

Electronic Supplementary Information (ESI) for:
**Synthesis of Stable Carboxy-terminated NaYF₄: Yb³⁺, Er³⁺@
SiO₂ Nanoparticles with Ultrathin Shell for Biolabeling
Applications**

Fuyao Liu,^{a,c} Qi Zhao,^{b,c} Hongpeng You^{*b} and Zhenxin Wang^{*a}

^aState Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China. E-mail: wangzx@ciac.jl.cn (ZW); Fax: (+86) 431-85262243.

^bState Key laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China, 130022, P. R. China. E-mail: hpyou@ciac.jl.cn (HY).

^cGraduate School of the Chinese Academy of Sciences, Beijing, 100039, P. R. China.

Contents: Additional Figure S1-S14

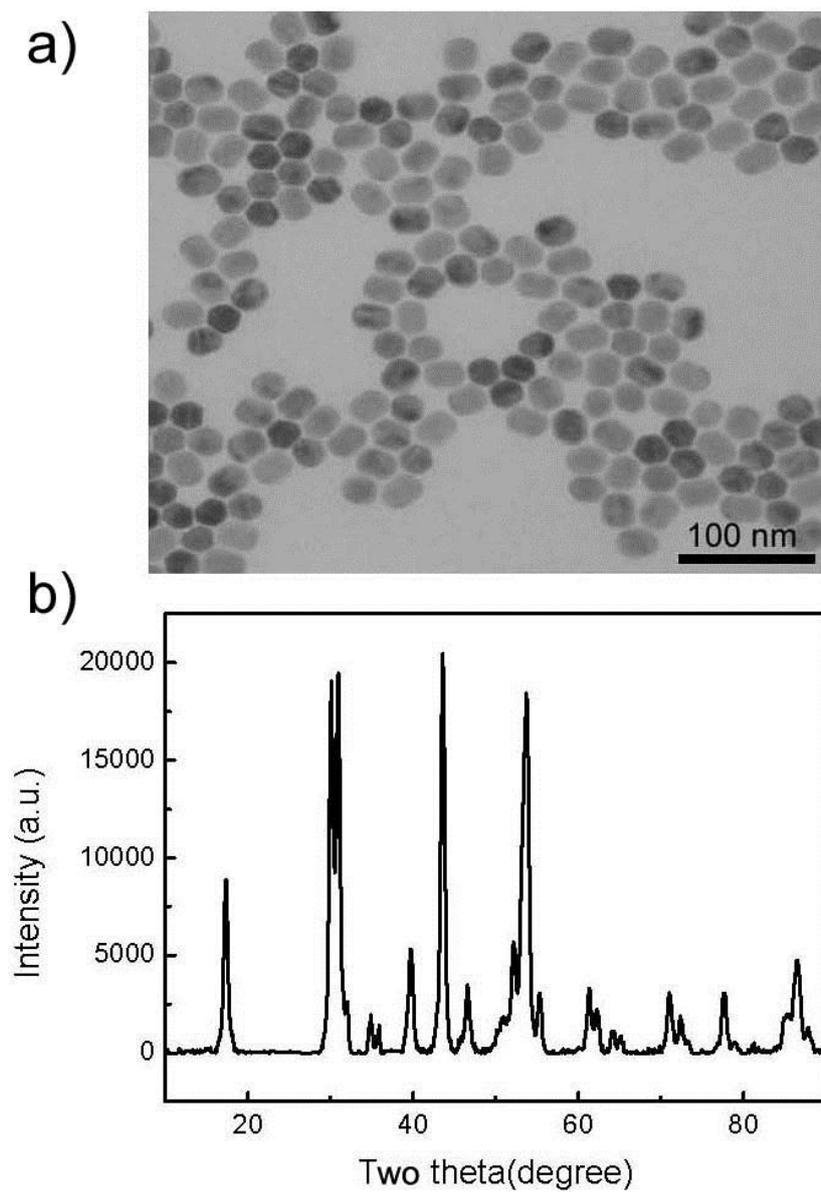


Fig. S1 TEM micrograph of UCNPs (a), and powder XRD pattern of UCNPs (b).

