

## Supporting Information

### Polycatechol Nanosheet: A Superior Nanocarrier for Highly Effective Chemo-Photothermal Synergistic Therapy in Vivo

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#### Calculation of the photothermal conversion efficiency of CuS/PCCNS.

The photothermal conversion efficiency of CuS/PCCNS was determined according to wang's report.<sup>[28]</sup> Detailed calculation was given as following:

The total energy balance of system obeys the following relation:

$$Q = Q_{NPs} + Q_0 - Q_{loss} = \sum_{i=1}^n m_i C_{p,i} \frac{dT}{dt} \quad (1)$$

where  $Q$  is the energy required for the system,  $m$  and  $C_p$  are the mass and heat capacity of each  $i$  component of the sample cell, and  $T$  is the solution temperature.  $Q_0$  is the heat energy of the quartz cell and solvent without nanoparticles, which is measured independently to be 20.0 mW.

$Q_{NPs}$  is the heat generated by NPs under laser irradiation:

$$Q_{NPs} = I\eta(1 - 10^{-A_{980}}) \quad (2)$$

Where  $I$  is the laser power,  $A_{980}$  is the extinction value of sample at 980 nm, and  $\eta$  is the photothermal conversion efficiency.

$Q_{loss}$  is the energy transferred from system to environment:

$$Q_{loss} = hA(T_{max} - T_0) \quad (3)$$

where  $h$  is the heat transfer coefficient,  $A$  is the surface area of the sample well,  $T_{max}$  is the equilibrium temperature,  $T_0$  is the ambient temperature.

When the system is heated to a maximum value in temperature ( $T_{\max}$ ), a heat transfer equilibrium with the environment can be established:

$$Q_{NPs} + Q_0 = Q_{loss} \quad (4)$$

Substituting Equation 2 and Equation 3 into Equation 4, the photothermal conversion efficiency ( $\eta$ ) can be determined:

$$\eta = \frac{hA(T_{\max} - T_0) - Q_0}{I(1 - 10^{-A_i})} \times 100\% \quad (5)$$

When the laser is shut down,  $Q_{NPs} + Q_0 = 0$ , and Equation 1 changed to:

$$Q_{loss} = -\sum_{i=1}^n m_i C_{p,i} \frac{dT}{dt} = hA(T_{\max} - T_0) \quad (6)$$

we herein introduce  $\vartheta$ , which is defined:

$$\theta = T_{\max} - T_0 \quad (7)$$

Substituting Equation 7 into Equation 6:

$$dt = -\frac{\sum_{i=1}^n m_i C_{p,i}}{hA} \frac{d\theta}{\theta} \quad (8)$$

Integrating Equation 8 gives the expression:

$$t = -\frac{\sum_{i=1}^n m_i C_{p,i}}{hA} \ln\theta + b \quad (9)$$

Therefore,  $hA$  can be determined by applying the linear time data from the cooling period vs  $-\ln\vartheta$  (Figure 2C and D).

$$hA = \frac{m_s C_s + m_w C_w}{k} \quad (10)$$

Where the  $m_s$  of the sample solution is 1.0 g, and its  $C_s$  value is approximated to be  $4.2 \text{ J g}^{-1} \text{ K}^{-1}$ . The  $m_w$  of quartz cell is 6.08 g, and its  $C_w$  value is approximated to be  $0.839 \text{ J g}^{-1} \text{ K}^{-1}$ .  $k$  is the slope of the linear Equation in Figure 2D, which is 280.

$$hA = \frac{1.0 \times 4.2 + 6.08 \times 0.839}{280} = 0.0332 \quad (11)$$

Finally, substituting  $hA$  value into Equation 5, the  $\eta$  can be calculated as following:

$$\begin{aligned} \eta &= \frac{hA(T_{\max} - T_0) - Q_0}{I(1 - 10^{-A_i})} \times 100\% \quad (5) \\ &= \frac{0.0332 \times (54.3 - 28.3) - 0.02}{2.0 \times (1 - 10^{-1.1})} \times 100\% \\ &= 45.7\% \end{aligned}$$

