Supporting Information

In situ synthesis of fluorescent polydopamine on biogenic MnO_2 nanoparticles as stimuli responsive multifunctional theranostics

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Characterization

The morphologies of the samples were observed by a HITACHI HT7700 operated at an acceleration voltage of 120 kV. HRTEM and energy dispersive spectrometry (EDS) were conducted using a Tecnai G2 F30 system operated at 200 kV in bright field mode. TEM images were analysed using Digital Micrograph software. Dynamic light scattering (DLS) of particles was measured by a Nano-Zetasizer (Malvern Instruments). Fluorescence spectra and UV-Vis-NIR spectra were recorded on a Lambda 750S spectrometer (PerkinElmer). Fourier transform infrared spectroscopy (FT-IR) was performed on an INVENIO-R (Bruker). Powder X-ray diffraction (XRD)

analysis was carried out on a SmartLab-SE (Rigaku Corporation). Mn concentrations of samples were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES 7000 Plus, Thermo Fisher, Waltham, MA, USA). Fluorescence images were obtained on a confocal laser scanning microscope system (CLSM) FV1000 (Olympus Company). T_1-weighted MRI images were acquired using a 4.7T MRI clinical MRI scanner (Bruker Biospin MRI GmbH, Ettlingen, Germany). NIR irradiation was performed using an MW-GX-808/5000 mW laser (Changchun Laser Optoelectronics Technology Co. Ltd.). The temperatures and thermal images were recorded on an infrared thermal imaging instrument (FLIR E50 camera, USA).

Calculation of Photothermal conversion efficiency

According to the previous report[1], the photothermal conversion efficiency (η) was calculated via equation 1:

$$\eta = \frac{hS(T_{\max} - T_{surr}) - Q_s}{I(1-10^{-A})} \qquad \text{(Eq 1)}$$

Where h is heat transfer coefficient. S represents surface area of the cell. T_{max} means the maximum steady-state temperature. T_{surr} is ambient temperature of surrounding. Q_s is heat dissipated from light absorbed by the cell itself, which is measured independently to be 0.27 mW. I is laser power (the area of the well was $3.14*(0.5)^2=0.785$ cm^2, the power density was 1.5 W/cm^2, the laser power was 0.785*1.5*1000=1177.5 mW), A means absorbance of Bio-MnO_2@F-PDA at the excitation wavelength of 808 nm, which is calculated to be 1.1486 (Figure 3d).

We define θ as the following:

$$\theta = \frac{T - T_{surr}}{T_{\max} - T_{surr}} \qquad \text{(Eq 2)}$$

Where ($T-\ T_{surr}$) represents the temperature increased compare to the surrounding, and ($T_{max}-T_{surr}$) means the temperature change at the maximum steady-state temperature.

$$\tau_s = -\frac{t}{\ln \theta} \qquad \text{(Eq 3)}$$

τ_s is the sample system time constant, which can be determined to be 187 s by the linear curve fitting of temperature cooling time according to Figure 3f.

$$hS = \frac{m_s C_s}{\tau_s} \qquad \text{(Eq 4)}$$

m_s (0.5 g) and C_s (4.2 J g^{-1}) are the mass and heat capacity of solvent, respectively. Putting this value into equation(4), the final photothermal-conversion efficiency (η) of Bio-MnO_2@PDA can be calculated to be 50.1%.

Table S1. Surface element composition of Bio-MnO_2@F-PDA analyzed by dot-scan EDS.

Element	Family	Atomic Fraction (%)	Mass Fraction (%)
C	K	56.15	42.79
N	K	19.56	24.15
O	K	16.41	16.96
P	K	5.33	9.30
S	K	0.91	1.76
Mn	K	1.65	5.04

Table S2. ICP-OES Result for Mn in Bio-MnO_2@F-PDA.

Sample	Mn/Bio-MnO_2@F-PDA
Mean value	5.93%
1	6.12%
2	5.43%
3	6.24%

Table S3. The photothermal conversion efficiency of polydopamine coating materials reported in this work and in previously reported literatures.

