Supporting Information

Black Phosphorus analogue Tin Sulfide nanosheets: Synthesis and Application as Near-Infrared Photothermal Agents and Drug Delivery Platforms for Cancer Therapy

Zhongjian Xie [a,1], Dou Wang [b,c,1], Taojian Fan [a1], Chenyang Xing [a], Zhongjun Li [a], Wei Tao [d,*], Liping Liu [b,*], Shiyun Bao [b,*], Dianyuan Fan [a], and Han Zhang [a,*]

1. Stability of SnS NSs

To characterize the crystal structure of exfoliated SnS NSs, Figure S1 shows the XRD pattern of bulk SnS and exfoliated SnS NSs. It was found that there was no destruction of crystal structure during exfoliation process. The stability of SnS NSs in deionized water was characterized in 10 days (Figure S2). The absorbance of SnS NSs showed a slight decrease, which indicated that the SnS NSs were relatively stable. Even though the SnS NSs were stable, they easily aggregate in deionized water. Before the measurement, the dispersion was stirred to avoid the aggregation of SnS NSs.

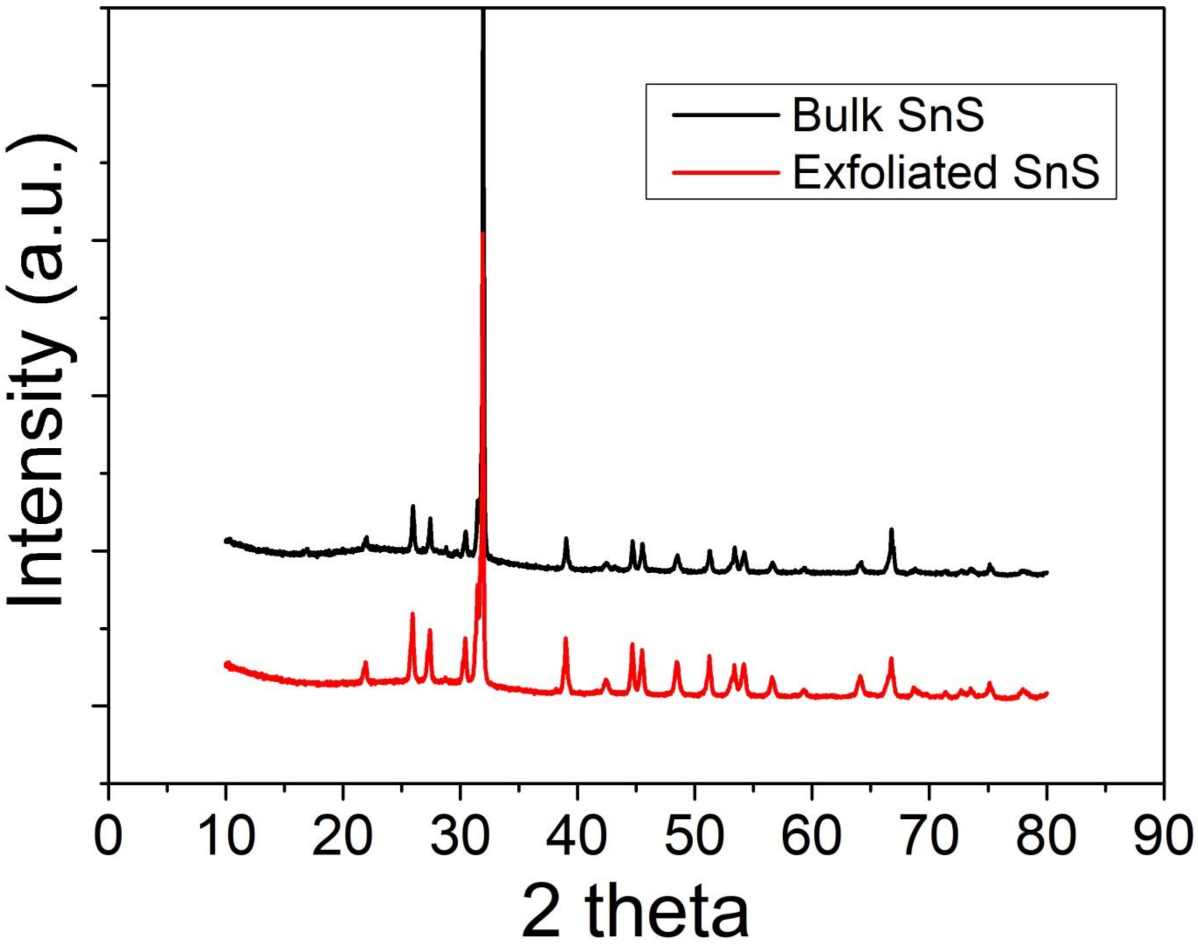

Figure S 1. The XRD pattern of bulk SnS and exfoliated SnS NSs.

