Supporting Information

Core-Shell Gold Nanorod@Mesoporous-MOF Heterostructures for Combinational Phototherapy

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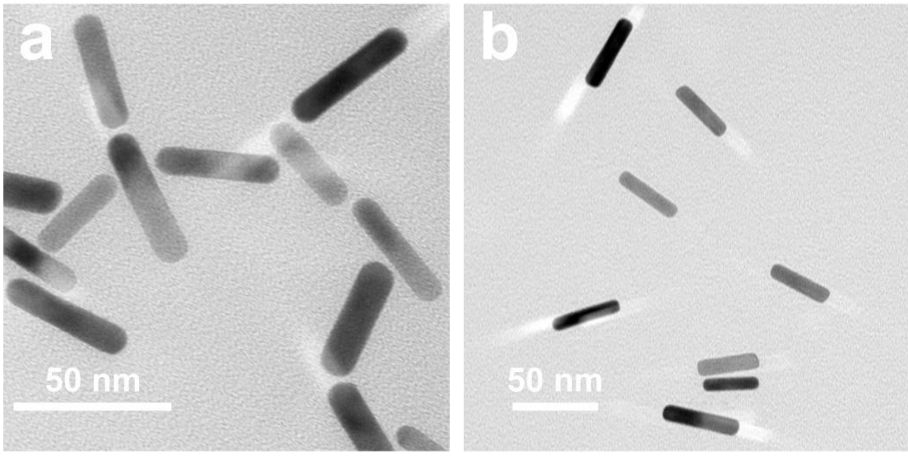

Figure S1. TEM images of the AuNRs coated with PVP and dispersed in (a) water and (b) DMF.

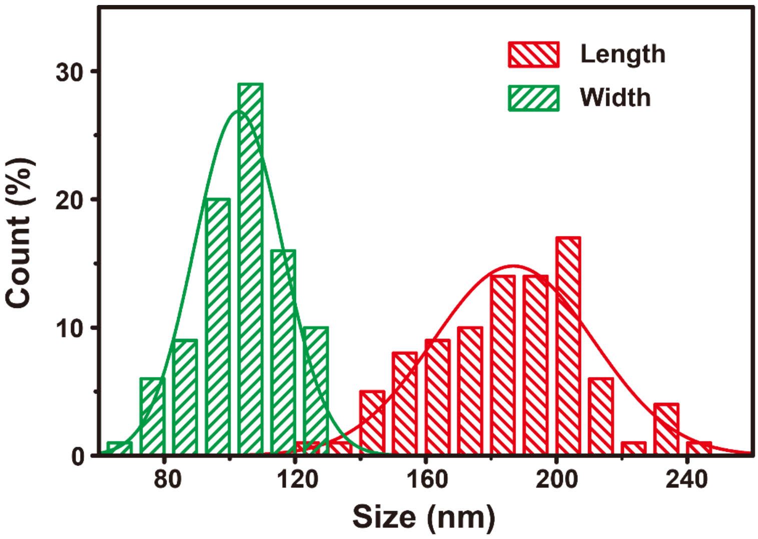

Figure S2. Size distribution of the AuNR@MOFs.

