

Supporting Information

Near-infrared light and magnetic field dual-responsive porous silicon-based nanocarriers to overcome multi-drug resistance of breast cancer cells with enhanced efficiency

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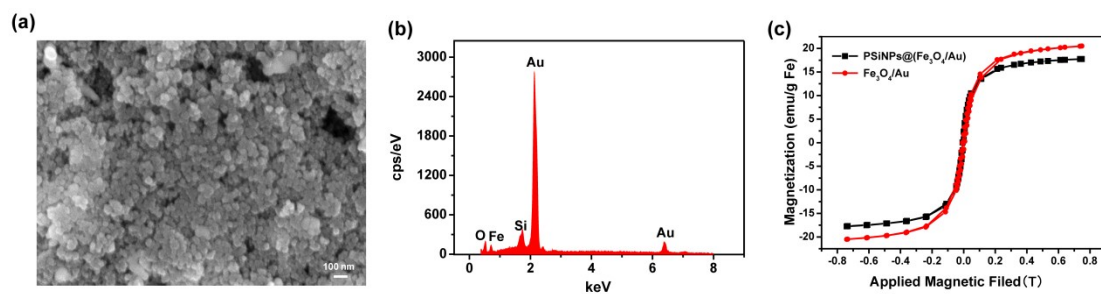


Fig. S1. (a) SEM image and (b) EDS of $\text{Fe}_3\text{O}_4/\text{Au}$ nanoparticles (Si signal attributed to the substrate of silicon wafer), and (c) VSM analysis of $\text{Fe}_3\text{O}_4/\text{Au}$ nanoparticles and $\text{PSiNPs}@\text{(Fe}_3\text{O}_4/\text{Au)}$ nanocomposites.

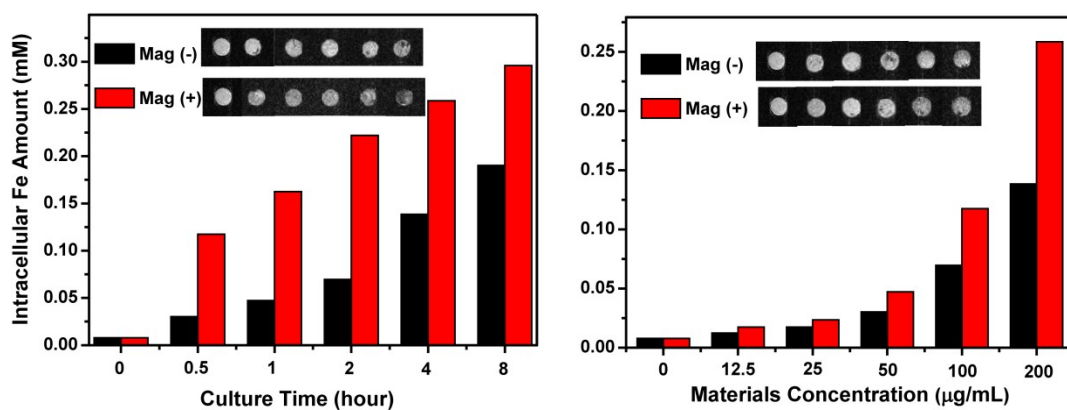


Fig. S2. Intracellular Fe amount of MCF-7 cells treated with $\text{PSiNPs}@\text{(Fe}_3\text{O}_4/\text{Au)}$ under different conditions, and their corresponding insert MRI images in the absence (Mag (-)) or presence (Mag (+)) of a magnetic field.

