Electronic Supplementary Material (ESI) for Biomaterials Science.
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Electronic Supplementary Information (ESI)

# Injectable hydrogel platform with biodegradable molybdenum polyoxometalate and R848 for combinational photothermal-immunotherapy of cancer

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## 1. Calculation of photothermal conversion efficiency

The photothermal conversion efficiency of three samples was be calculated by using the following formula according to the methods of these articles[1, 2].

$$\eta = \frac{hS(T_{max} - T_{max,\ water})}{I(1 - 10^{-A_{808}})}$$

$$hS = \sum mC_p/\tau_s$$

$$\tau_s = (-t)/ln\theta$$

$$\theta = （T_{amb} - T）/（T_{amb} - T_{max}）$$

$h$ is the heat transfer coefficient;

$S$ is the surface area of the photothermal test vessel;

$\tau_s$ is the time constant of samples;

$m$ is the mass of samples (1.0 g);

$C_p$ is the specific heat capacity of water ($C_p$ = 4.2 J·mol$^{-1}$);

$A_{808}$ is the absorbance at 808 nm of different samples.

According to the first heating-cooling process in the photothermal cycle, $\tau_s$ is obtained by the linear relationship between the cooling period and natural logarithm of driving force temperature ($T_{max,\ water}$ = 22.8 °C).

For POM@GG hydrogel, $T_{amb}$ is the temperature of the surroundings (21.0 °C), $T_{max}$ is the equilibrium temperature of POM@GG hydrogel (42.6 °C), and the value of $\tau_s$ is 281.69 (Figure S5), $hS$ is calculated from the above equation ($hS$ = 0.01491). The deviation of $T_{max}$ and $T_{max,\ water}$ is 21.6 °C. $I$ is 0.45 W where the area of light spot was 1.5 cm$^2$, and $A$ is the absorbance of POM@GG hydrogel at 808 nm ($A_{808}$ = 1.41). The photothermal conversion efficiency $\eta$ is obtained from the first formula ($\eta$ = 63.1%).

## 2. Supplementary Figures

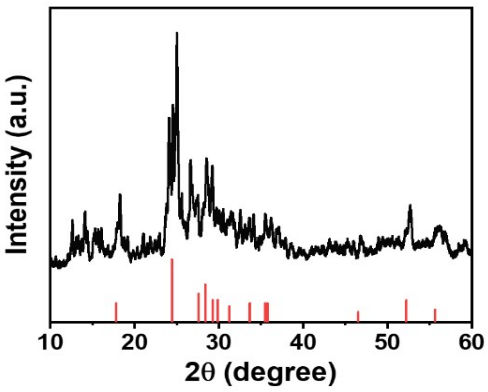


**Figure S1.** Powder X-ray diffraction (PXRD) analysis of ox-POM using Cu Kα in the range of 10−60° with a scanning rate of 10°/min.

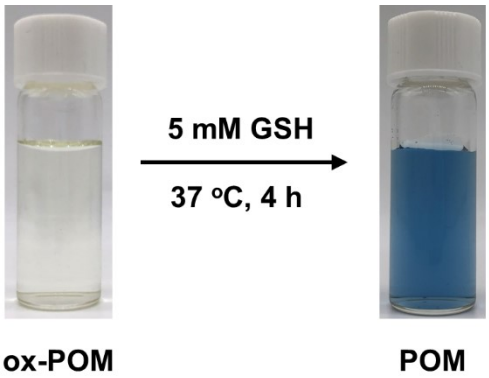


**Figure S2.** Color change of POM before and after reduction.

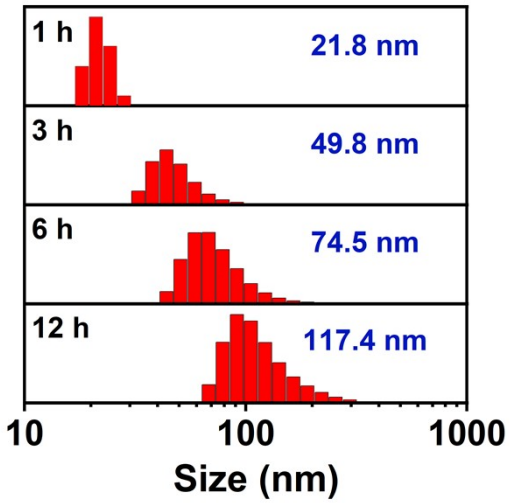


**Figure S3.** Size distribution of POM clusters as a function of time in the reduction process measured by the dynamic light scattering (DLS).

