Supplementary materials

Amplified Oxidative Stress Therapy of Degradable Copper Phosphate Nanozyme Coated by in situ Polymerization of PEGDA

Ning Nie,†[a] Yifan Liu,†[a] Bing Li,[a,c] Zhentao Hua,[a,c] Jianfeng Liu,*[a,b] Jinjian Liu,*[b] Wei Wang*[a]

[a]Lab of Functional and Biomedical Nanomaterials, College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China
[b]Tianjin Key Laboratory of Radiation Medicine and Molecular Nuclear Medicine, Institute of Radiation Medicine, Chinese Academy of Medical Sciences and Peking Union Medical College, Tianjin 300192, China
[c]State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China
†The authors contributed equally to this work

Keywords: copper phosphate, nanozymes, oxidative stress therapy, photothermal therapy;

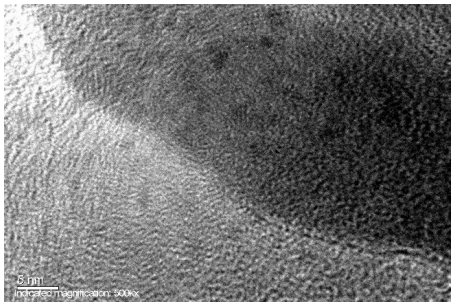

Fig. S1 High-resolution TEM image of the $Cu_3(PO_4)_2$.

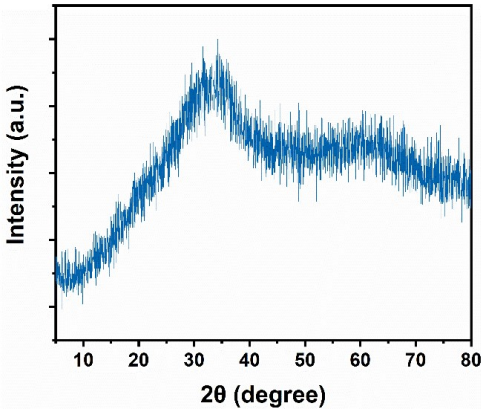

Fig. S2 XRD pattern of $Cu_3(PO_4)_2$.

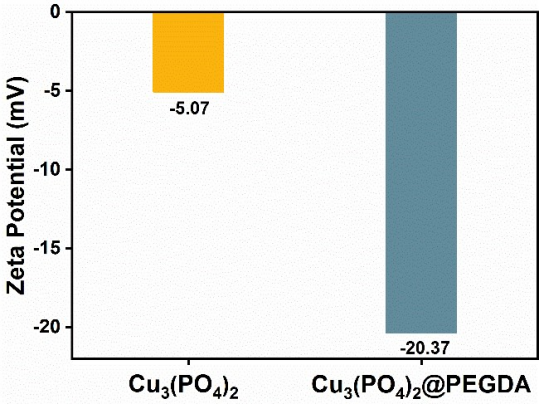

Fig. S3 Zeta potential of $Cu_3(PO_4)_2$ and $Cu_3(PO_4)_2$@PEGDA.

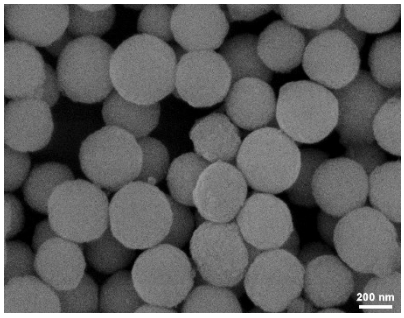

Fig. S4 SEM image of the $Cu_3(PO_4)_2$ after five cycles of on-off laser irradiation procedure (808 nm, 2.0 W/cm^2).

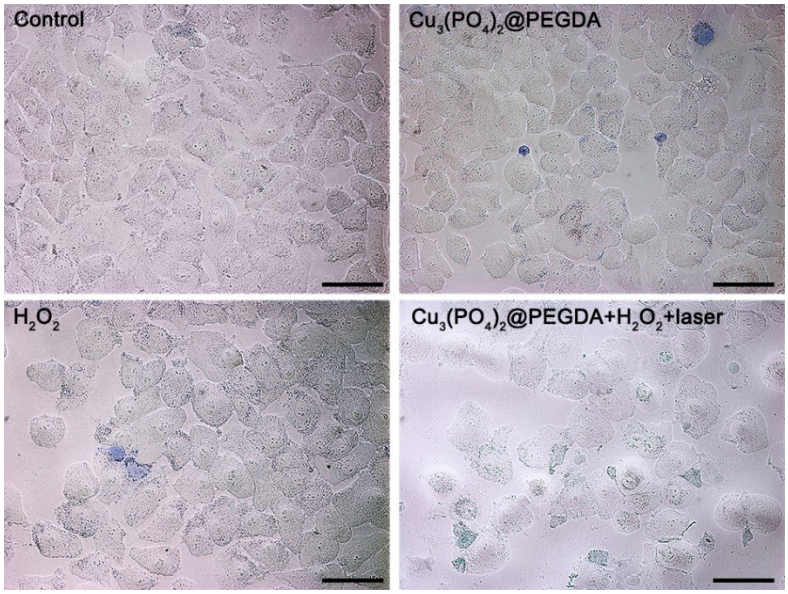

Fig. S5 Optical microscopy images of HUVEC cells stained by trypan blue. Scale bars: 100 μm.

