

## Supporting Information

### **Urchin-like Tungsten Suboxide for Photoacoustic Imaging- Guided Photothermal and Photodynamic Cancer Combination Therapy**

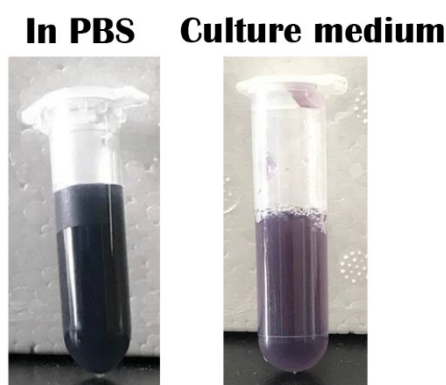
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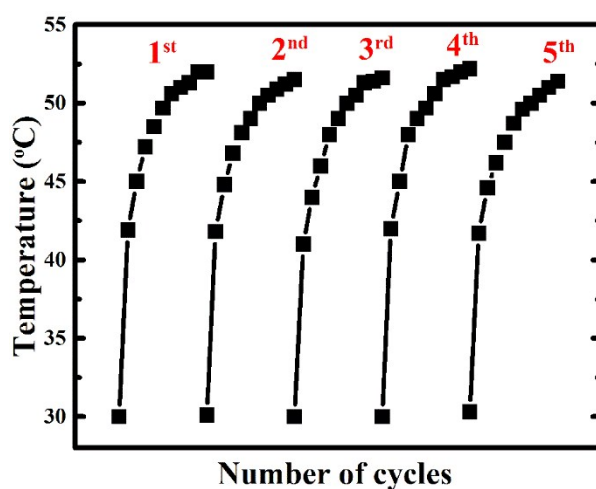
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**Figure. S1** Photographs of  $W_{18}O_{49}$  dispersed in PBS solution and culture medium.



**Figure S2** Cycling stability test of the photothermal conversion for 5 cycles.

The photothermal conversion efficiency,  $\eta$ , can be determined by following equation:

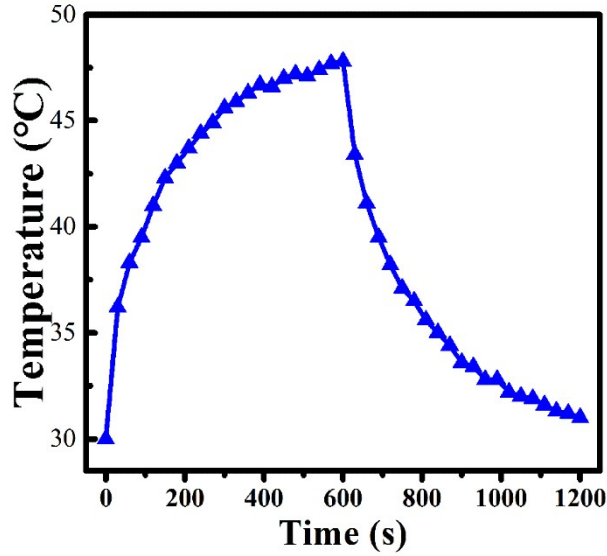
$$\eta = [\text{hS} (T_{max} - T_{surr}) - Q_{dis}] / I(1 - 10^{-A_{1064}}) \quad \text{Eqn.S1}$$

where h is heat transfer coefficient; S is the surface area of the container;  $T_{max}$  is the equilibrium temperature;  $T_{surr}$  is ambient temperature of the surroundings;

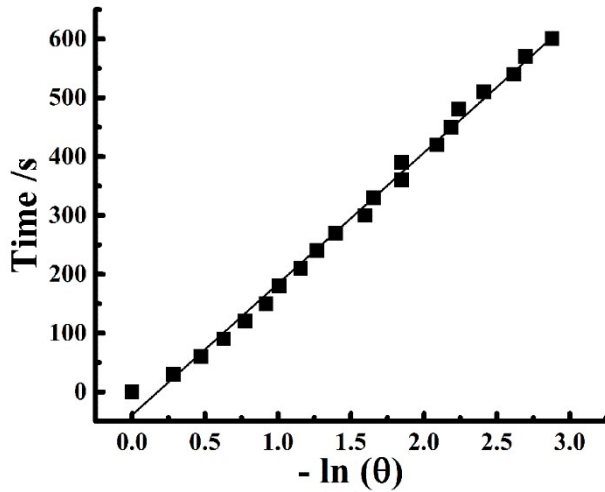
$Q_{dis}$  is heat dissipated from light absorbed by the quartz sample cell itself (it was measured independently to be 13.25 mW using a quartz cell containing pure water);

I is incident laser power ( $2 \text{ W/cm}^2$ )

$A_{1064}$  is the optical absorbance of nanocubes at 1064 nm, which to be 0.95 in this work.