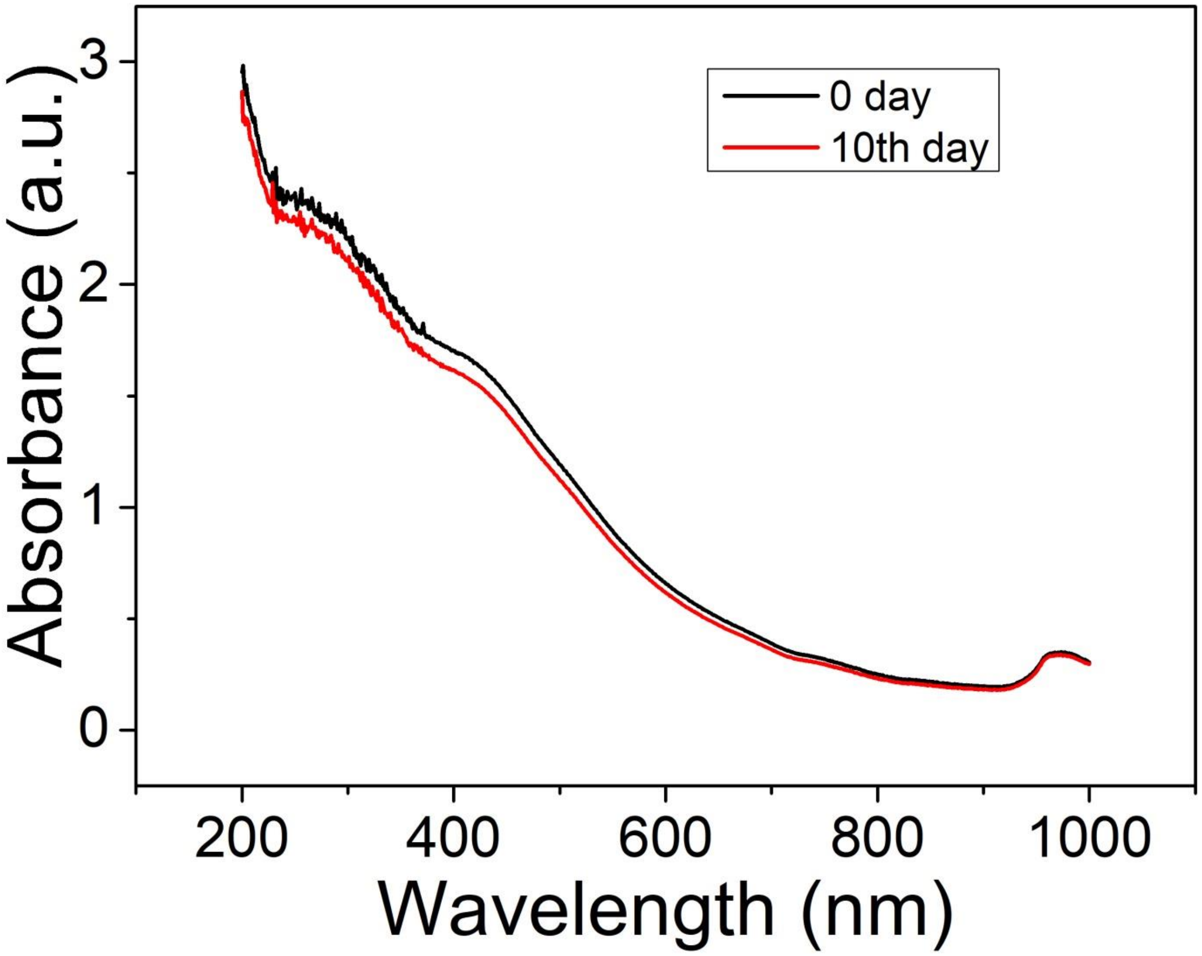

Figure S 2. The stability of naked SnS NSs without surface modification in deionized water.

2. Photodegradation of SnS NSs

In Figure S3, the low laser power and high laser power were both used for one point of the SnS sample. It was found that a new peak at 307 cm^{-1} appeared. This peak confirmed the presence of SnS_2.[1] It indicated that the photo-degradation property of SnS NSs.