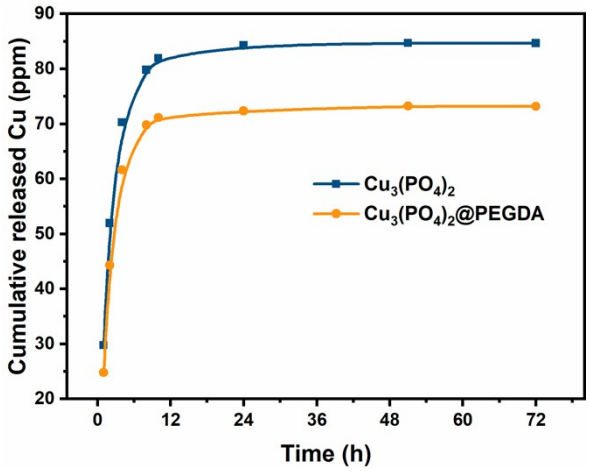

Fig. S6 Release profiles of Cu ions from $Cu_3(PO_4)_2$ and $Cu_3(PO_4)_2$@PEGDA soaked in citric acid-Na_2HPO_4 buffer (pH=5.6).

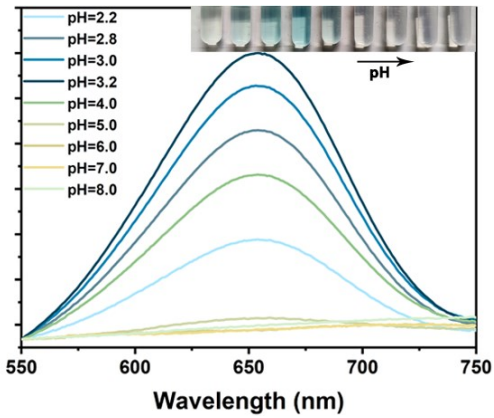

Fig. S7 Typical UV-Vis spectra and inset of TMB-H_2O_2-$Cu_3(PO_4)_2$@PEGDA reaction system (50 μL of 25 mM TMB, 50 μL of 25 mM H_2O_2, 50 μL of 1 mg/mL $Cu_3(PO_4)_2$@PEGDA, 2350 μL of citric acid-Na_2HPO_4 buffer solution).

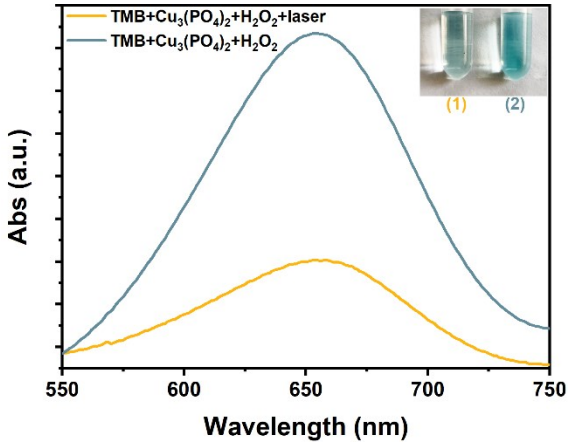

Fig. S8 Typical UV-Vis spectra of TMB-H_2O_2-$Cu_3(PO_4)_2$@PEGDA reaction system before and after laser irradiation for 30 min in citric acid-Na_2HPO_4 buffer solution (pH=3.2) (0.5 mM TMB, 0.5 mM H_2O_2, 20 μg/mL $Cu_3(PO_4)_2$@PEGDA).

