Supporting Information

In Situ Crystal Growth of Gold Nanocrystals on Upconversion Nanoparticles for Synergetic Chemo-Photothermal Therapy

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1. The photothermal conversion effect of UCNPs@Au-DOX

According to Roper's report,[1] the photothermal conversion efficiency η of UCNPs@Au-DOX nanocomposites was calculated using the following eq 1:

$$\eta = \frac{\mathrm{h}S(T_{max} - T_{surr}) - Q_{Dis}}{I(1 - 10^{-A_{808}})} \quad (1)$$

Where h is heat transfer coefficient, S is the surface area of the container, T_{max} is the equilibrium temperature, T_{surr} is ambient temperature of the surroundings. Q_{Dis} is heat losted from light absorbed by the container itself, which was measured independently containing pure water without UCNPs@Au-DOX. And A_{808} is the absorption intensity of UCNPs@Au-DOX at 808 nm. The value of hS is derived according to eq 2:

$$\tau_s = \frac{m_D C_D}{\mathrm{h}S} \quad (2)$$

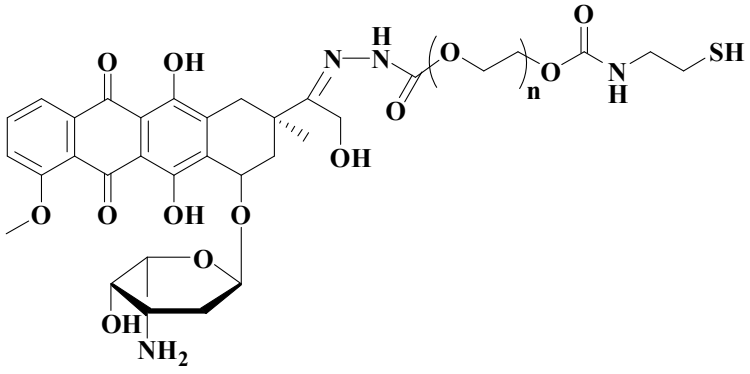
Where τ_s is the sample system time constant, m_D and C_D are the mass and heat capacity of ultrapure water used as the solvent, respectively.

And, τ_s can be calculated by eq 3:

$$t = -\tau_s ln\theta \quad (3)$$

Time constant for heat transfer from the system is determined to be τ_s = 221.1 s applying the linear time data from the cooling period (after 600 s) *vs* negative natural logarithm of driving force temperature (Fig. 3d). Substituting the value of τs into eq 2, hS can be obtained. And the value of hS replaced into eq 1, 808 nm laser heat conversion efficiency (η) of UCNPs@Au-DOX nanocomposites can be calculated to be 12%.

2. Molecule structure of SH-PEG-DOX: `



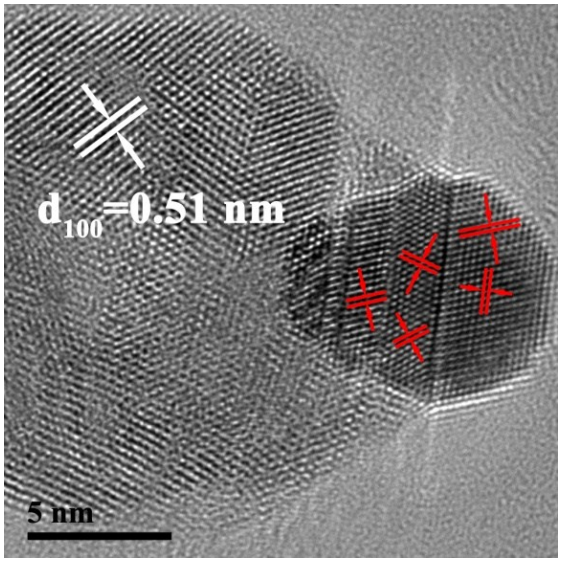


Fig. S1. HRTEM image of cit-UCNPs@Au. All of the crystal lattice fringes of gold nanopartiles were displayed with red arrows.

