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Supplementary Information

SnS Nanosheets for Efficient Photothermal Therapy

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1 Synthesis of SnS nanosheets

SnS nanosheets were prepared by a modified solvothermal route and subsequent exfoliation by an ultrasonication method.[1] In a typical procedure, $SnCl_2 \cdot 2H_2O$ (2 mmol), NaOH (25 mmol), and thiourea (4 mmol) were dissolved in distilled water (50 mL). The resulting solution was then transferred to a poly(tetrafluoroethylene) (Teflon)-lined stainless steel autoclave, sealed, and treated at 220 ^{o}C for 6 h. Bulk SnS was collected by centrifuging the mixture, washed with distilled water and absolute ethanol many times, and then dried in vacuum overnight for later use. Subsequently, bulk SnS powders (40 mg), distilled water (20 mL) and ethanol (20 mL) were added into a flask. The flask was then sealed and sonicated at an ultrasonic machine for 12 h. The dispersions were centrifuged at 700 rpm for 20 min. After centrifugation, the supernatant was collected and centrifuged at 1200 rpm for 10 min. For PEG coating, 50 mg of SnS nanosheets dispersed in 10 mL water was mixed with 50 mg SH-PEG. After stirring overnight, excess SH-PEG molecules were removed by centrifugation at 14000 rpm for 10 min and repeated water washing.

2 Characterization

The morphology, size, and microstructure of the SnS nanosheets were determined by HRTEM (JEOL JEM-2010F). XRD measurements were performed on a Bruker D4 X-ray diffractometer using Cu K α radiation (λ = 0.15418 nm). UV-vis absorption spectra were measured on a Shimadzu UV-2550 UV-visible-NIR spectrophotometer

using quartz cuvettes with an optical path of 1 cm. Content of tin irons released (from SnS) in the solution was determined by a Leeman Laboratories Prodigy high-dispersion inductively coupled plasma atomic emission spectroscopy (ICP-AES).

To measure the photothermal conversion performances of SnS nanosheets and bulk SnS, radiation from an 808 nm laser was sent through an aqueous dispersion (0.1 mL) with different concentrations (0 - 50 ppm); the light source was a 808 nm-wavelength semiconductor laser device (Shanghai Xilong Optoelectronics Technology Co. Ltd., China) whose power could be adjusted externally (0-2 W). The output power was independently calibrated using a hand-held optical power meter (Newport model 1918-C, CA, USA) and was found to be ~ 0.34 W for a spot size of ~ 0.34 cm^2. A thermocouple with an accuracy of ± 0.1 ^oC was inserted into the aqueous dispersion at such a position that the direct irradiation of the laser on the probe was avoided. The temperature was recorded by an online type thermocouple thermometer (DT-8891E Shenzhen Everbest Machinery Industry Co., Ltd., China) every 5 s. For comparison, the photothermal conversion efficiency of bulk SnS was also measured using a similar method.

To investigate the photostability of the SnS nanosheets, 25 ppm SnS nanosheets solution (3 mL) were irradiated with an 808 nm laser (2 W) for 5 min (LASER ON), followed by naturally cooling without irradiation for 18 min (LASER OFF). The temperature was measured every 5 s. This cycle repeated for four times.

3 In vitro photothermal therapy of cancer cells with SnS nanocrystals

SK-OV-3 cells were seeded into a 24-well plate at a density of 10, 000 cells/mL in RPMI-1640 culture medium at 37 °C in the presence of 5% CO_2 for 24 h prior to treatment. After incubation, the cell medium was removed, and the cells were washed with PBS buffer solution for three times. 100 μL of the PEGylated SnS nanosheets dispersed in a PBS solution was then added into the wells at gradient concentrations (0, 5, 10, 25, 50, and 100 ppm). After incubation for another 12 h, SnS nanosheets in the cell medium were washed away with PBS solution, the cells were then irradiated for 0 min and 5 min, respectively, using a 808 nm laser with an output power density of 1 Wcm^{-2} (~ 0.34 W for a spot size of ~ 0.34 cm^2). Cell viability was measured using the CCK8 assay. All of the tests were independently performed 3 times.

After laser irradiation, the SK-OV-3 cells were also stained with calcein acetoxymethyl ester (calcein AM, 1μM, Molecular Probes, USA) to observe the distribution of live cells through a fluorescence microscope (Olympus, Japan). Fluorescence images of more than three different areas in each sample were obtained.

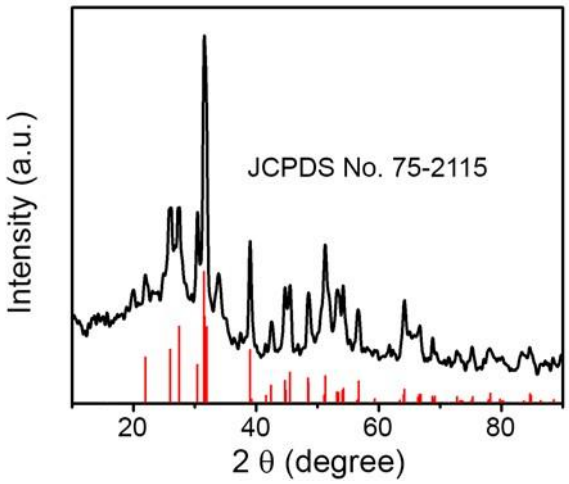

Fig. S1 XRD patterns of the as-prepared bulk SnS (black line) and the standard SnS powders (red bar) on a JCPDS card (no. 75-2115).

