Supporting Information

Au-Cu_{2-x}Se Heterogeneous Nanocrystals for Efficient Photothermal Heating for Cancer Therapy

Dewei Zhu[a,b], Maixian Liu[b,c], Xin Liu[a], Yang Liu[a,b], Paras N. Prasad[b,c], Mark T. Swihart[a,b*]*

[a] *Department of Chemical and Biological Engineering,* [b]*Institute for Lasers, Photonics, and Biophotonics, and* [c]*Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York, 14260-4200, USA.*

[*] Corresponding authors: swihart@buffalo.edu (MTS), pnprasad@buffalo.edu (PNP)

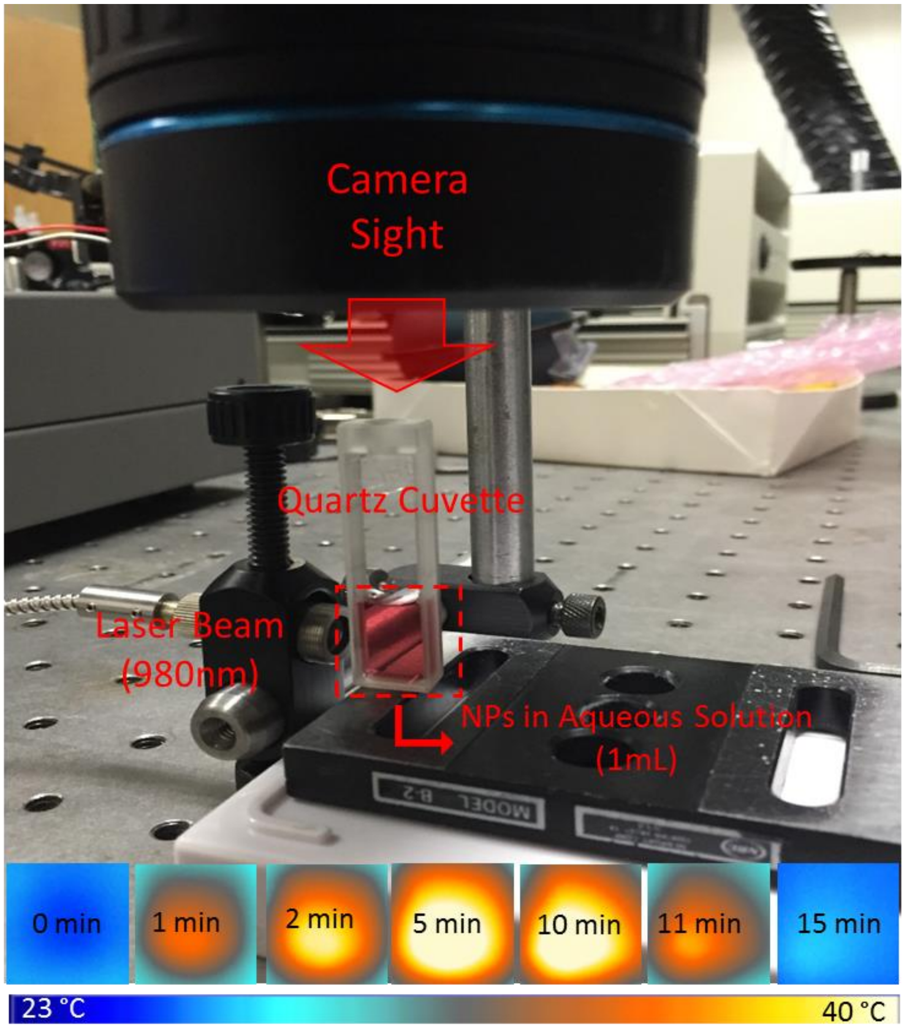

Fig. S1 Annotated photograph of the system for photo-thermal heating experiments.