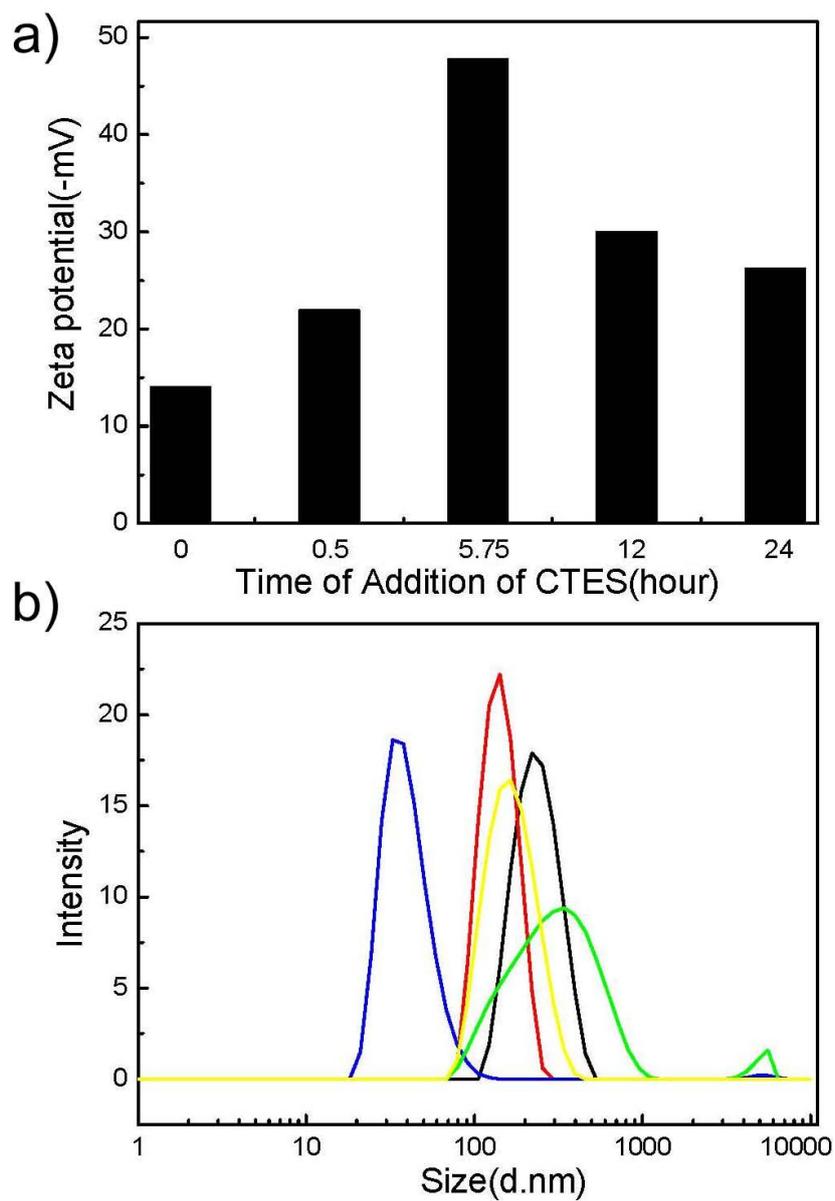


Fig. S2 Zeta-potential as a function of the time of addition of CTES (a), and DLS size distribution as a function of the time of addition of CTES (blue line 5.75 h, red line 12 h, yellow line 24 h, black line 0.5 h, green line 0 h.) (b), respectively.