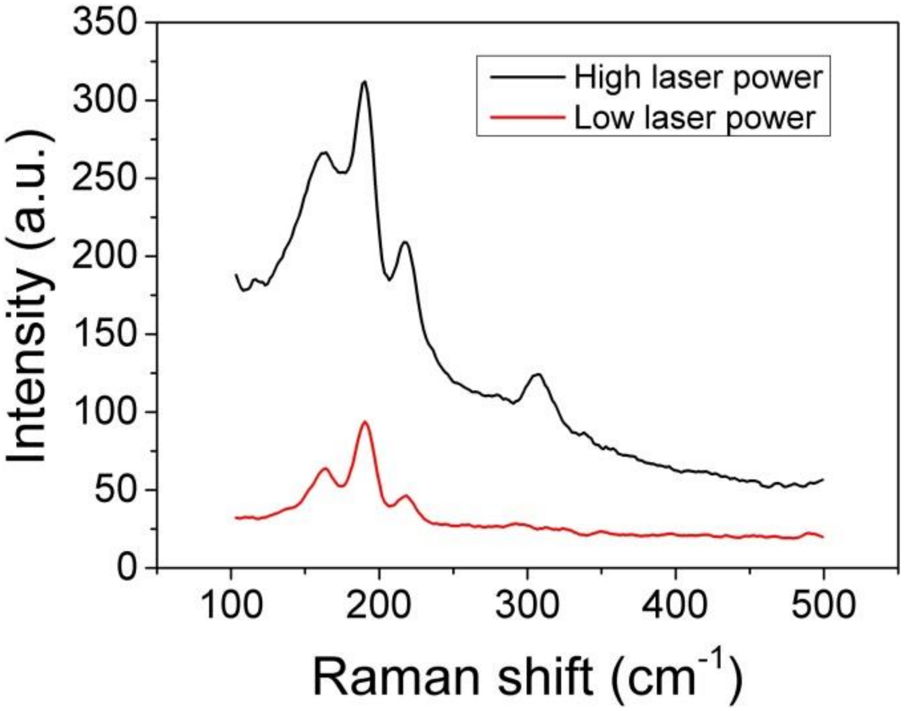

Figure S 3 Photodegradation of SnS NSs at strong laser power.

3. FITC-PEG-FA coating on SnS NSs

To obtain the *in vitro* cell imaging, the SnS-FITC-PEG-FA NSs were prepared. 4 mg of FITC-PEG-FA was dispersed in 4 ml of SnS NSs/H_2O solution at SnS concentration of 100 ppm. The mixture underwent bath sonication for 5 min and stirring for 4 h. Then, in order to remove the excess FITC-PEG-FA molecules, the resulting mixture was centrifuged in Amicon tubes (MWCO 100kDa; Millipore) at 4000 rpm (10 °C) for 30 min, and was washed 2 times using the same method. The pure SnS-FITC-PEG-FA NSs sample was re-suspended in deionized water and stored under 4 °C for further use.

In Figure S4 was shown the absorbance of FITC-PEG-FA. The peak at 275 nm indicated the absorbance of FA and the peak at 450 nm indicated the absorbance of FITC. The whole absorbance spectra from 250 nm to 1100 nm decreased as stirring time increased. After 4h's stirring, the absorbance was lower than the pure SnS NSs dispersion. It was because of the encage effect of FITC-PEG-FA on SnS NSs.