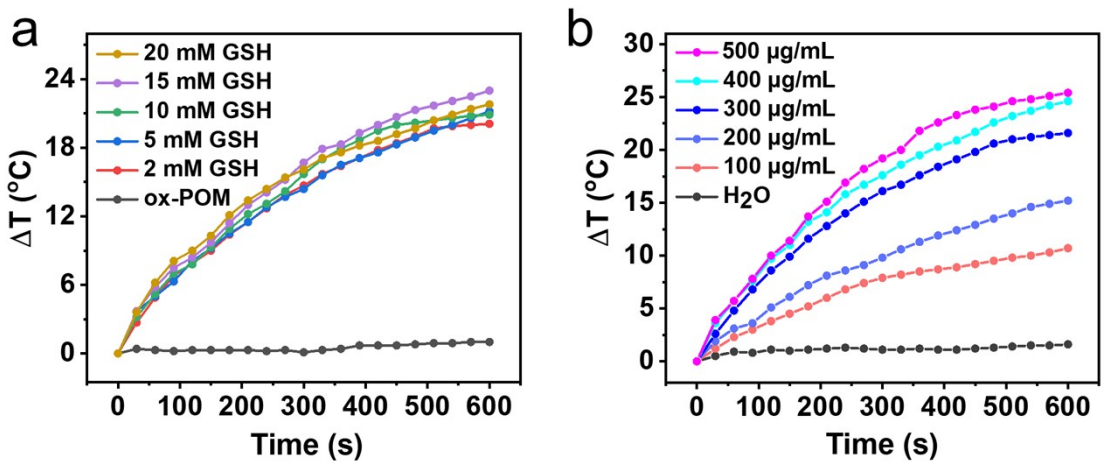


**Figure S4.** (a) Temperature rises of 300 μg/mL POM solution under different GSH concentrations and (b) the temperature rises in different concentration POM solutions.

