Supporting Information

Plasmonic Caged Gold Nanorods for Near-infrared Light Controlled Drug Delivery

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SERS enhancement factor

The density of nile red (ρ_n) and 1-tetradeconal (ρ_t) are 1.23 and 0.824 g/cm³, respectively. The molar mass of nile red (M_n) is 318.37 g/mol.

The enhancement factor (*EF*) of each CGNR was calculated using the following expression:

$$EF = \frac{I_{SERS} \times N_{bulk}}{I_{bulk} \times N_{SERS}}$$

Where I_{SERS} and I_{bulk} are the intensities for the SERS spectra of CGNRs and bulk, respectively, while N_{SERS} and N_{bulk} are the number of nile red molecules probed. SERS spectra of CGNRs with nile red and nile red in bulk were collected with 50x objective (NA=0.75).

Calculation of N_{bulk}

The approximate laser spot size for 50x objective was estimated as followed.^[1,2]

$$\omega_0 = \frac{0.61\lambda}{NA}$$

Where ω_0 is the minimum waist diameter for a laser beam of wavelength λ focused by an objective with a numerical aperture *NA*. *N*_{bulk} is approximated from the following expressions.

The depth of focus $Z_0 = \frac{2\pi\omega_0^2}{\lambda}$

The focal volume $\tau = \left(\frac{\pi}{2}\right)^{1.5} \omega_0^2 Z_0$

$$N_{bulk} = \frac{\rho_n \tau}{M_n} = 1.23 \times 10^{-14} \ mol$$

Calculation of NSERS

The CGNRs used had outer length of 98.4 ± 11.5 nm, width of 43.7 ± 4.7 nm and wall thickness of 5.4 ± 1.1 nm, while the length and width of gold nanorods in the center are 81.0 ± 10.9 nm, width of 13.3 ± 1.4 nm, respectively. The volume of individual CGNR (V_{CGNR}) can be estimated:

$V_{CGNR} = 8.36 \times 10^4 nm^3$

Based on the assumption that CGNRs were filled with nile red and 1-tetradeconal with the weight ratio of 1:10, the number of nile red in each CGNR is estimated to be

$$N_{SERS} = \frac{V_{CGNR} \left(\frac{\frac{1}{\rho_n}}{\frac{1}{\rho_n} + \frac{10}{\rho_t}}\right) \rho_n}{M_n} = 2.03 \times 10^{-20} mol$$

Calculation of EF

$$EF = \frac{I_{SERS} \times N_{bulk}}{I_{bulk} \times N_{SERS}} = \frac{8300 \times 1.23 \times 10^{-14}}{430 \times 2.03 \times 10^{-20}} = 1.17 \times 10^{7}$$



Figure S1. UV-vis spectra of gold nanorods and templated CGNRs. (a) gold nanorods with 4 different aspect ratios with londidual SPR band ranging from 645 nm to 1089 nm; (b) CGNRs using nanorods in (a) with SPR ranging froom 674 nm to 831 nm; (c) reduce the cage wall thickness by increasing HAuCl₄ precursor (110, 130, 150, 170, and 190 μ L). The redshift of the lonfidual SPR band indicated the increase of the aspect ratio of gold nanorods in Figure S1a. The redshift shown in Figure S1b and c indicated the increase of length of CGNRs and the decrease of thickness of naged, resoectively.



Figure S2. TEM images of CGNR



Figure S3. SERS of nile reds after thermally-induced release from CGNRs. The incubation temperature is 42°C and the laser wavelength is 830 nm.



Figure S4. (a-b) Dark-field images of HeLa cell after being treated with nile red-loaded CGNRs. (c) Raman spectra of nile reds after applying the laser with a power of 23.7 mW. (d) Plots of $-\ln(I/I_0)$ vs laser exposure time under laser power of 23.7 and 2.4 mW.

Reference

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- [2] P. H. Camargo; C. M. Cobley; M. Rycenga; Y. N. Xia, Nanotechnology 2009, 20,

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