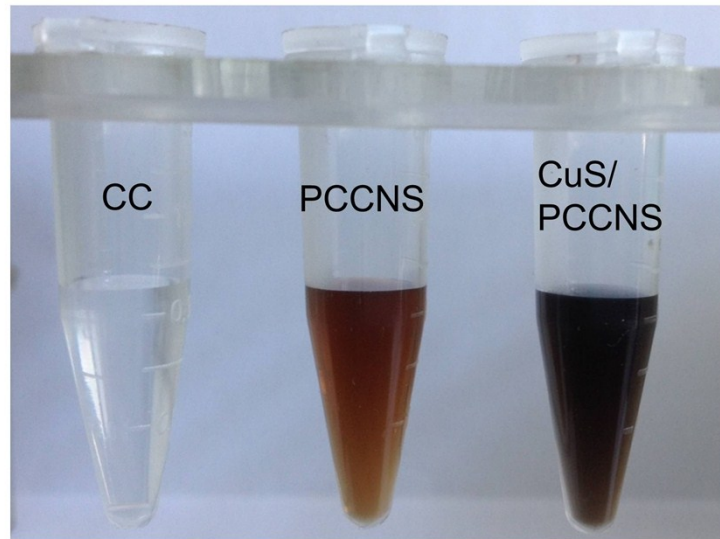


Fig. S1 Photos of CC, PCCNS and CuS/PCCNS nanocomposites in water solution.

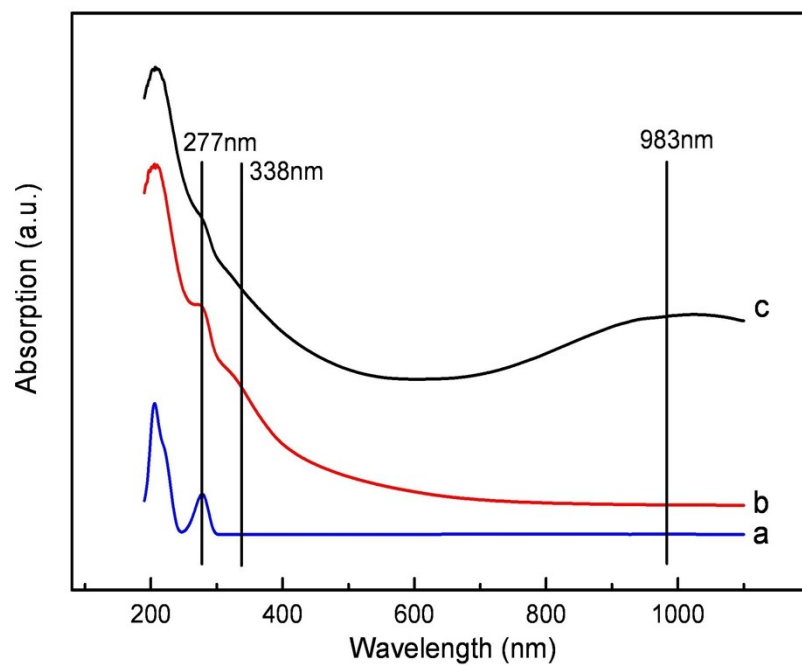


Fig. S2 UV-vis absorption spectra of CC (a), PCCNS (b) and CuS/PCCNS nanocomposites (c).

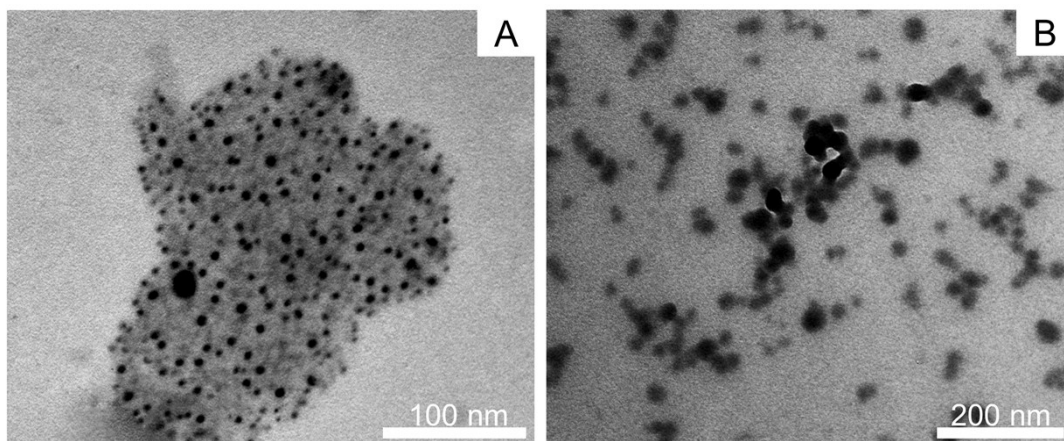


Fig. S3 TEM images of polycatechol after polymerization reaction at (A) 10°C and (B) 30°C.