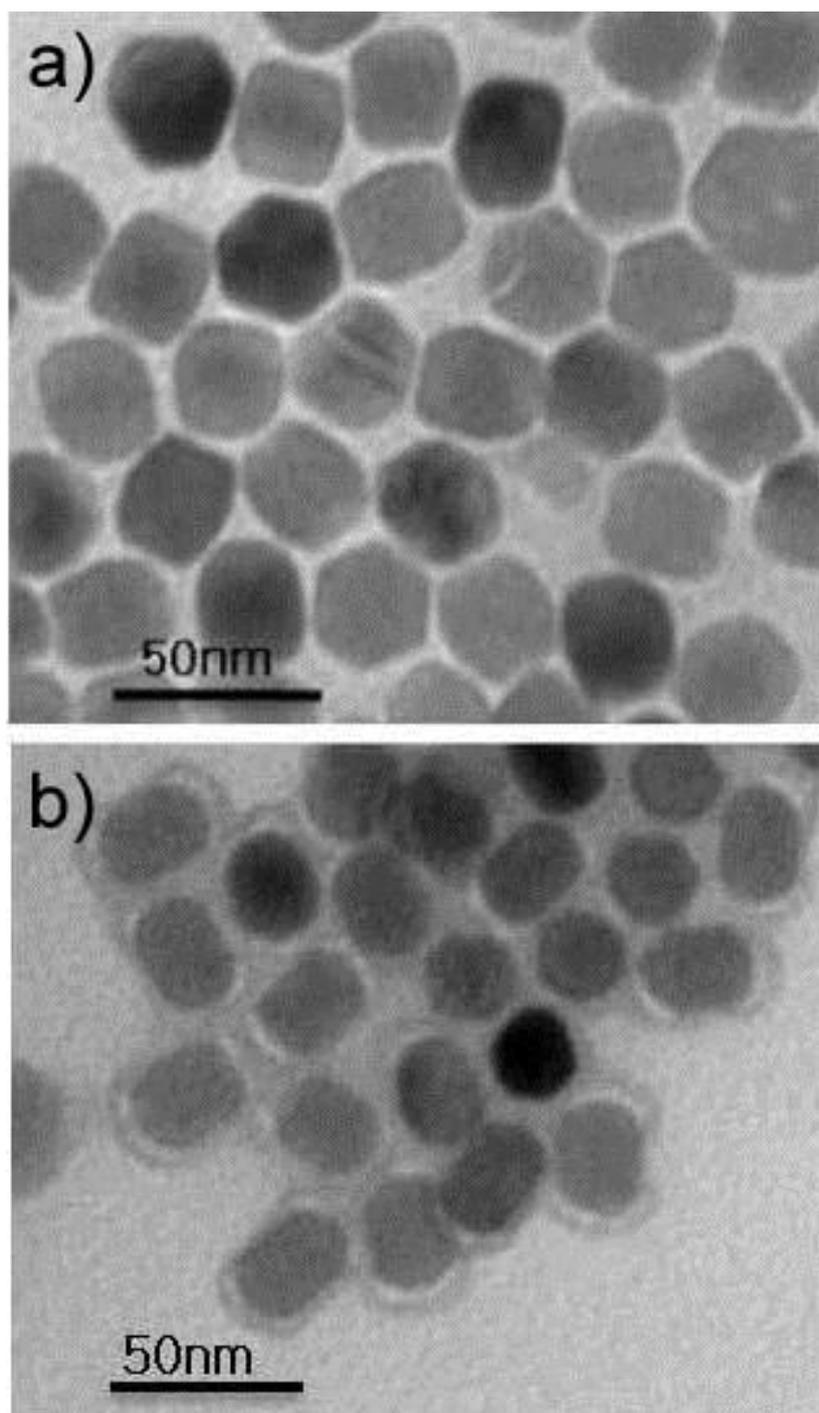


Fig. S3 TEM micrographs of UCNP@SiO₂ with varied shell thickness obtained by changing the amount of Igepal CO-520 (a, 0.15+0.5 mL; and b, 0.1+0.4 mL), respectively. The reaction mixture also contains 20 μL TEOS, 0.08 mL ammonium hydroxide (28 wt% in water), 10 mL cyclohexane, and 20 μL CTES.

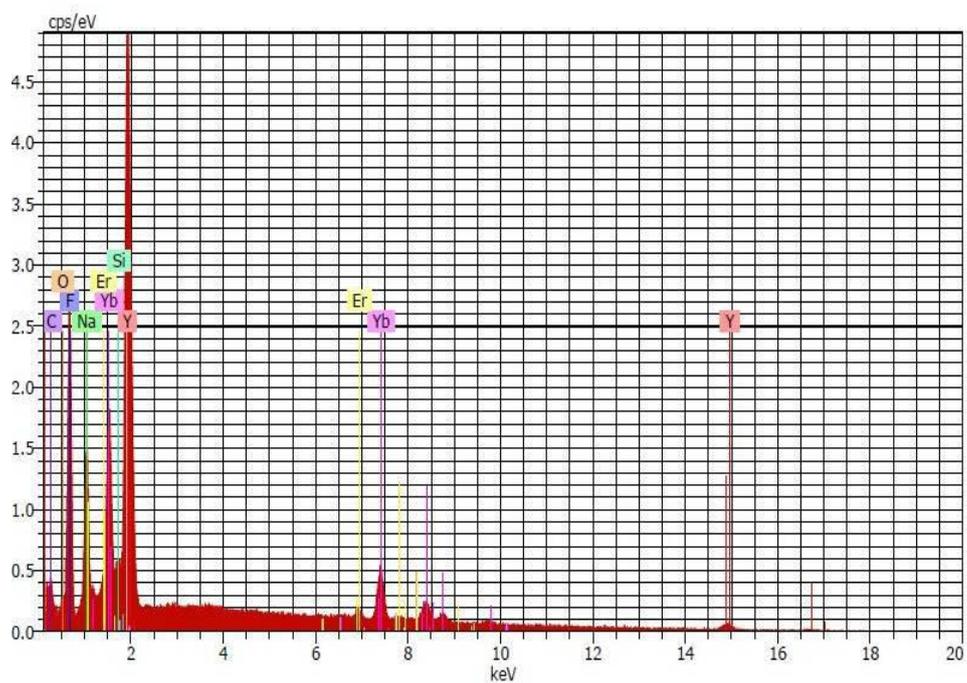


Fig. S4 The energy-dispersive X-ray spectroscopy (EDS) analysis of UCNP@SiO₂-1.5.

