H_2O_2 self-supplying degradable epitope imprinted polymer for targeted fluorescence imaging and chemodynamic therapy

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Experimental section

Characterization. The transmission electron microscope (TEM) images were obtained from digital transmission electron microscope (Hitachi, Japan). The content of copper and calcium in MIP were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The UV-Vis absorption spectra were obtained from UV-2450 spectrophotometer (Shimadzu, Japan). Photoluminescence (PL) spectra were obtained from F-4500 fluorescence spectrophotometer (Hitachi, Japan). Fluorescence lifetime (τ) was measured by a FLS-920 spectrophotometer (Edinburgh, UK). Cell microplates in CCK-8 experiments were determined by a microplate reader (Sunrise, Austria). Fluorescence images of cells were obtained from a confocal laser scanning microscopy (Nikon, Japan).

Preparation of silicon nanoparticles (SiNPs). 300 mg of sodium citrate was dissolved in 10 mL deionized water, stirred under the atmosphere of N_2 for 15 min. Then, 3 mL of N-(2-aminoethyl-3-aminopropy) trimethoxysilane (DAMO) was added to the above system. After 20 min, the precursor solution was transferred to the polytetrafluoroethylene-lined autoclave and reacted at 180℃ for 4 h. The product was cooled to room temperature and dialyzed in a dialysis bag (MWCO 1000 Da) for 12 h to obtain SiNPs aqueous solution. Adjust pH of SiNPs aqueous solution to 6.6 with

0.1 M HCl and refrigerate it.

Cell culture and fluorescence imaging. CD47-positive human breast cancer cells (MCF-7) and normal human renal epithelial cells (293T) were cultured in DMEM containing 10% (V/V) of fetal bovine serum (FBS) and 1% (V/V) of penicillin streptomycin in a CO_2 incubator (5% CO_2, 37℃). MCF-7 cells and 293T cells were respectively seeded in laser confocal dishes with a density of 1×10^5/mL for 24 h. MCF-7 cells were treated with different concentrations of MIP and NIP (40 and 60 μg mL^{-1}) for 4 h. 293T cells were treated with 60 μg mL^{-1} of MIP and NIP for 4 h. The cells were washed several times with PBS (pH=7.4) and fixed with 4% paraformaldehyde solution (PFA) for 15 min. Confocal laser scanning microscope (CLSM) was used for cell imaging. The fluorescence channel was set to blue and the excitation wavelength was 408 nm.

Monitoring the transportation pathway of MIP. MCF-7 cells were seeded in 24-well plates at a density of 4×10^4 cells per well and these plates were maintained at 37°C under 5% CO_2 atmosphere for 24 h, following by co-incubation with the MIP at 37°C for 0.5 h, 1.5 h, 3 h or 5 h. Then, these plates were washed three times with PBS and stained with Lyso Tracker Green DND-26 (100 nM) for 1 h. Finally, the confocal laser microscope was used to observe the intracellular localization. The MIP and Lyso Tracker Green DND-26 were excited under 408 nm and 488 nm, respectively.

Fig. S1 The yellow of the extracellular CD47 structure (PDB: 4KJY) was the

sequence of the peptide template (KWKFGRDIY) used for MIP.

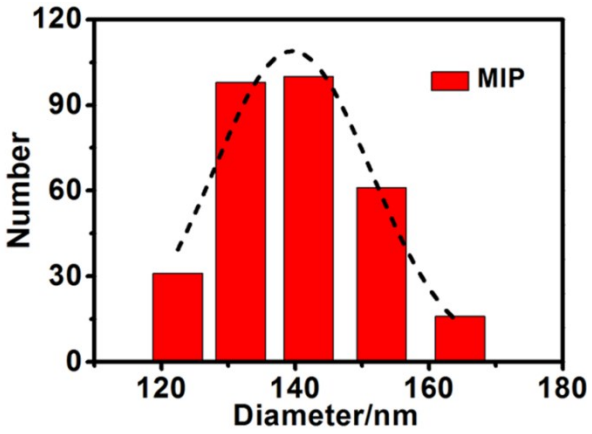

Fig. S2 DLS characterization of MIP.