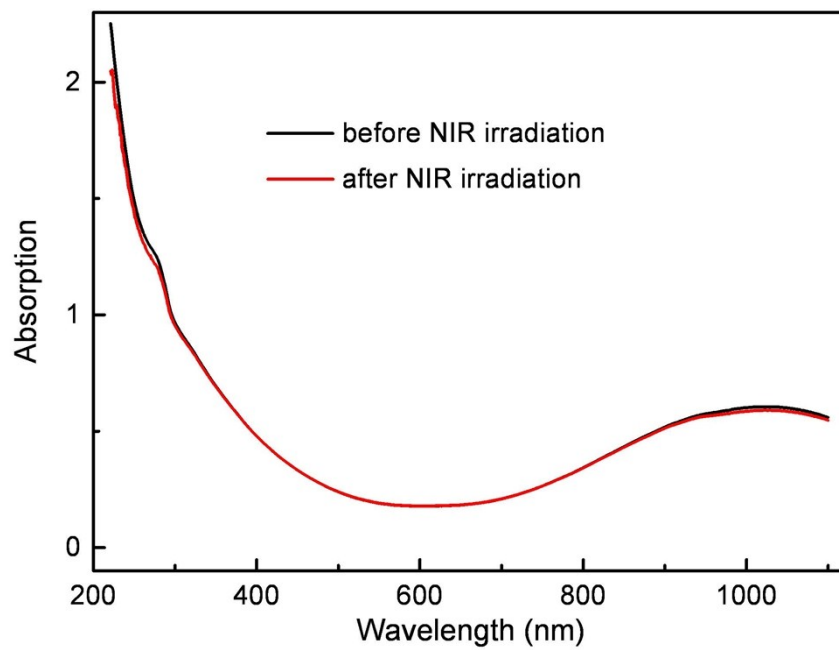


Fig. S4 UV-vis absorption spectra of CuS/PCCNS nanocomposites before (black line) and after (red line) NIR irradiation.

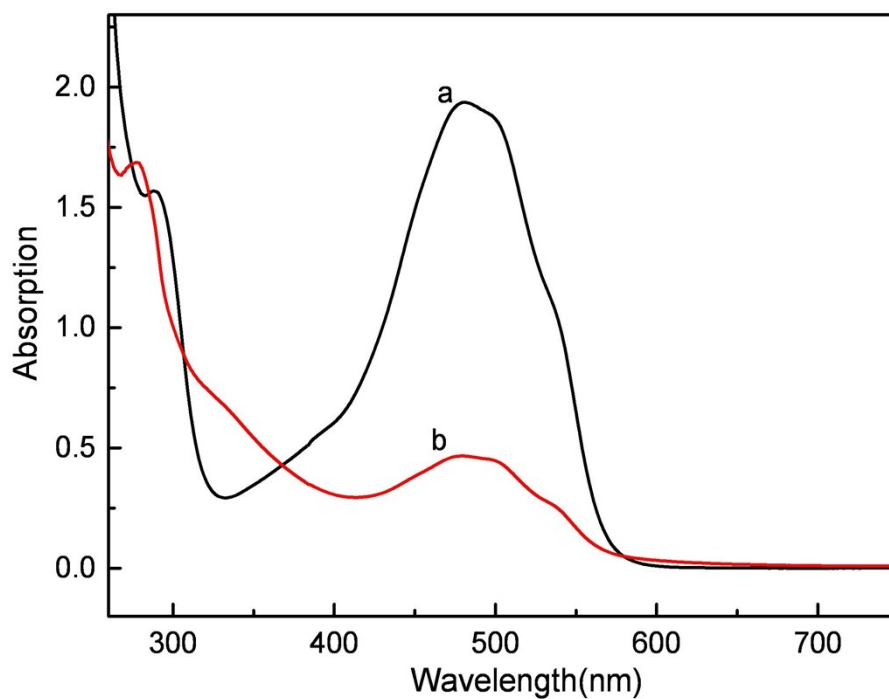


Fig. S5 UV-vis of before (a) and after (b) Dox loading onto CuS/PCCNS nanocomposites in aqueous solution.