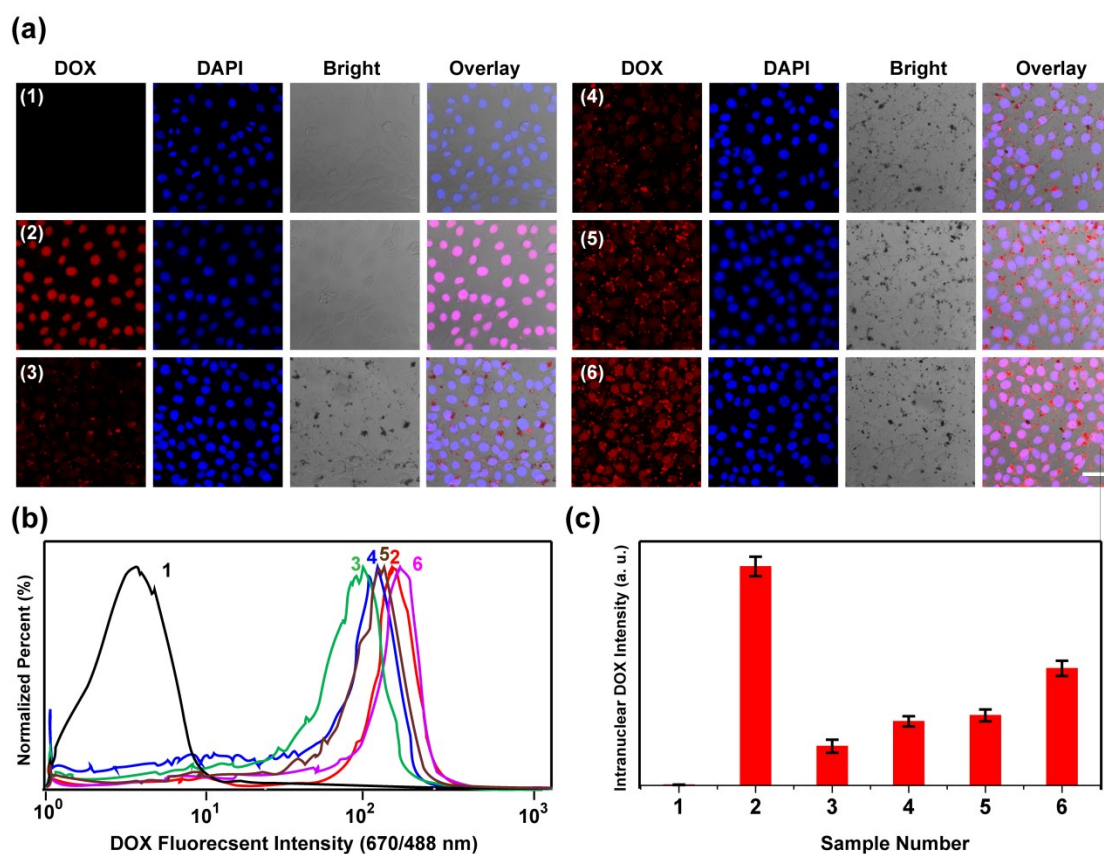


Fig. S3. (a) Typical LSCM images (scale bars in all images = 20 μm), (b) flow cytometry analysis, and (c) MFI analysis in the nuclei of MCF-7 cells in different groups treated with: (1) no treatment/control; (2) free DOX + Mag + NIR; (3) DOX/PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$); (4) DOX/PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$) + NIR; (5) DOX/PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$) + Mag; and (6) DOX/PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$) + Mag + NIR.

Table S1. Atomic concentration, elemental amount, size and zeta-potential of PSiNPs, $\text{Fe}_3\text{O}_4/\text{Au}$, and PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$) samples.

Materials	XPS (w/w)						ICP-MS (w/w)		DLS	
	C 1s (%) (284.5 eV)	O 1s (%) (531.5 eV)	N 1s (%) (392.1 eV)	Si 2p (%) (98.5 eV)	Fe 2p (%) (710.1 eV)	Au 4f (%) (97.9 eV)	Fe (%)	Au (%)	Size (nm)	Surface Potential (mV)
PSiNPs	38.7	20.4	0.0	36.3	4.6	0.0	1.6	0.0	209.5 \pm 46.8	-15.7 \pm 5.4
$\text{Fe}_3\text{O}_4/\text{Au}$	35.2	23.9	3.0	2.5	26.4	9.0	70.4	23.5	38.8 \pm 7.0	+16.8 \pm 2.3
PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$)	36.3	27.0	1.0	26.3	7.2	2.1	39.6	12.8	367.4 \pm 40.2	-8.7 \pm 2.6

Calculation of the photothermal conversion efficiency

The calculation method about the photothermal conversion efficiency of PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$) nanocomposites was referred to these references (H. Chen, et al., *Small*, 2010, 6, 2272; Y. Liu, et al., *Adv. Mater.*, 2013, 25, 1353; J. Zhou, et al., *Biomaterials*, 2013, 34, 9584; W. Ren, et al., *Adv. Healthcare Mater.*, 2015, 4, 1526), the details were followed:

The total energy balance of this system as in Eq. (1):

$$\sum_i m_i C_{p,i} \frac{dT}{dt} = Q_{NPs} + Q_s - Q_{loss} \quad (1)$$

where, m and C_p are the mass and heat capacity, respectively. The suffix “ i ” of m and C_p refer to solvent (water) or dispersed matter (nanoparticles). T is the solution temperature. Q_{NPs} is the photothermal energy absorbed by PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$) per second (Eq. (2)):

$$Q_{NPs} = I(1 - 10^{-A_\lambda})\eta \quad (2)$$

where, I is the laser power, A_λ is the absorbance of PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$) at the wavelength of 808 nm in aqueous solution, and η is the photothermal conversion efficiency of PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$), which means the ratio of absorbed light energy converting to thermal energy.

Q_{loss} is the thermal energy last to surroundings (Eq. (3)):

$$Q_{loss} = hA\Delta T \quad (3)$$

where, h is, the heat transfer coefficient, A is the surface area of the container, and ΔT is the changed temperature, which is referred to $T - T_{surr}$ (T and T_{surr} are the solution temperature and ambient temperature of the surrounding, respectively).

