Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2019

Supporting Information

One-pot synthesis of SiO_2-coated $Gd_2(WO_4)_3$: Yb^{3+}/Ho^{3+} nanoparticles for simultaneous multi-imaging, temperature sensing and tumor inhibition

Guofeng Liu[a,b], Yeqing Chen[c], Mochen Jia[a], Zhen Sun[a], Binbin Ding[b], Shuai Shao[b], Fan Jiang[b], Zuoling Fu*[,a], Ping'an Ma*[,b], Jun Lin*[,b]

[a]Coherent Light and Atomic and Molecular Spectroscopy Laboratory, Key Laboratory of Physics and Technology for Advanced Batteries, College of Physics, Jilin University, Changchun 130012, China

[b]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China.

[c]School of Applied Physics and Materials, Wuyi University, Jiangmen, Guangdong 529020, China.

*Corresponding author. Email: zlfu@jlu.edu.cn, mapa675@ciac.ac.cn, jlin@ciac.ac.cn

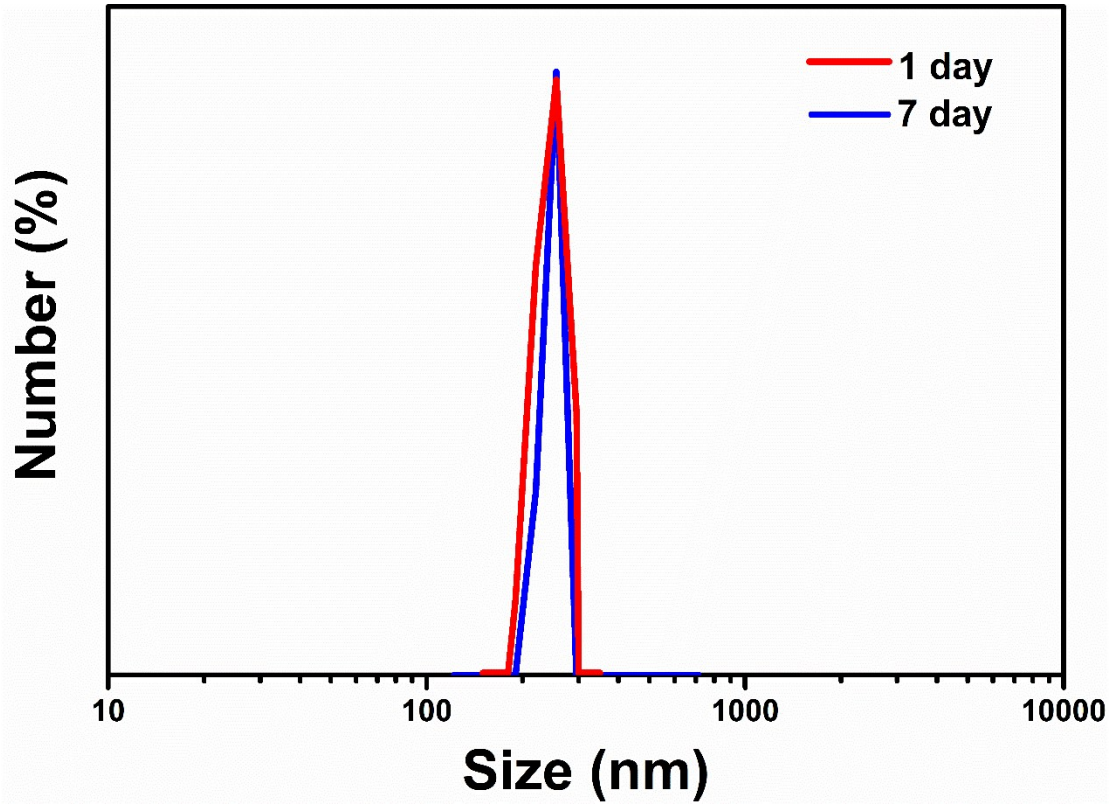

Figure S1. The size distribution of $Gd_2(WO_4)_3$@SiO_2 nanoparticles in water for different times.