**Figure S3.** Temperature variations of solution containing 0.5 mg/ml tungsten suboxide with 2 W/cm<sup>2</sup> laser irradiation. The NIR laser irradiation lasted 10 min and then was turned off.



**Figure S4.** Linear relation between the  $t$  and  $\ln\theta$ .

It easily found that only the  $hS$  remains unknown for calculating  $\eta$ . To obtain the value of  $hS$ , a dimensionless driving force temperature,  $\theta$  is introduced using the maximum system temperature.

$$\Theta = (T - T_{surr}) / (T_{max} - T_{surr}) \quad \text{Eqn.S2}$$

At the cooling stage of the aqueous dispersion, the cooling time  $t$  and  $\theta$  abide by the following equation;

$$t = -\tau_s \ln(\Theta) \quad \text{Eqn.S3}$$

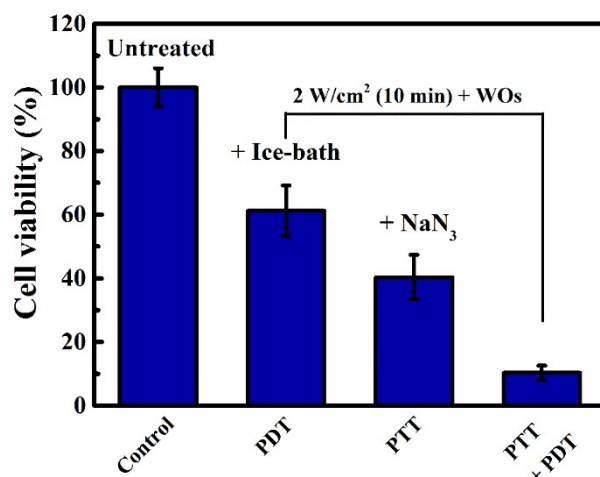
Time constant for heat transfer from the system could be determined by plotting linear time data from the cooling period against negative natural logarithm of driving force temperature.

The  $\tau_s$  is calculated to be 223s.

$$hS = \sum m_i C_{p,i} / \tau_s \quad \text{Eqn.S4}$$

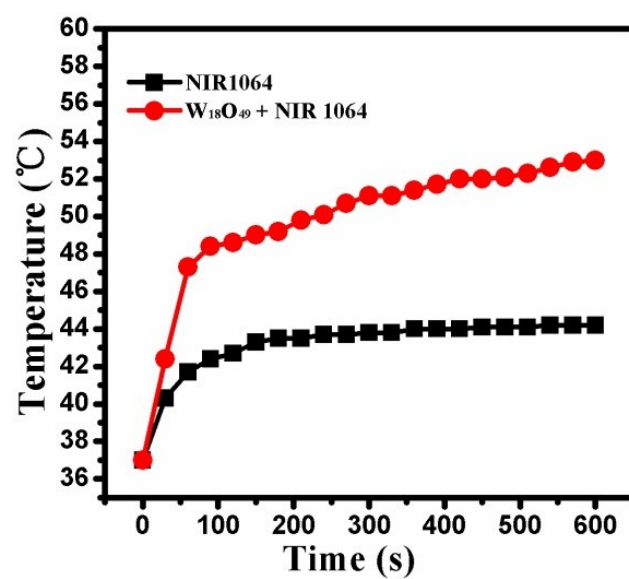
Where  $m$ ,  $C_p$ ,  $\tau_s$  are the mass, heat capacity of water and time constant, respectively. The  $m$  is 3 g and  $C$  is 4.2 J/g. The  $hS$  is determined to 56.5 mW/ °C according to Equ.S4. Substituting  $hS = 56.5$  mW/ °C into Equ.S1 produces  $\eta = 49.5$  %.

