Supplementary Information

Precise Synthesis of Unique Polydopamine/Mesoporous Calcium Phosphate Hollow Janus Nanoparticles for Imaging-Guided Chemo-Photothermal Synergistic Therapy

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Photothermal Conversion Efficiency

To evaluate the photothermal conversion efficiency, the PEG-ICG-PDA/mCaP H-JNPs (1 mL, 200 μg mL^{-1}) in centrifuge tubes were exposed to an 808 nm NIR laser (1 W cm^{-2}, 540 s). The temperature of the solutions was measured by a digital thermometer and recorded every 30 s. The photothermal conversion efficiency (η) was calculated by Equation (1):[1-2]

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

in which h is the heat-transfer coefficient, S is the surface area of the container, the equilibrium temperature is T_{max}, T_{Surr} is the ambient temperature of the surroundings, Q_{dis} expresses the heat associated with the light absorbance by the solvent, I expresses the incident laser power (1 W cm^{-2}), and A_{808} is the absorbance of the PEG-ICG-PDA/mCaP H-JNPs at 808 nm. The value of hS is derived according to Equation (2)

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

where τ_s is the sample system time constant, m_D and C_D are the mass and heat capacity of water used as the solvent, respectively.

Fig. S1 Photographs of PAA NPs (left) and PDA/PAA JNPs (right).

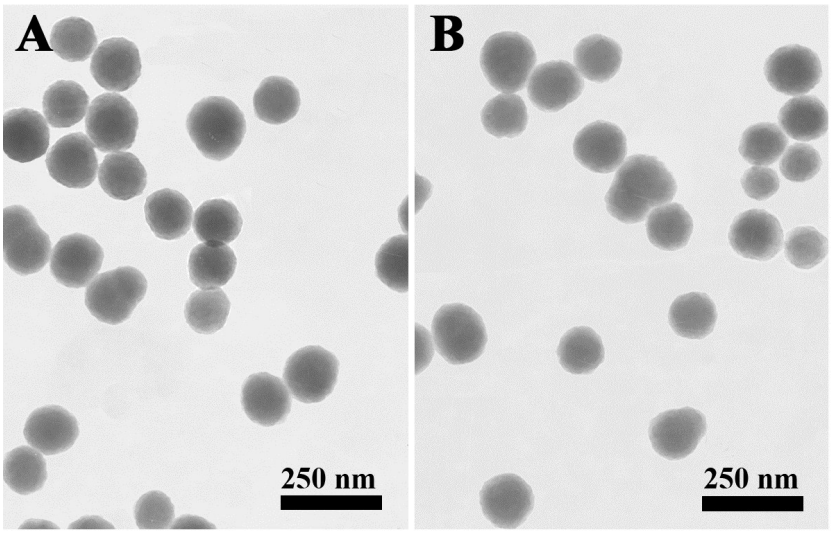

Fig. S2 TEM images of PDA nanospheres prepared without adding the template (PAA NPs) for 3.5 h at 50 °C (A) before and (B) after washing with water.

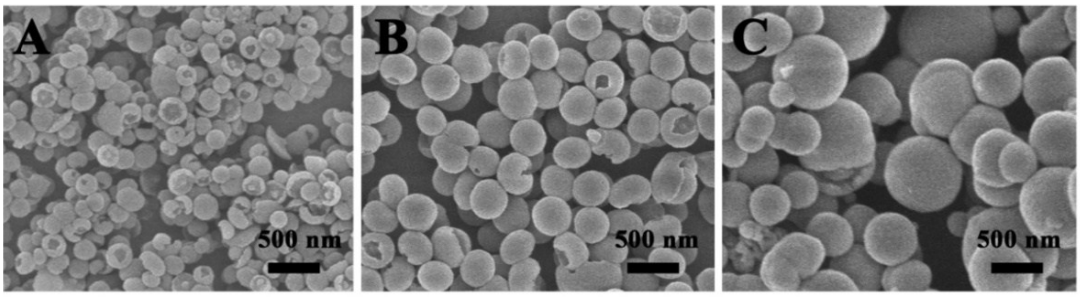

Fig. S3 SEM images of PDA NPs with different morphologies prepared with different amounts of dopamine hydrochloride (A) 5 mg mL^{-1}, 3 mL, (B) 8 mg mL^{-1}, 3 mL and (C) 13 mg mL^{-1}, 3 mL, respectively.