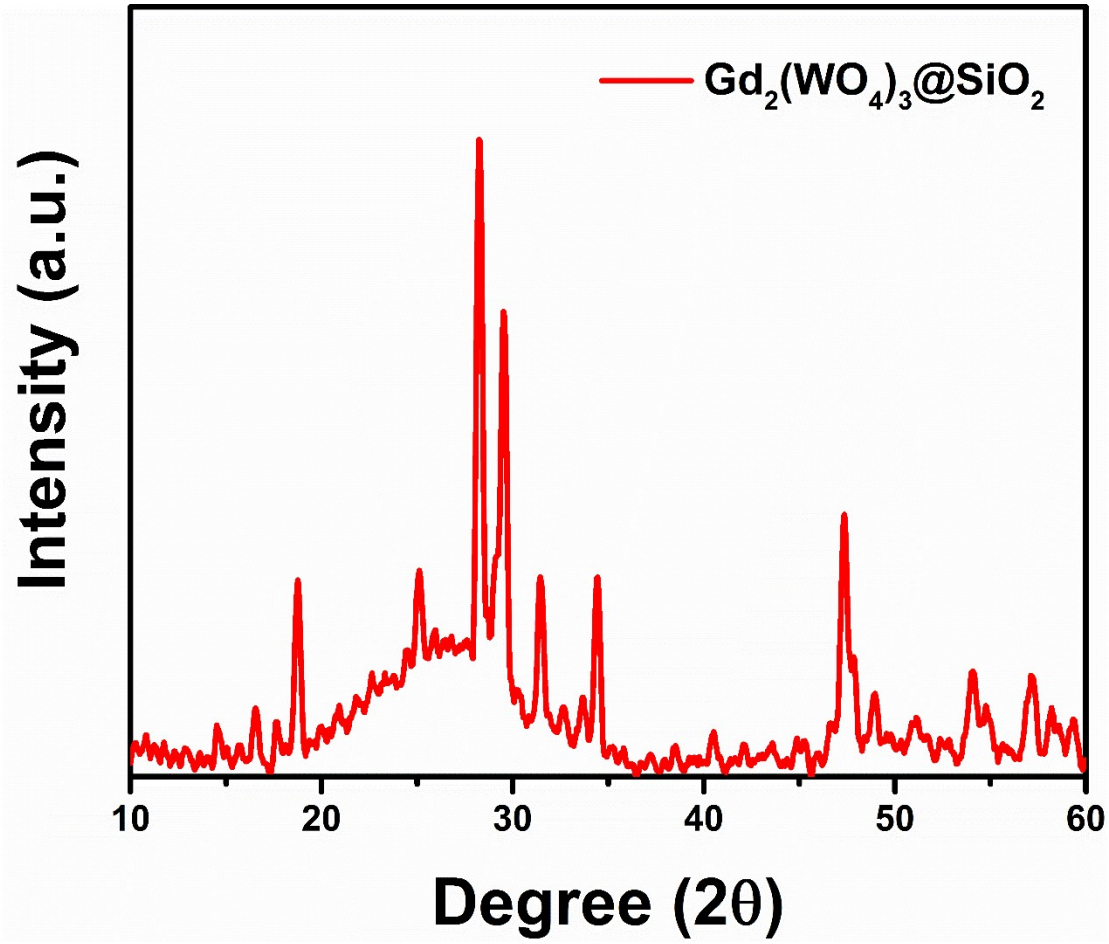

Figure S2. The XRD patterns of $Gd_2(WO_4)_3$ nanoparticles with thick SiO_2 shell.