Q_s is the heat associated with the light absorbed by solvent per second. In the situation of heating pure water, the heat input is equal to the heat output at the maximum steady-state temperature, so the equation can be (Eq. (4)):

$$Q_s = Q_{loss} = hA\Delta T_{max, H_2O} \quad (4)$$

where, $\Delta T_{max, H_2O}$ is the temperature change of water at the maximum steady-state temperature.

As it to the experiment of PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$) dispersion, the heat inputs are the heat generated by nanoparticles (Q_{NPs}) and the heat generated by water (Q_s), is equal to the heat out-put at the maximum steady-state temperature, so the equation can be (Eq. (5)):

$$Q_{NPs} + Q_s = Q_{loss} = hA\Delta T_{max, mix} \quad (5)$$

where, $\Delta T_{max, mix}$ is the temperature change of the PSiNPs@($\text{Fe}_3\text{O}_4/\text{Au}$) dispersion at the maximum steady-state temperature. According to the Eqs. (2), (4) and (5), the photothermal conversion efficiency (η) can be expressed as in Eq. (6):

$$\eta = \frac{hA\Delta T_{max,mix} - hA\Delta T_{max,H_2O}}{I(1 - 10^{-A\lambda})} = \frac{hA(\Delta T_{max,mix} - \Delta T_{max,H_2O})}{I(1 - 10^{-A\lambda})} \quad (6)$$

in this equation, only hA is unknown. In order to get the hA , we introduce θ , which is defined as the ratio of ΔT to ΔT_{max} (Eq. (2)):

$$\theta = \frac{\Delta T}{\Delta T_{max}} \quad (7)$$

Substituting Eq. (7) into Eq. (1):

$$\frac{d\theta}{dt} = \frac{hA}{\sum_i m_i C_{p,i}} \left[\frac{Q_{NPs} + Q_s}{hA\Delta T_{max}} - \theta \right] \quad (8)$$

where, the laser was shut off, the $Q_{NPs} + Q_s = 0$, equation (8) could be expressed to (Eq. (9)):

$$\frac{dt}{d\theta} = - \frac{\sum_i m_i C_{p,i}}{hA} \frac{d\theta}{\theta} \quad (9)$$

Eq. (9) changes the expression (Eq. (10)):

$$t = - \frac{\sum_i m_i C_{p,i}}{hA} \ln \theta \quad (10)$$

where, $\frac{\sum_i m_i C_{p,i}}{hA}$ can be calculated by linear relationship of time versus $-\ln(\theta)$ in Fig. S4. Compared with solvent (water, 2×10^{-3} kg), mass of NPs (2×10^{-7} kg) was too little. Generally, the m_{NPs} and $C_{p,NPs}$ of PSiNPs@(Fe_3O_4/Au) were neglected. m_{H_2O} was 2×10^{-3} kg. C_{p,H_2O} was 4.2×10^3 J kg⁻¹. So we can get hA equals 0.01335.

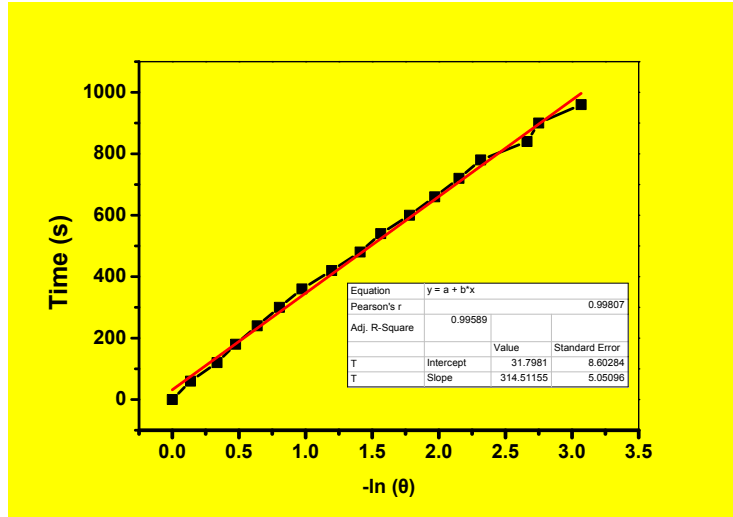


Fig. S4. The relationship of irradiation time and $\ln(\theta)$.

Now, from Eq. (6), every parameter is clear now. $\Delta T_{max,mix}$ is 17.2 and $\Delta T_{max,H_2O}$ is 1.7. I was 1.6 W, where the area of light spot was 1 cm^2 . A_λ was 0.33545, which was calculated by UV at 808 nm. Thus, the photothermal conversion efficiency (η) of P $\text{SiNPs@}(\text{Fe}_3\text{O}_4/\text{Au})$ is calculated as 24.0%.