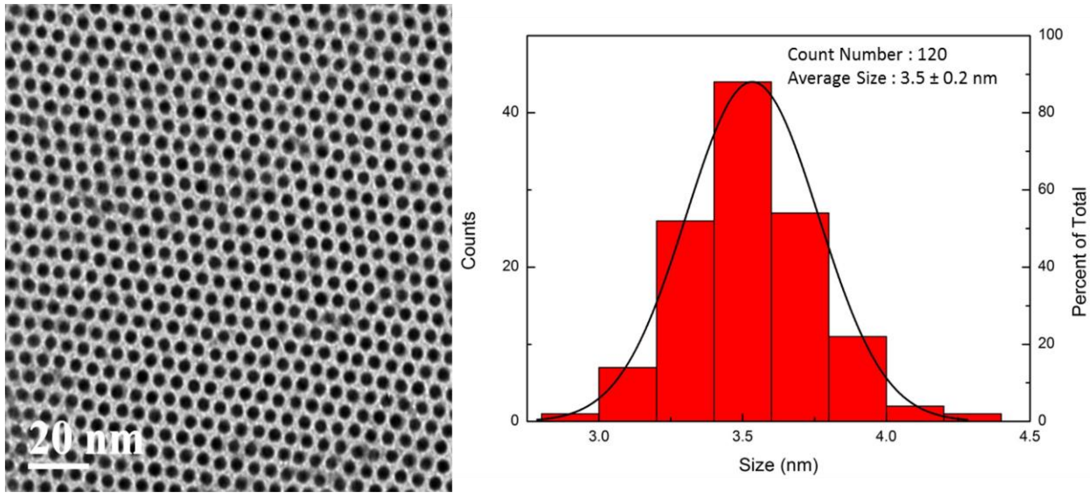

Fig. S2 TEM images and size distribution of Au Nanoseeds.

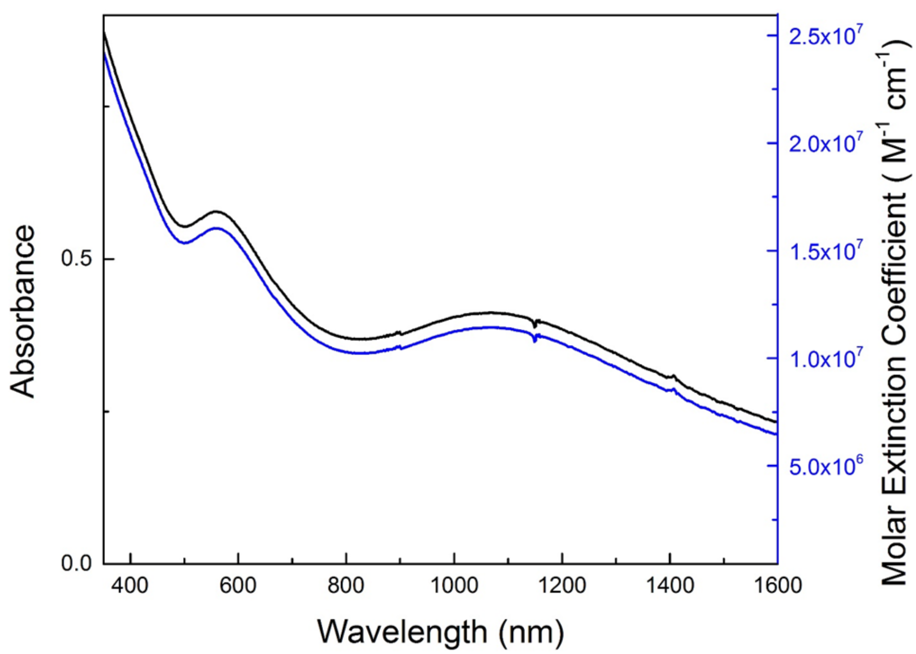

Fig. S3 Absorbance (black) and molar extinction coefficient (blue) for Au-$Cu_{2-x}Se$ NCs in chloroform solution plotted against wavelength.

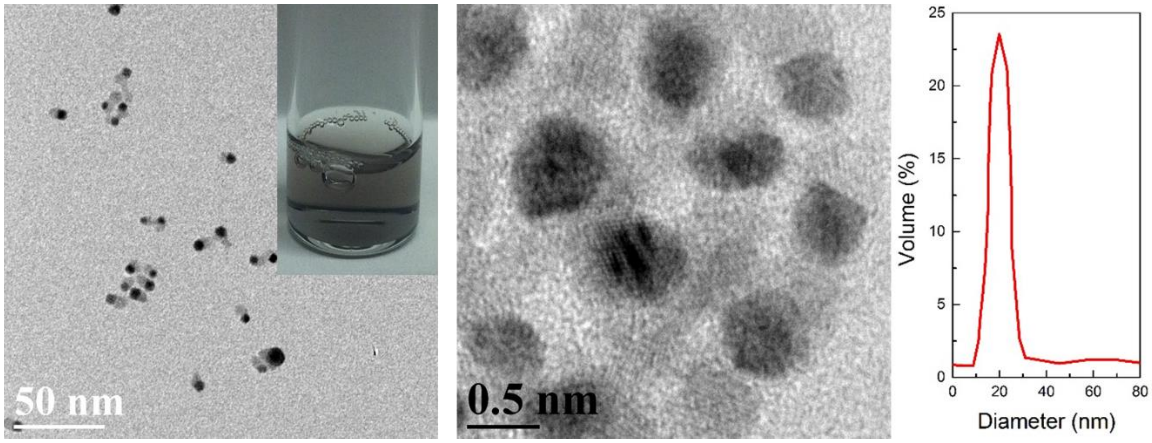

Fig. S4 TEM and HR TEM of PEGylated Au-$Cu_{2-x}Se$ NPs in water and a photograph of the aqueous dispersion. The inset shows results of dynamic light scattering, showing that the hydrodynamic diameter of Au-$Cu_{2-x}Se$ NPs is about 20 nm.