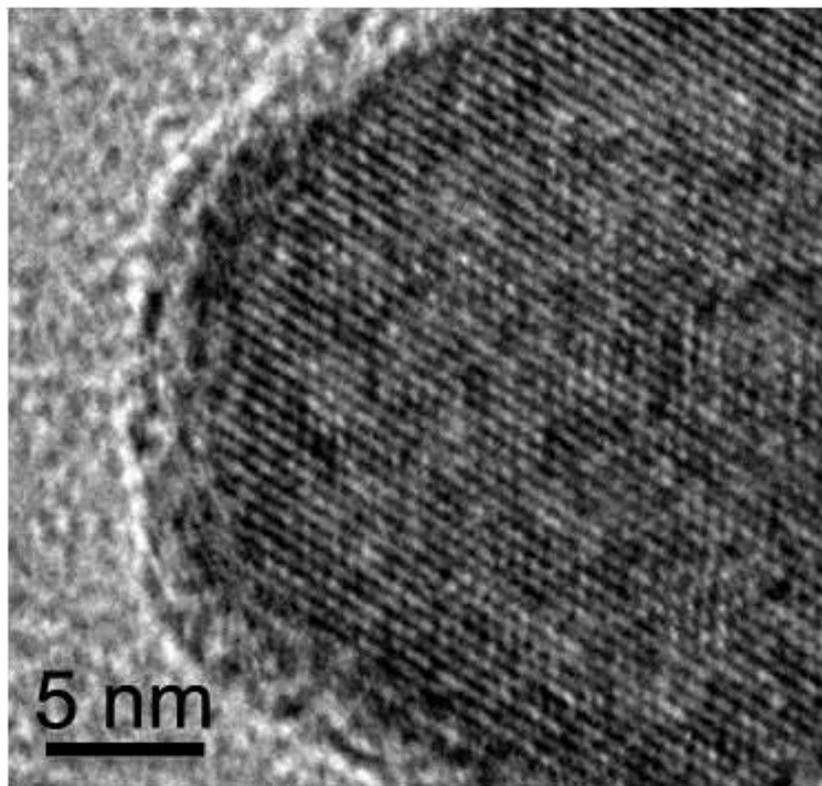


Fig. S5 HRTEM micrograph of UCNPs@SiO₂-1.5.

The ultrathin shell is clearly observed by HRTEM.

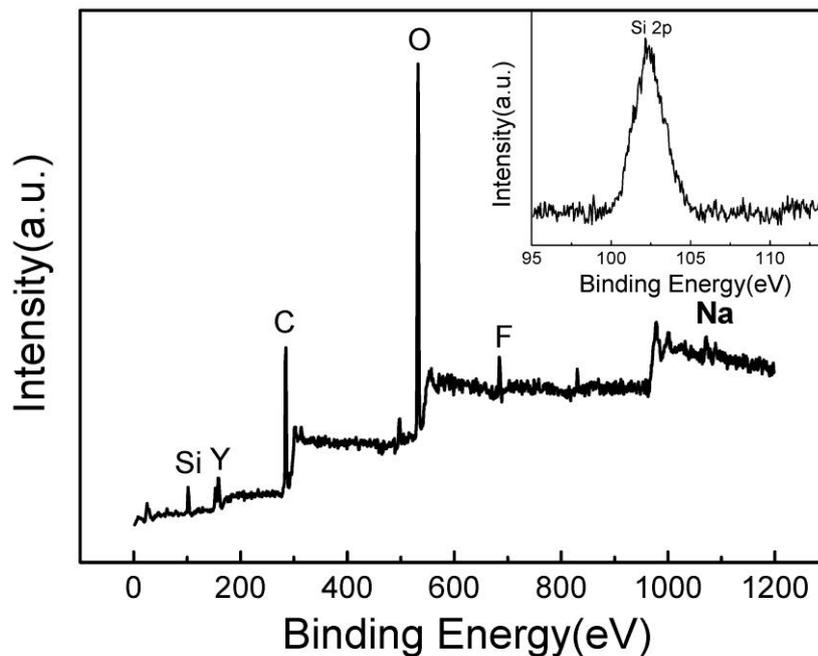


Fig. S6 The wide scan and high resolution (inset) XPS analysis of UCNP@SiO₂-1.5. The XPS spectral analysis provides detailed information on the chemical composition of UCNP@SiO₂-1.5. The XPS spectrum shows Si, Y, C, O, F and Na elements in the nanoparticles.

X-ray photoelectron (XPS) measurements were performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom).