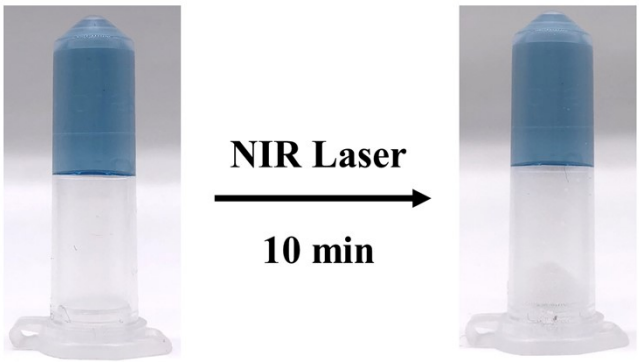


**Figure S5.** The image of POM@GG hydrogel before and after the NIR laser irradiation (808 nm, 0.3 W/cm$^2$, 10 min).

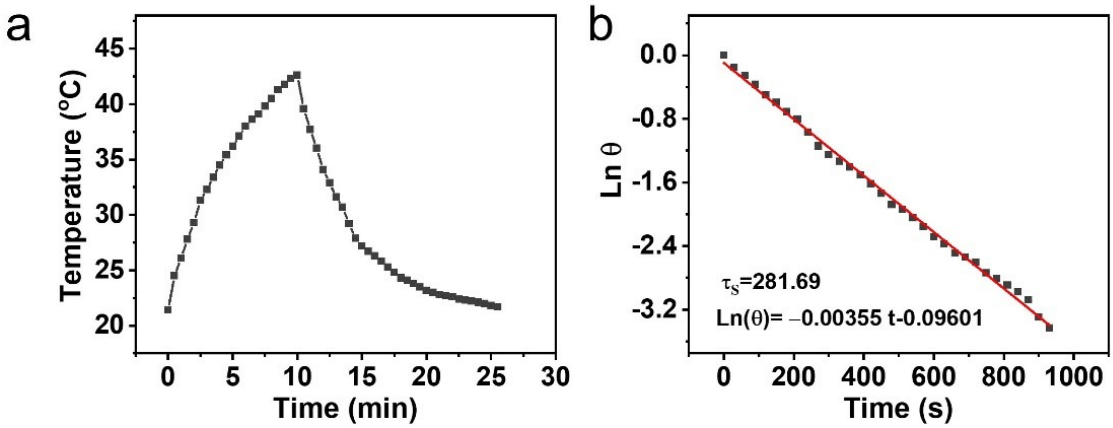


**Figure S6.** Calculation of photothermal conversion efficiency using the first photothermal cycle of POM@GG.

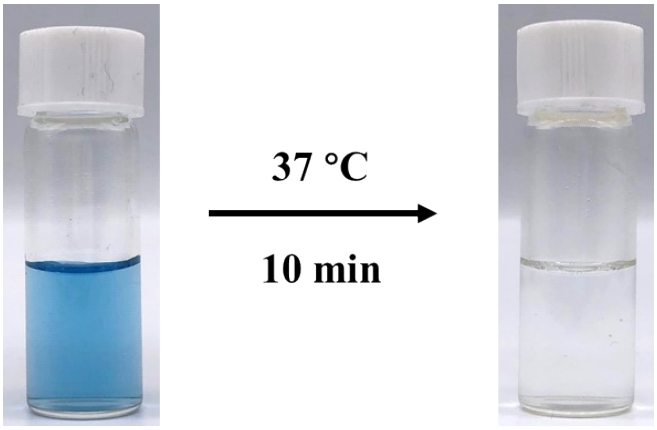


**Figure S7.** The color change of POM (300 μg/mL, 1 mL) after being dispersed in the $H_2O_2$ solution (10 mM, 1 mL).

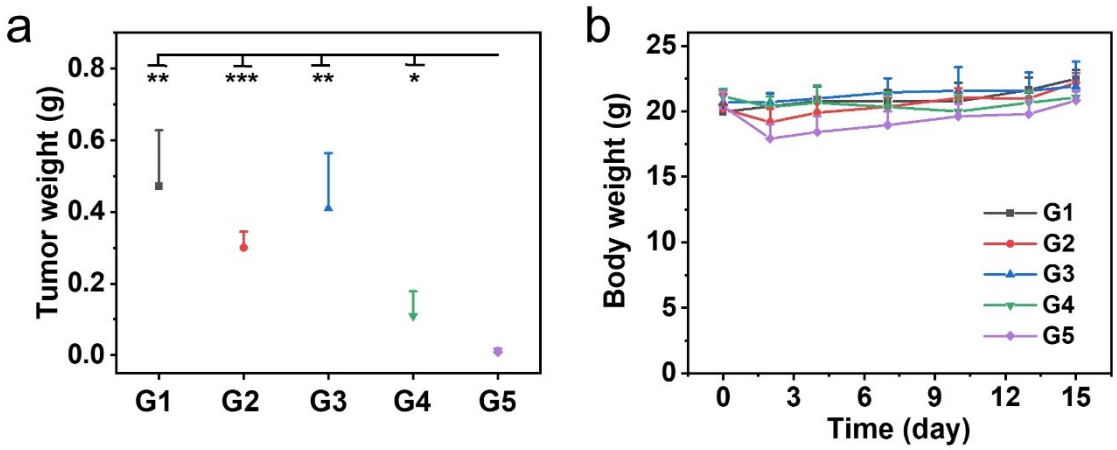


**Figure S8.** (a) The residual tumor weights after the treatment and (b) body weights of mice during the treatment. G1: untreated; G2: R848@GG; G3: POM@GG; G4: POM@GG with NIR; G5: R848/POM@GG with NIR.

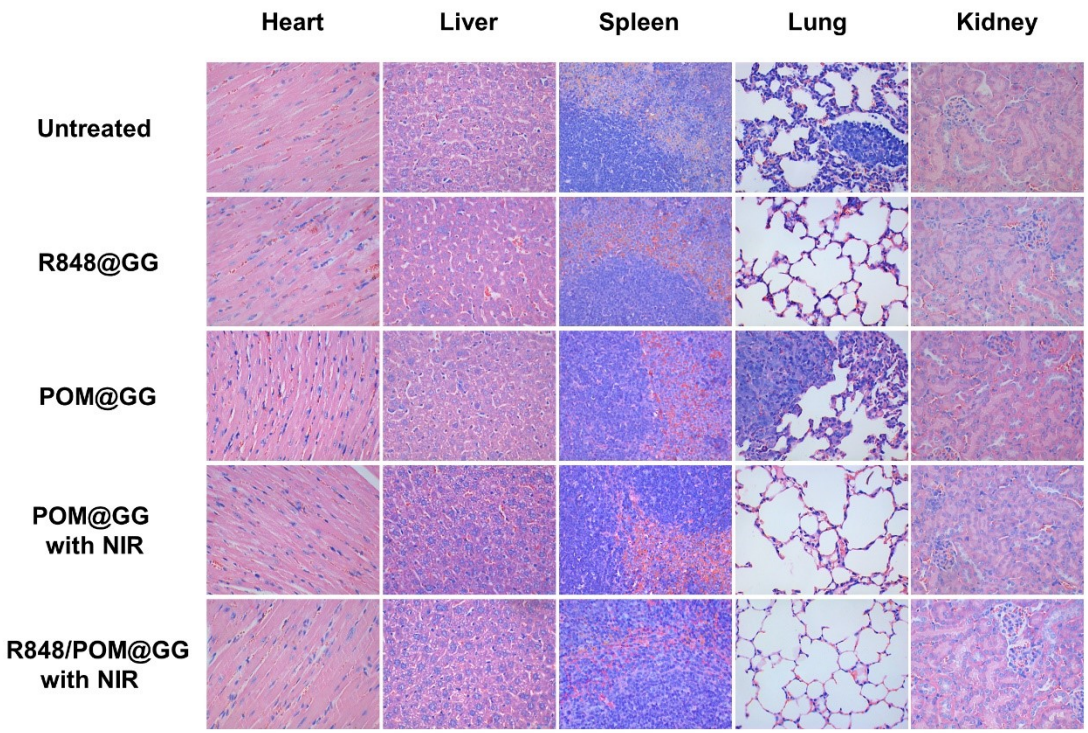


**Figure S9.** H&E staining images of major organs (heart, liver, spleen, lung, and kidney) in different groups after the treatment.

## References

1. C. Sun, L. Wen, J. Zeng, Y. Wang, Q. Sun, L. Deng, C. Zhao and Z. Li, *Biomaterials*, 2016, **91**, 81-89.
2. W. Ren, Y. Yan, L. Zeng, Z. Shi, A. Gong, P. Schaaf, D. Wang, J. Zhao, B. Zou, H. Yu, G. Chen, E. M. B. Brown and A. Wu, *Adv. Healthcare Mater.*, 2015, **4**, 1526-1536.