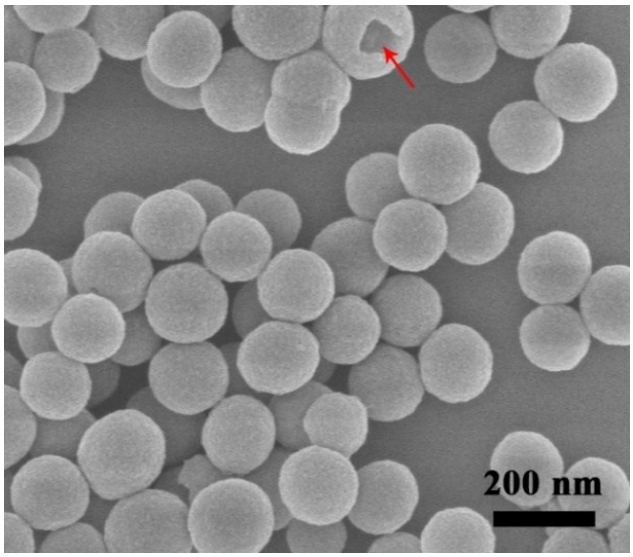

Fig. S4 SEM image of as-prepared PDA/mCaP H-JNPs (a purposely selected broken H-JNP with red arrow).

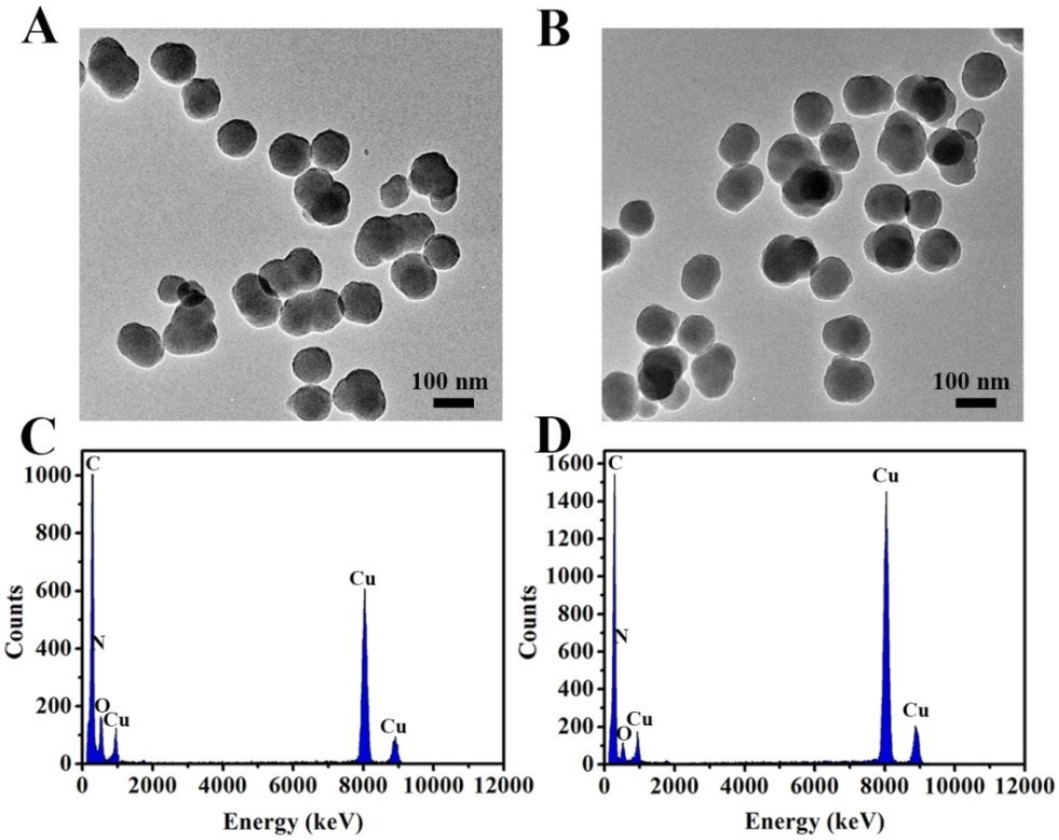

Fig. S5 TEM images and corresponding EDX spectra of PDA NPs (A, C) before and (B, D) after the addition of $CaCl_2$ and Na_2HPO_4.

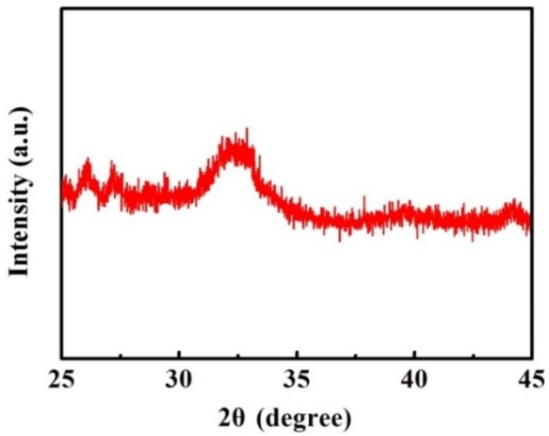

Fig. S6 XRD pattern of PDA/mCaP H-JNPs.

