Electronic Supplementary Material

Cu-chelated polydopamine nanoparticle as photothermal medium and "immunogenic cell death" inducer for combined tumor therapy

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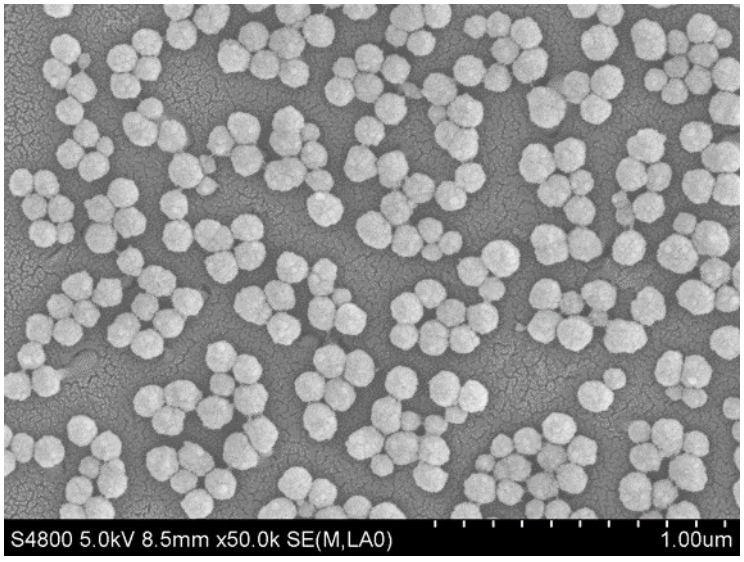

Figure S1. SEM image of Cu-PDA-FA NPs.

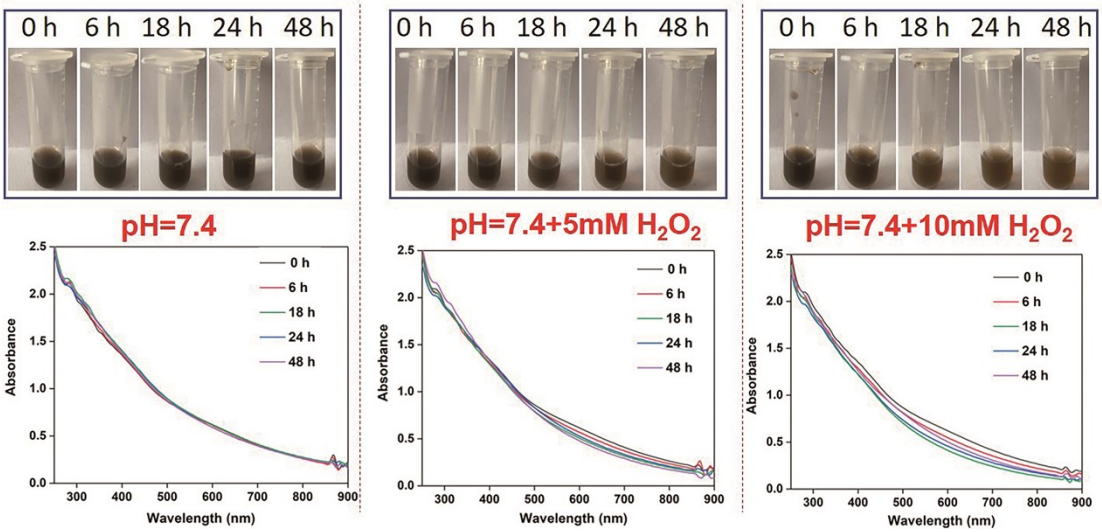

Figure S2 H_2O_2-triggered degradation assay of PDA. UV-vis absorption spectra of PDA dispersion in different concentration H_2O_2 for different times. The digital photographs showed the Color change of PDA dispersion.