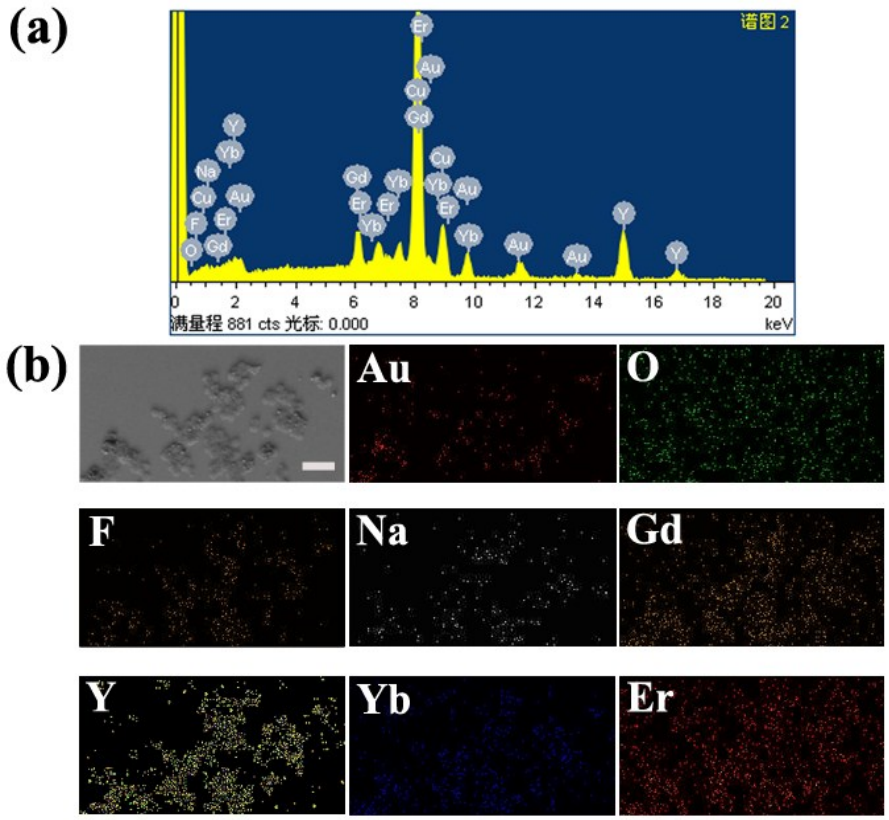


Fig. S2. The energy dispersive X-ray (EDX) spectrum (a) and elemental mapping images of cit-UCNPs@Au (b).

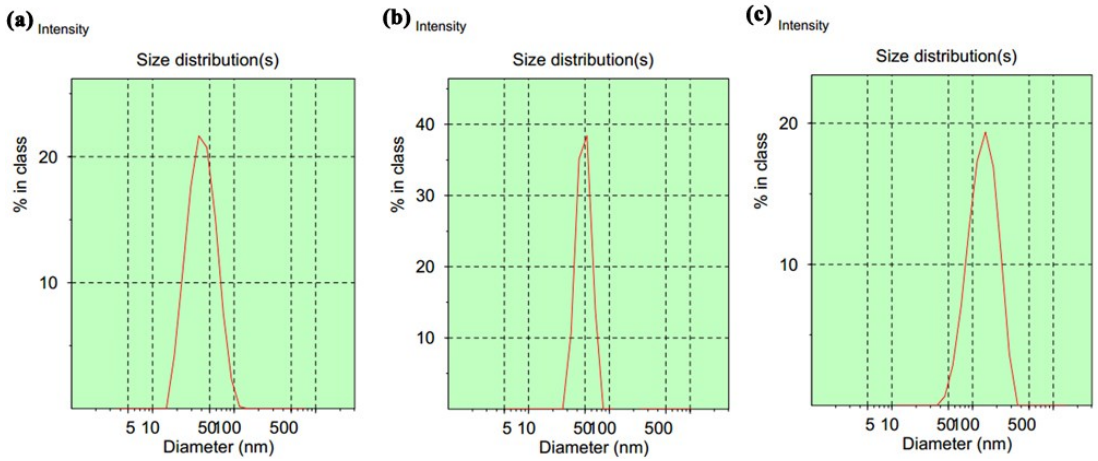


Fig. S3. Dynamic light scattering (DLS) of cit-UCNPs (a) cit-UCNPs@Au (b) and UCNPs@Au-DOX (c) in water (200 μg/mL).

