Electronic Supplementary Information for

PEGylated rhenium nanoclusters: a degradable metal photothermal nanoagent for cancer therapy

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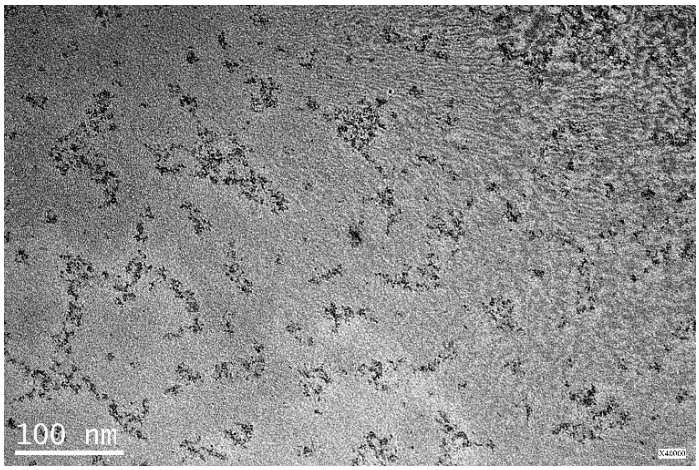

Figure S1. TEM image of PEGylated Re nanoclusters

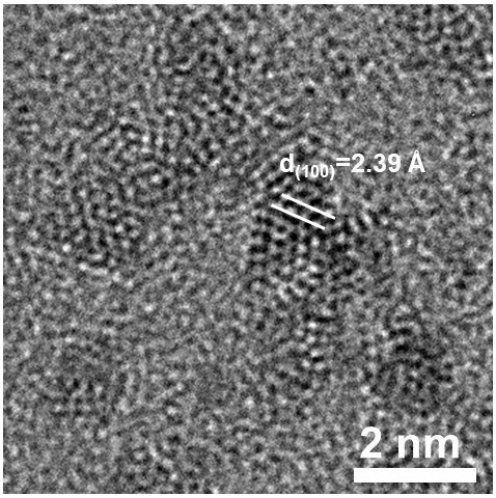

Figure S2. HRTEM image of hexagonal Re nanoclusters

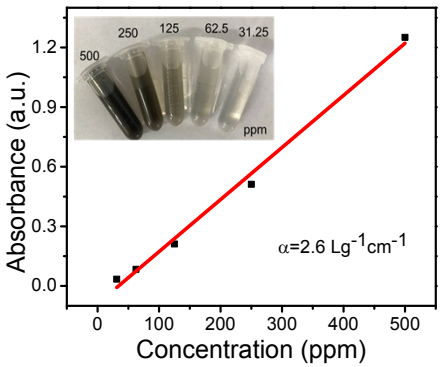

Figure S3. The fitting curve of the absorbance at 808 nm vs different concentrations of Re dispersions, inset the digital image of Re NCs dispersions at different concentrations.