Name	Composition	Efficiency (%)	Ref.
Bio-MnO_2@F-PDA	biogenic MnO_2, PDA	50.1	This work
Bio-MnO_2 NPs	biogenic MnO_2	44	16
Dpa-melanin CNSs	PDA	40	20
Fe_3O_4@PDA composite	Fe_3O_4, PDA	13.1	21
PFP-PDA-PEG	Perfluoropentane (PFP), PDA, mPEG-NH_2	40.9	37
Au-PEI@pD NSs	Au, PEI, PDA	49.9	38

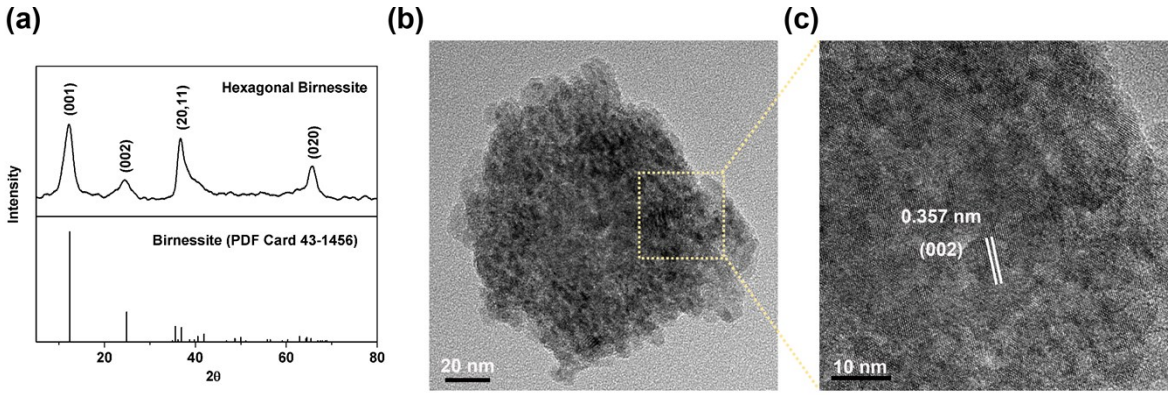

Figure S1 (a) XRD profile of Bio-MnO_2 NPs (30 min) and (b,c) the corresponding HRTEM images.

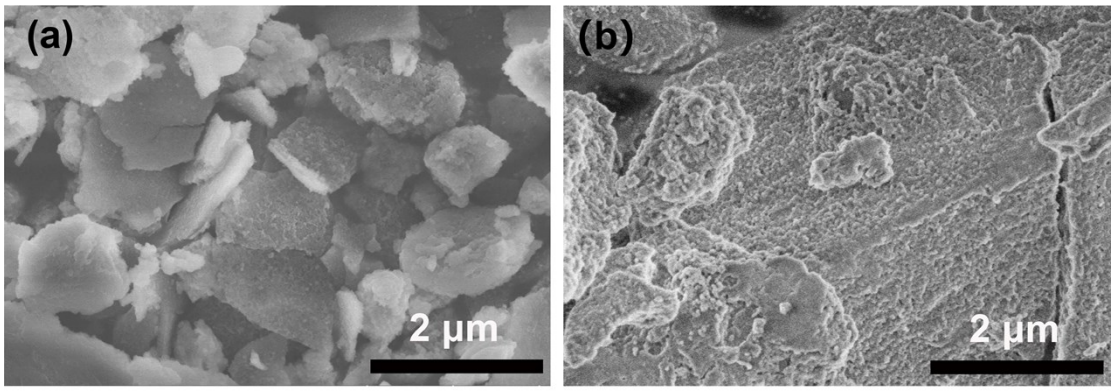

Figure S2. SEM images of (a) Bio-MnO_2 NPs and (b) Bio-MnO_2@F-PDA.