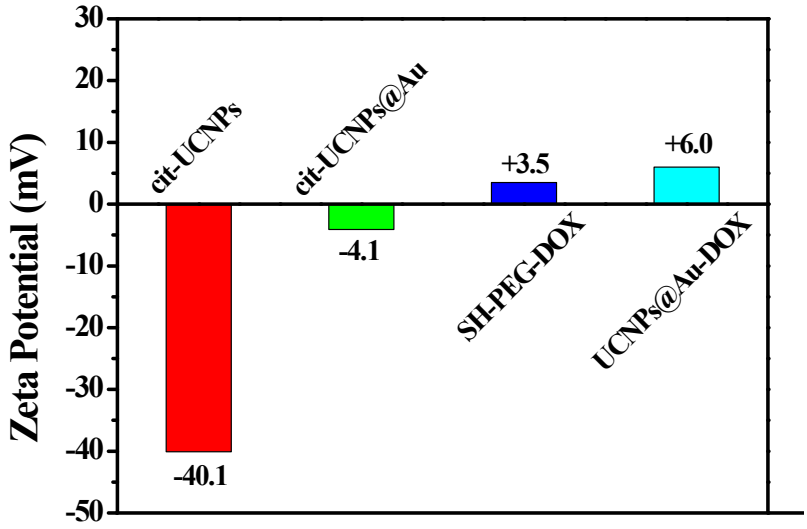


Fig. S4. The zeta potentials of cit-UCNPs, cit-UCNPs@Au, SH-PEG-DOX, and UCNPs@Au-DOX in water (200 μg/mL).

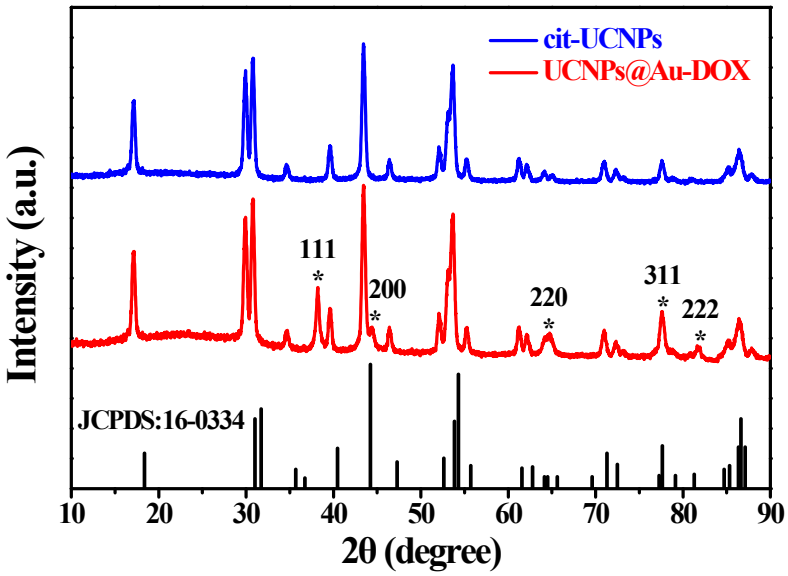


Fig. S5. XRD patterns of cit-UCNPs, UCNPs@Au-DOX and the standard card of β-$NaYF_4$ (JCPDS: 16-0334), *: the peaks of gold nanoparticles.

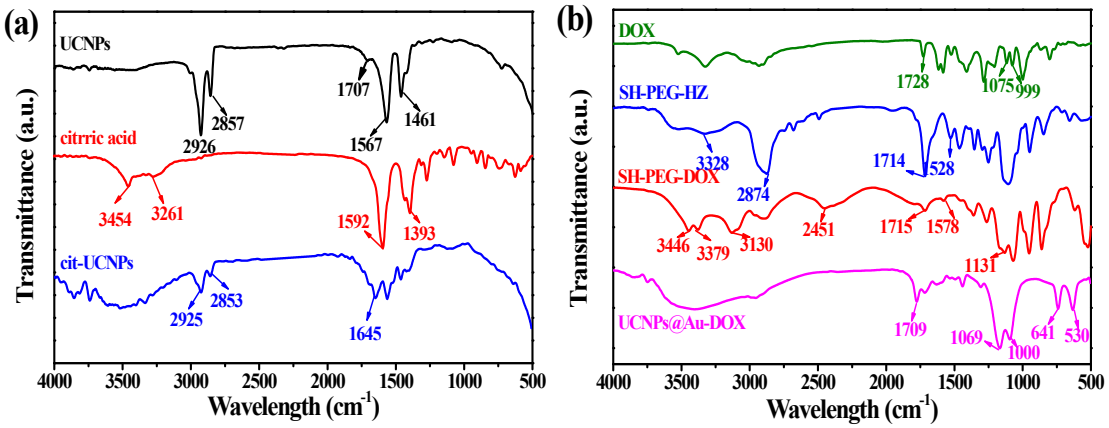


Fig. S6. FT-IR spectra of UCNPs, citric acid, and cit-UCNPs (a); FT-IR spectra of DOX, SH-PEG-HZ, SH-PEG-DOX, and UCNPs@Au-DOX (b).