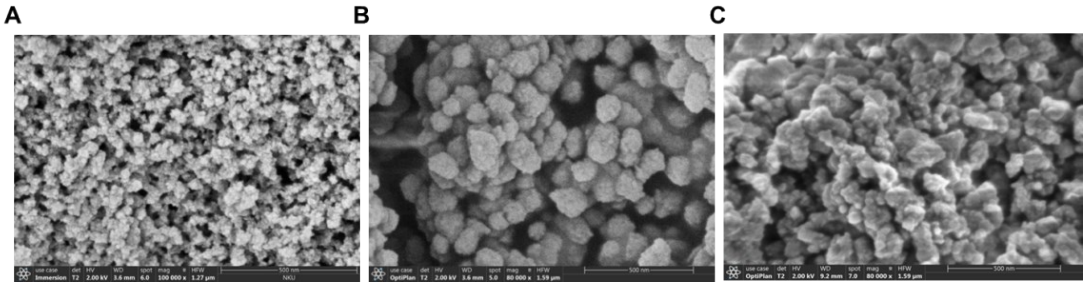

Fig. S3 SEM images of (A) $FCaO_2$, (B) MIP and (C) NIP.

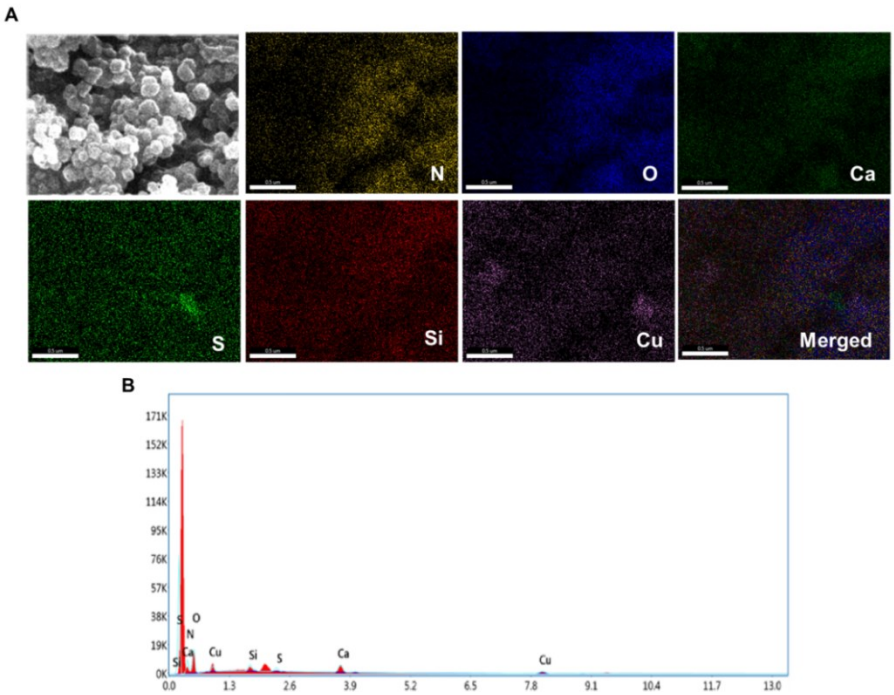

Fig. S4 (A) Element mapping and (B) EDS of MIP.

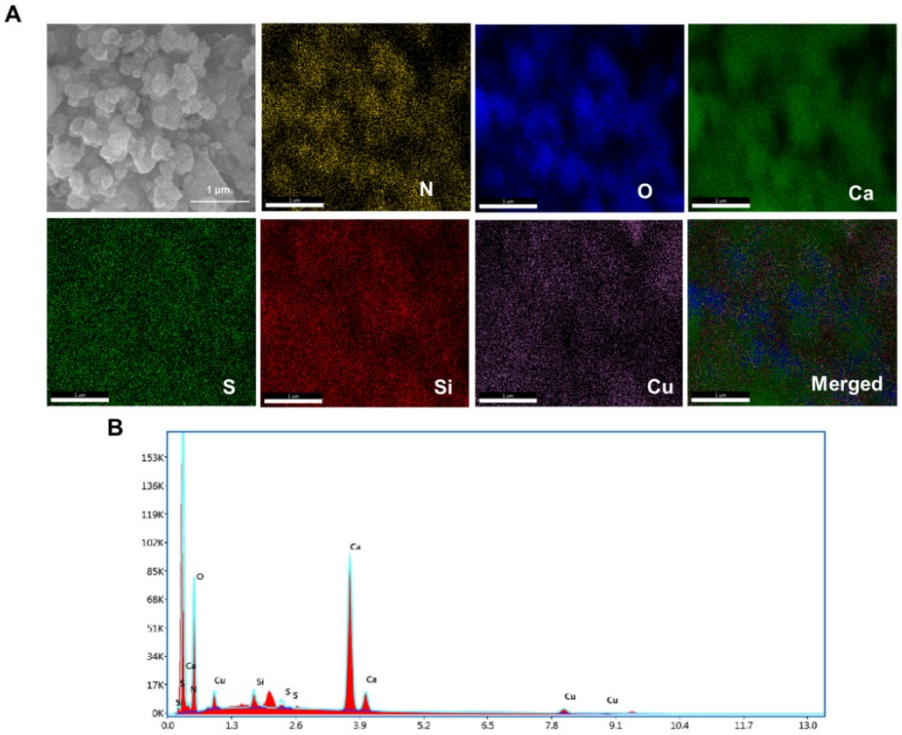

Fig. S5 (A) Element mapping and (B) EDS of the NIP.