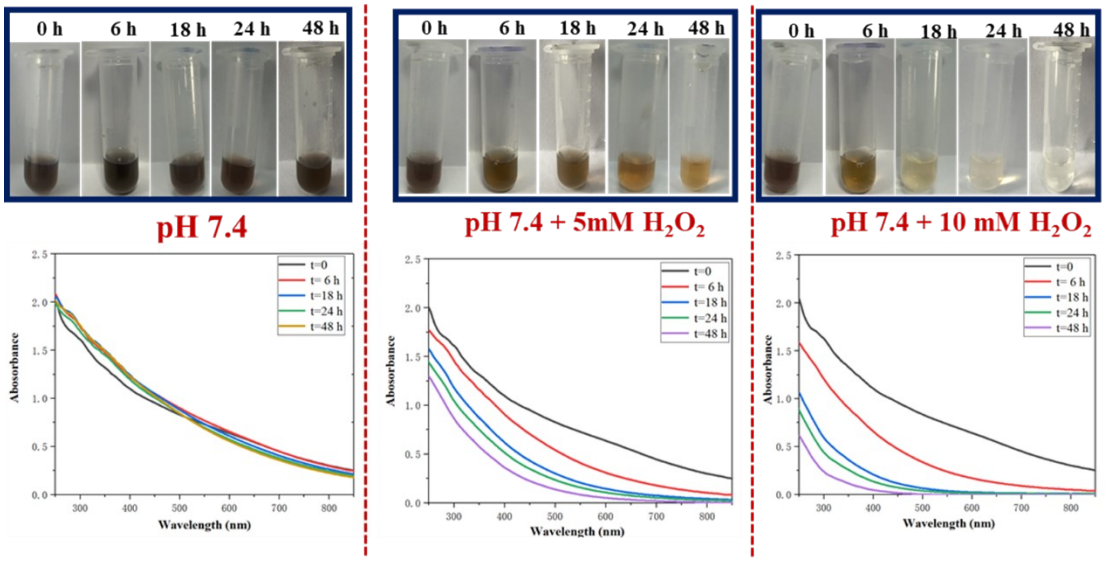

Figure S3. H_2O_2-triggered degradation assay of Cu-PDA. UV-vis absorption spectra of Cu-PDA dispersion in different concentration H_2O_2 for different times. The digital photographs showed the Color change of Cu-PDA dispersion.

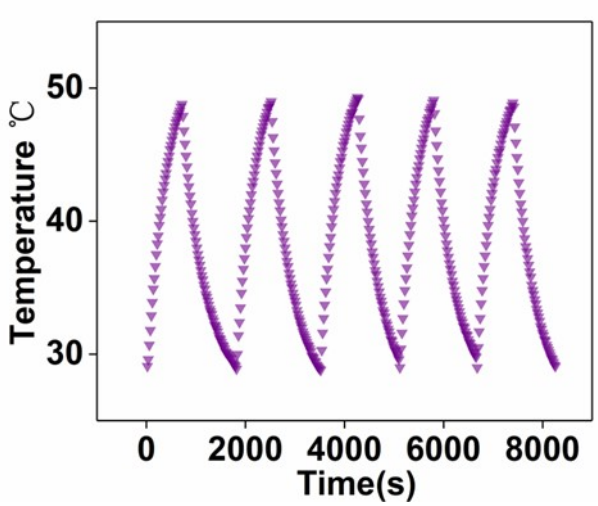

Figure S4 Fives cycles of an on-off laser irradiation curves

The photothermal conversion efficiency could be determined by Eq.1

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

where h was the heat transfer coefficient, A was the surface area of the container, ΔT_{max} was the temperature change of the Cu-PDA NPs dispersion at the maximum steady-state temperature, I was the laser power, A_λ was the absorbance of Cu-PDA NPs dispersion at 808 nm, ΔT_{water} was the temperature change value of solvent water under the same conditions. Qs was the heat associated with the light absorbance of the solvent, which was measured independently to be 25.2 mW using pure water. In this equation, only *hA* was unknown for calculation. hA was a constant, which could be obtained by the cooling curve of the Cu-PDA. For

calculating *hA*, τs and θ were introduced according the previous method:

$$\tau_s = \frac{\sum_i m_i c_{p,i}}{hA} \quad (2)$$

$$\theta = \exp\left(\frac{t}{\tau s}\right) \quad (3)$$

therefore, we could get:

$$t = -\tau_s \, ln\theta \quad (4)$$

where m was the mass of Cu-PDA dispersion (1 g) and Cp was heat capacity of solvent (4.2 J/g °C). hA could be determined by the slope of the linear time data from the cooling period vs –lnθ. The photothermal conversion efficiency (η) of Cu-PDA was 46.84%, which was higher than that of pure PDA (η = 36.00%).