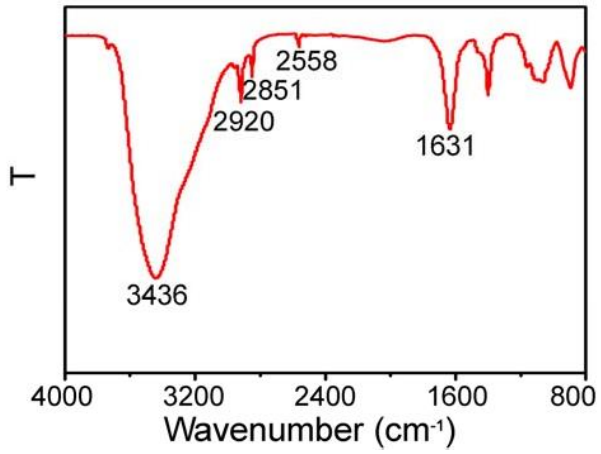

Figure S2. FTIR spectrum of the SnS nanosheets.

This FTIR spectrum of the SnS nanosheets is shown in Fig. S2. It consists of several bands, i.e., a broad band at 3436 cm^{-1} is due to OH stretching,[2] the bands at 2920 cm^{-1} and 2851 cm^{-1} correspond to CH_2 asymmetric stretching and symmetric stretching, respectively,[3] the band at 2558 cm^{-1} is attributed to SH stretching,[4] and the band at 1631 cm^{-1} is assigned to C=O symmetric stretching. [2, 3]

Based on the above results, it is concluded that the SH-PEG has been successfully coated on SnS nanosheets.

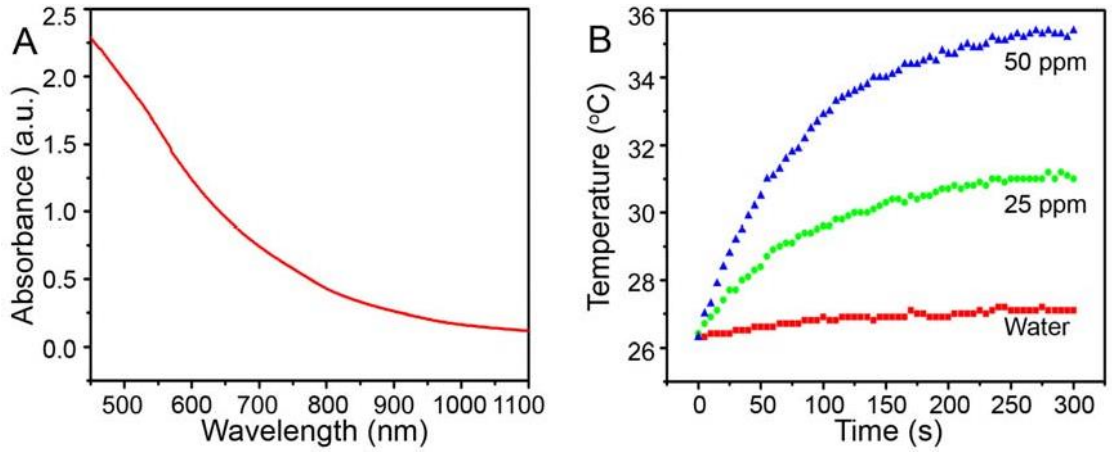

Fig. S3 (A) UV-vis absorbance spectrum for the aqueous dispersion of 50 ppm SnS nanosheets. The extinction coefficient of bulk SnS was calculated to be 8.2 Lg^{-1} cm^{-1}. (B) Temperature elevation of the aqueous dispersion of bulk SnS with a concentration of 25 ppm and 50 ppm under an irradiation of 808 nm laser at a power density of 1.0 W cm^{-2}.

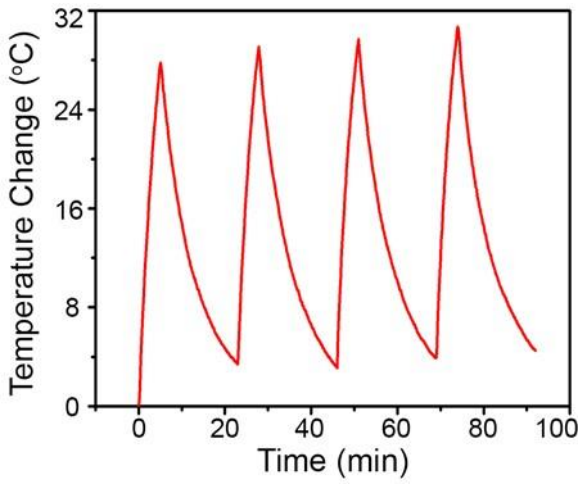

Fig. S4 Temperature elevation of SnS nanosheets over four LASER ON/OFF cycles of NIR laser irradiation.

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