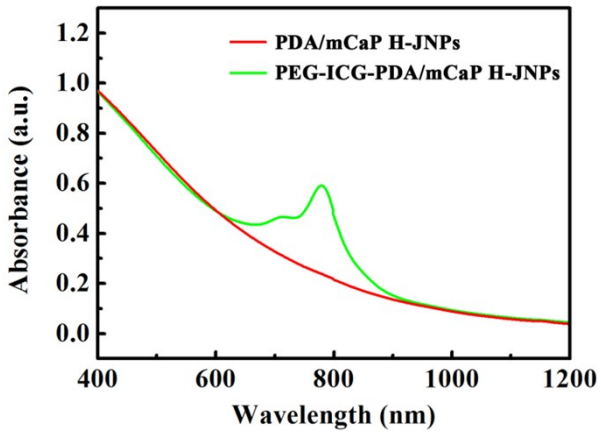

Fig. S7 UV-vis-NIR spectra of PDA/mCaP H-JNPs and PEG-ICG-PDA/mCaP H-JNPs.

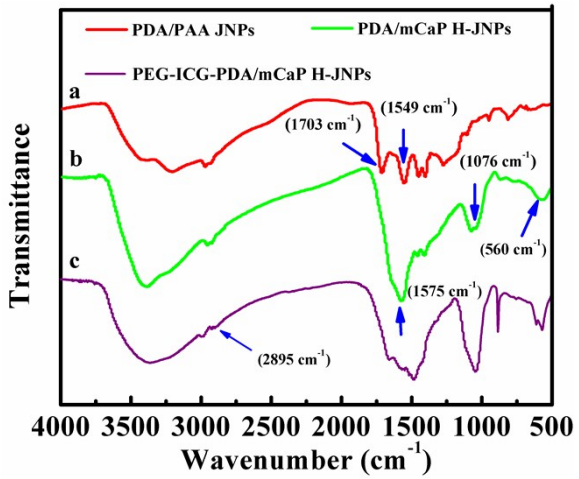

Fig. S8 FTIR spectra of (a) PDA/PAA JNPs, (b) PDA/mCaP H-JNPs and (c) PEG-ICG-PDA/mCaP H-JNPs. A new band centered at 560 and 1076 cm^{-1} in (b) can be observed, which are attributed to the characteristic peaks of O-P-O bending and asymmetric stretching of PO_4^{3-} ions. The band at 2895 cm^{-1} in (c) is assigned to the symmetric stretching vibrations of $-CH_3$ groups, indicating the successful modification of PEG on the surface of PDA domains.

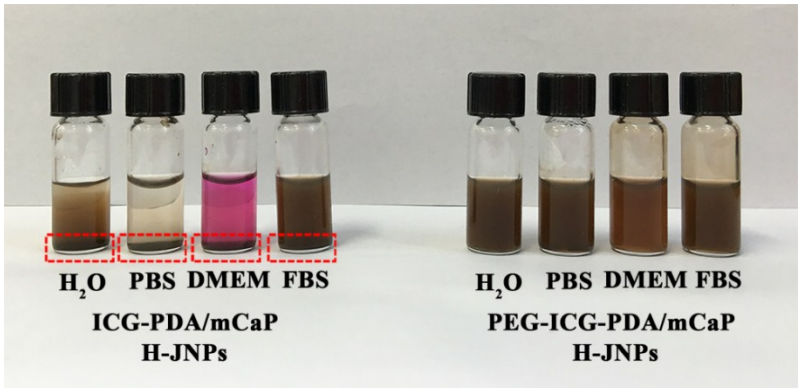

Fig. S9 Photographs of ICG-PDA/mCaP H-JNPs and PEG-ICG-PDA/mCaP H-JNPs in different solutions even after one week. The red squares indicate the location of the precipitation of ICG-PDA/mCaP H-JNPs. No precipitation of PEG-SH modified ICG-PDA/mCaP H-JNPs was observed in water, PBS buffer, fetal bovine serum (FBS) or culture medium even after one week, in comparison with the ICG-PDA/mCaP H-JNPs under the same conditions, indicating that the PEG-SH was successfully modified and effectively improved the stability of ICG-PDA/mCaP H-JNPs.