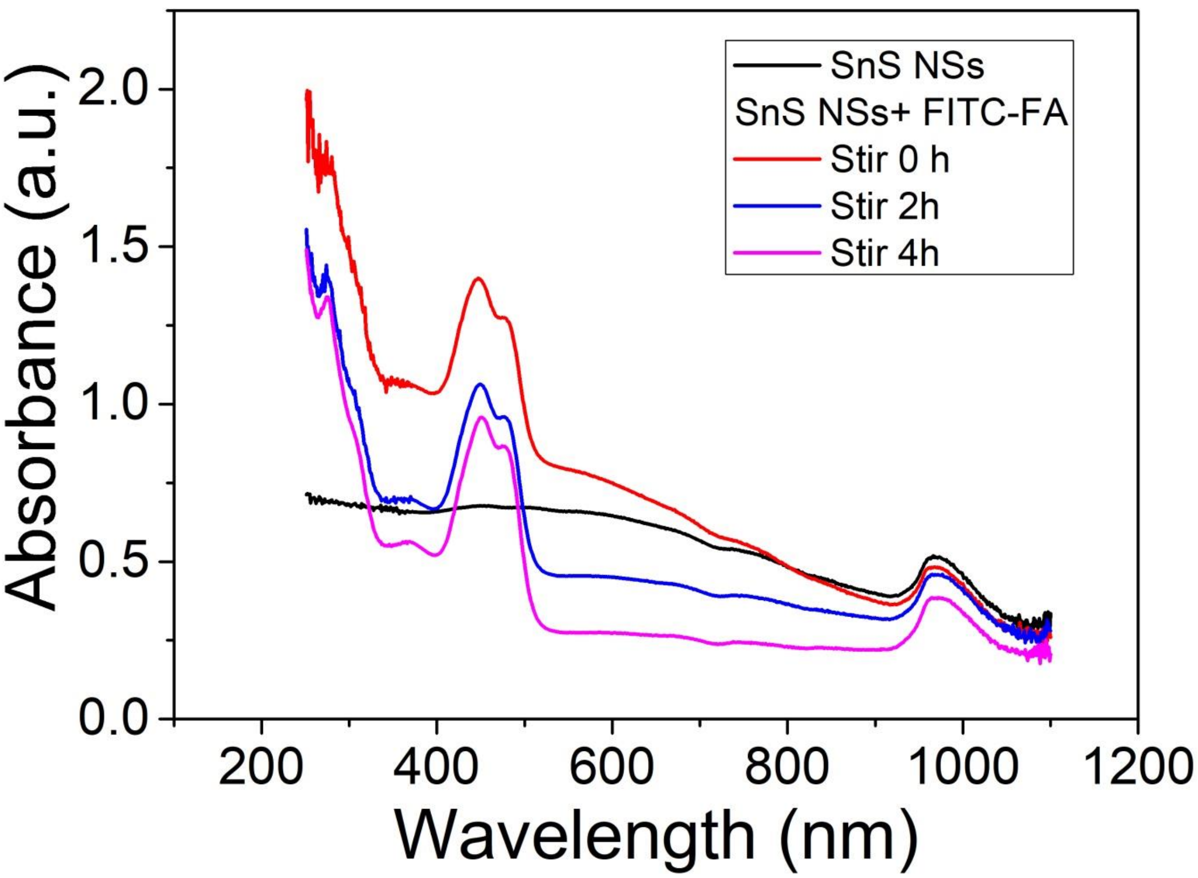

Figure S 4 Loading process of FITC-PEG-FA on SnS NSs.

The fluorescence of FITC coating of SnS NSs was then measured. In Figure S5, the fluorescence of FITC coating of SnS NSs can be excited under 480 nm and 490 nm and the emission peak occurs at 520 nm.