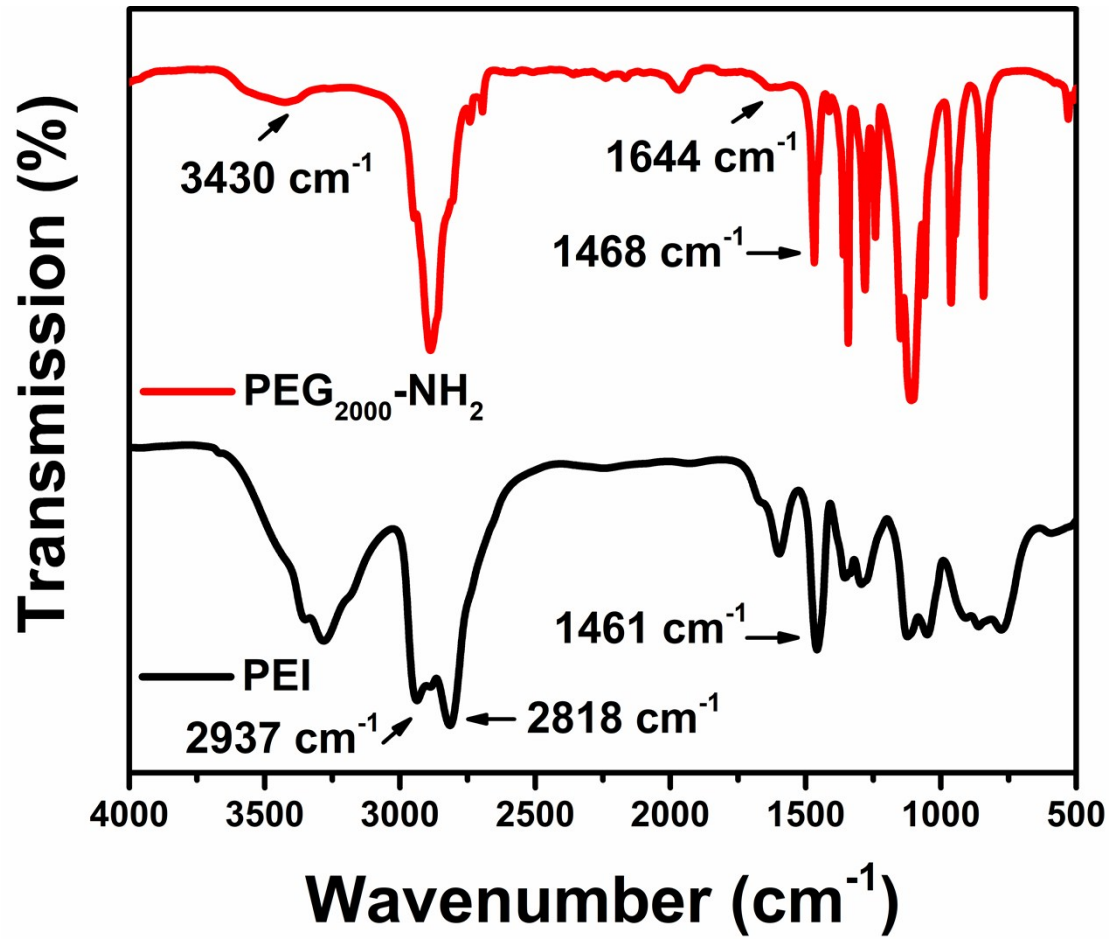

Figure S3. The FTIR spectra of PEI and PEG_{2000}-NH_2.