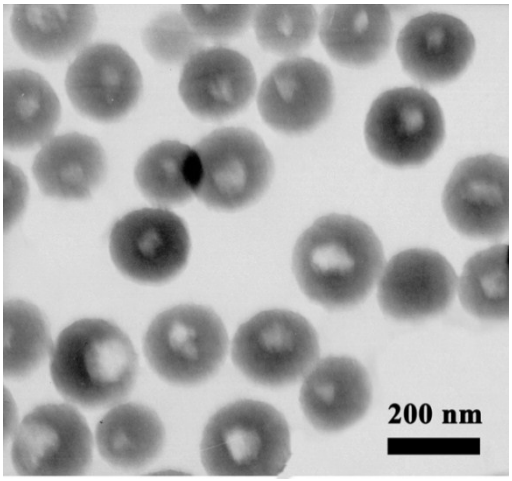

Fig. S10 TEM image of the PEG-ICG-PDA/mCaP H-JNPs after irradiation by an 808 nm NIR laser at power density of 1 W cm^{-2} for 5 min.

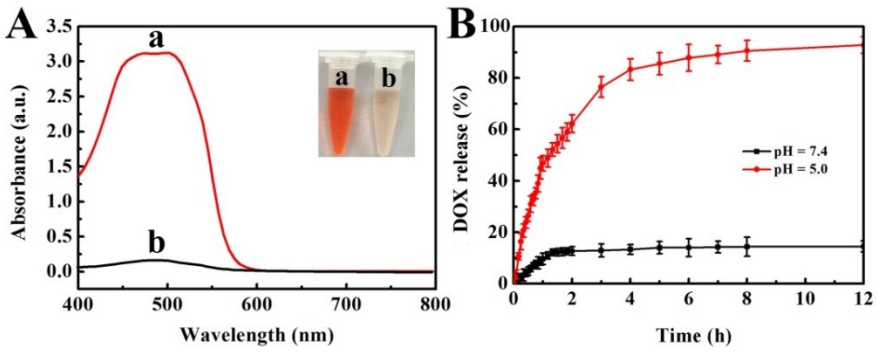

Fig. S11 (A) UV-vis absorption spectra and photographs (inset) of DOX solutions before (a) and supernatant after centrifugation of interacting with the PEG-ICG-PDA/mCaP H-JNPs (b). (B) DOX release profiles from DOX-loaded PEG-ICG-PDA/mCaP H-JNPs at different PBS solutions at 37 °C.

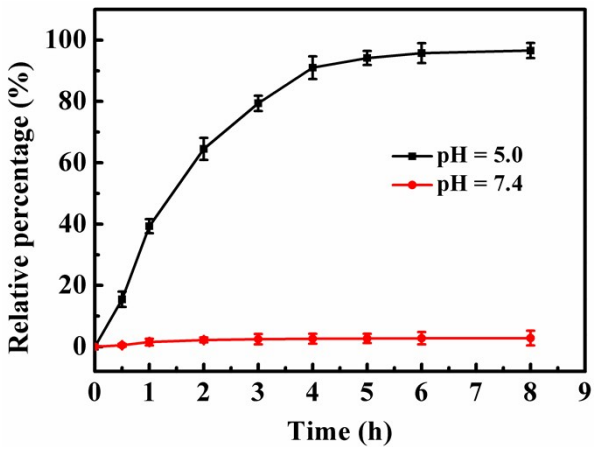

Fig. S12 The Ca^{2+} dissolution percentages of PEG-ICG-PDA/mCaP H-JNPs measured in PBS buffer at pH values of 7.4 and 5.0 at 37 °C, respectively.

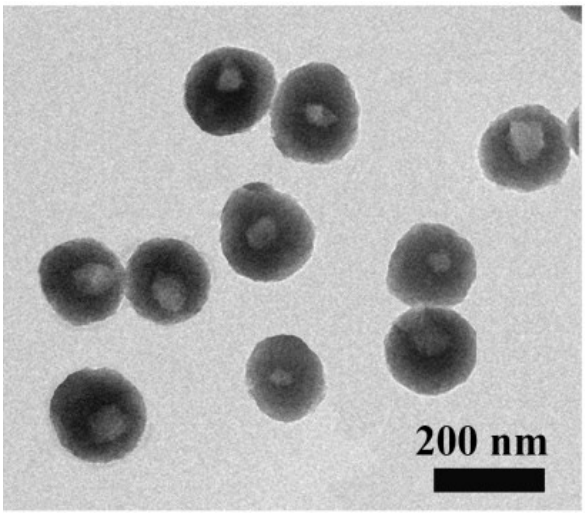

Fig. S13 TEM image of PEG-ICG-PDA/mCaP H-JNPs after being immersed in PBS buffers at pH 7.4.