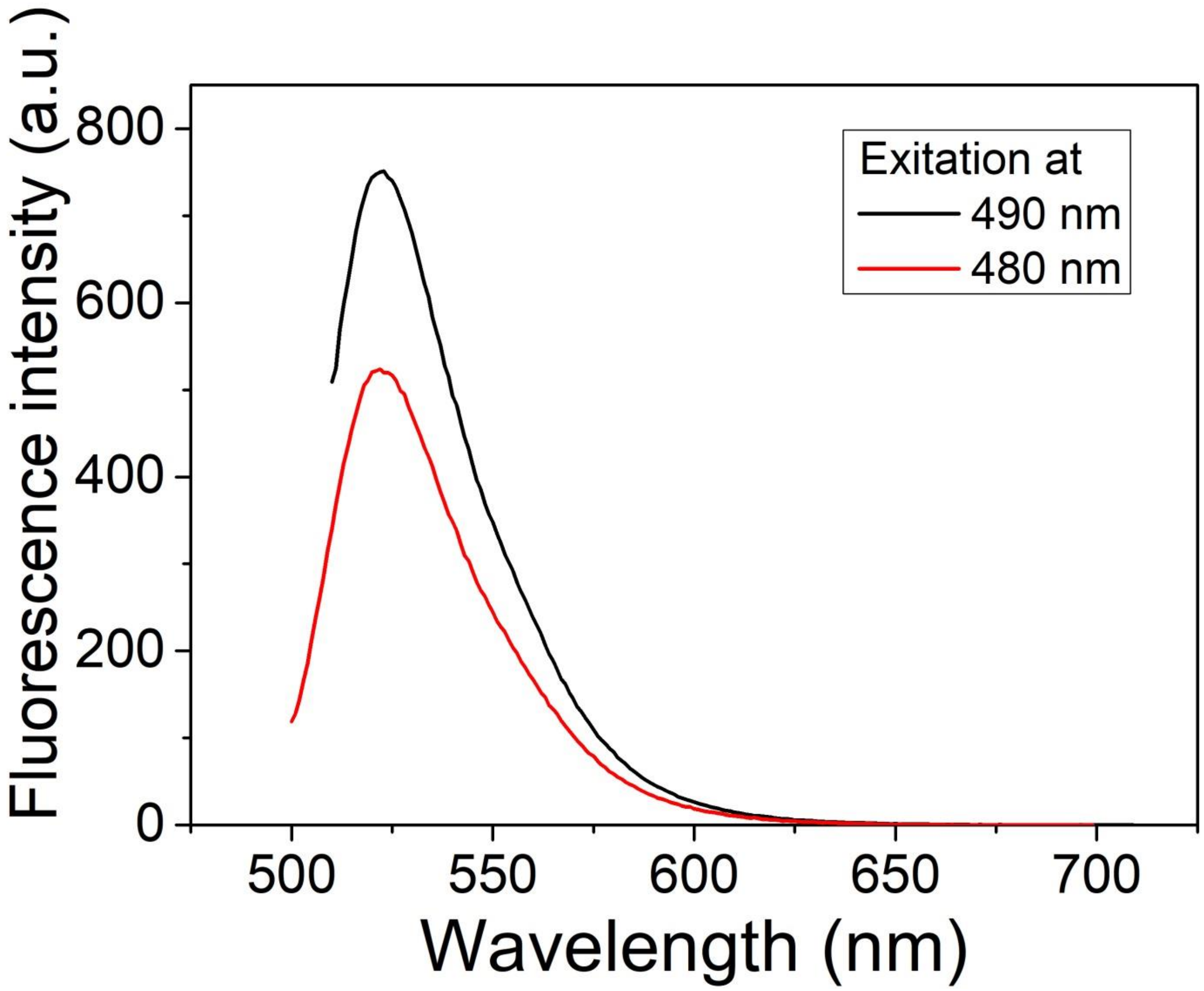

Figure S 5 Fluorescence of FITC coating of SnS NSs excited at 480 nm and 490 nm respectively.

4. NIR Laser-Induced Heat Conversion

The photothermal experiment was measured on a custom setup. 1 mL of the sample was contained in a 1 cm path length quartz cuvette. A fiber-coupled continuous semiconductor diode laser (808 nm, LSR808H, Lasever Inc. Jiangsu, China) provided the laser source. An infrared thermal imaging camera (FLIR E-60) was used to monitor the temperature change.

Furthermore, the photothermal conversion efficiency (η) of SnS NSs was measured and calculated according to previous reported method.[2] It was calculated as follows,

$$\eta = \frac{hA\Delta T_{\max} - Q_s}{I(1-10^{A_{808}})}$$

Where h is the coefficient of heat transfer, A is surface area of container, ΔT_{max} is the maximum temperature change of the sample, I is the incident laser power, A_{808} is the absorbance of the sample at 808 nm, and Q_s is the heat produced by the water upon laser. According to this equation, the η value of SnS NSs was determined to be 39.3% (Figure S6).