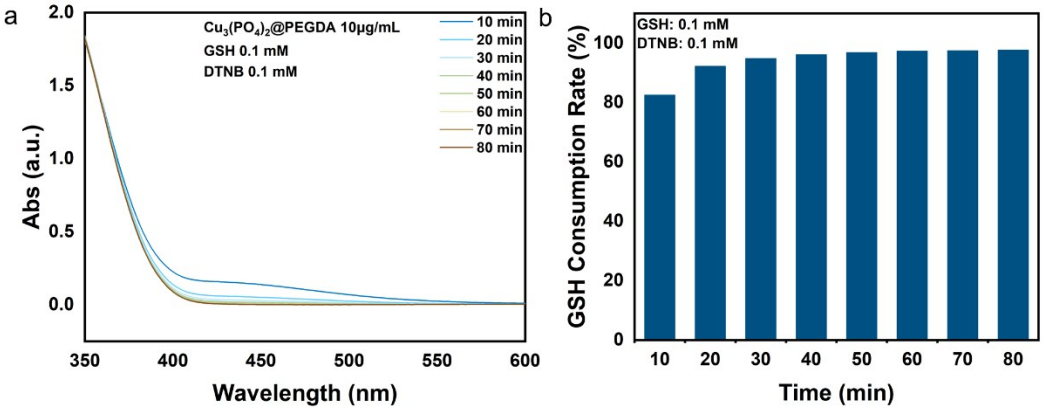

Fig. S9 (a) Concentration-dependent GSH depletion and (b) GSH consumption rate by $Cu_3(PO_4)_2$@PEGDA nanozyme.

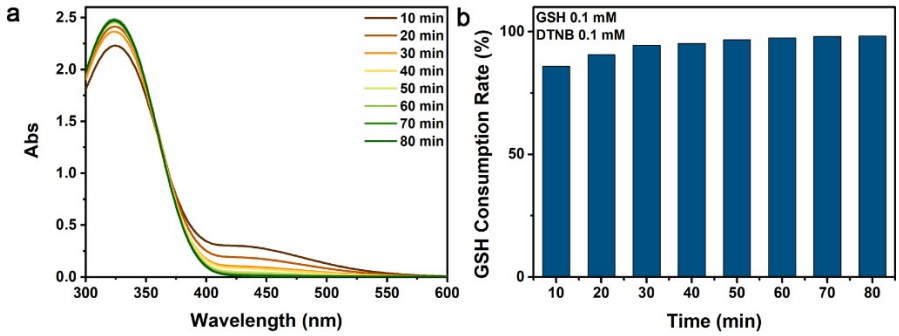

Fig. S10 (a) Concentration-dependent GSH depletion and (b) GSH consumption rate by $Cu_3(PO_4)_2$ nanozyme.

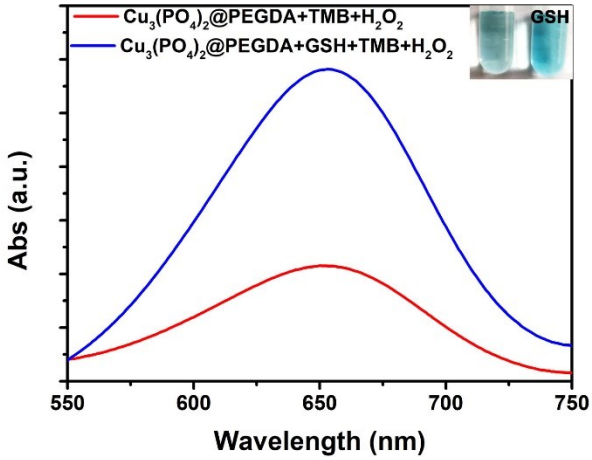

Fig. S11 Reaction of GSH with the generated ·OH-induced enhancement of Fenton-like reaction.

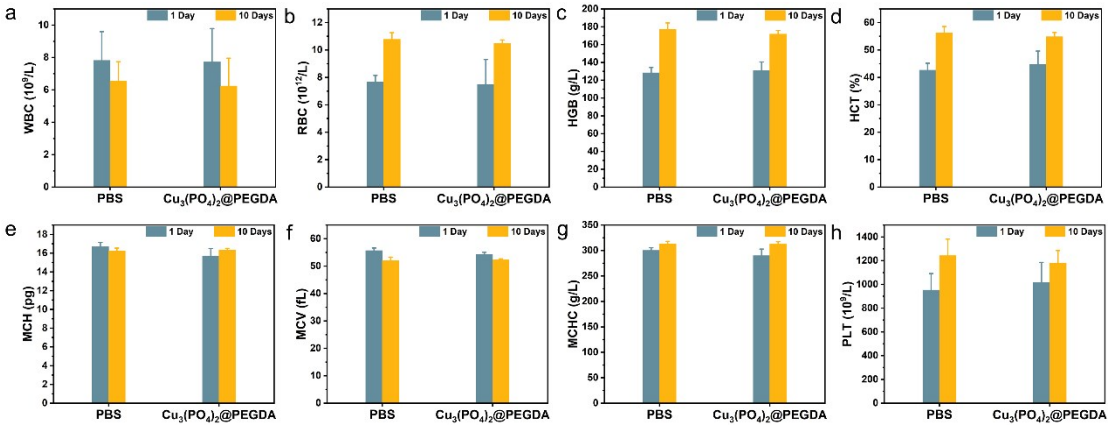

Fig. S12 Hematological indicators of WBC (a), RBC (b), HGB (c), HCT (d), MCH (e), MCV (f), MCHC (g), and PLT (h) of mice performed on the 1st and 10th day of the treatment.