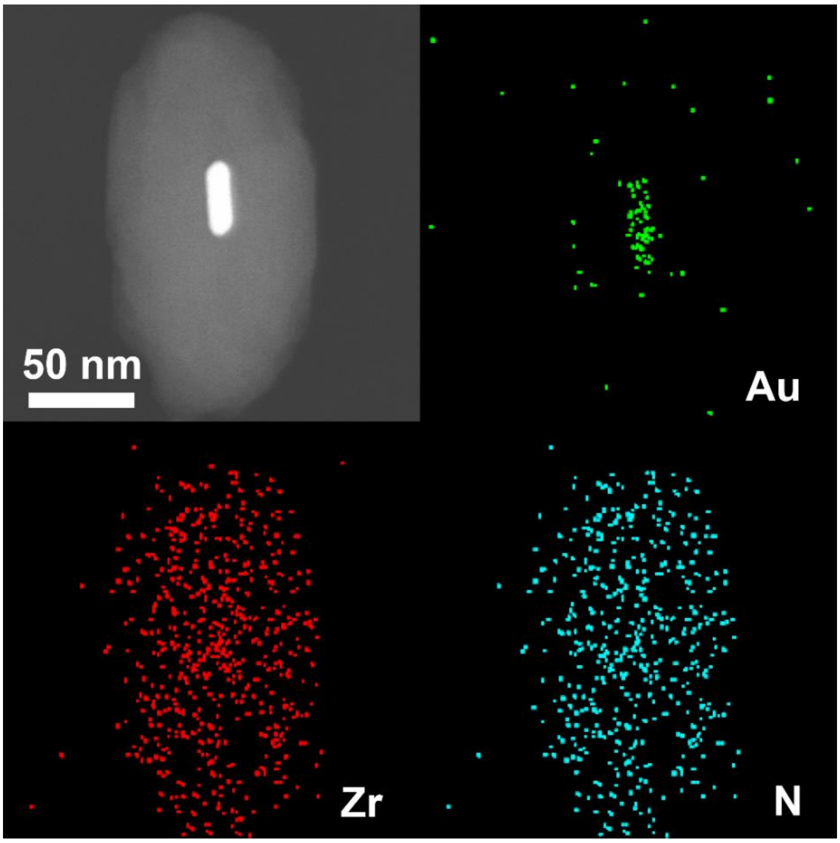

Figure S3. HAADF-STEM image and the corresponding STEM-EDS elemental mapping images (green for Au, red for Zr and cyan for N) of a single AuNR@MOFs nanoparticle.

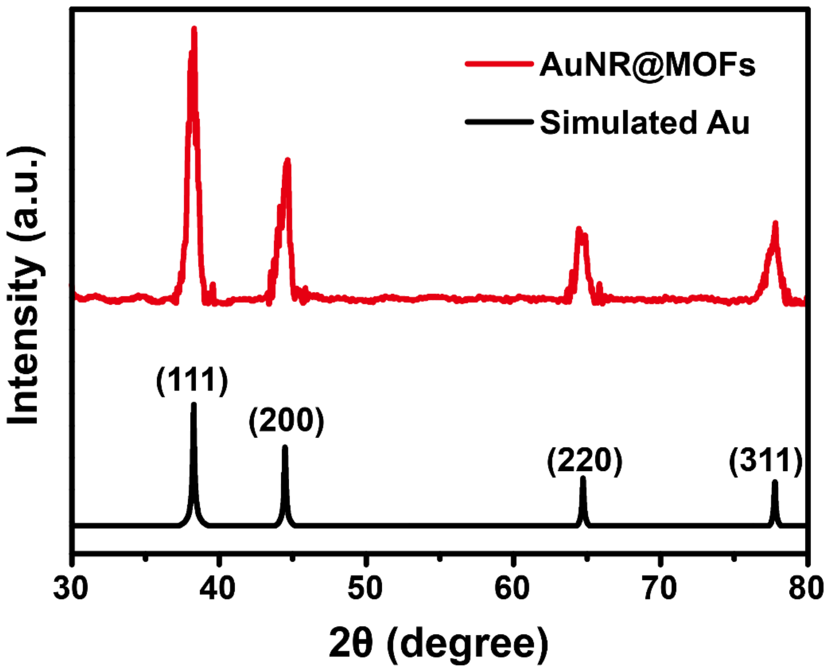

Figure S4. PXRD patterns of AuNR@MOFs and corresponding simulation result.