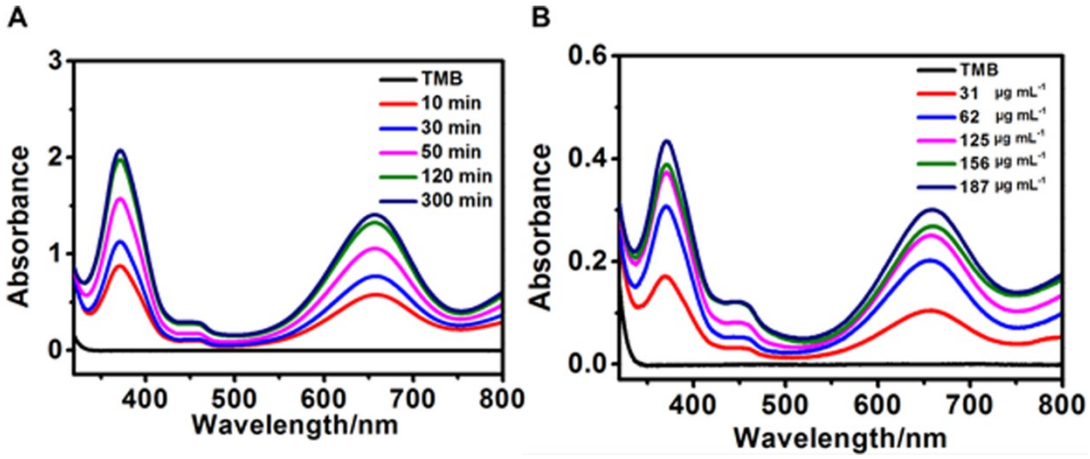

Fig. S6 (A) The UV-Vis absorption spectra of ox-TMB formed by $FCaO_2$ and copper acrylate in acetic acid buffer solution (pH=5.0) containing TMB (40 μg mL^{-1}) for different times (10, 30, 50, 120 and 300 min). (B) The UV-Vis absorption spectra of ox-TMB formed by $FCaO_2$ and different concentrations of copper acrylate (Cu^{2+}: 31, 62, 125, 156 and 187 μg mL^{-1}) in acetic acid buffer solution (pH=5.0) containing TMB (10 μg mL^{-1}) for 120 min.

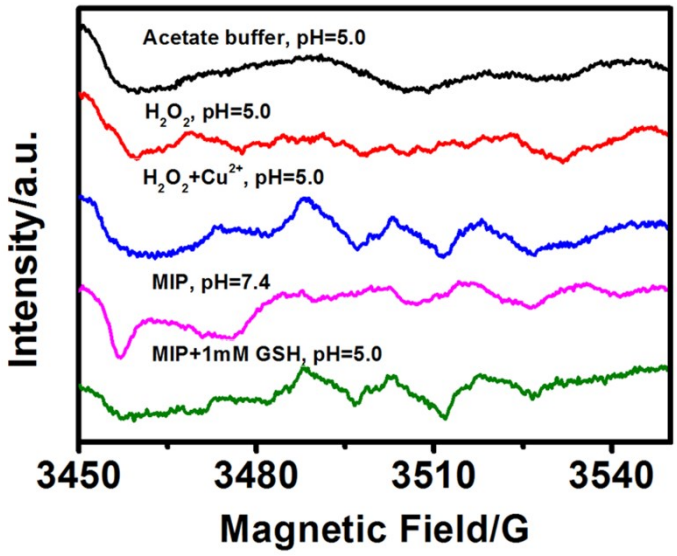

Fig. S7 EPR analysis of •OH production in each group with different treatment. DMPO was used as the spin-trapping agent.

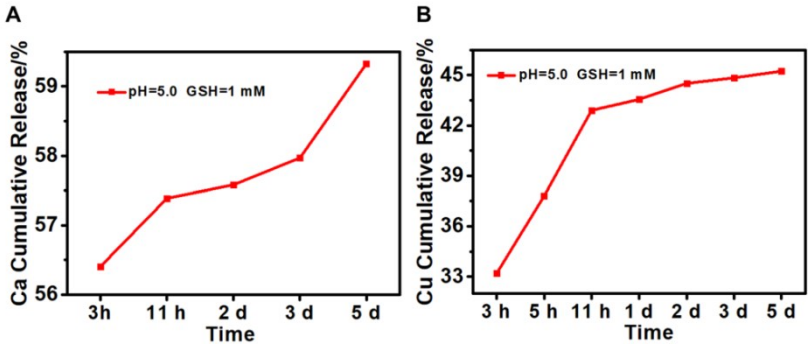

Fig. S8 The curves of cumulative release of (A) calcium ion and (B) copper ion from MIP in buffer solution with pH=5.0 and GSH=1 mM.