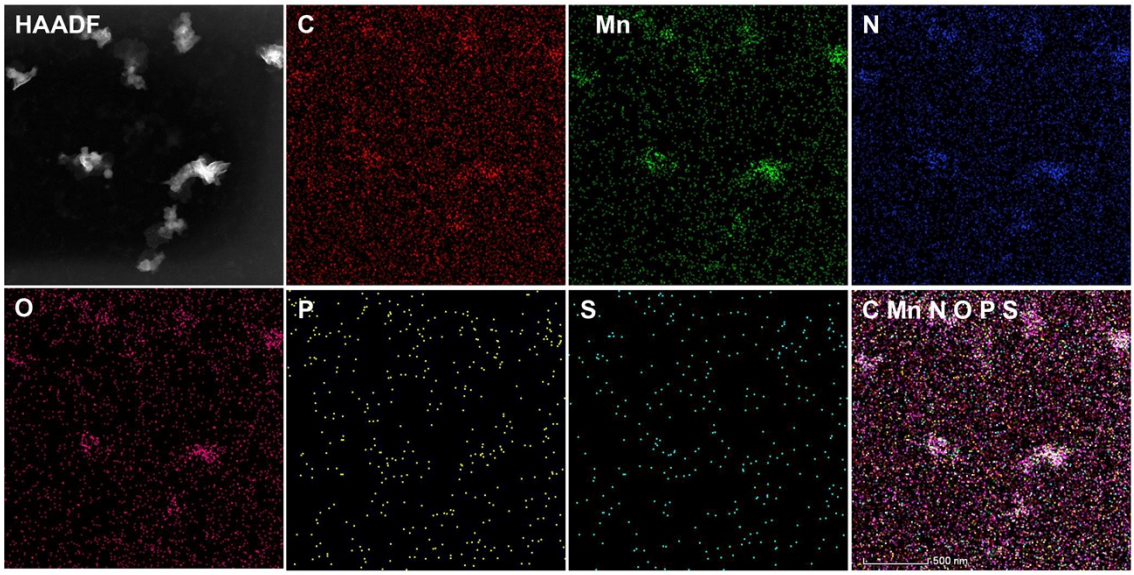

Figure S3 EDS mapping of Bio-MnO_2@F-PDA. (Scale bar: 500 nm in all images)