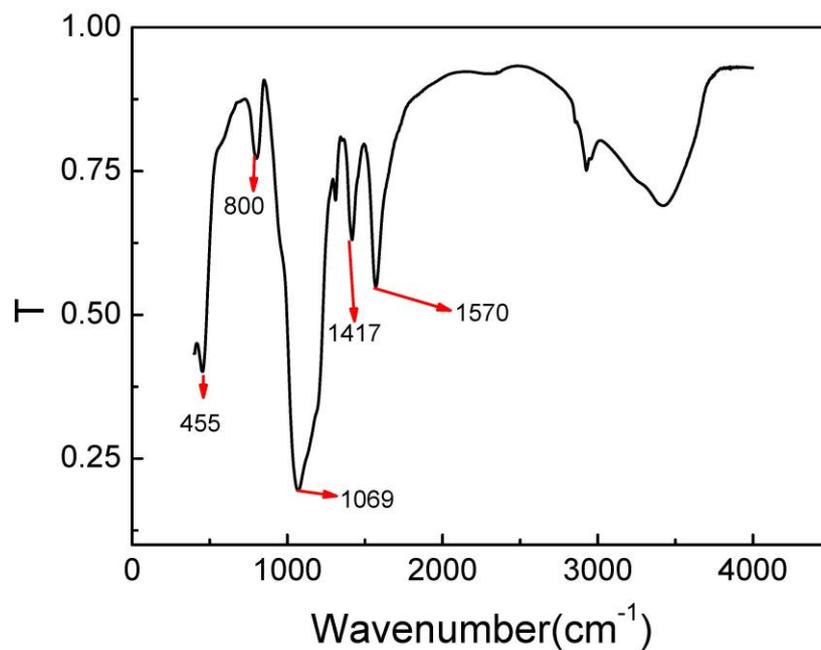


Fig. S7 FTIR spectrum of carboxy-terminated UCNP@SiO₂-1.5.

Two bands at 1417 cm⁻¹ and 1570 cm⁻¹ are observed, which are associated with the asymmetric and symmetric stretching vibrations of carboxylate anions. The band at 1069 cm⁻¹ is attributed to Si–O–Si asymmetric stretching vibration modes of SiO₂. Bands at 800 cm⁻¹ and 455 cm⁻¹ are attributed to the deformation vibration δSi–O.

FTIR analysis was performed on a Bruker Vertex 70 spectrometer (Bruker Co., Germany).

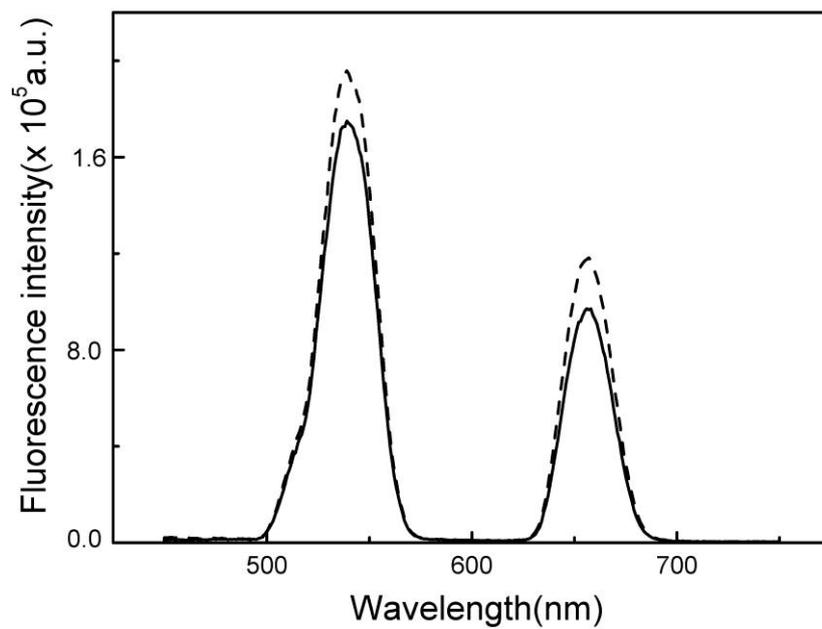


Fig. S8 UCL spectra of UCNP@SiO₂-1.5 (solid line) in water and UCNPs in cyclohexane (dash line), respectively.