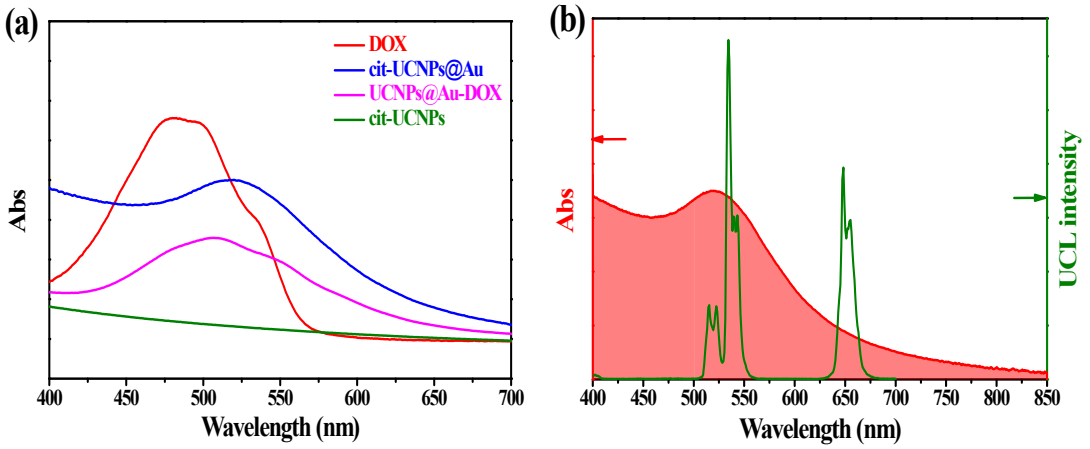


Fig. S7. (a) Visible absorption spectra of cit-UCNPs, DOX, cit-UCNPs@Au, and UCNPs@Au-DOX; (b) Spectral overlap between the upconversion luminenscence (UCL) spectrum of cit-UCNPs (green line) and absorption spectrum of cit-UCNPs@Au (red line).

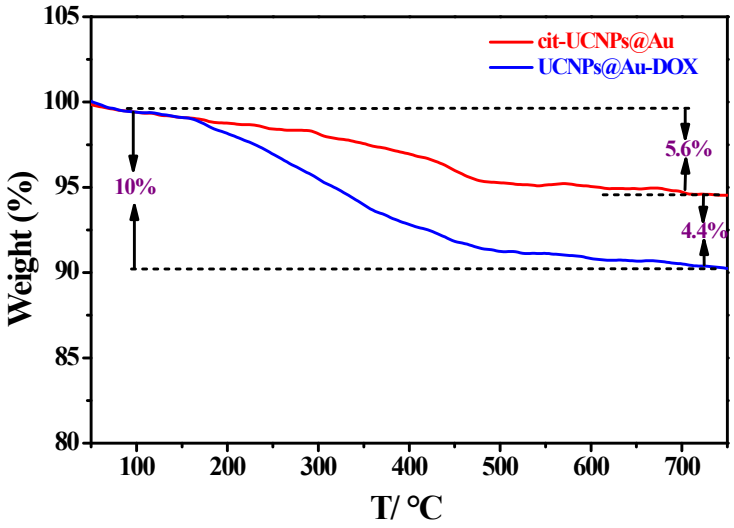


Fig. S8. Thermogravimetric (TG) curves of cit-UCNPs@Au and UCNPs@Au-DOX.

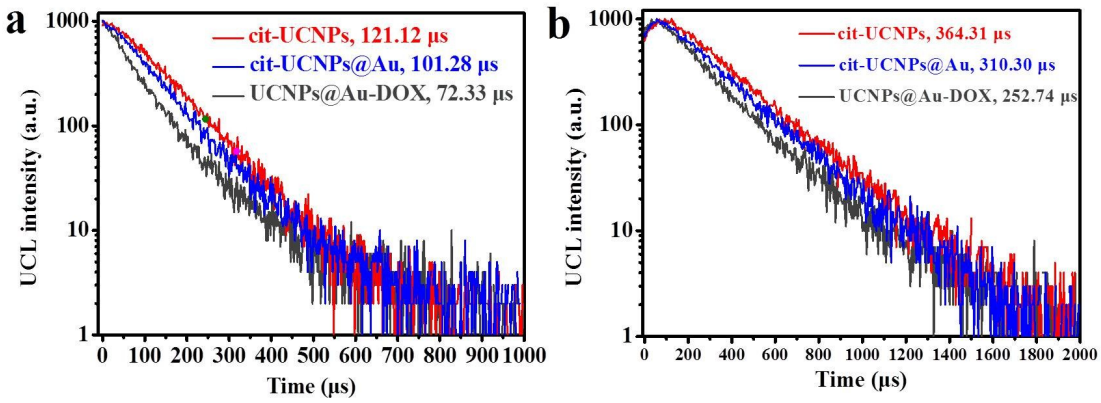


Fig. S9. The upconversion luminescence (UCL) decay profiles of $^4S_{3/2}$ (a) and $^4F_{9/2}$ (b) levels of Er^{3+} ion under excitation of 980 nm pulsed laser (1.5 W/cm^2).

