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,\textsuperscript{1} the photothermal conversion efficiency $\eta$ of UCNPs@Au-DOX nanocomposites was calculated using the following eq 1:

$$\eta = \frac{hS(T_{\text{max}} - T_{\text{surr}}) - Q_{\text{Dis}}}{I(1 - 10^{-A_{808}})}$$  \hspace{1cm} (1)

Where $h$ is heat transfer coefficient, $S$ is the surface area of the container, $T_{\text{max}}$ is the equilibrium temperature, $T_{\text{surr}}$ is ambient temperature of the surroundings. $Q_{\text{Dis}}$ 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:

$$\tau_s = \frac{m_D C_D}{hS}$$  \hspace{1cm} (2)

Where $\tau_s$ 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, $\tau_s$ can be calculated by eq 3:

$$\tau = -\frac{\ln \theta}{\tau_s}$$  \hspace{1cm} (3)

Time constant for heat transfer from the system is determined to be $\tau_s = 221.1$ 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 $\tau_s$ into eq 2, $hS$ can be obtained. And the value of $hS$ replaced into eq 1, 808 nm laser heat conversion efficiency ($\eta$) of UCNPs@Au-DOX nanocomposites can be calculated to be 12%.

2. Molecule structure of SH-PEG-DOX: 

\begin{center}
\[ \text{Molecule structure of SH-PEG-DOX} \]
\end{center}
Fig. S1. HRTEM image of cit-UCNPs@Au. All of the crystal lattice fringes of gold nanoparticles 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-NaYF₄ (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 luminescence (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, $\lambda_{ex} = 980$ nm, 500 mW.
Reference