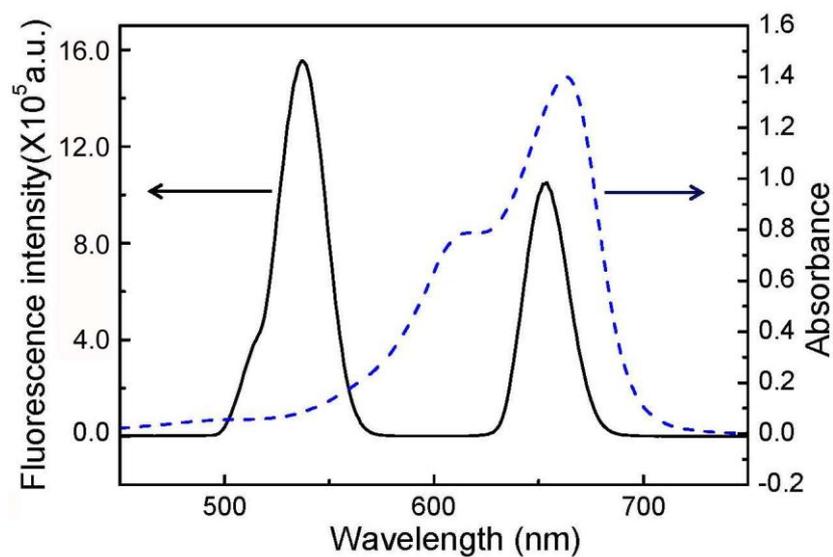


Fig. S9 UCL spectra of UCNP@SiO₂-1.5 with NIR-laser excitation (980 nm, solid line), and UV/Vis absorption spectrum of methylene blue in water (dashed line).

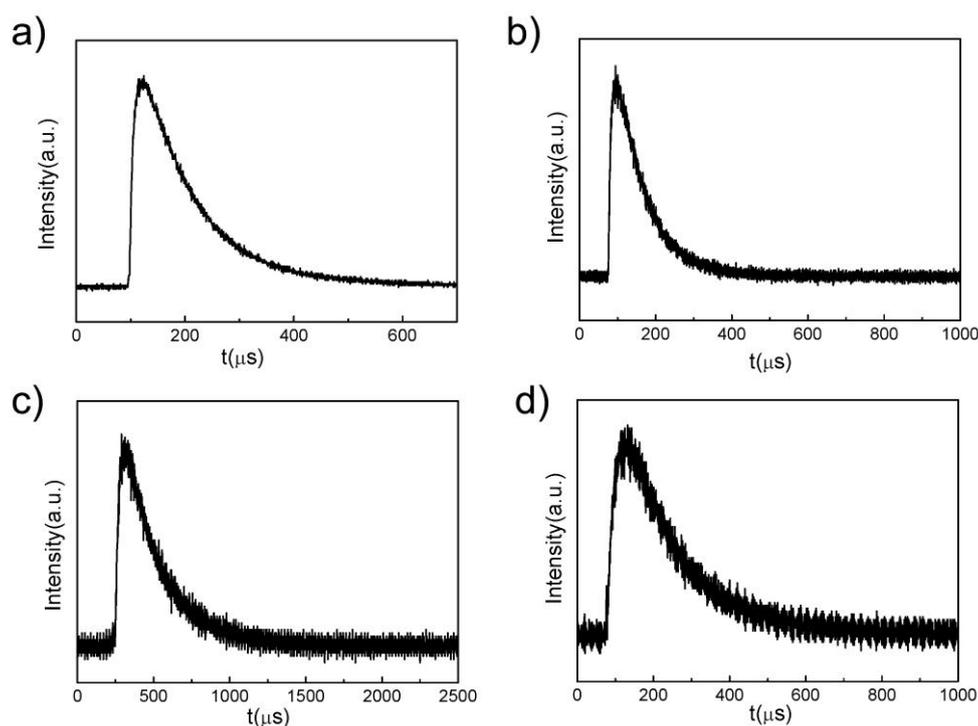


Fig. S10 Luminescence decay curves of UC emission intensity at 544 nm of 2.5mg/mL UCNP@SiO₂-1.5 in the absence of methylene blue (a) and in the presence of 0.1 mM methylene blue (b), and Luminescence decay curves of curves of UC emission intensity at 660 nm of 2.5mg/mL UCNP@SiO₂-1.5 in the absence of methylene blue (c) and in the presence of 0.1 mM methylene blue (d).

The luminescence lifetime were investigated by a laser-system consisting of a Nd:YAG pumping laser (1064 nm), the third-order Harmonic-Generator (355 nm) and a tunable optical parameter oscillator (OPO, Continuum Precision II 8000). It was with a pulse duration of 10 ns, repetition frequency of 10 Hz and line width of 4-7 cm⁻¹.