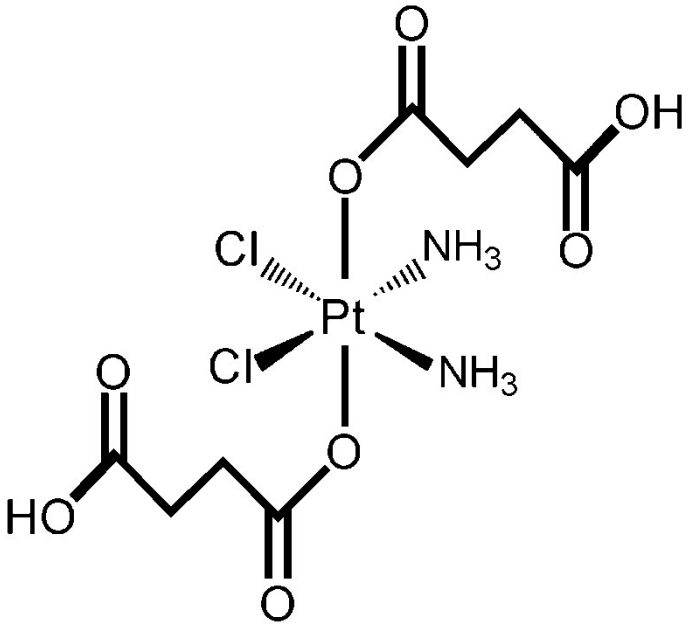

Figure S4. The structure of DSP

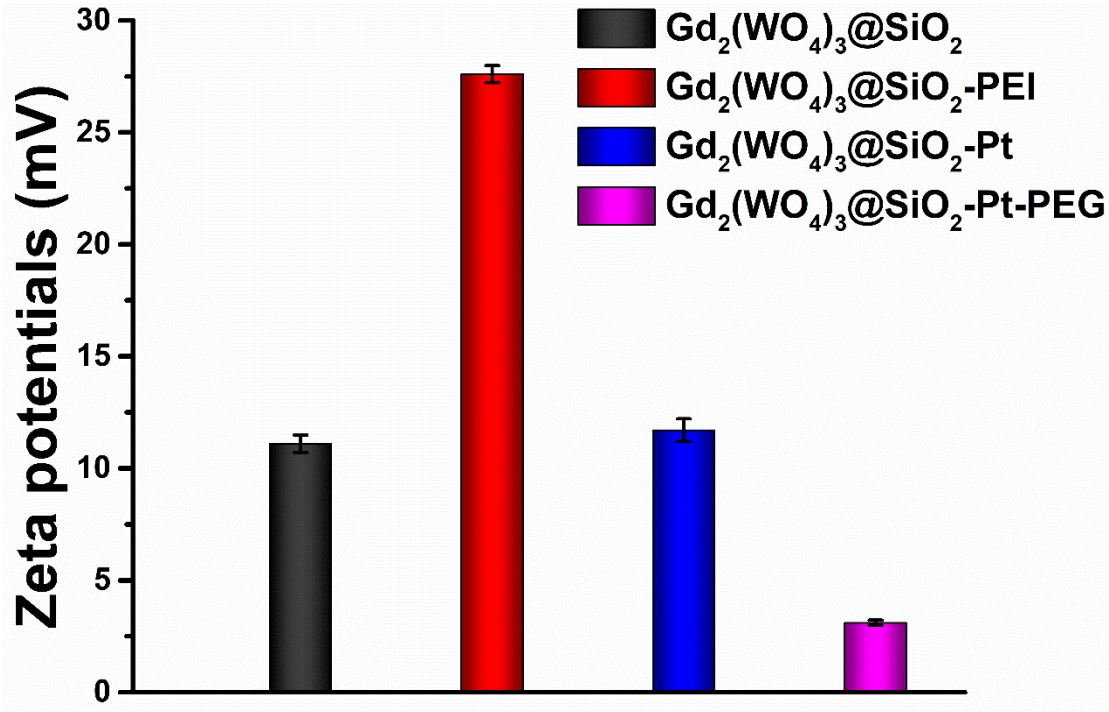

Figure S5. The zeta potentials of $Gd_2(WO_4)_3@SiO_2$, $Gd_2(WO_4)_3@SiO_2$-PEI, $Gd_2(WO_4)_3@SiO_2$-Pt, and $Gd_2(WO_4)_3@SiO_2$-Pt-PEG.