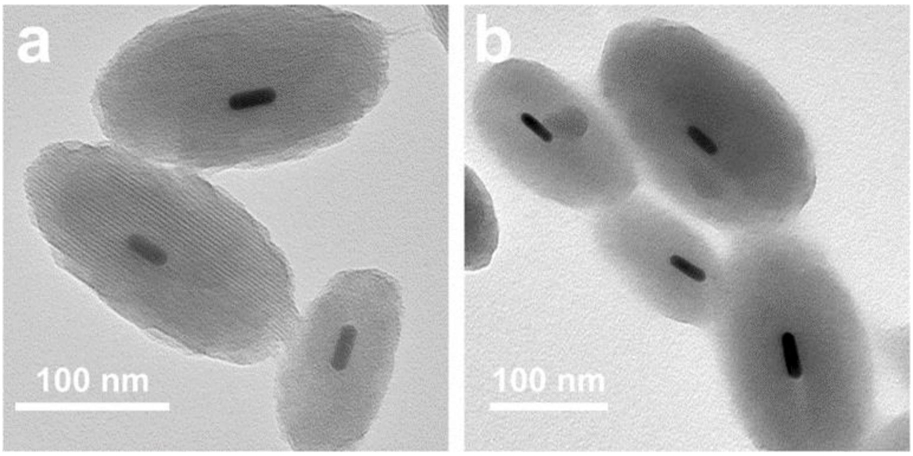

Figure S5. TEM images of AuNR@MOFs incubated in water (pH = 7.4) for (a) 0 h and (b) 24 h, respectively.

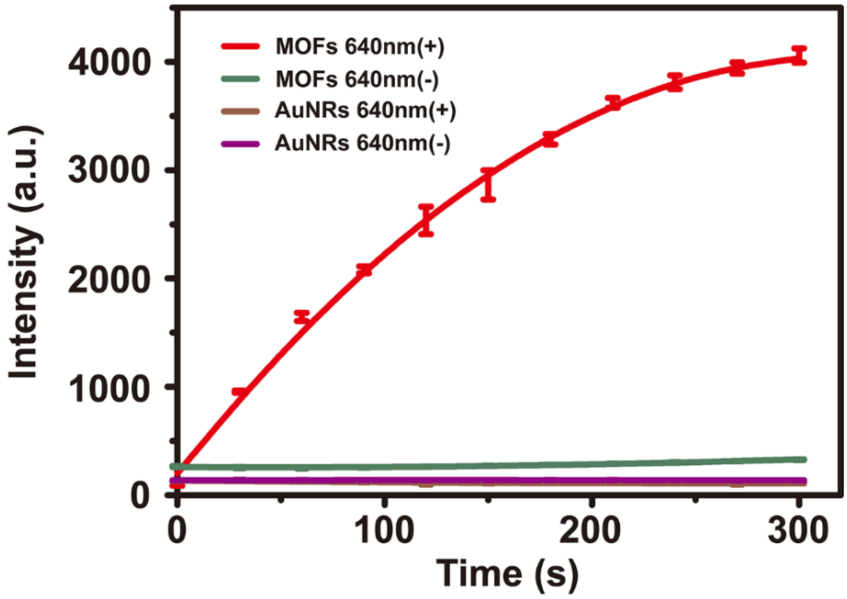

Figure S6. Singlet oxygen generation by MOF NPs and PVP-AuNRs with (+) and without (-) 640 nm irradiation (20 mW/cm^2), detected by SOSG assay. Data are means ± SD (N = 3).

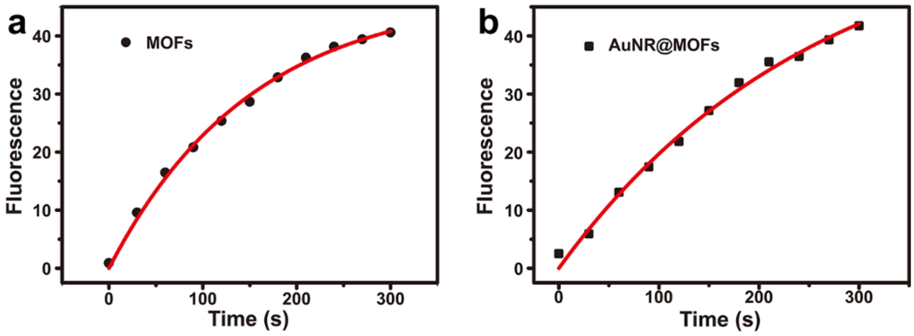

Figure S7. Singlet oxygen generation by (a) MOFs and (b) AuNR@MOFs, respectively. The dots are experimental data and solid lines are fitting curves.