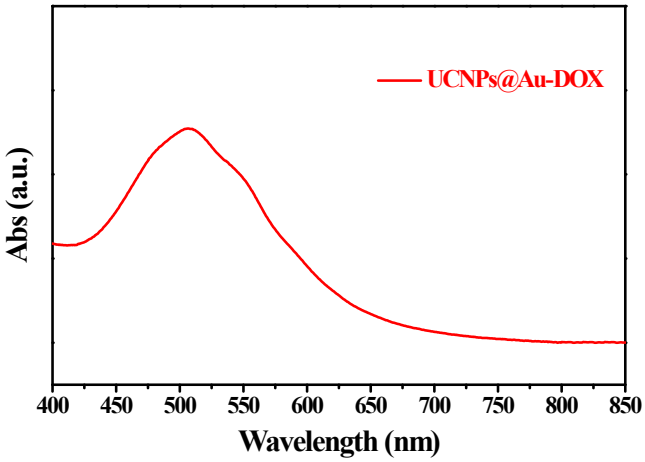


Fig. S10. Visible absorption spectrum of UCNPs@Au-DOX (400 μg/mL) in water.

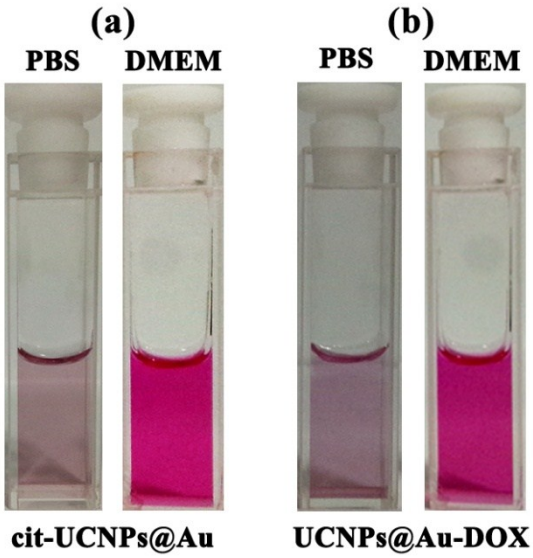


Fig. S11. The photographs of cit-UCNPs@Au (a) and UCNPs@Au-DOX (b) in PBS and DMEM culture solution (200 μg/mL), respectively; There are no obvious aggregation after 24 h.

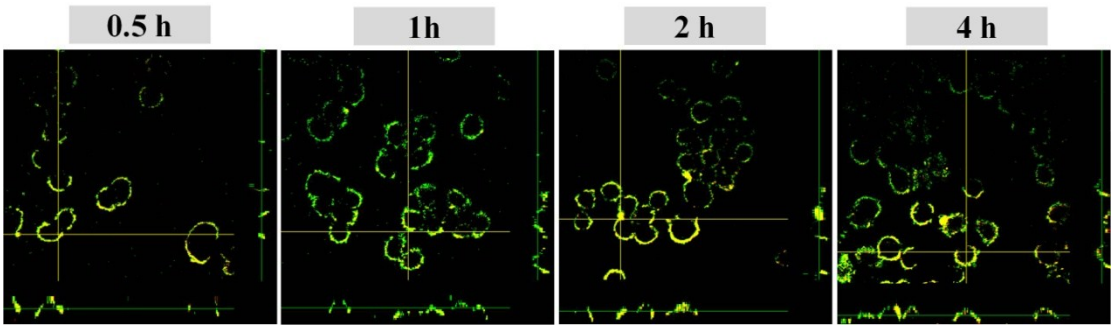


Fig. S12. The three-dimensional confocal luminescence reconstructions of HeLa cells after incubation with cit-UCNPs@Au for 0.5, 1, 2, and 4 h collected as a series along the Z optical axis, λ_{ex} = 980 nm, 500 mW.

Reference

1. D. K. Roper, W. Ahn and M. Hoepfner, *J. Phys. Chem. C*, 2007, **111**, 3636-3641.