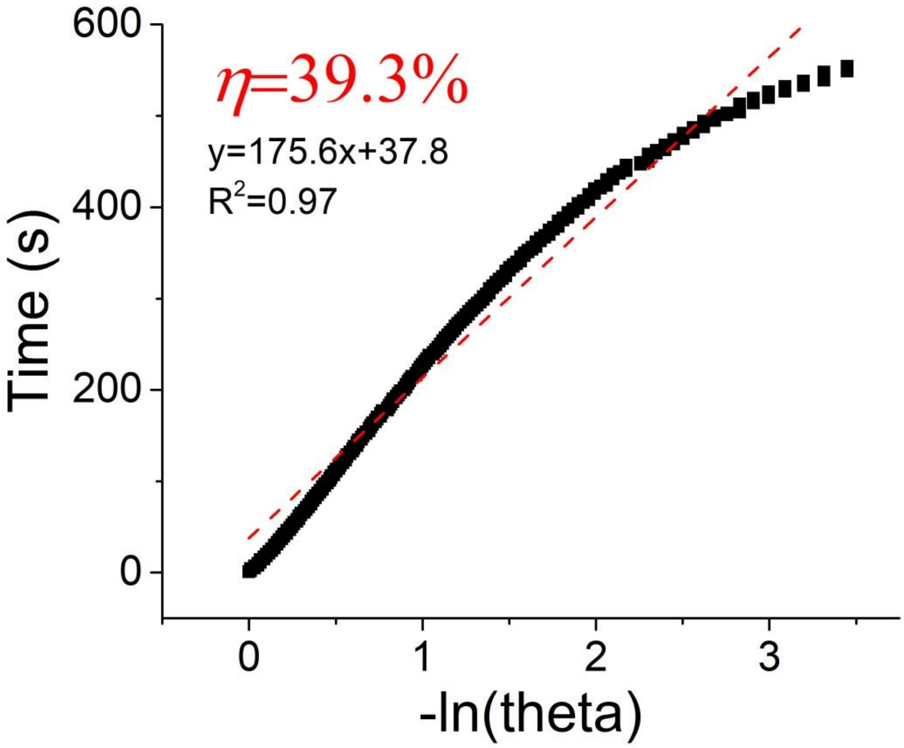

Figure S 6 Linear fitting between time and –ln(theta) for caculating PTCE.

5. Preparation of theranostic delivery platform based on SnS NSs

To measure the loading ratio of DOX on SnS NSs, the absorbance and fluorescence of DOX should be characterized firstly. Figure S7 showed the absorbance and fluorescence of DOX at different concentrations. It was found that the absorbance increased as the concentration increased and a linear relation between absorbance at 482 nm and DOX concentration can be obtained (Figure S7b). For fluorescence, it first increased and then decreased as DOX concentration increased. The maximum fluorescence occurred at DOX concentration of 25-50 ppm.

