Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B. This journal is © The Royal Society of Chemistry 2015

Supporting Information

NIR light responsive core-shell nanocontainers for drug delivery

Liru Cui, Huiming Lin*, Chunyu Yang, Ting Zhang, Ruihan Tong, Na An, Fengyu Qu*

College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin, 150025, P. R. China.

Tel (Fax): +86 451 88060653 *E-mail: qufengyu@hrbnu.edu.cn and linhuiming@hrbnu.edu.cn*

Fig. S1



Fig. S1 Schematic drawing of NIR-triggered drug delivery experiments performed on Hela cells.

Fig. S2



Fig. S2 FT-IR spectra of UCNP@mSiO₂ (a) before and (b) after the removal of surfactant.

Fig. S2 shows the FT-IR spectra of UCNP@mSiO₂ before and after the removal of

surfactant. Compared with FT-IR spectra of the two samples, the absence of C-H characteristic peaks in the 2929 and 2853 cm⁻¹ suggests the remove of CTAB, successfully. It is believed that the strategy adopted in this paper is effective to remove CTAB.

Fig. S3



Fig. S3 Thermal gravity analysis (TGA) curves of different nanoparticles: (a) UCNP @mSiO₂, (b) UCNP@mSiO₂-NH₂, (c) UCNP@mSiO₂-COOH, (d) UCNP@mSiO₂ -NO₂, (e) UCNP@mSiO₂@α-CD and (f) DOX- UCNP@mSiO₂@α-CD.

Thermal gravity analysis (TGA) was selected to confirm the modification and drug loading. As shown in Fig. S3, the weight loss values of UCNP@mSiO₂, UCNP@mSiO₂-NH₂, UCNP@mSiO₂-COOH, UCNP@mSiO₂-NO₂, UCNP@mSiO₂ @ α -CD and DOX-UCNP@mSiO₂@ α -CD are 2.60 %, 8.36 %, 9.79 %, 11.85 %, 16.04 % and 31.26 %, respectively. Compared with UCNP@mSiO₂-NO₂, the increased weight loss of UCNP@mSiO₂@ α -CD indicates that α -CD was successfully immobilized onto the surface of the nanoparticles. In addition, the drug loading efficiency (15.2 %) can be calculated based on the weight loss of UCNP@mSiO₂@ α -CD and DOX-UCNP@mSiO₂@ α -CD, which is consistent with the value determined by UV/vis spectroscopy (15.0 ± 0.5 %).

Fig. S4



Fig. S4 DLS measurements of DOX- UCNP@mSiO₂@α-CD in the conditions of
(A) PBS (pH 7.4), (B) PBS (pH 7.4, containing 1M NaCl) and (C) DMEM. (D)
The photographs of DOX-UCNP@mSiO₂@α-CD scattered in the three conditions:
(a) PBS (pH 7.4), (b) PBS (pH 7.4, containing 1M NaCl) and (c) DMEM.





Fig. S5 DLS measurements of UCNP@mSiO₂@α-CD in the conditions of (A) PBS (pH 7.4), (B) PBS (pH 7.4, containing 1M NaCl) and (C) DMEM. (D) The photographs of UCNP@mSiO₂@α-CD scattered in the three conditions: (a) PBS (pH 7.4), (b) PBS (pH 7.4, containing 1M NaCl) and (c) DMEM.

In order to verify the long-term dispersion stability, the hydrodynamic diameters of DOX-UCNP@mSiO₂@ α -CD and UCNP@mSiO₂@ α -CD in PBS (pH 7.4), PBS (pH 7.4, containing 1M NaCl) and DMEM were measured. As shown in Fig. S4 and Fig. S5, the hydrodynamic diameters of the three conditions are 121 nm, 126 nm, 130 nm and 119 nm, 125 nm and 128 nm, respectively, which are larger than that observed from TEM because of the hydrate layer in aqueous environment. However, there was no significant difference between them, suggesting that no obvious aggregation occurred in the presence of DMEM. The digital photos reveal the good stability of the sample.





Fig. S6 Cumulative release rates of DOX-UCNP@mSiO₂@ α -CD under dark condition with various amount of α -CD.





Fig. S7 Cumulative release rates of DOX-UCNP@mSiO₂@α-CD (blue line) and DOX-UCNP@mSiO₂-NO₂ (green line) under alternative NIR light irradiation/dark for every 1 h and only under dark condition.





Fig. S8 CLSM images of the photocontrolled DOX release in HeLa cells. The cells were exposed to the 980 nm light (1.4 W/cm2) for 0 to 20 min before CLSM observations. For each panel, the images from left to right show cell nuclei stained by DAPI (blue), DOX-UCNP@mSiO₂@ α -CD stained by FITC (green), DOX fluorescence in cells (red) and merged. All images share the same scale bar

 $(50 \ \mu m)$. The last line represents the control experiment with free DOX.

. In this paper, 20 min irradiation induces about 8 % (1.4 W/cm²) of drug release (Fig. 7) and the concentration of the free DOX is calculated to be 500 μ g/ mL×15.2 % (drug loading efficiency)×8 % = 6.1 μ g/ mL at this condition. For comparison, the control experiment with free DOX (6.1 μ g/ mL, 80 min incubation) was also carried out as shown in Fig. S8. From Fig. S8, both the cytoplasm and nucleus show the red color derived from DOX molecule, owing to its small molecular structure and easy diffusion into cells rapidly.