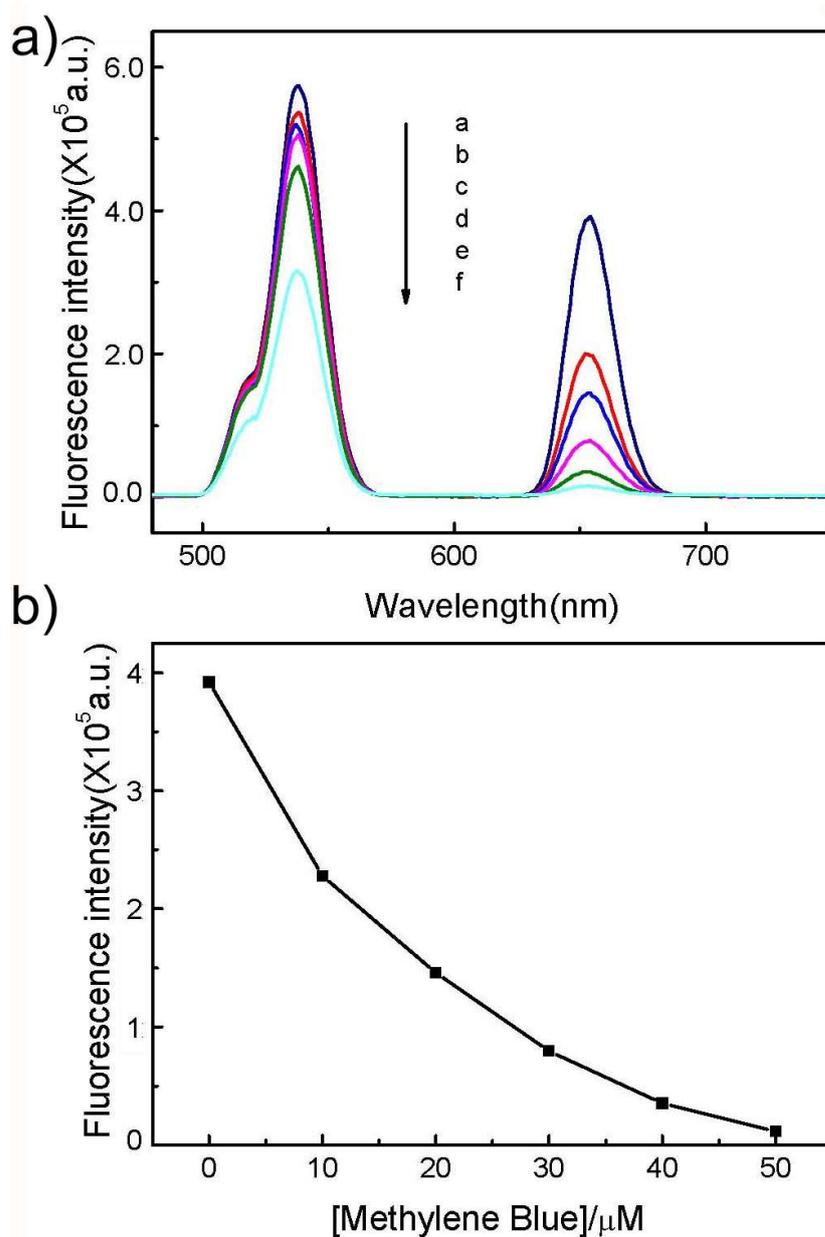


Fig. S11 (a) UCL spectra of the 0.5 mg/mL UCNPs@SiO₂-1.5 in the presence of various concentrations (a, 0; b, 10; c, 20; d, 30; e, 40; and f, 50 μM) of methylene blue, and (b) corresponding UCL intensity at 654 nm as a function of the concentration of methylene blue, respectively.

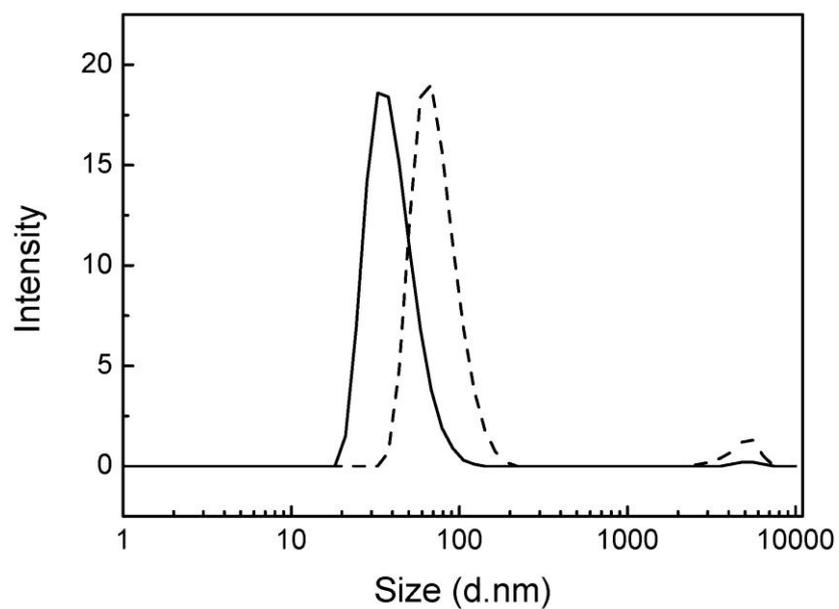


Fig. S12 DLS size distribution of UCNP@SiO₂-1.5 (solid line) and RCA 120 conjugated UCNP@SiO₂ (dashed line), respectively.