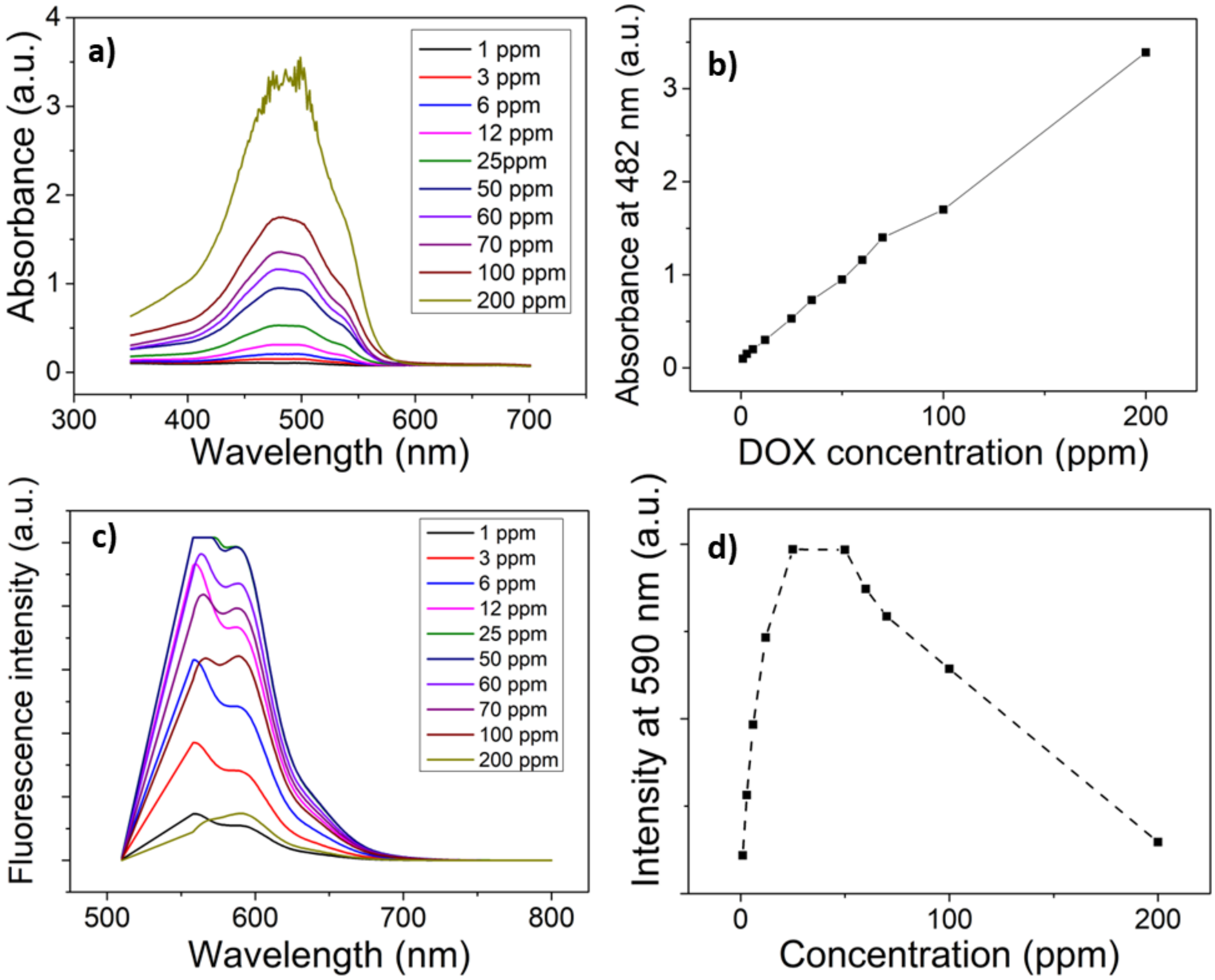

Figure S 7 a) Absorbance spectra of DOX at different concentrations. b) Normalized absorbance at wavelength = 482 nm. c) Fluorescence spectra of DOX at excitation wavelength of 482 nm for different concentrations. d) Normalized fluorescence spectra at wavelength = 590 nm.

Drug loading efficiency was determined by using UV-Vis spectra and fluorescence spectra. After stirring 24 h, the mixture of SnS and DOX was dialyzed. The unloaded DOX can be measured by using normalized absorbance at 482 nm at different concentrations of DOX (Figure S7b).

6. Loading process of DOX on naked and PEGylated SnS NSs

The loading process of naked SnS NSs and PEGylated SnS NSs were compared. It is found that there is no large difference of loading process for naked SnS NSs and PEGylated SnS NSs. After mixing one hour, the absorbance had been decreased to a saturated value (Figure S8). For the mixture of PEG and DOX, the absorbance has a slight decrease.

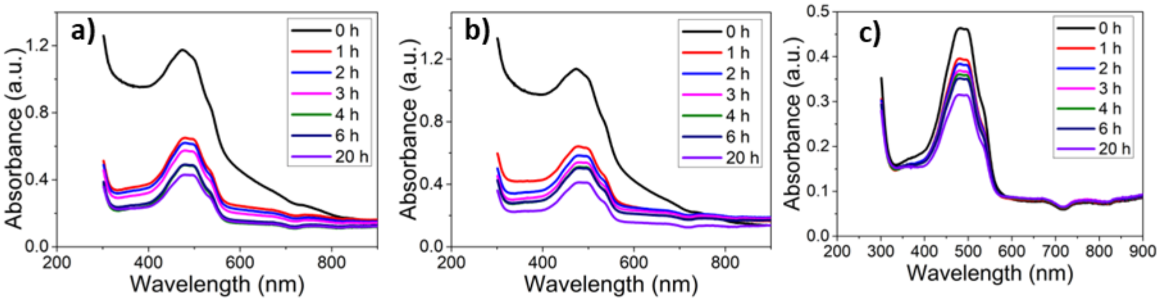

Figure S 8 Comparison of the DOX loading process of a) naked SnS NSs, b) PEGylated SnS NSs and c) PEG.

7. Drug release kinetics

The DOX release kinetics of SnS NSs with and without laser irradiation was characterized. 1ml of SnS NSs/DOX was packaged in a dialysis bag (MWCO = 14 kDa) and incubated in 20 ml PBS (pH = 7.4). The laser was used to promote the drug release and switched on and off in every ten minutes. In every time nodes, 1 ml of the external solution was collected to measure the concentration of released DOX via absorbance, and 1 ml of fresh PBS was added to keep its constant volume. The drug release kinetics can be shown in Figure S9. It can be shown that large quantities of drug can be released at first laser cycles and the drug release saturated gradually as laser on/off cycle increased.