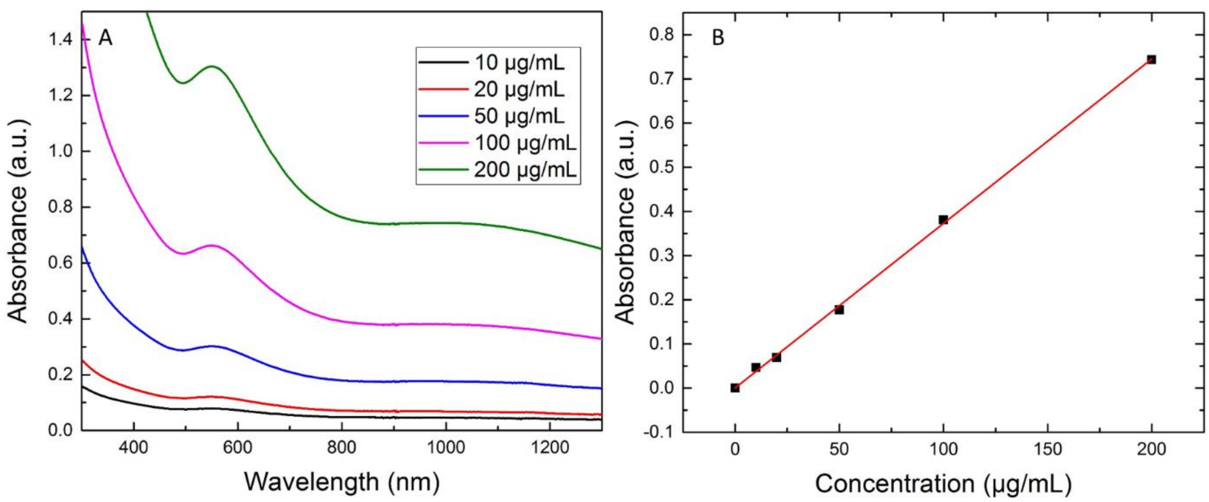

Fig. S5 (A) Absorbance spectra of PEGylated Au-$Cu_{2-x}Se$ nanocrystals dispersed in HPLC water at concentrations of 10, 20, 50, 100 and 200 μg/mL. (B) Plot of absorbance of Au-$Cu_{2-x}Se$ NCs dispersions at 980 nm versus concentration, used for obtaining the extinction coefficient.