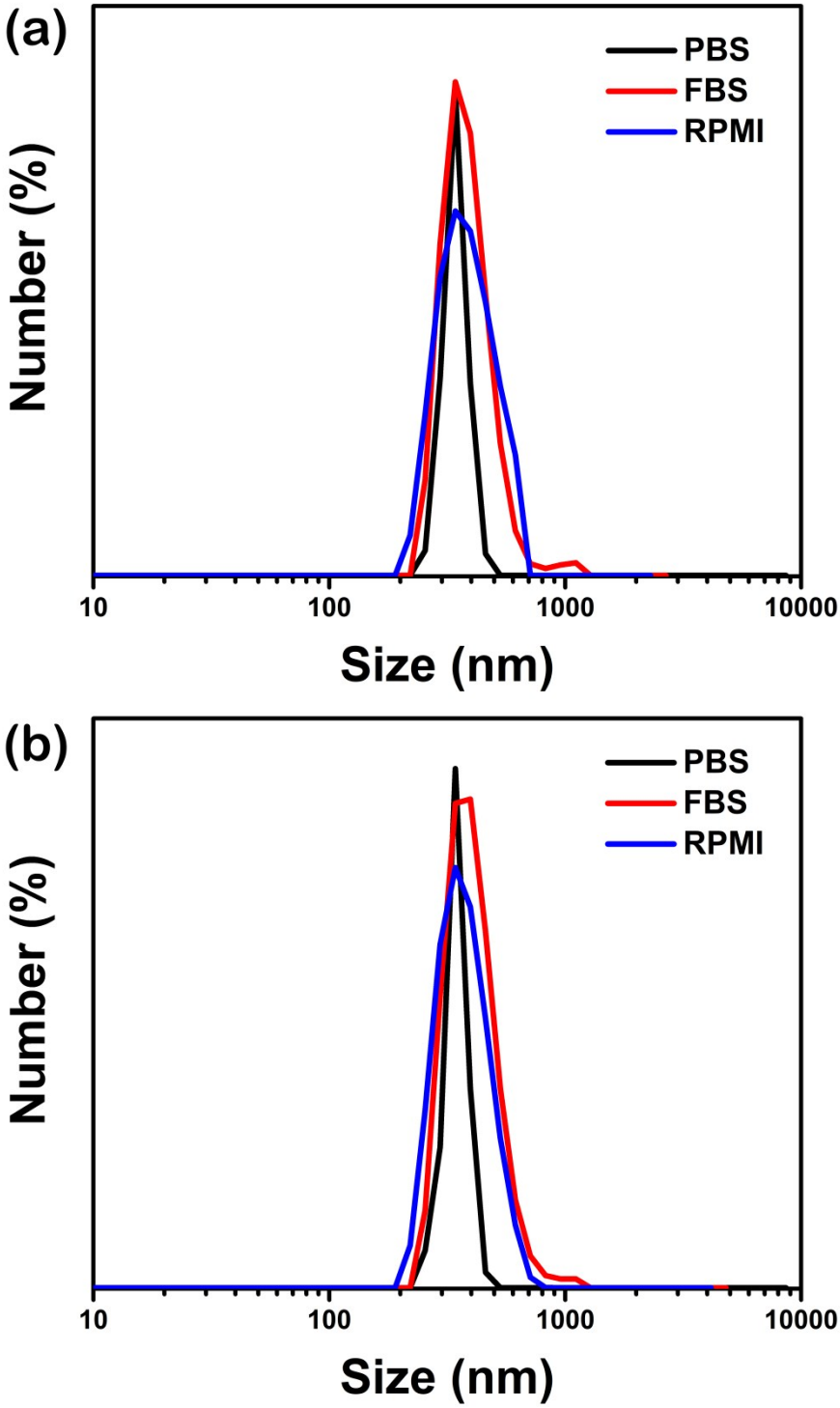

Figure S6. The size distribution of $Gd_2(WO_4)_3$@SiO_2-Pt-PEG nanoparticles in different mediums for different times. (a) The first day in PBS, FBS and RPMI; (b) The seventh day in PBS, FBS and RPMI.