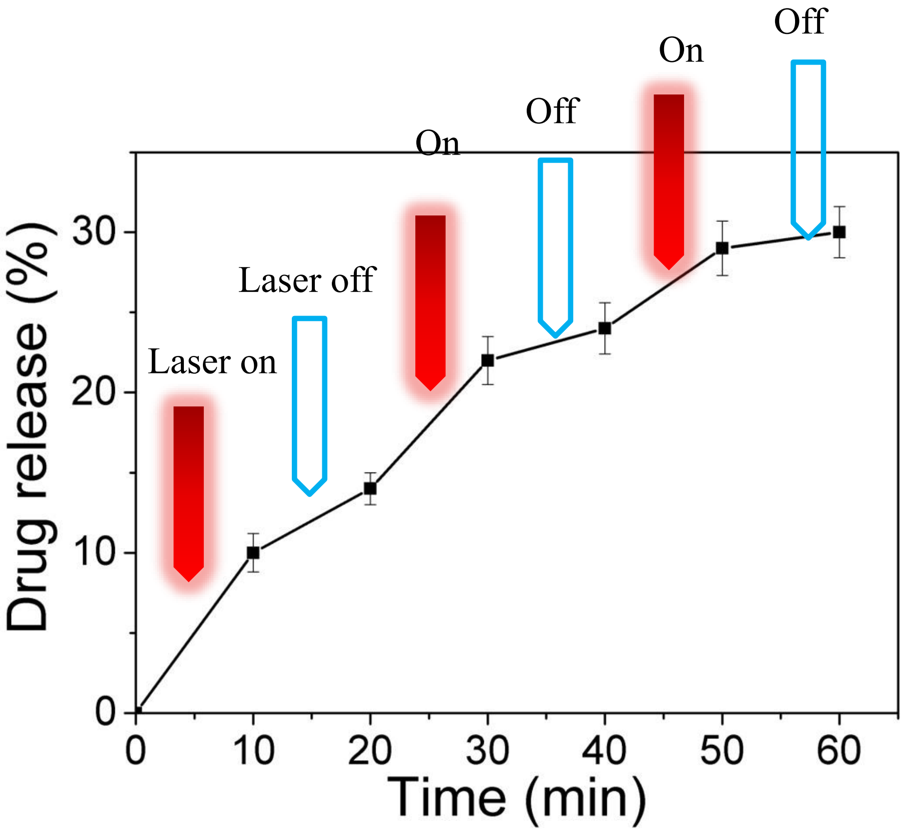

Figure S 9 Drug release kinetics under laser on/off cycle.

8. Photodynamic study

The reactive oxygen species (ROS) produced by nanomaterials can react with 1,3-diphenylisobenzofuran (DPBF), and further generate colorless *ortho*-dibenzoylbenzene, accompanied with the decay of the absorption at 410 nm. Thus, the photodynamic activity of NMs can be tested using DPBF as a probe for ROS.[3,4]

5 mL of DPBF solution (20 ug/mL) in ethanol was mixed with SnS nanosheets solution (20 ug/mL) and stirred in dark for 2 h. A continuous semiconductor diode laser (660 nm, LSR 660NL-FC-1.2 W, Jiangsu China) at power density of 0.2 and 0.3 W/cm was used as the illuminant. Afterward, the samples were taken for UV-Vis measurements at different time points (Figure S10). When the SnS NSs dispersion was irradiated under the laser power of 0.2 W/cm^2 and 0.3 W/cm^2 for 10 min, the absorbance was decreased 14%, 26%, respectively.

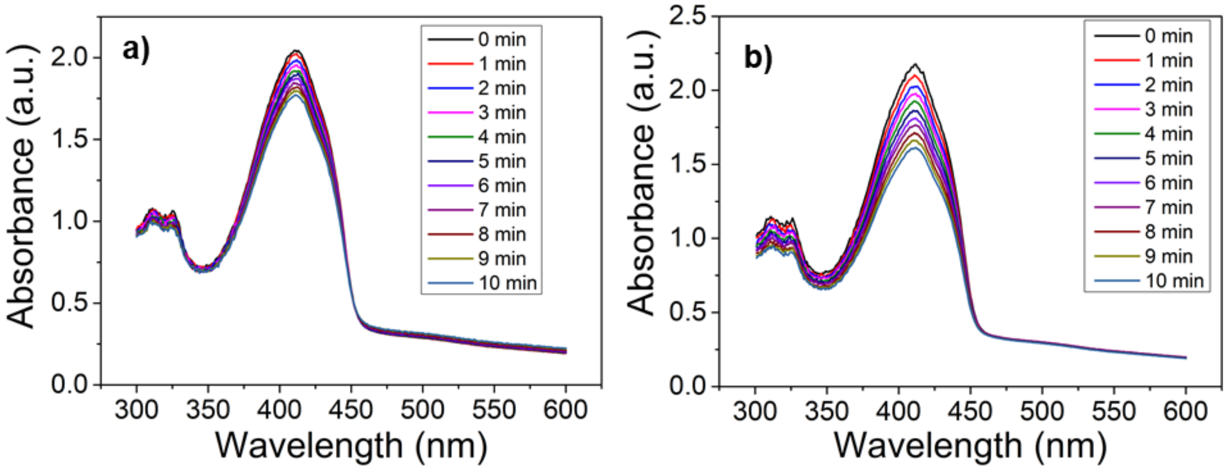

Figure S 10 PDT of SnS NSs under 660 nm laser irradiation at a) 0.2 W and b) 0.3 W.

References

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