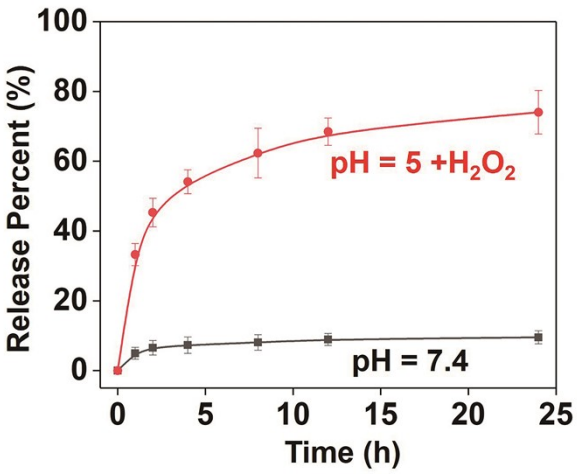

Figure S5. Cu(II) release curves in different media.

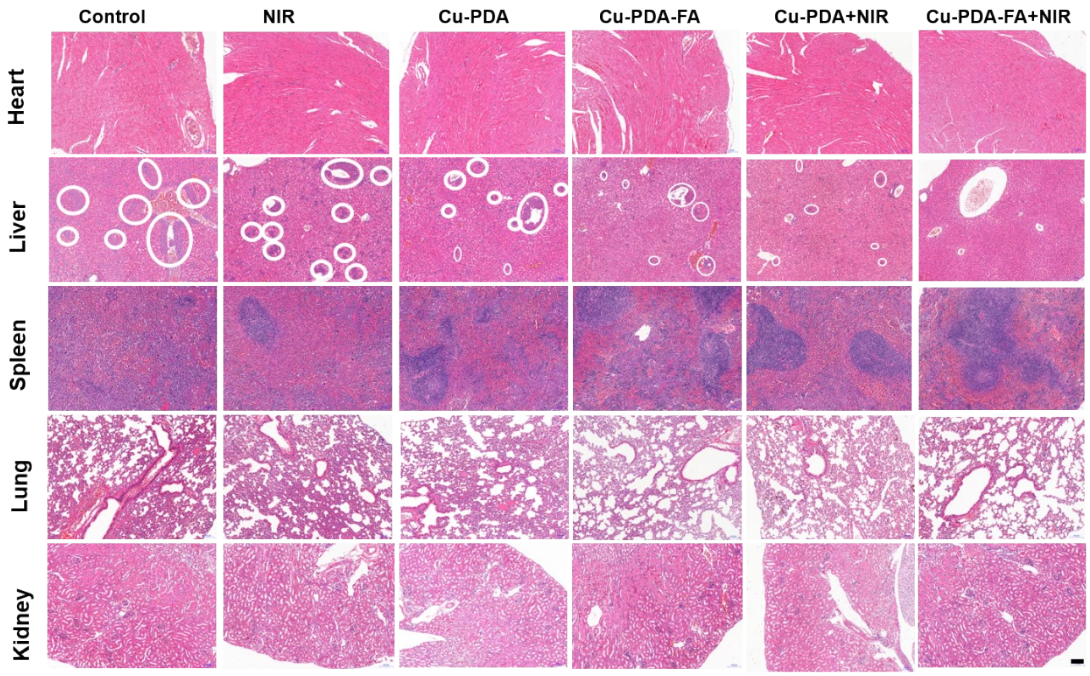

Figure S6 H&E staining of main organs (heart, liver, spleen, lung, kidney) of different treatments. Scale bar, 100 μm.