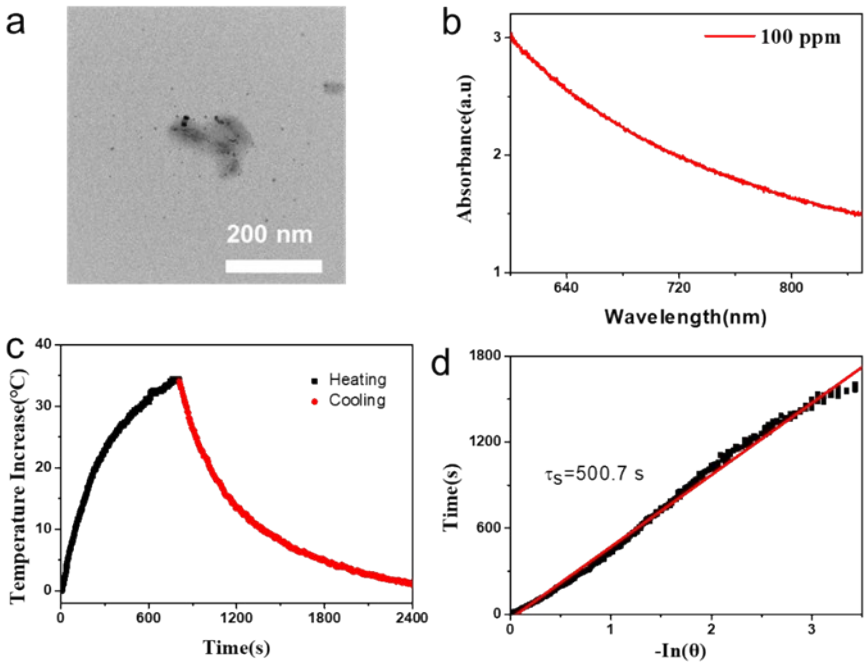

Figure S4. (a) TEM image of black phosphorus, (b) UV-vis-NIR absorption curve of black phosphorus (100 ppm), (c) the heating/cooling curves of black phosphorus under laser irradiation (2 W, 808 nm); (d) The fitting linear curve of time data vs –lnθ from the cooling period of black phosphorus.

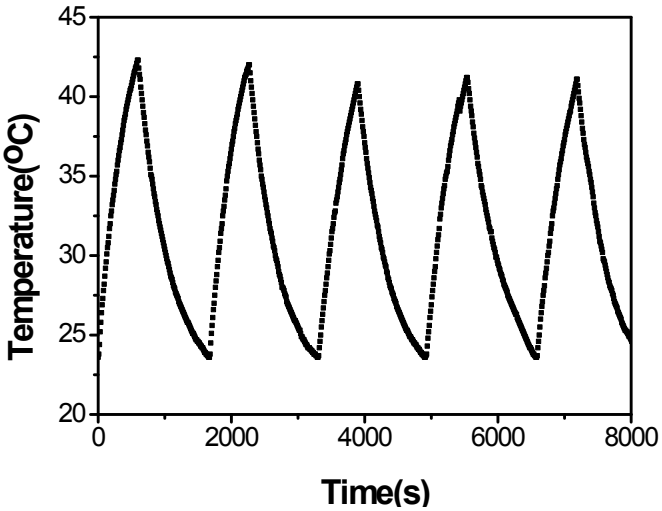

Figure S5. Five irradiation cycles of Re nanoclusters with a concentration of 125 ppm.

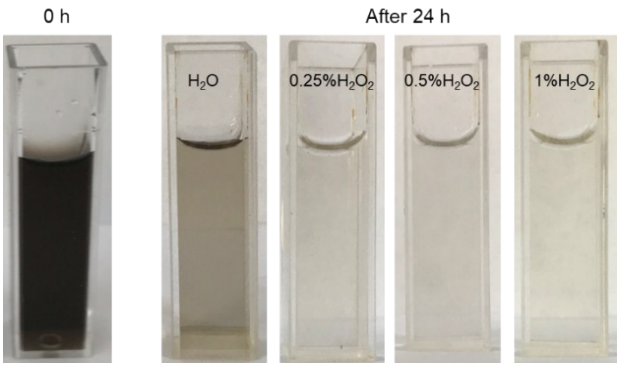

Figure S6. Digital photographs of Re nanoclusters dispersions with a concentration of 500 ppm after incbuation in H_2O, 0.25%, 0.5% and 1% H_2O_2 solution for 24 h.

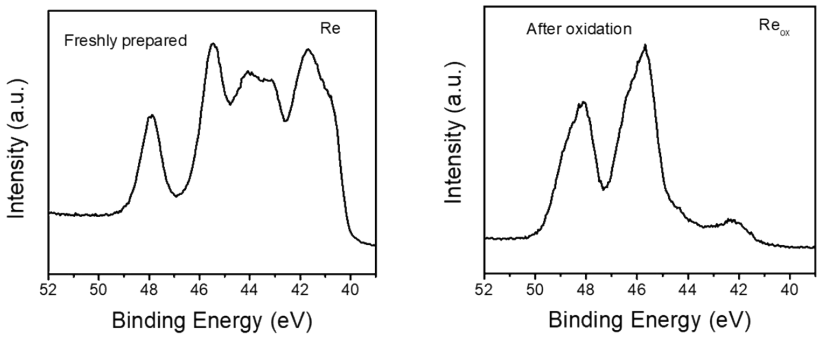

Figure S7. XPS spectra of freshared prepared and after the oxidiation of Re nanoclusters. The oxidiation process is conducted by incubation of Re nanoclusters dispersions (2 mg/mL) in H_2O_2 (0.5%) for 24 h.