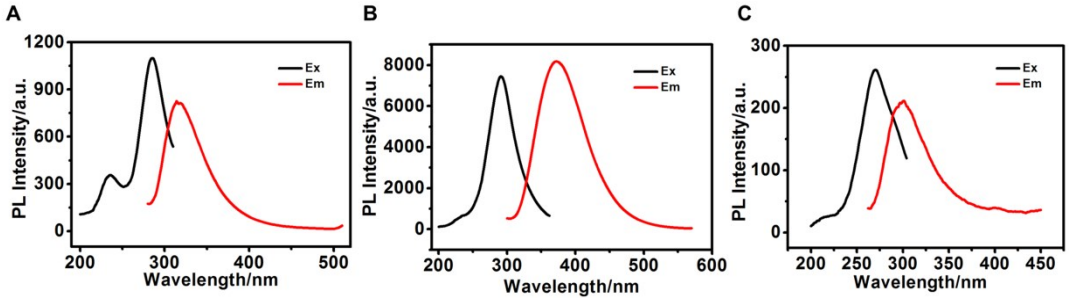

Fig. S9 The fluorescence excitation spectra and PL spectra of (A) L-tyrosine, (B) L-tryptophan and (C) L-phenylalanine.

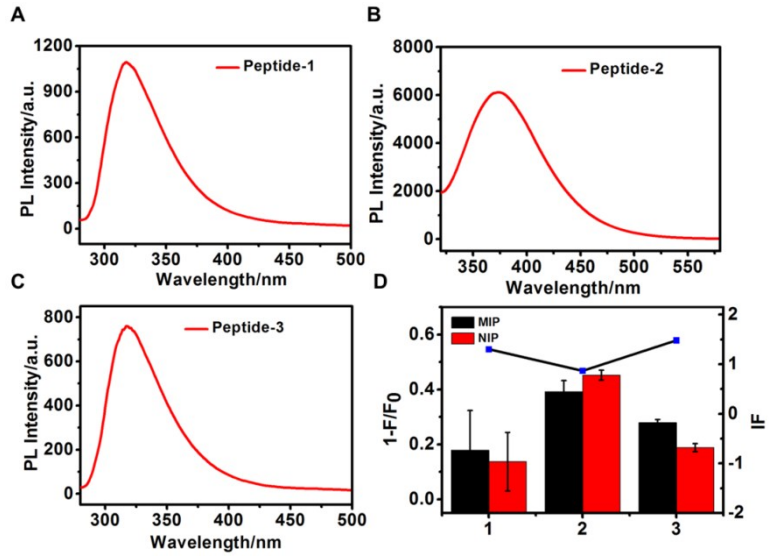

Fig. S10 The PL spectra of (A) peptide-1, (B) peptide-2 and (C) peptide-3. (D) The ($1-F/F_0$) values of the supernatant before and after adsorption of different peptides by MIP and NIP.

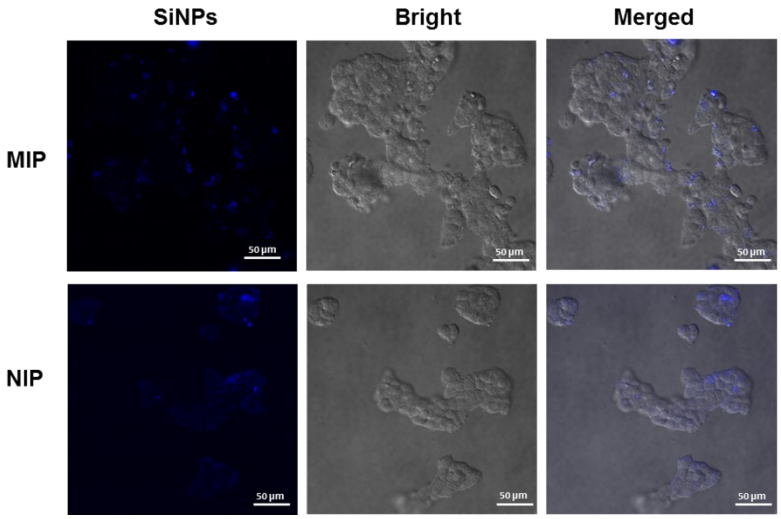

Fig. S11 The fluorescence images of 293T cells after incubation with 60 μg mL^{-1} of MIP and NIP for 4 h. Scale bar: 50 μm.