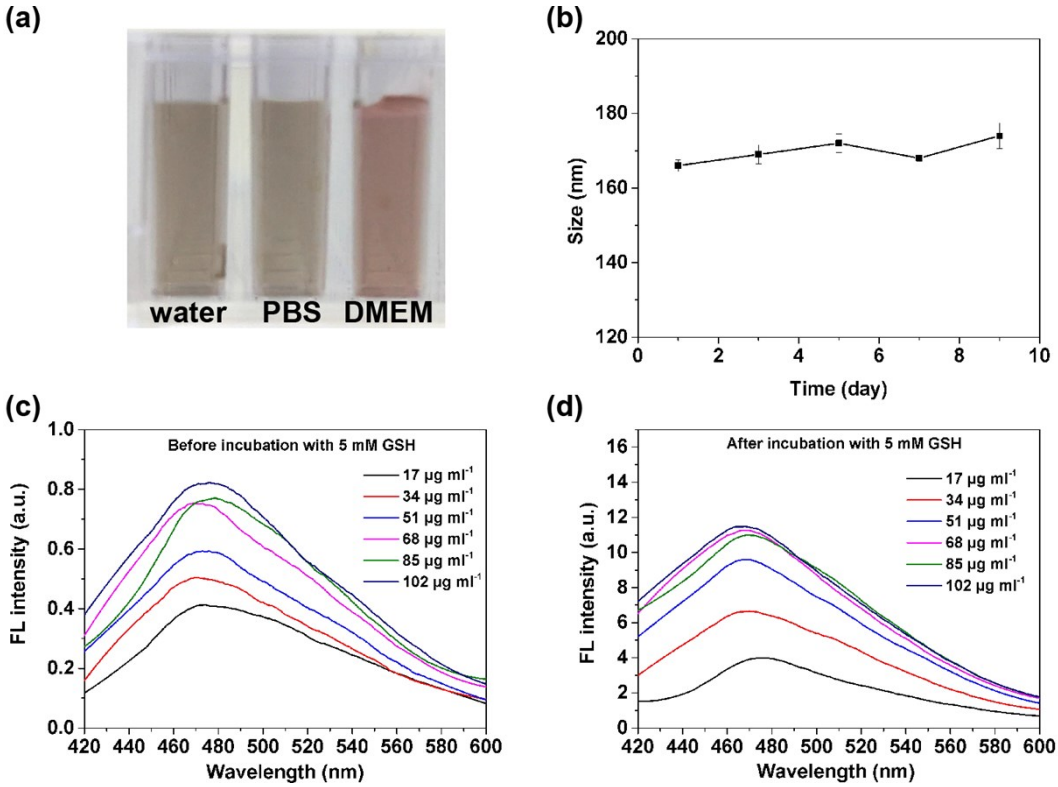

Figure S4 (a) The photographs of Bio-MnO_2@F-PDA dispersed in water, PBS and DEME medium. (b) The hydrodynamic diameter of Bio-MnO_2@F-PDA as a function of incubation time. (c) Fluorescence emission spectra of Bio-MnO_2@F-PDA synthesized from a series of different Bio-MnO_2 concentrations (excitation: 400 nm) and the corresponding fluorescence recovery after incubation with 5 mM GSH.

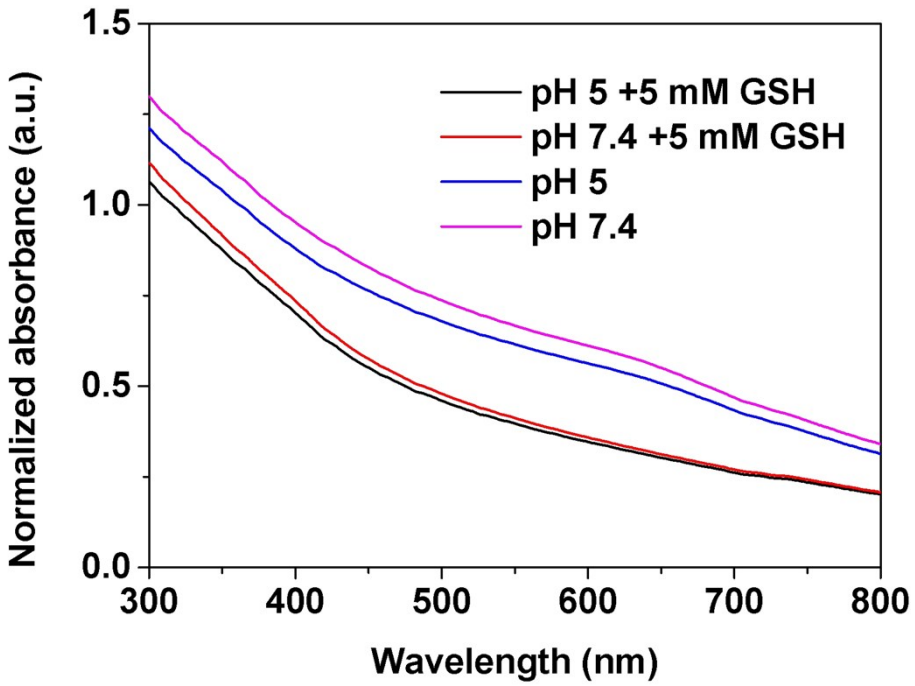

Figure S5 UV-vis-NIR spectra of Bio-MnO_2@F-PDA (250 μg mL^{-1}) after incubation in different buffer for 24 h.

