## PEGylated Cu<sub>3</sub>BiS<sub>3</sub> Hollow Nanospheres as a New Photothermal Agent for 980 nm-Laser-Driven Photothermochemotherapy and Contrast Agent for X-Ray Computed Tomography Imaging

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Fig. S1 EDS spectrum of Cu<sub>3</sub>BiS<sub>3</sub> hollow nanospheres. Ni grid was used as the sample support.



**Fig. S2** XPS spectra of Cu<sub>3</sub>BiS<sub>3</sub> hollow nanospheres: (a) survey spectrum, (b) core level spectrum of Bi 4f, (c) core level spectrum of Cu 2p, and (d) core level spectrum of S 2p.



Fig. S3 FT-IR spectrum of PEGylated Cu<sub>3</sub>BiS<sub>3</sub> hollow nanospheres.



Fig. S4 TG curve of PEGylated Cu<sub>3</sub>BiS<sub>3</sub> hollow nanospheres.



**Fig. S5** The digital photo of PEGylated Cu<sub>3</sub>BiS<sub>3</sub> hollow nanospheres dispersed in different solvents (a). The digital photo of Cu<sub>3</sub>BiS<sub>3</sub> colloid aqueous solution after 30 minutes' standing (b).



**Fig. S6** UV-vis absorption spectra of various concentrations of PEGylated Cu<sub>3</sub>BiS<sub>3</sub> HNSs (a). The corresponding Beer's law plot at 980 nm (b).

Synthesis of Cu<sub>9</sub>S<sub>5</sub> and CuS flower-like superstructures. In a typical process for the synthesis of Cu<sub>9</sub>S<sub>5</sub> superstructures, 1 mmol of CuCl<sub>2</sub> were dispersed into 55 mL of ethylene glycol under vigorous stirring. The solution was refluxed at 200 °C for 1 h. Then mixed solvents of PEG 2000 (2 mL) and ethylene glycol (5 mL) containing 0.5 mmol of thioacetamide were quickly injected into the above-mentioned solution. The solution was refluxed at 200 °C for another 1.5 h. The final precipitate was separated by centrifugation and washed with deionized water and absolute ethanol for several times. Then the products were dried at 60 °C for 4 h under vacuum for further characterizations. As for the synthesis of CuS superstructure, keeping all other conditions unchanged except that the dosage of thioacetamide was increased to 1 mmol.



Fig. S7 XRD patterns of the as-synthesized products.



Fig. S8 FESEM image of the as-synthesized Cu<sub>9</sub>S<sub>5</sub>.



Fig. S9 FESEM image of the as-synthesized CuS.



Fig. S10 UV-vis absorption spectra of the as-synthesized  $Cu_9S_5$  and CuS flower-like superstructures .

From the results of XRD patterns and UV-vis absorption spectra analyses and FESEM observations of the samples, it could be concluded that the obtained products were flower-like  $Cu_9S_5$  and CuS superstructures, respectively.



Fig. S11 Temperature profiles of  $Cu_3BiS_3$  HNSs,  $Cu_9S_5$  and CuS superstructures aqueous solution under irradiation of a 980 nm laser.



**Fig. S12** Temperature changes of  $Cu_3BiS_3$  HNSs aqueous solution (100 µg/mg) over five laser on/off cycles under NIR laser irradiation.



Fig. S13  $N_2$  adsorption and desorption isotherm (a) and pore-size distribution curve (b) of PEGylated  $Cu_3BiS_3$  HNSs.



Fig. S14 Zeta potential of the sample measured in neutral water.



**Fig. S15** In vivo CT images of Balb/c mice bearing melanoma tumor: without injection of the solution of the PEGylated Cu<sub>3</sub>BiS<sub>3</sub> HNSs (a) and with intratumoral injection of the solution of the PEGylated Cu<sub>3</sub>BiS<sub>3</sub> HNSs (b).