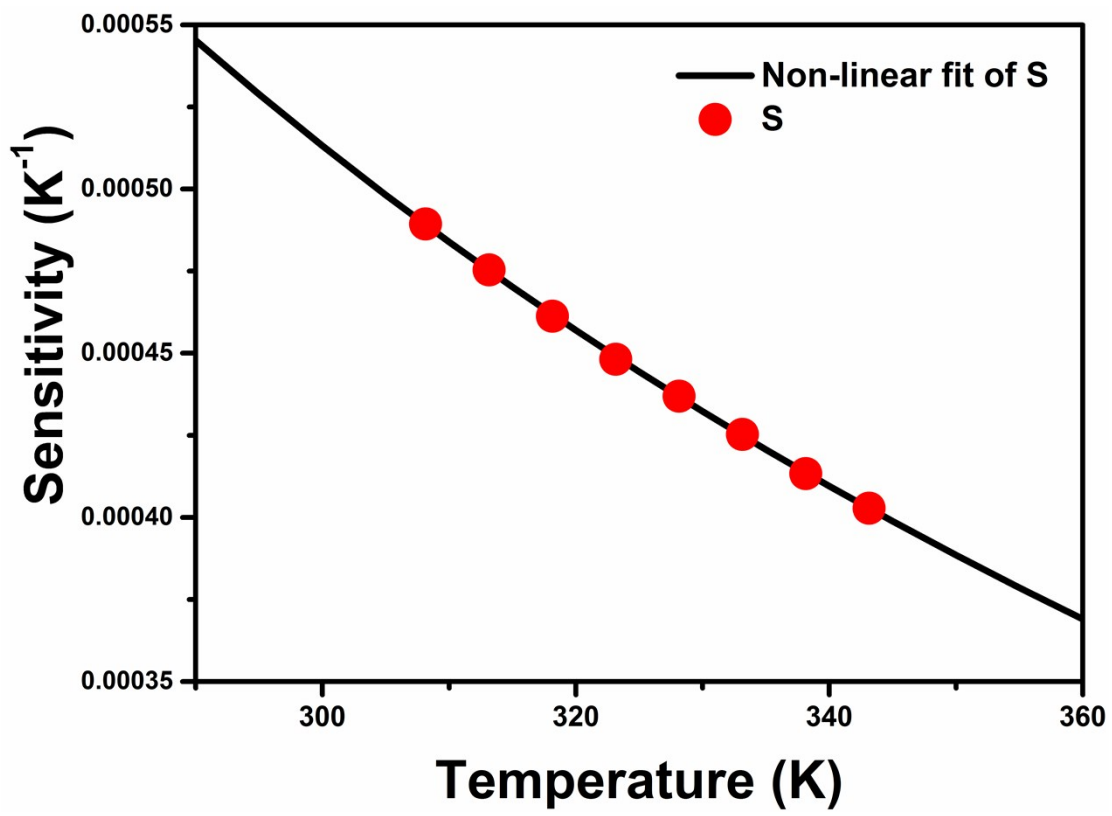

Figure S7. The evolution of sensitivity of $Gd_2(WO_4)_3$@SiO_2-Pt-PEG with temperature rising.

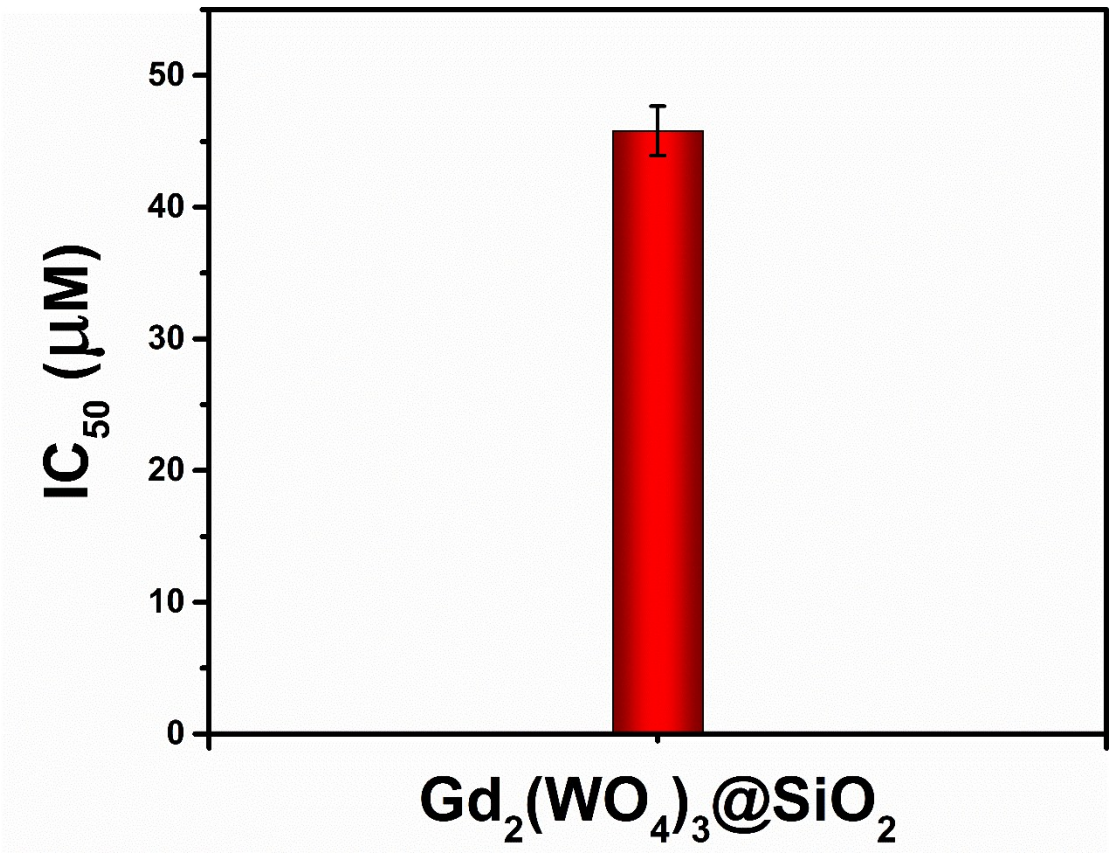

Figure S8. The 50% inhibitory concentration (IC_{50}, Pt) of $Gd_2(WO_4)_3@SiO_2$.