Secondly, the photo-stability was investigated by applying 5 heating cycles on 1 mg/ml tungsten suboxide under 2W/cm<sup>2</sup> laser irradiation. As shown in Figure. R4, there was no obvious change on temperature rise after 5 cycles, indicating a good photostability of tungsten suboxide.

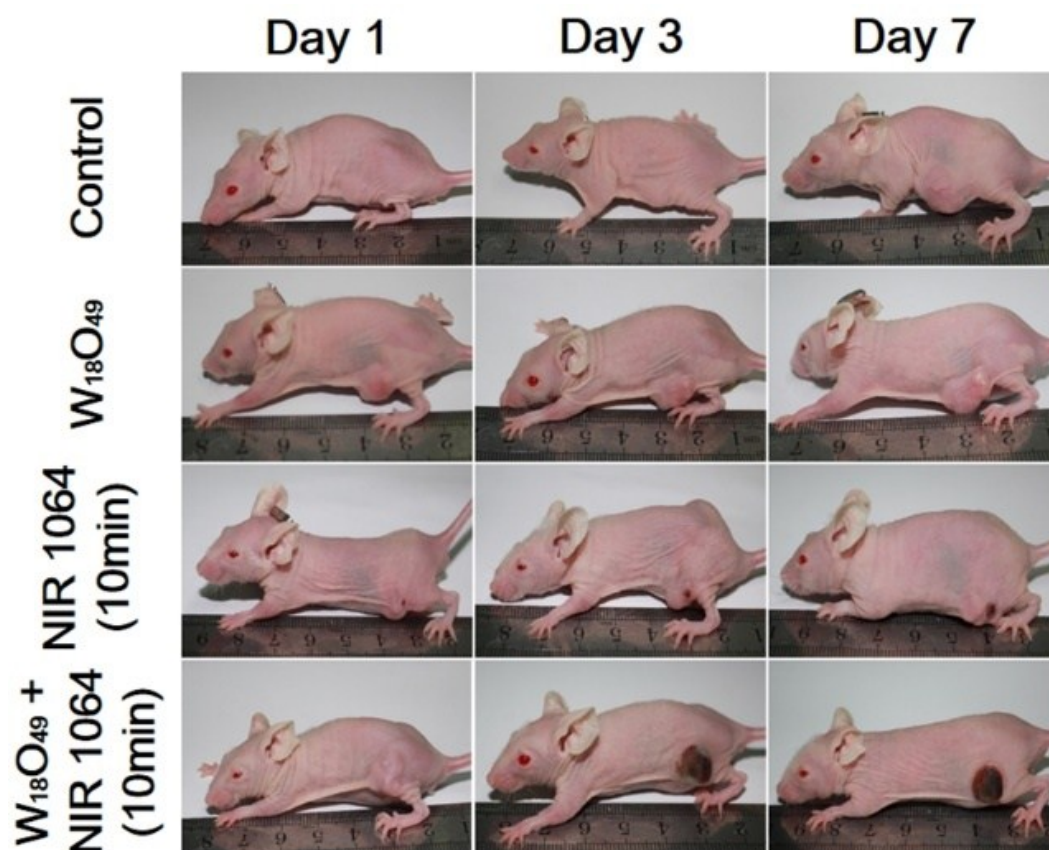


**Figure S5** Cell viability after different treatments.

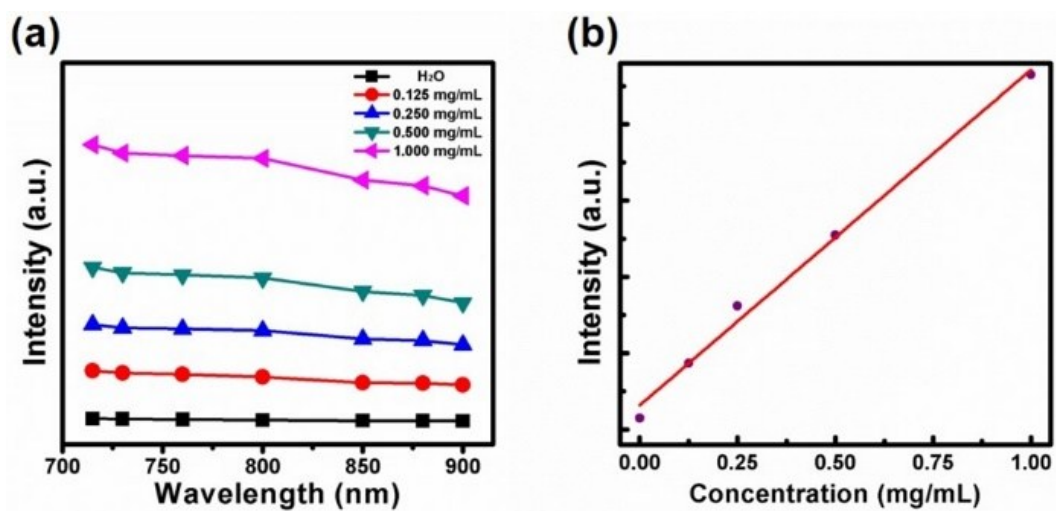
The therapeutic effect in each group was reflected by a MTT method. For internalizing WOs, cells were seeded in 96-well plate and incubated with BSA-MoS<sub>2</sub> for 24 h. After removing the excessive WOs by PBS washing, cells were irradiated with a 1064 nm laser for 10 min, resulting in a combined PTT/PDT treatment effect. As to PDT group, the cells were set at a