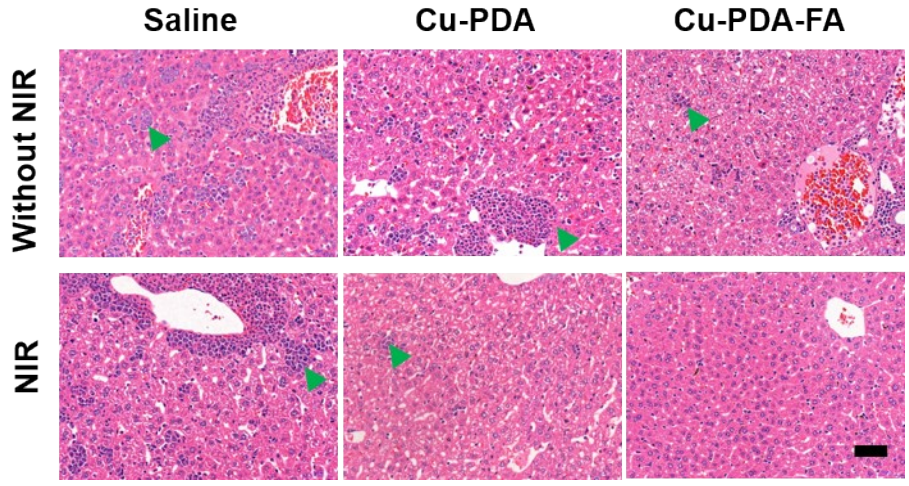

Figure S7 The H&E staining in the tumor site after 1 day of different treatments. Scale bar is 50 μm. The green clippers point to tumor-like cells.

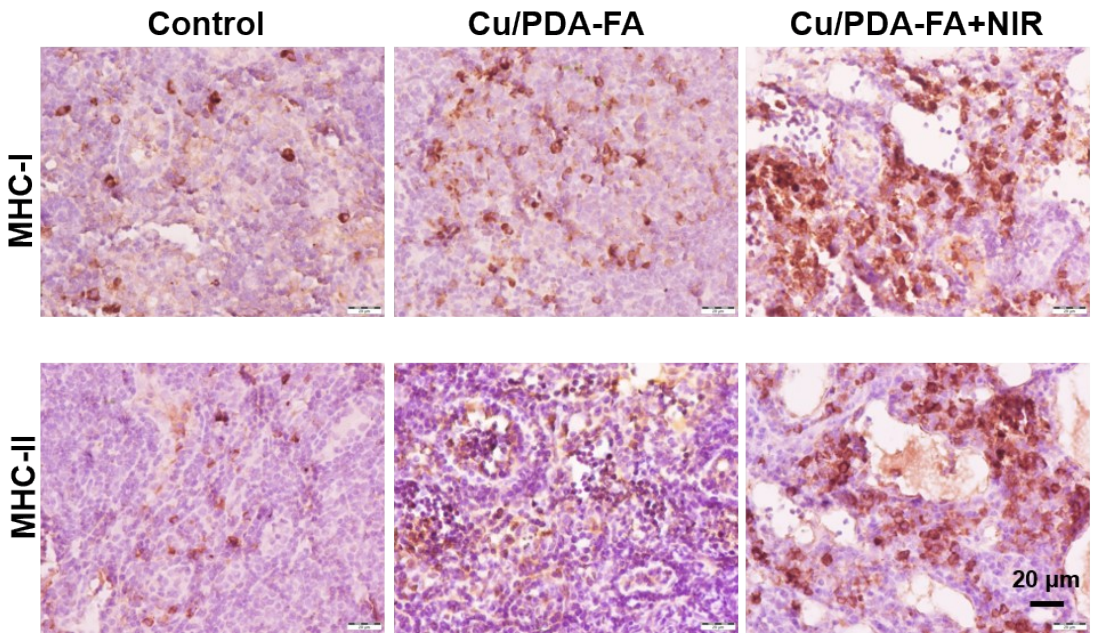

Figure S8 Immunohistochemical staining of MHC-I and MHC-II in lymph node. Scale bar: 20 μm.