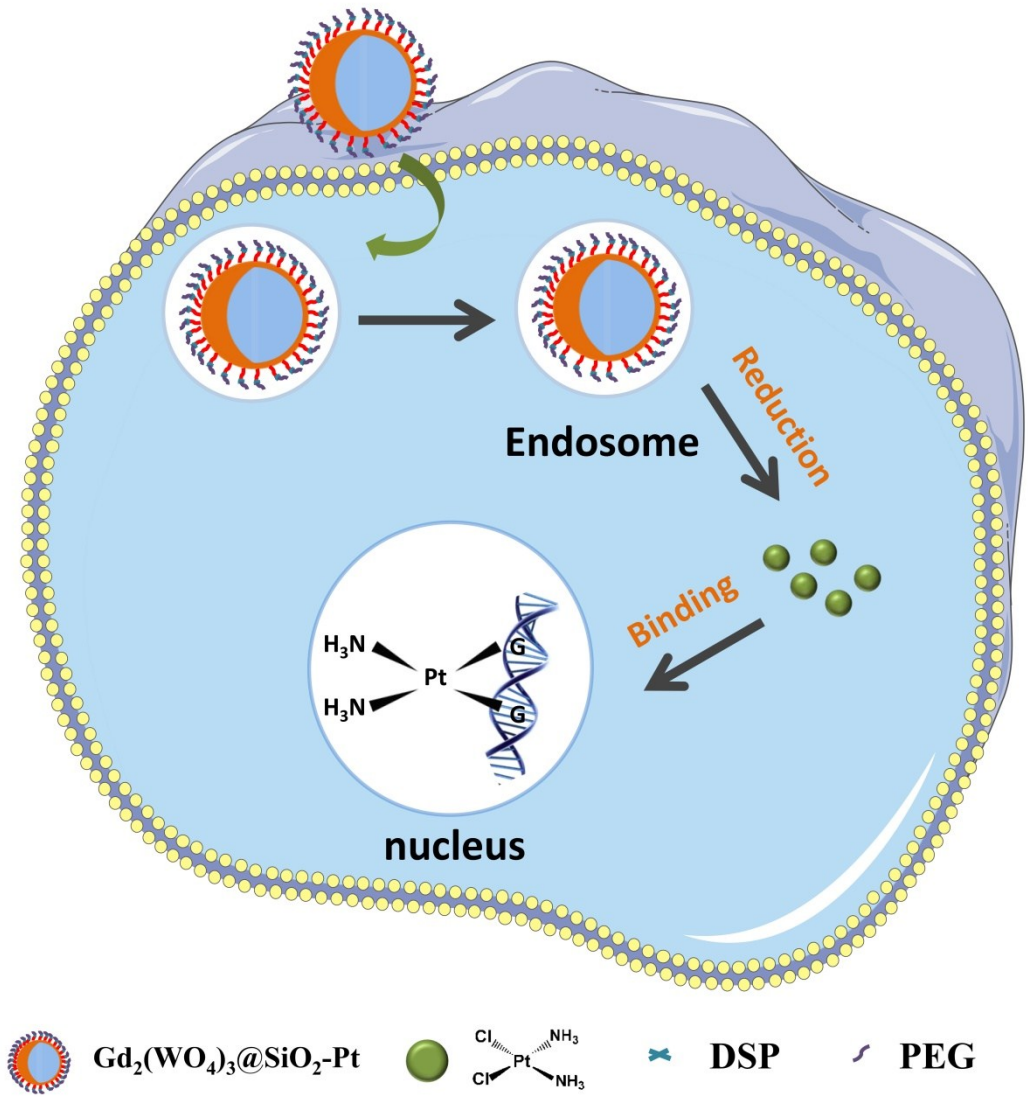

Figure S9. The therapeutic mechanism of $Gd_2(WO_4)_3$@SiO_2-Pt-PEG UCNPs for tumor cells.