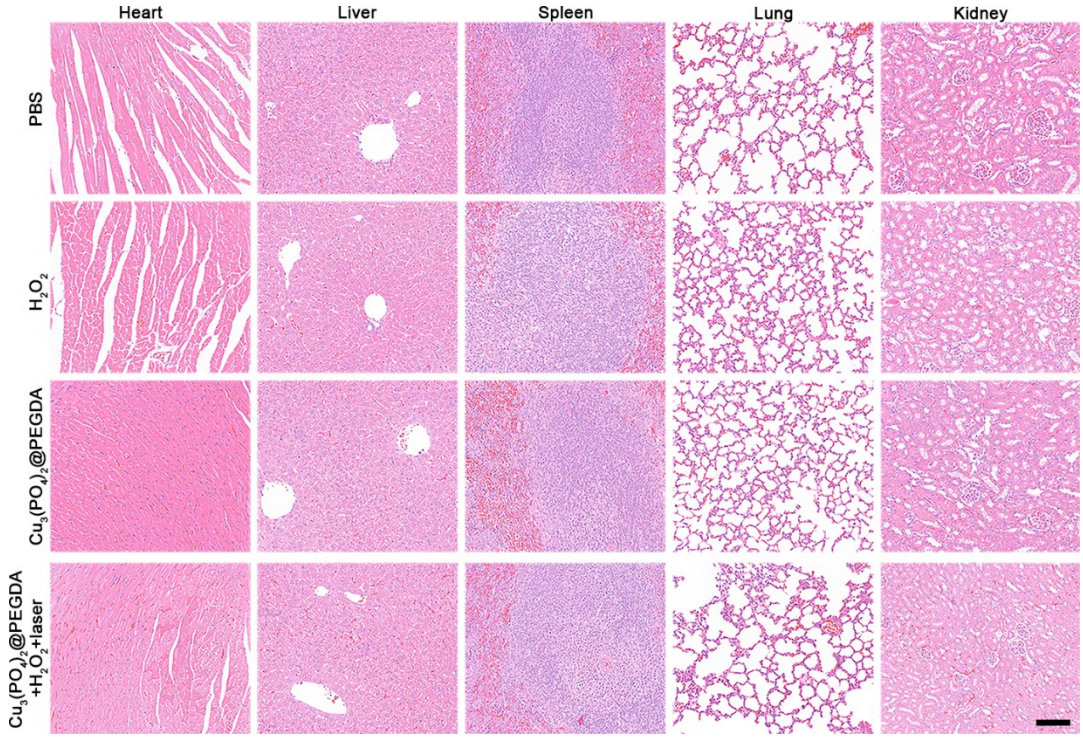

Fig. S13 Microscopy images of tissue sections (heart, liver, spleen, lung, and kidney) stained by H&E sampled at the 20th day of the anti-tumor treatment. Scale bar: 100 μm.

Table S1 The XPS peak area analysis results of $Cu_3(PO_4)_2$.

Spectrum	Area (P) CPS.eV	RSF	Area/RSF	Atomic ratio
Cu 2p	829775.34	3.38	245495.6627	2.953287633
P 2p	58188.36	0.35	166252.4571	2.000000001
O 1s	514725.98	0.71	724966.169	8.721268626

$$\theta = \frac{T - T_{surr}}{T_{max} - T_{surr}} \qquad \text{Equation S1}$$

$$\tau_s = \frac{t}{-ln\theta} \qquad \text{Equation S2}$$

$$hS = \frac{cm}{\tau_s} \qquad \text{Equation S3}$$

$$Q_{dis} = hS(T_{max} - T_{surr}) \qquad \text{Equation S4}$$

$$\eta = \frac{hS(T_{max} - T_{surr})}{I(1 - 10^{-A_{808}})} \qquad \text{Equation S5}$$

In Equation S1-5, T is an instant temperature of the time (t), T_{surr} is initial particle temperature, T_{max} is maximum temperature, c is specific heat capacity of water, m is the mass of the prepared $Cu_3(PO_4)_2$-water dispersion (3.75 mg/mL), h is heat-transfer coefficient, S is the area cross section perpendicular to conduction, and the value of hS is obtained from the Equation S1-3. The Q_{dis} represents external heat flux in the system. I is incident laser power density (2.5 W/cm^2), and A_{808} is the absorbance intensity of the $Cu_3(PO_4)_2$-water dispersion at 808 nm which was measured as shown in Fig. 2f. η is the photothermal conversion efficiency, which was calculated by Equation S5.