Following Lu's report.[1] The singlet oxygen generation curve was fitted with the following equation (1):

$$I_F = A(1 - e^{-kt}) \qquad (1)$$

Where I_F is fluorescence intensity of SOSG and t is irradiation time, A and k are fitting parameters. The product of Ak represents the singlet oxygen generation efficiency. In our experiment, the singlet oxygen generation efficiency of MOFs and AuNR@MOFs were calculated as 0.3128 S^{-1} and 0.2377 S^{-1}, respectively, indicating that the singlets oxygen generation efficiency of MOFs is about 1.3 times higher than that of AuNR@MOFs.

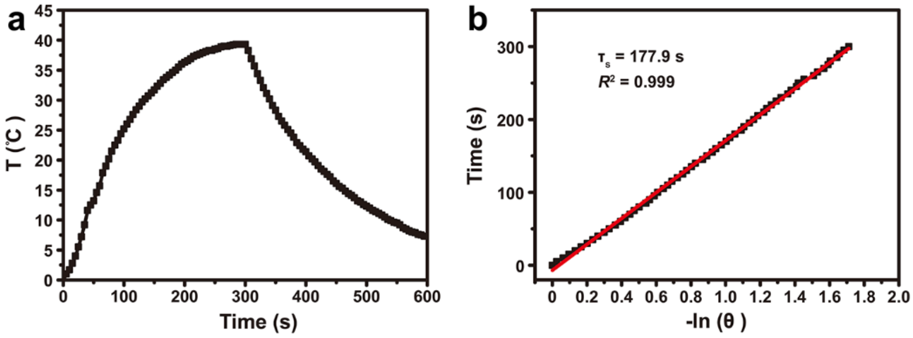

Figure S8. (a) Photothermal effect of AuNR@MOFs aqueous solution (200 μL, 1.4 mg/mL) under irradiation of 808 nm laser with the power density of 0.75 mW/cm^2 and shutting of laser after irradiation for 300 s. (b) Time constant for heat transfer from the system is determined to be τ_s = 177.9 s by applying the linear time data from the cooling period of (a) versus negative logarithm of the driving force temperature.

Following Roper's report,[2] the photothermal conversion efficiency (η) was calculated using equation (2):

$$\eta = \frac{hA(T_{max} - T_{amb}) - Q_0}{I(1 - 10^{-A_\lambda})} \qquad (2)$$

Where h is heat transfer coefficient (mW/(m^2 °C)), A is the surface area of the container (m^2), T_{max} is the equilibrium temperature (°C) , T_{amb} is ambient temperature of the surroundings (°C). According to the Figure S8a, T_{max}-T_{amb} is 39.3 °C. Q_0 is the heat from light absorbed by the water and cuvette sample walls (mW), and it was measured approximately 17 mW. I is the incident laser power (750 mW) and A_λ is the absorbance at an excitation wavelength of 808 nm. In our experiment, A_λ is so large that 10^{-A_λ} is close to zero.

In order to get hA, θ is introduced according to the equation (3):

$$\theta = \frac{T - T_{amb}}{T_{max} - T_{amb}} \qquad (3)$$

And we also introduced τ_s as the sample system time constant:

$$\tau_s = \frac{m_D C_D}{hA} \qquad (4)$$

In equation (4), m_D represents the sample mass (0.2 g) and heat capacity of water used as solvent (4.2 J/g) respectively.

And τ_s is calculated by using equation (5):

$$t = -\tau_s \ln(\theta) \qquad (5)$$

Where t represents the cooling time, and the equation (4) is the fitting curve of Figure S8b. τ_s is 177.9 s and hA is 0.00472 W/K.

Finally, the photothermal conversion efficiency of AuNR@MOFs is calculated as 22.5%.