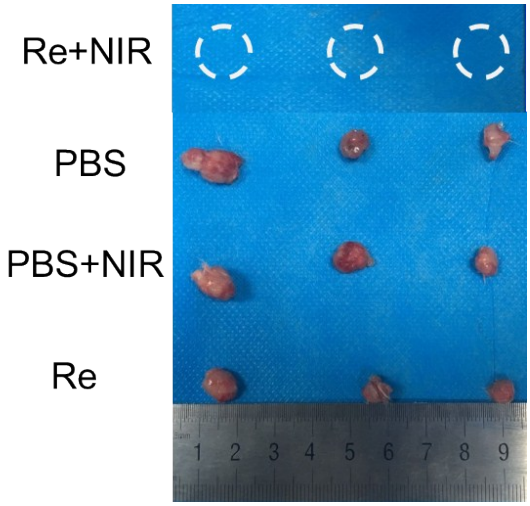

Figure S8. Digital photographs of tumors extracted from different groups after the PTT treatment.

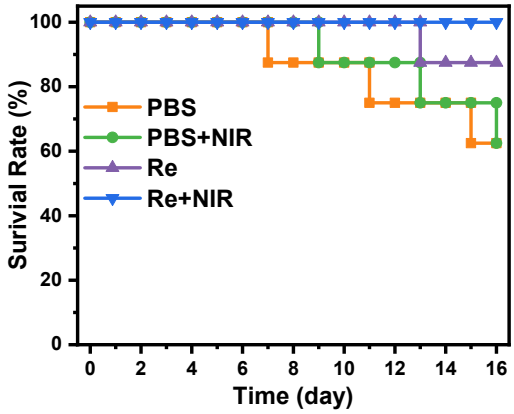

Figure S9. The survival rate of mice after various treatments.

Figure S10. Digital photographs of major organs (heart, liver, spleen, lung and kidney) of representative mice from different groups as indicated.

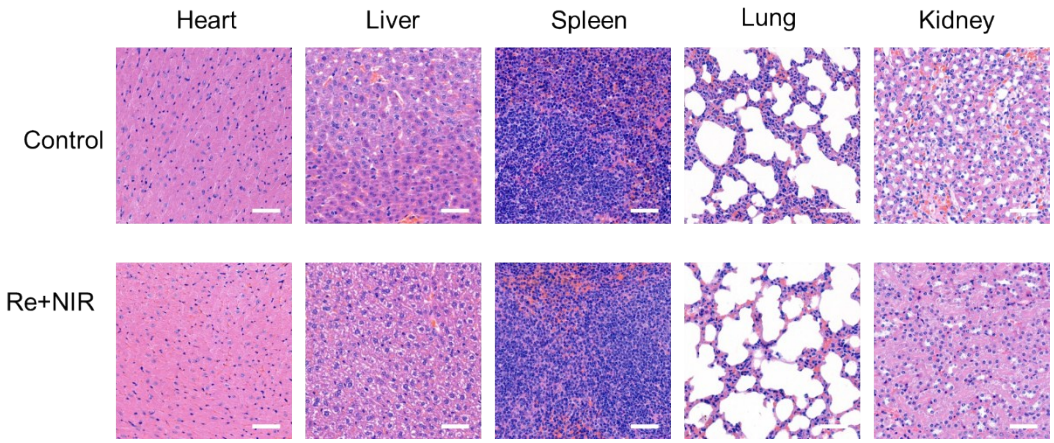

Figure S11. Representative H&E images of major organs (heart, liver, spleen, lung and kidney) of representative mice from healthy group and "Re+NIR" group. Scale bar is 50 μm