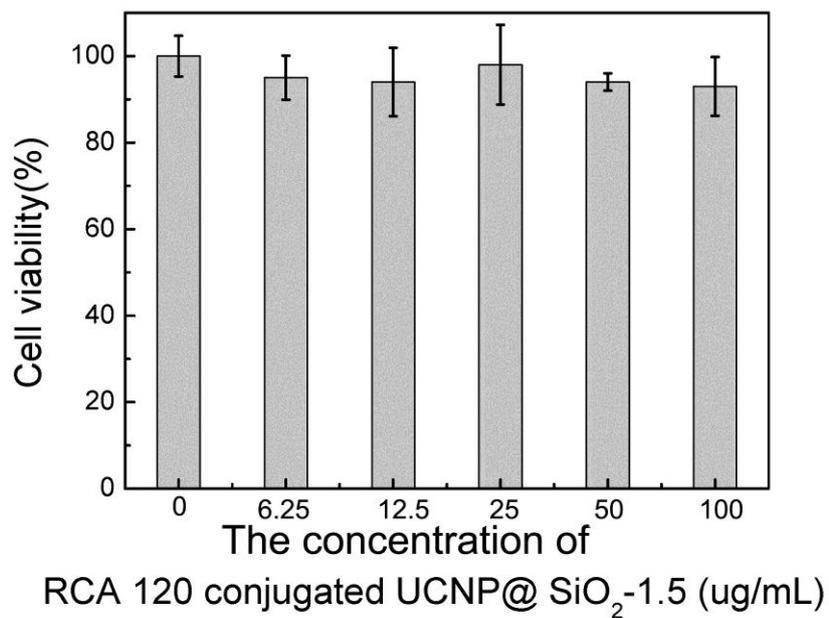


Fig. S13 *In vitro* cell viabilities of HeLa cells incubated with various concentrations (0, 6.25, 12.5, 25, 50, 100 $\mu\text{g/mL}$) of RCA 120 conjugated UCNP@SiO₂-1.5 for 24 h, respectively. The error bars mean standard deviations (n=4).

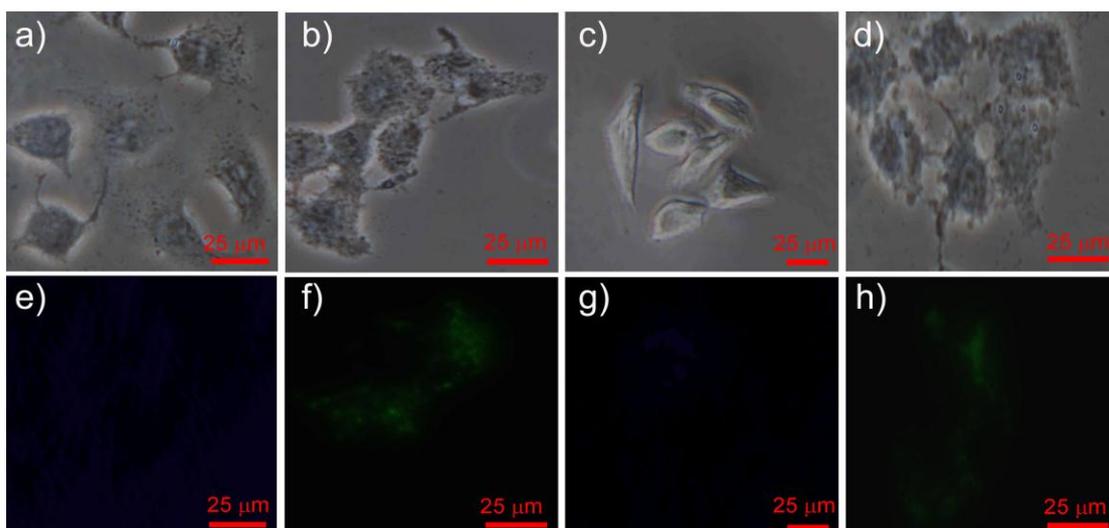


Fig. S14 UCL microscopic imaging of HeLa cells after incubated with 12.5 $\mu\text{g}/\text{mL}$ carboxy-terminated UCNP@SiO₂-3 (a and e), RCA 120 conjugated UCNP@SiO₂-3 (b and f), carboxy-terminated UCNP@SiO₂-6 (c and g), and RCA 120 conjugated UCNP@SiO₂-6 (d and h) for 0.5 h, respectively. Up row are images in bright field mode and bottom row are UCL images in dark field mode.