chamber temperature of 4 °C during the NIR irradiation. For PTT experiments, 50  $\mu$ L of sodium azide (10  $\mu$ M) was added into the cells that had been incubated with BSA-MoS<sub>2</sub>.



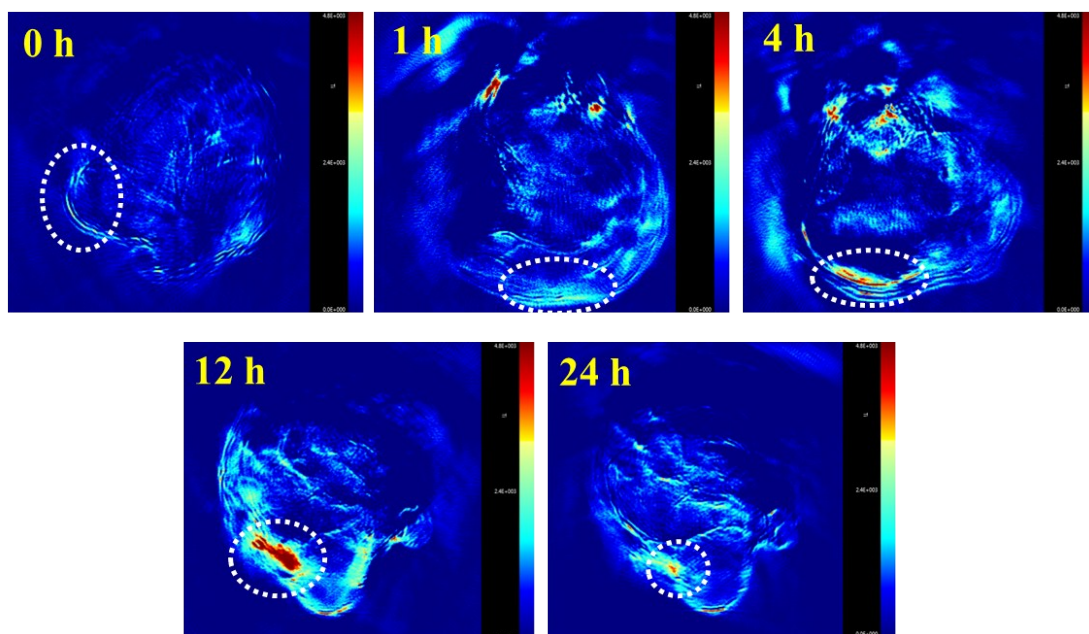
**Figure S6** Temperature evaluation of tumors intratumorally injected with 100  $\mu$ L of PBS or WOs (1 mg/mL) recorded by an IR thermal camera under irradiation of NIR 1064 nm laser.



**Figure S7** Representative photographs of mice taken before treatment (day 1), at day 3 and day 7 after various treatments.



**Figure S8** (a) PA signal of WOs solutions of various concentrations. (b) Plot of PA signal at 880 nm versus WOs concentrations.



**Figure S9** In vivo PA imaging of HeLa tumor-bearing mice before and after intravenous injection of WOs for varied time.