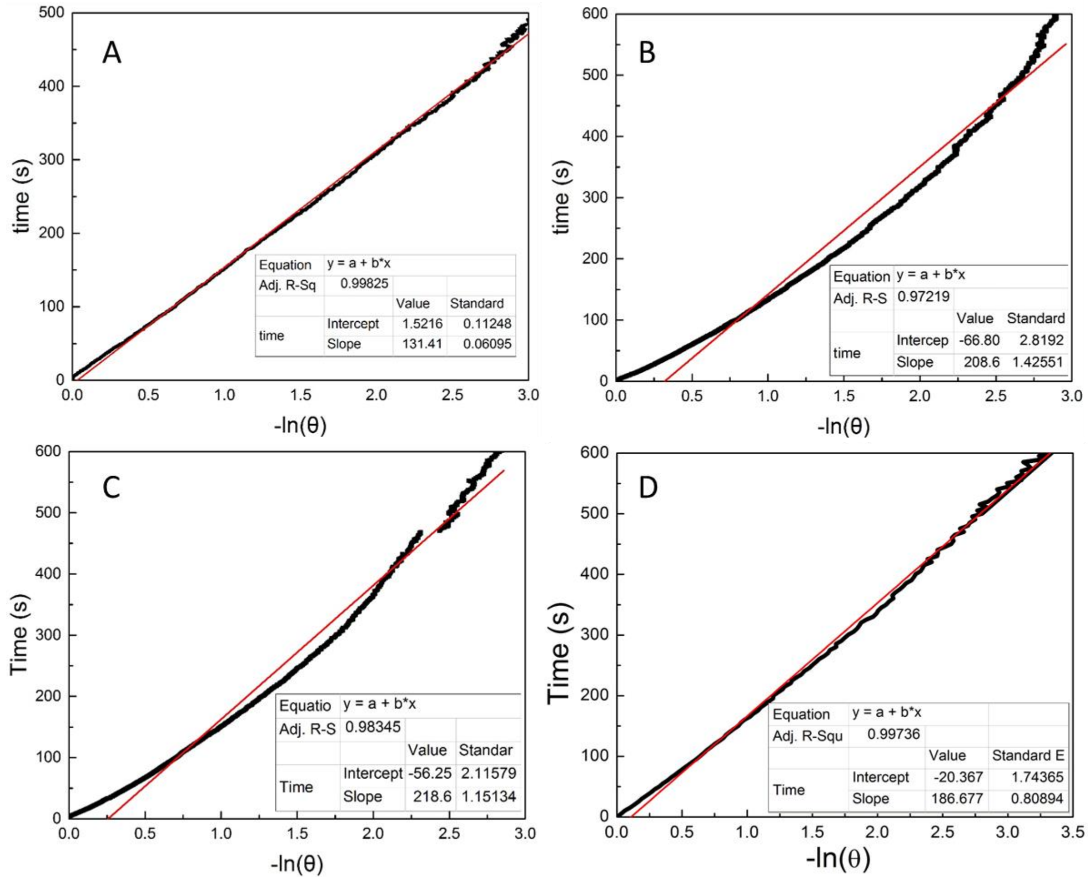

Fig. S6 Plot of time versus negative natural logarithm of the temperature increment for the cooling cycle (after 10 min heating) for Au-$Cu_{2-x}Se$ NCs (A), Au NRs (B), Au NPs (C) and $Cu_{2-x}Se$ (D) NPs each at a concentration of 200 µg/mL. The linear fit of the data points results in a half-life time τ_s (slope) as shown in the tables shown in the insets.

Sample	Element	Atomic (%)	Weight (%)
Au-$Cu_{2-x}Se$	Cu	56.2	41.3
	Se	29.9	27.2
	Au	14.0	31.5

Table S1 EDS analysis of Au, Cu, and Se composition in the heterogeneous nanoparticles (analysis excludes C and O).

Calculation of molar extinction coefficient

To compare the NIR photoabsorption capability of the Au-$Cu_{2-x}Se$ NCs with that of previously reported photothermal agents, such as gold nanorods and nanoshells, the extinction coefficient $\varepsilon(\lambda)$ of the Au-$Cu_{2-x}Se$ NCs, dispersed in chloroform, was calculated according to eq.1 [1]

$$A(\lambda) = \varepsilon(\lambda)LC \tag{1}$$

where $A(\lambda)$ is the absorbance at a wavelength λ, $\varepsilon(\lambda)$ is the molar extinction coefficient at a wavelength λ, L is the path length (1 cm), C (M) is the molar concentration of the nanocrystals. The molar concentration of the Au-$Cu_{2-x}Se$ NCs is calculated by eq. 2

$$\mathrm{C} = \frac{Mass\ ratio\ of\ Au\ in\ Au{-}Cu_{2-x}Se\ NCs \times C_{wt}}{\frac{Volume\ of\ Au\ nanoseeds}{Volume\ of\ Au\ unit\ cell} \times M_{Au} \times Atom\ number\ of\ Au\ in\ unit\ cell} \tag{2}$$

$$\text{Volume of Au nanoseeds} = \frac{1}{6}\pi d^3 \tag{3}$$

$$\text{Volume of Au unit cell} = abc \tag{4}$$

where the mass ratio of Au in Au-$Cu_{2-x}Se$ NCs is determined from EDS analysis as 31.5%, C_{wt} is the mass concentration of the Au-$Cu_{2-x}Se$ NC dispersion, the volume of Au nanoseeds is calculated by eq. 3, d is the diameter of gold nanoseeds (3.5 nm), the volume of the Au unit cell is calculated by eq. 4, a=b=c=0.407 nm, M_{Au} is the molar mass of gold (197 g/mol), and the FCC unit cell of gold contains 4 Au atoms. The calculation showed that the molar extinction coefficient of Au-$Cu_{2-x}Se$ NCs in chloroform was 1.1×10^7 M^{-1} cm^{-1} at 980 nm. For the Au nanorods (r = 10 nm, L = 75 nm) and nanoparticles (d = 10 nm), the mass ratio of Au is 1. The volume of Au NRs is $\pi r^2 L$ and the volume of Au NPs is $\pi d^3/6$.

Reference:

1. Zhao, Y.; Pan, H.; Lou, Y.; Qiu, X.; Zhu, J.; Burda, C. J. Am. Chem. Soc. 2009, 131, 4253–4261.