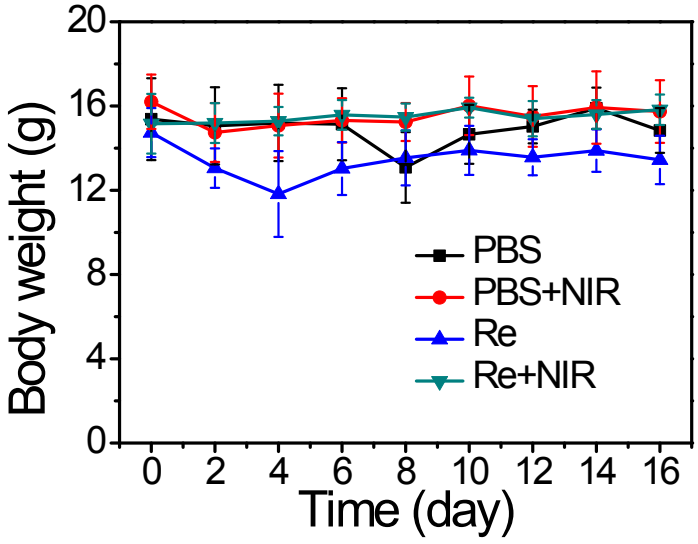

Figure S12. Body weight of mice from different groups within 16 days

Additional Experiments

Synthesis of Gold Nanoparticles

The fabrication of Au nanoparticles with an average dimeter of 3 nm was according to a previous report.[1] 1.0 mL of $HAuCl_4$ aqueous solution (1% w/v) was added into 100 mL of DI water under vigorous stirring for 1 min, followed by the addition of 1 mL of sodium citrate solution (1% w/v). After stirred for another one minute, 1.0 mL of $NaBH_4$ (0.075% w/v) in sodium citrate (1% w/v) solution was added and continuously stirred for 5 min. Then, 2 mL of PEG-SH solution (5 mg/mL) was added and stirred for 6 h. At last, PEG-SH modifided Au nanoparticles were obtained by ultrafiltration centrifugation (4500 rpm, 10 min) and washed with D.I water for four times.

Photothermal Performance of Rhenium Nanoclusters

2 mL of Re nanoclusters aqueous dispersion with different concentrations was put in a quartz cuvette, and then irradiated by a 808 nm laser (2 W) for 10 min. D.I. water was used as control. A thermocouple probe with a digital thermometer was used to record the temperature of aqueous dispersions every 10 s.

To calculate the photothermal conversion efficiency (η), a previously reported method was adapted[2]. In brief, 2 mL of Re nanoclusters aqueous dispersion (250 ppm) was continuously irradiated by a NIR laser (808 nm, 2 W) until the temperature reached a plateau, and then the laser was shut off. The heating/cooling period was recorded every 10 s. Base on the temperature change vs time, the value of η can be calcuated as follows by equation S1:

$$\eta = \frac{hS(T_{max} - T_{surr}) - Q_s}{I(1 - 10^{-A_{808}})} \quad (1)$$

where h is the heat transfer coefficient of the whole system, S is the surface area of the quartz tube, T_{max} is the highest temperature in plateau period, T_{surr} is the surrounding temperature, Qs is the heat related with the light absorbance of water, I is the power (2 W) of NIR laser, and A_{808} represents the absorbance of Re nanoclusters aqueous dispersion.

The value of hS can be determined by the following equation S2:

$$\tau s = \frac{m_D C_D}{hS} \quad (2)$$

where τ_s is time constant of the whole system, m_D and C_D are the mass of water (2 g) and heat capacity of water (4.2 J/(g□ºC)), respectively. In order to accquire the value of hS, the parameter of θ is defined by the following equation S3:

$$\theta = \frac{T - T_{surr}}{T_{max} - T_{surr}} \quad (3)$$

where T is the real-time temperature of Re nanoclusters aqueous dispersion during the irradiation period. Hence, hS can be determined by linearly fitting time data vs $-\ln\theta$ during the cooling period.

References

1 H. Ke, J. Wang, Z. Dai, Y. Jin, E. Qu, Z. Xing, C. Guo, X. Yue and J. Liu, *Angewandte Chemie International Edition*, 2011, **50**, 3017.

2 D. K. Roper, W. Ahn and M. Hoepfner, *The Journal of Physical Chemistry C*, 2007, **111**, 3636.