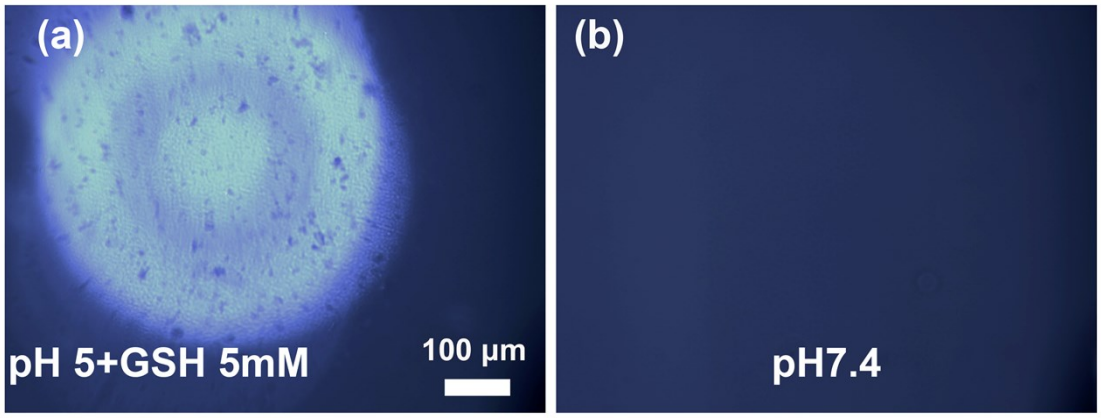

Figure S6 Fluorescence microscopy photos of Bio-MnO_2@F-PDA after incubation in (a) PBS (pH 5.0) supplemented with 5mM GSH and (b) PBS (pH 7.4) for 24 h, respectively. (Scale bar: 100 μm in all images)

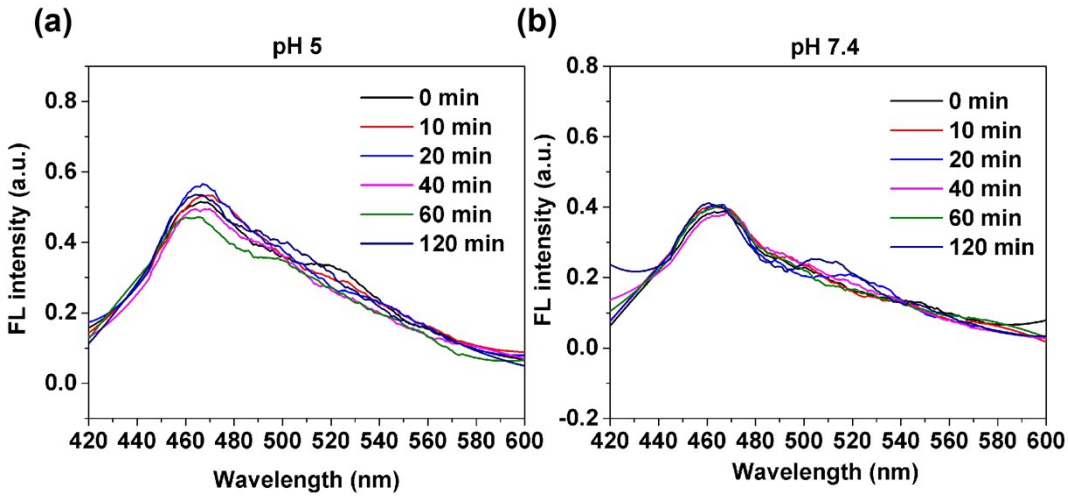

Figure S7 The fluorecence spectra of Bio-MnO_2@F-PDA excited by 400 nm light after incubation in buffer solutions of (a) pH5 and (b) pH 7.4 at different time.