S10. Fluorescence intensity ratio technique (FIR)

FIR is an excellent method for temperature sensing, an experiment is carried out in order to calculate FIR. Briefly, quartz cuvette containing $Gd_2(WO_4)_3$@SiO_2-Pt-PEG solution (2 mL, 1 mg/mL) is placed in Andor SR-500i (Andor Technology Co, Belfast, U.K.) spectrometer. The solution is heated by an external temperature controller from 305-345 K and the spectra is recorded from 630-670 nm under a pulse 980 nm laser irradiation (1W/cm^2).

The ratio of fluorescence intensity from two thermally coupled energy levels can be written as follows:[1, 2]

$$FIR = \frac{N_2}{N_1} = \frac{I_{2j}}{I_{1j}} = \frac{g_2\sigma_{2j}\omega_{2j}}{g_1\sigma_{1j}\omega_{1j}} exp(-\frac{\Delta E}{k_B T}) = Bexp(-\frac{\Delta E}{k_B T}) \quad (1)$$

Where

$$B = \frac{g_2\sigma_{2j}\omega_{2j}}{g_1\sigma_{1j}\omega_{1j}}$$

N represents populations of upper ($^5F_{5(1)}$) and lower ($^5F_{5(2)}$) levels, g denotes degeneracy, σ denotes emission cross-section, ω is angular frequency. I_{645} and I_{658} are the integrated intensities of the $^5F_{5(1)} \rightarrow {}^5I_8$ and $^5F_{5(2)} \rightarrow {}^5I_8$, respectively. The energy separation ($^5F_{5(1)}$/ $^5F_{5(2)}$) can be labeled by ΔE, k_B represents the Boltzmann constant and T is the absolute temperature.[2] In addition, the Eq. (1) can be rearranged as follow:

$$ln(FIR) = lnB - \frac{\Delta E}{k_B T} \quad (2)$$

Where all the terms have been mentioned in the Eq. (1). The value of FIR ($^5F_{5(1)}$/ $^5F_{5(2)}$) and inverse absolute temperature can be fitted by a straight line. Furthermore, the sensitivity S can be defined as follow:[3, 4]

$$S = \frac{d(FIR)}{dT} = FIR(\frac{\Delta E}{k_B T^2}) = B\frac{\Delta E}{k_B T^2} exp(-\frac{\Delta E}{k_B T}) \quad (3)$$

S11. Drug loading of DSP on the surface of $Gd_2(WO_4)_3@SiO_2$

$Gd_2(WO_4)_3@SiO_2$-Pt is dispersed in deionized water (7 mL), The inductively coupled plasma-mass spectrometry (ICP-MS) is employed for the measurement of platinum concentration (Table S1). The drug loading rate can be calculated by the following formula:[5]

$$\eta = \frac{m_1}{m_1 + m_2} \times 100\% \tag{4}$$

In particular, the η denotes the drug loading rate, m_1 is the amount of DSP, and the m_2 represents the amount of $Gd_2(WO_4)_3@SiO_2$.

Table S1. The element concentrations of $Gd_2(WO_4)_3@SiO_2$ NPs after conjugated with DSP.

Element	Gd	Ho	Pt	W	Yb
Concentration (ppm)	112.8	0.8531	3.442	142.2	58.07

References

1. Collins, S. F.; Baxter, G. W.; Wade, S. A.; Sun, T.; Grattan, K. T. V.; Zhang, Z. Y.; Palmer, A. W. *J. Appl. Phys.* 1998, **84**, 4649-4654.
2. Yang, Y.; Mi, C.; Yu, F.; Su, X.; Guo, C.; Li, G.; Zhang, J.; Liu, L.; Liu, Y.; Li, X. *Ceram. Int.* 2014, **40**, 9875-9880.
3. Du, P.; Luo, L.; Yu, J. S. *Ceram. Int.* 2016, **42**, 5635-5641.
4. Dong, B.; Cao, B.; He, Y.; Liu, Z.; Li, Z.; Feng, Z. *Adv. Mater.* 2012, **24**, 1987-1993.
5. L. Liang, A. Care, R. Zhang, Y. Lu, N. H. Packer, A. Sunna, Y. Qian and A. V. Zvyagin, *ACS Appl. Mater. Interfaces.*, 2016, **8**, 11945-11953.