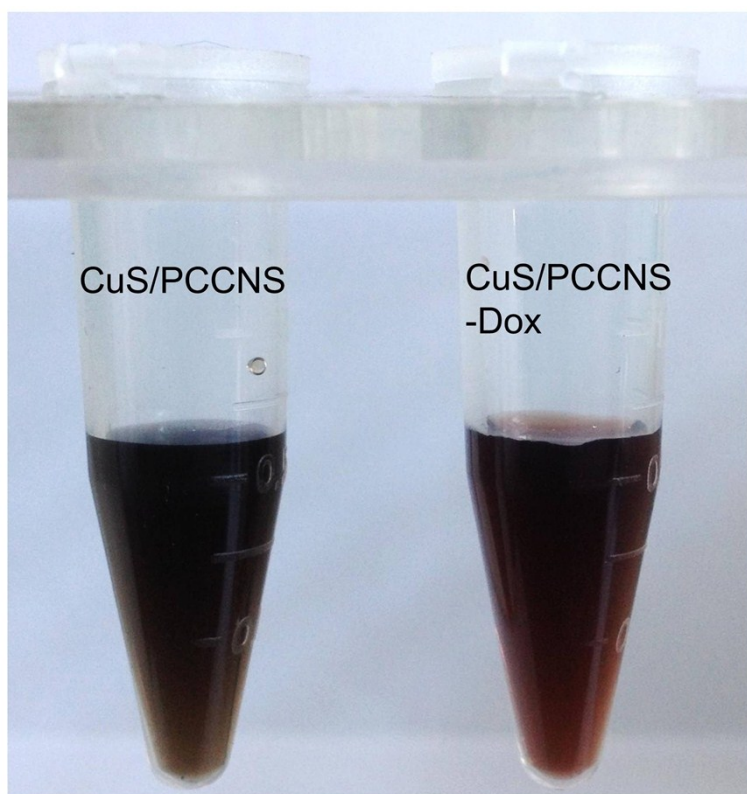


Fig. S6 Photos of CuS/PCCNS and CuS/PCCNS-Dox nanocomposites dispersed in water.

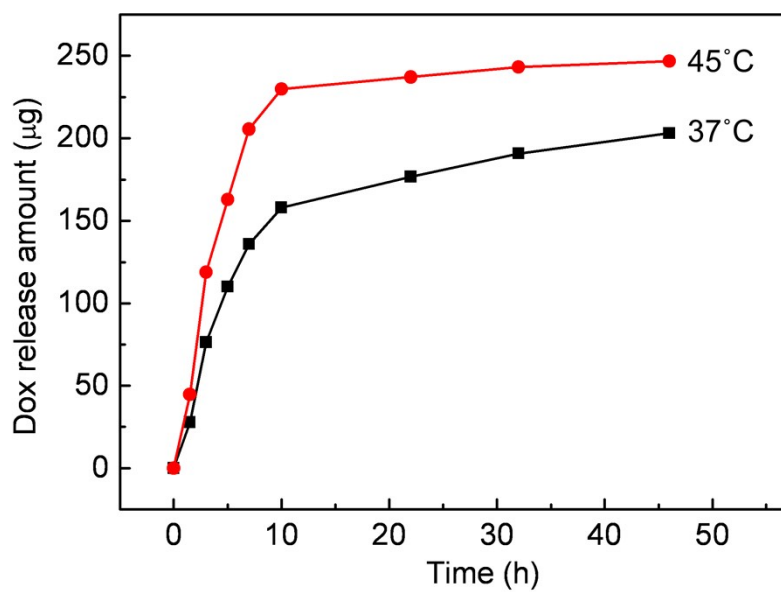


Fig. S7 Dox-release profiles from CuS/PCCNS-Dox nanocomposites at 37°C and 45°C in PBS at pH 5.5.

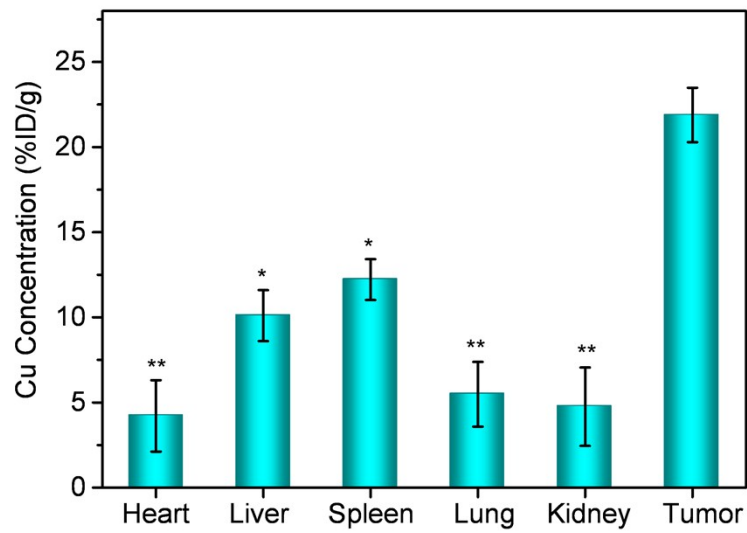


Fig. S8 Biodistribution of CuS/PCCNS after intratumoral injection into U14 tumor-bearing mice for 24 h as determined Cu concentrations by ICP-MS in various organs and tumor. The results were shown as mean values  $\pm$  standard deviation (SD, n = 3). P values were calculated by the methodology of Student's t test (\* $p < 0.05$ , \*\* $p < 0.01$ , or \*\*\* $p < 0.001$ ).