Cation-exchange Controlled Core-shell MnS@Bi₂S₃ Theranostic Platform for Multimodal Imaging Guided Radiation Therapy with Hyperthermia Boost

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Figure S1. (a) TEM image of MnS NPs. (b) Corresponding HR-TEM image of MnS NPs. The elemental mapping images of Mn (c), S (d), and combined Mn and S (e), respectively.



Figure S2. EDS spectra of MnS and MnS@Bi₂S₃ NPs.



Figure S3. Powder XRD pattern of MnS.



Figure S4. HAADF-STEM image of core-shell MnS@Bi₂S₃ NPs prepared at 160 °C for 30 min.



Figure S5. Fast Fourier transform (FFT) image of MnS@Bi₂S₃ HR-TEM image.



Figure S6. XPS patterns of MnS@Bi₂S₃ for the element of (a) Mn, (b) Bi and S.



Figure S7. Statistics data of Bi_2S_3 shell thickness acquired under various reaction temperatures for 30 min

Reaction Condition	140 °C,	30 min	160 °C,	30 min	180 °C,	30 min
Element	Wt %	Atomic %	Wt %	Atomic %	Wt %	Atomic %
S	32.84	54.34	29.84	54.27	23.65	54.05
Mn	40.18	38.81	33.43	35.48	19.5	26.02
Bi	26.98	6.85	36.74	10.25	56.84	19.93
Total:	100	100	100	100	100	100
Similar Formula	Mn _{11.3} S _{11.3} @Bi ₂ S ₃		Mn ₇ S ₇ @Bi ₂ S ₃		Mn _{2.6} S _{2.6} @Bi ₂ S ₃	
MnS:Bi ₂ S ₃	11.3 : 1		7:1		2.6 : 1	

 Table S1. MnS@Bi₂S₃ EDS data of Bi, Mn, and S element compositions acquired

 under various reaction temperatures for 30 min

Table S2. MnS@Bi₂S₃ ICP-OES data of Bi and Mn elements composition acquired under various reaction temperatures for 30 min

	140 °C, 30 min	160 °C, 30 min	180 °C, 30 min
Mn	39.95%	33.55%	19.41%
Bi	27.10%	36.80%	56.99%



PMHC₁₈-mPEG₂₀₀₀

poly(maleic anhydride-alt-1-octadecene)poly(ethylene glycol) methyl ethers)





Figure S9. ¹H-NMR of PMHC₁₈-mPEG₂₀₀₀



Figure S10. (a) DLS diameter and (b) zeta potential distribution of MnS@Bi₂S₃-PEG NPs in different solvents.



Figure S11. (a) UV-vis absorption of MnS in cyclohexane and MnS@Bi₂S₃-PEG in H₂O. (b) UV-vis absorption of MnS@Bi₂S₃-PEG in different concentration. (c) UV-vis absorption vs. concentration plot of MnS@Bi₂S₃-PEG in H₂O at 808 nm. (PMHC₁₈-mPEG₂₀₀₀ was also modified on the MnS NPs surface according to the similar procedure of fabrication of PMHC₁₈-mPEG₂₀₀₀ modified MnS@Bi₂S₃NPs.)



Figure S12. PA signal changing of MnS@Bi₂S₃-PEG excited under different absorption wavelength from 680 nm to 970 nm.



Figure S13. The relationship between different concentrations of MnS@Bi₂S₃-PEG NPs in H₂O vs increased temperature under the irradiation of 808 nm laser (800 mW cm⁻²) for 10 min.



Figure S14. The temperature change curves of $MnS@Bi_2S_3$ -PEG H₂O solutions (0.8 mg mL⁻¹) after multiple cycles of exposure to the 808 nm NIR laser irradiation (power density = 800 mW cm⁻²).



Figure S15. The H&E stained slices of different organs for a control group, and intravenous (i.v.) injected MnS@Bi₂S₃-PEG (20 mg kg⁻¹) after 24 h or 21 d including $100 \times$ magnifications.



Figure S16. Blood analysis data of healthy BALB/c mice were intravenous (i.v.) injected MnS@Bi₂S₃-PEG (20 mg kg⁻¹) after 1d or 21 d. Healthy BALB/c mice were intravenous (i.v.) injected saline (200 μ L) as control.