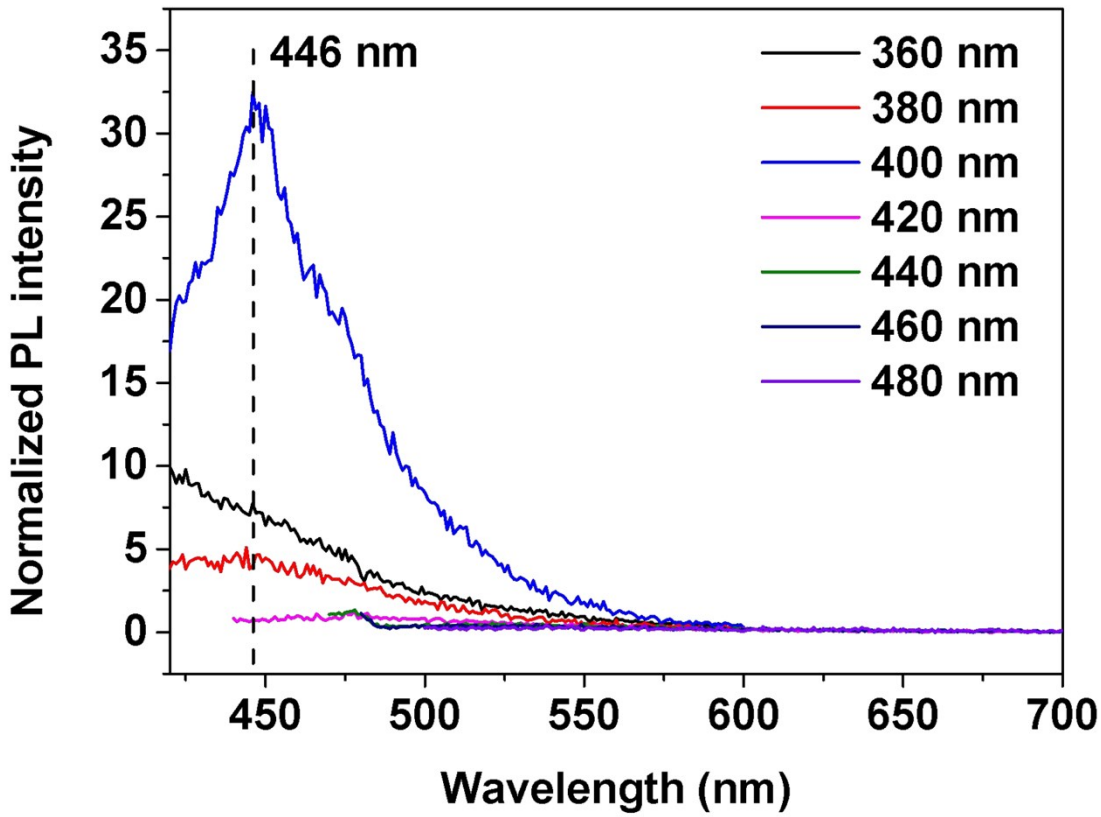

Figure S8 Fluorescence emission spectra (with gradually increased excitation wavelengths from 360 nm to 480 nm) of the Bio-MnO_2@F-PDA after incubation in PBS (pH 5.0) supplemented with 5mM GSH for 24 h.

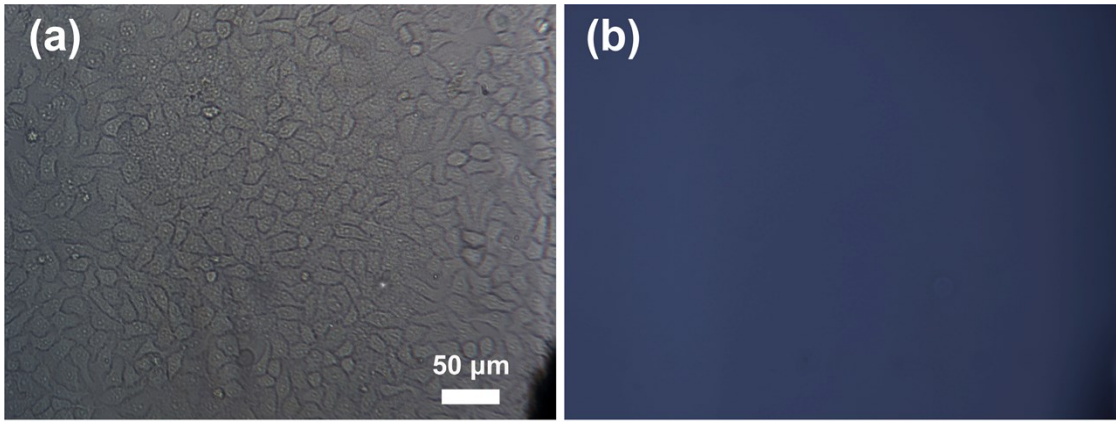

Figure S9 (a) and (b) are fluorescence images of Hela cells incubation without Bio-MnO_2@F-PDA under bright field and UV excitations, respectively. (Scale bar: 50 μm in all images)