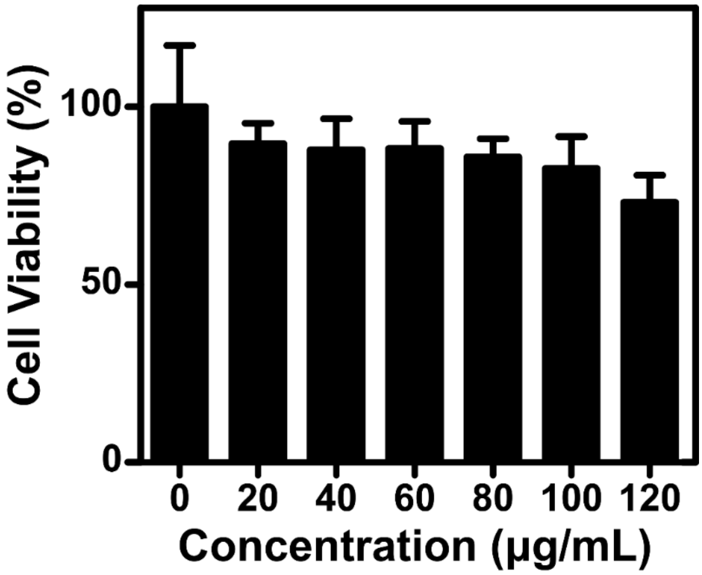

Figure S9. Cell viability of 4T1 cells with treatment of AuNR@MOFs of different concentration. Data are means ± SD; N = 4.

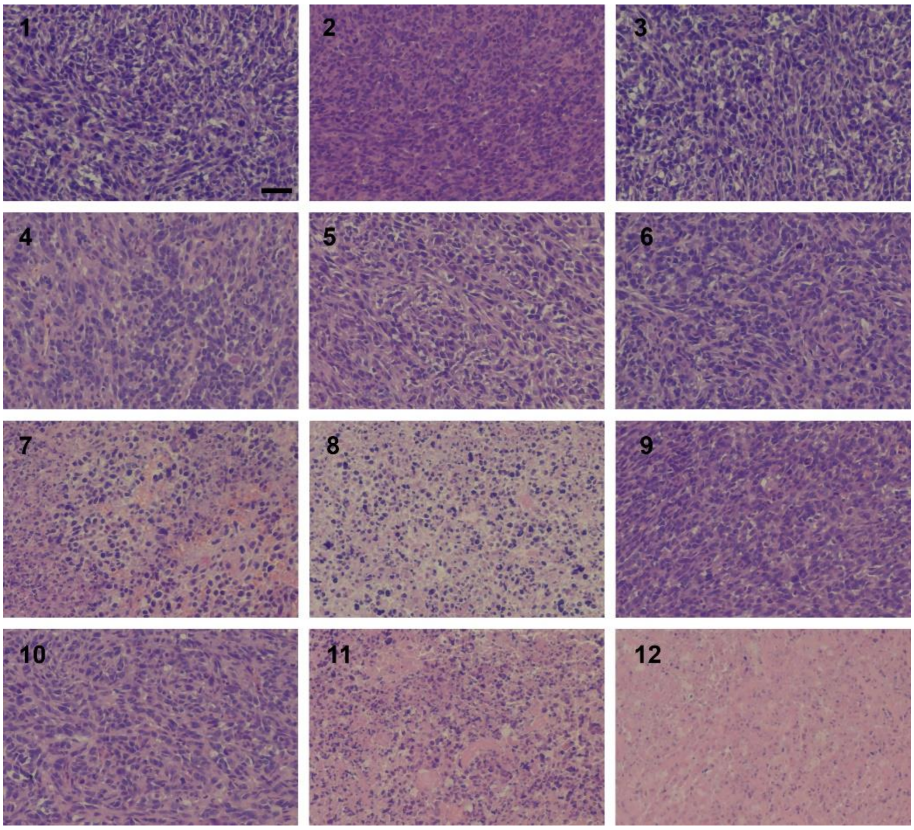

Figure S10. Representative H&E stained tumor sections after different treatments (1: Saline, 2: Saline + 640 nm + 808 nm, 3: PVP-AuNRs, 4: PVP-AuNRs + 808 nm, 5: PVP-AuNRs + 640 nm + 808 nm, 6: MOF NPs, 7: MOF NPs + 640 nm, 8: MOF NPs + 640 nm + 808 nm, 9: AuNR@MOFs, 10: AuNR@MOFs + 640 nm, 11: AuNR@MOFs + 808 nm, 12: AuNR@MOFs + 640 nm + 808 nm). Scale bars = 100 μm.

References

1 K. Lu, C. He and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 16712-16715.

2 D. K. Roper, W. Ahn and M. Hoepfner, *J. Phys. Chem. C*, 2007, **111**, 3636-3641.