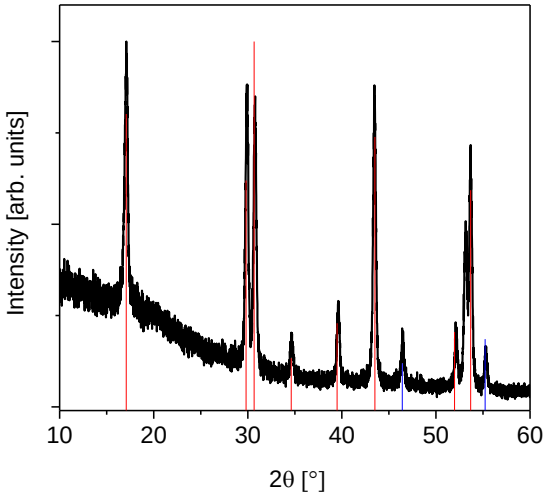

Figure S1: XRD diffractogram of the $NaYF_4$: Yb, Er cores (red lines: hexagonal phase peaks (ICDD no. 28-1192); blue lines: cubic phase peaks (ICDD no. 06-0334).

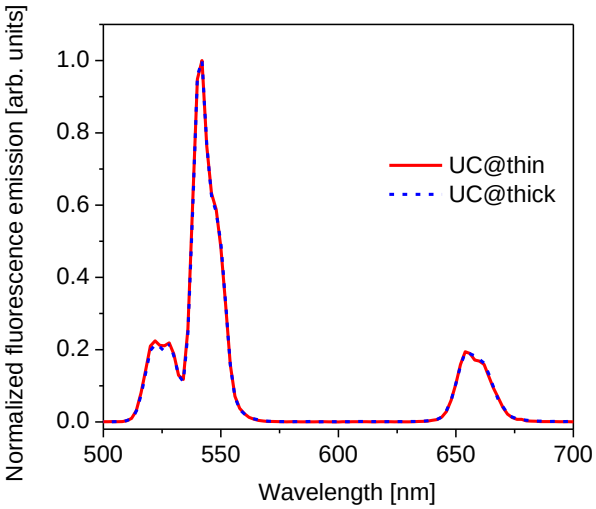

Figure S2: Upconversion luminescence spectra of UC@thin_NH_2 (r_{SiO2} = 8±2 nm) and UC@thick_NH_2 (r_{SiO2} = 21±2 nm) in ethanol. The cores of both particles are $NaYF_4$: 18 % Yb, 2 % Er nanoparticles. The spectra are normalized at 655 nm for better comparison. The excitation power density was 2 W/cm^2 at 980 nm.

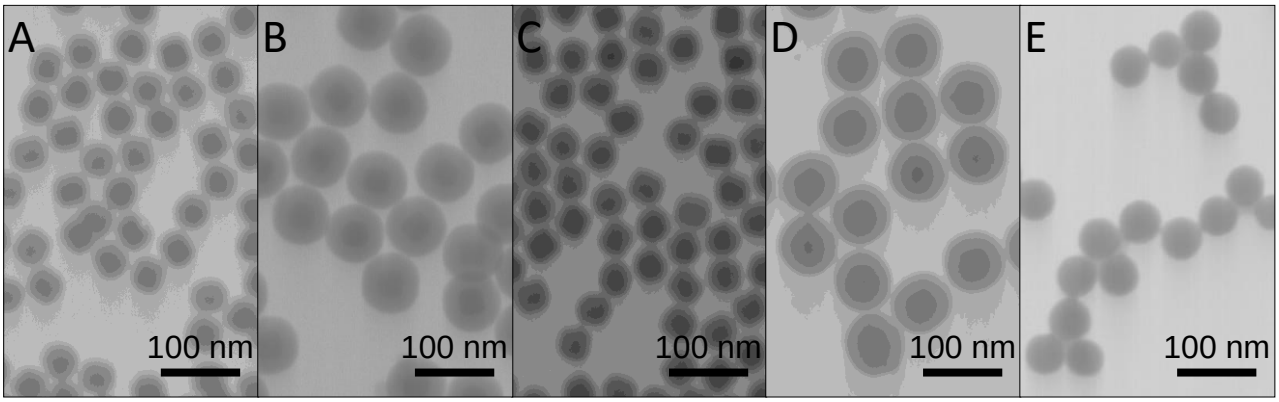

Figure S3: STEM images of A: UC@thin_NH_2 (r_{SiO2} = 8±2 nm); B: UC@thick_NH_2 (r_{SiO2} = 21±2 nm; C: UC@thin_RBITC_NH_2 (r_{SiO2} = 9±2 nm); D: UC@thick_RBITC_NH_2 (r_{SiO2} = 22±2 nm) and E: functionalized SiO_2-nanoparticles SiO_2@RBITC_NH_2 (average STEM-diameter = 52±3 nm). The cores of all particles are $NaYF_4$: 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	
Concentration [ppm]	Concentration [mmol/L]	Ions filtered [%]	Concentration [mmol/L]	Ions filtered [%]	Concentration [mmol/L]	Ions filtered [%]
1	$[4.30\pm0.05]\cdot10^{-3}$	38±3	$[1.00\pm0.01]\cdot10^{-3}$	17±2	$[3.32\pm0.05]\cdot10^{-4}$	6.0±0.6
2	$[1.00\pm0.01]\cdot10^{-2}$	45±4	$[2.40\pm0.01]\cdot10^{-3}$	21±2	$[7.48\pm0.05]\cdot10^{-4}$	6.4±0.6

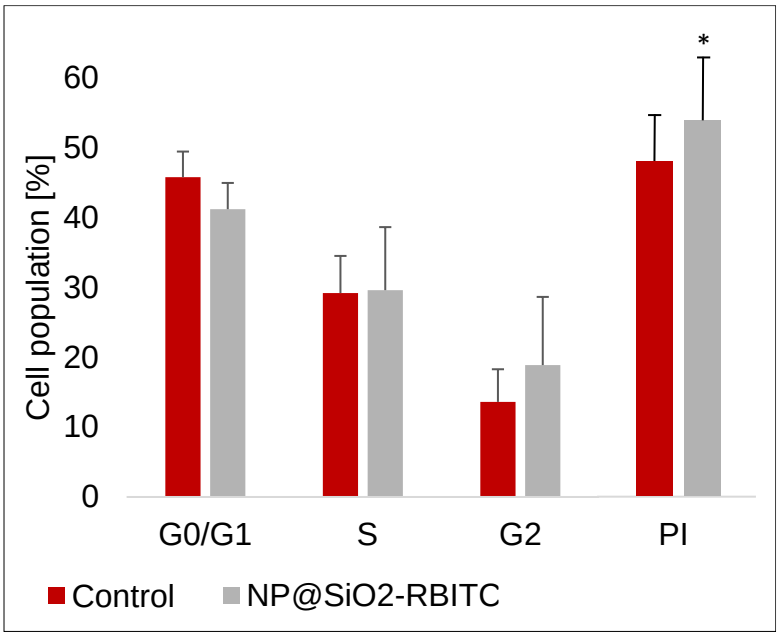

Figure S4: Effect of silica particles without a UCNP core (NP@SiO_2-RBITC-NH_2) on the cell cycle dynamics of RAW 264.7 macrophages after 24 h of exposure. The concentration was 200 µg/mL.