Supplementary information for

A Multi-responsive Au NCs@PMLE/Ca^{2+} Antitumor Hydrogel Formed *in Situ* interior/surface of Tumor for PT-imaging Guided Synergistic PTT/ enhanced PDT Effects

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1. Experimental section

Reagents and materials. Fresh PMLs were purchased from Chongqing Yanglan Tofu wood Royal Kitchen. Auric acid chloride ($HAuCl_4 \cdot 3H_2O$, 99.99%), calcium chloride ($CaCl_2$), hydrogen peroxide (H_2O_2, >30%), anhydrous ethanol (CH_3CH_2OH) and methylene chloride (CH_2Cl_2) were purchased from Sinopharmaceutical Chemical Reagents Co., Ltd. 1, 3-diphenylisobenzofuran (DPBF), vitamin C (V_C), dimethyl sulfoxide (DMSO) indocyanine green (ICG) and N, N-dimethylformamide (DMF) were obtained from Aladdin Biochemical Technology Co., Ltd. Trypsin solution (25%), hoechst 33342, propidium iodide (PI), pyimonidazole hydrochloride (Hypoxyprobe), streptomycin and phosphate buffered saline (PBS) were gotten from Sigma-Aldrich, USA. FBS fetal bovine serum and Dulbecco's modified eagle's medium (DMEM), 2',7'-dichlorodihydrofluorescein diacetate (DCFH-DA), 2,2,6,6-tetramethylpiperide (TEMP), fluorescein isothiocyanate (FITC) were purchased from Hyclone Corporation, USA. All the reagents were analytically pure without further purification. ICR (Institute of Cancer Research) mice were acquired from the Animal Experiment Center of Anhui Medical University. Deionized (DI) water with a resistance of 18.2 MΩ·cm was gained from a Milli-Q water purification system. Glassware was washed in aqua regia, then rinsed with DI water and dried.

Experimental instruments. The pH values of fresh prepared solutions were detected via a PHS-3C digital display pH meter (Tianda, Shanghai, China). The UV-vis-NIR spectra of samples were obtained by using a U-1800 UV spectrophotometer (Shimadzu, Japan) at the range of 200-1200 nm. The morphologies and structure of samples were performed on a 100SX high-resolution transmission electron microscope (TEM, Electronics Co., Ltd., Japan) operated at a 200kV acceleration voltage and a Zeiss Supra 40 scanning electron microscope (SEM) with the acceleration voltage of 5 kV. The Fourier transform infrared (FT-IR) spectra were collected on a NEXUS-870 spectrometer (Thermo Fisher, USA) at the frequency ranges from 4500 to 500 cm^{-1}) through the method of KBr pellet. The potential and stability of samples were measured by a Zeta Sizer Nano ZS90 analyzer (Malvern Instrument, Worcs, UK). Electron spin resonance spectroscopy (ESR) was carried out with Bruker E500 at microwave frequency of 9.78 GHz and power of 10 mW. The infrared thermal imaging photos of the products were acquired by using a Fluke Ti32 infrared imager (Fluke, Everett, USA). The MTT assay were calibrated with a RT-2100C spectro-photometric micro-plate (Rayto, Shenzhen, China). The fluorescence images were recorded through a DMI3000B confocal electron microscope (CLSM, Leica, Germany).

2. Additional figures

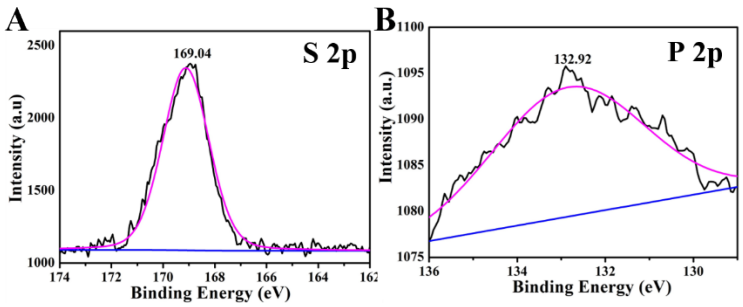

Fig. S1 The high-resolution XPS spectra of (A) S 2p, (B) P 2p of the as-synthesized Au NCs@PMLE

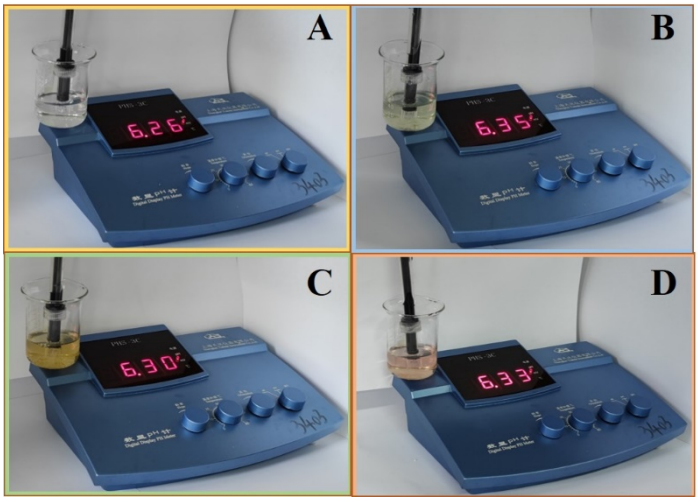

Fig. S2 Digital photos for the pH values of (A) $CaCl_2$ (0.333 mg/mL) solution, (B) PMLE (45 mg/mL) dispersion, (C) PMLE/Ca^{2+} and (D) Au NCs@PMLE/Ca^{2+} measured by the pH meter. In mixtures (C and D), the volume ratio of PMLE to $CaCl_2$ is 5:1.

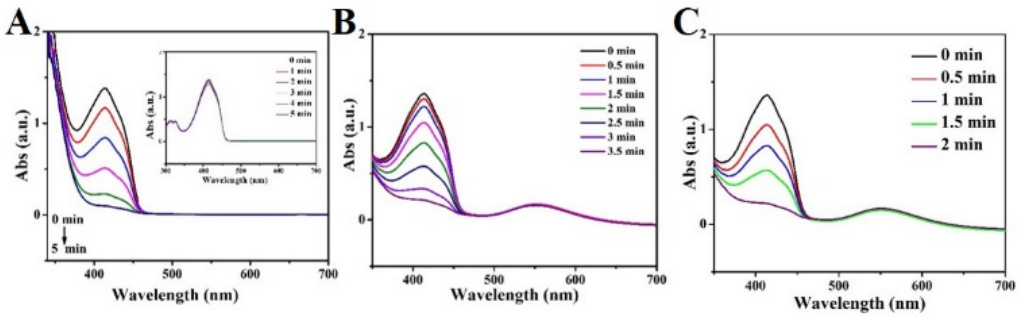

Fig. S3 PDT effect of (A) PMLE/DPBF (The inset in Fig. S3-A presents UV spectra of DPBF), (B) Au NCs@PMLE/DPBF and (C) Au NCs@PMLE/DPBF+H_2O_2 dispersions at 410nm after 808 nm laser irradiation. The concentration of DPBF was 5 μg/mL.