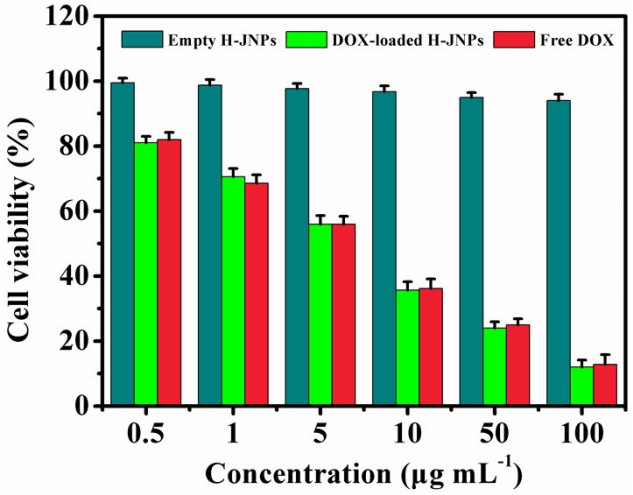

Fig. S14 The cytotoxicity of HepG-2 cells treated with free DOX, empty PEG-ICG-PDA/mCaP H-JNPs and DOX-loaded PEG-ICG-PDA/mCaP H-JNPs with different concentrations after 24 h.

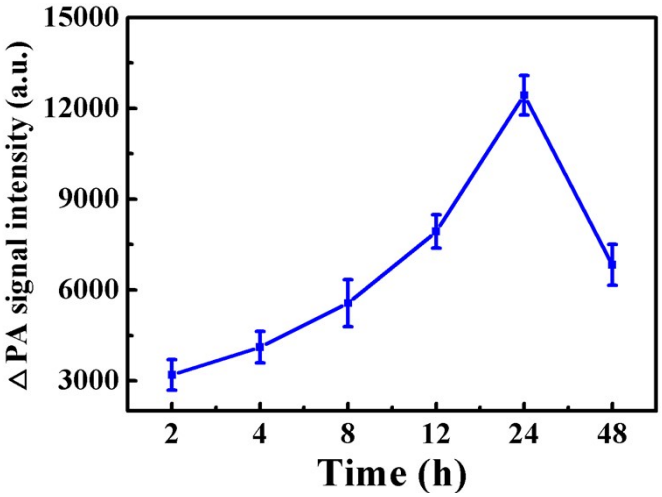

Fig. S15 Quantified PA signals of the tumorous sites of mice.

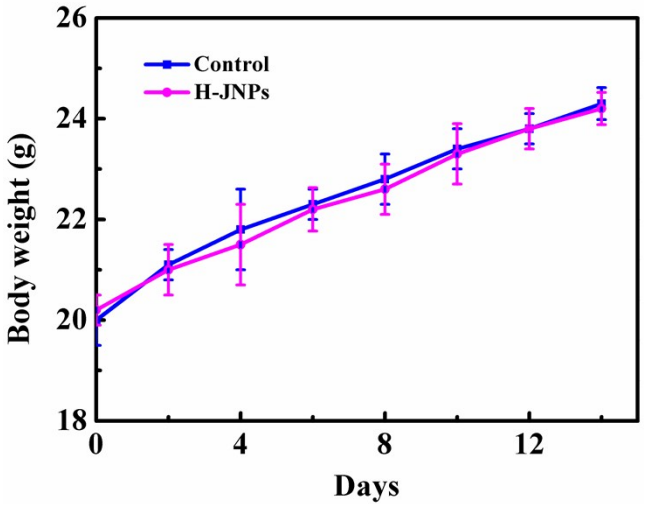

Fig. S16 Body weight changes of mice after intravenous injection of PBS (control) and PEG-ICG-PDA/mCaP H-JNPs (20 mg kg^{-1}), respectively. No noticeable body weight losses were observed in the control and PEG-ICG-PDA/mCaP H-JNPs groups, suggesting no abnormalities in eating, drinking, grooming, activity, exploratory behavior, urination, or neurological status.

1 Q. W. Tian, F. R. Jiang, R. J. Zou, Q. Liu, Z. G. Chen, M. F. Zhu, S. P. Yang, J. L. Wang, J. H. Wang, J. Q. Hu, *ACS Nano* 2011, **5,** 9761;

2 F. L. Gao, M. Z. Sun, L. G. Xu, L. Q. Liu, H. Kuang, C. L. Xu, *Adv. Funct. Mater.* 2017, **27,** DOI: 10.1002/adfm.201700605.