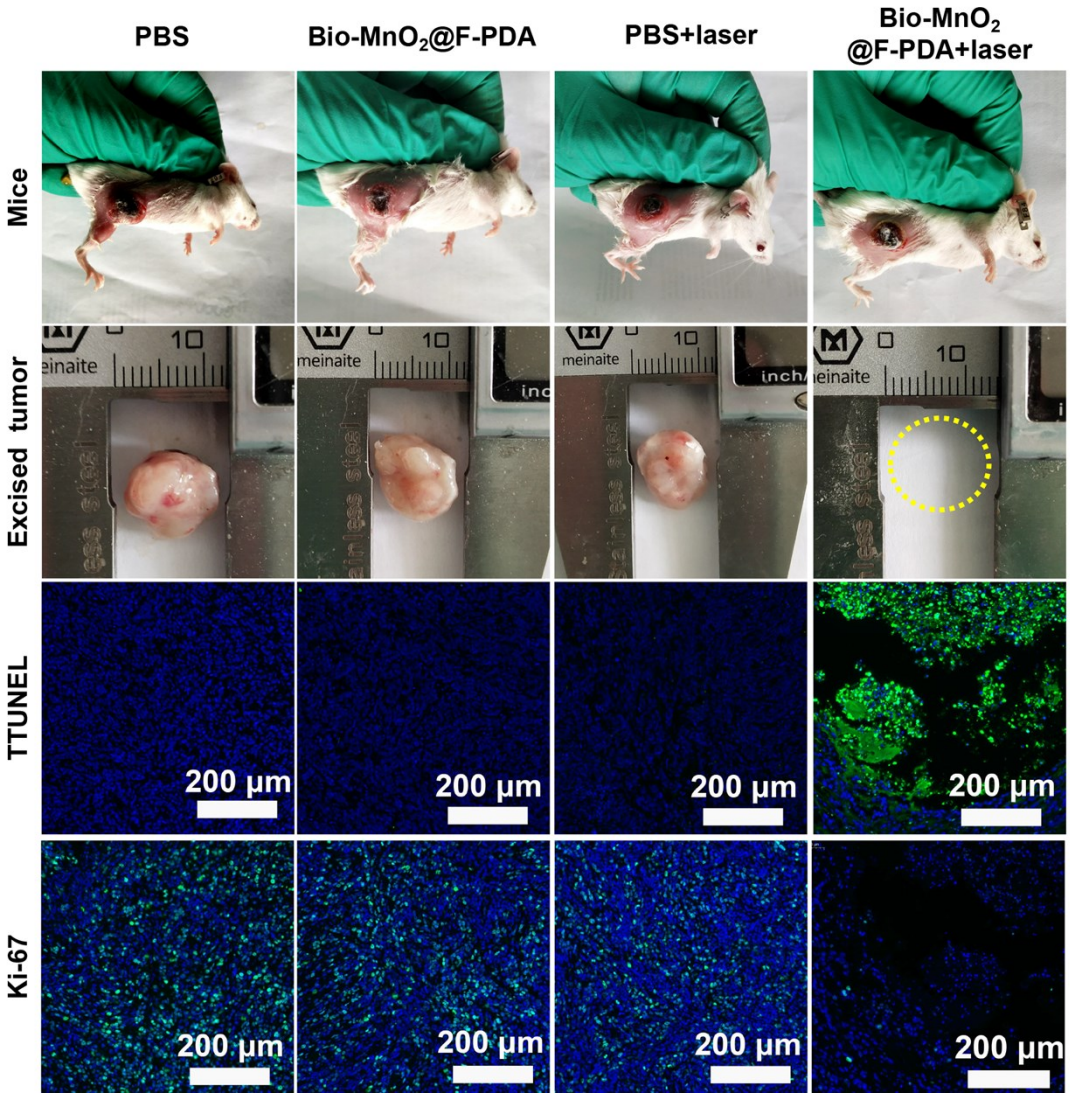

Figure S10 Photographs of representative mice after different treatments (16 days after the first treatment), excised Hela tumours from tumour-bearing mice and the results of TUNEL and antigen Ki-67 immunofluorescence staining of tumour tissues.

References

[1] Roper, D. K.;Ahn, W.; Hoepfner, M. Microscale Heat Transfer Transduced by Surface Plasmon Resonant Gold Nanoparticles. *J. Phys. Chem. C Nanomater. Interfaces* **2007**, *111*, 3636-3641.