Supplementary Material

Yolk-Shell Magnetic Composites Fe_3O_4@Co/Zn-ZIF for MR Imaging-Guided Chemotherapy of Tumors in Vivo

Ying Li, Lu-Lu Jiang, Ya-Xian Qiao, Dong wan and Yan-Feng Huang*

State Key Laboratory of Separation Membranes and Membrane Processes, and College of Chemistry and Chemical Engineering, Tiangong University, 399 West Binshui Road, Tianjin 300387, China.

*Corresponding author.

E-mail: *huangyanfeng@tiangong.edu.cn* (Y.-F. Huang)

Materials and Chemicals

Analytical grade zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and doxorubicin hydrochloride (DOX) were obtained from Shanghai Macklin Biochemical Co. Ltd. (Shanghai, China). Ferric chloride ($FeCl_3 \cdot 6H_2O$), 2-Methylimidazole (99%), dopamine hydrochloride (DA, 98%), ethylene glycol and diethylene glycol were bought from Shanghai Aladdin Chemistry Co. Ltd. (Shanghai, China). Methanol, sodium acetate anhydrous (NaOAc) and dimethyl sulfoxide were supplied by Tianjin fine Chemical R&D Center.

Characterization

The shape and size of the samples were recorded on transmission electron microscope (TEM: Hitachi H7650) and scanning electron microscopy (SEM: Hitachi S4800). The elemental composition of the samples was measured using energy dispersive spectrometer. The sizes distribution and surface charge property of these crystals were measured by the Nano Size and Zeta-potential Tester (Zetasizer Nano ZSE Malvern, England). The X-ray diffraction (XRD) patterns were surveyed through a Rigaku Miniflex 600 X-ray diffractometer with $Cu_{K\alpha}$ radiation source (λ=1.5418 Å). The magnetization curves were taken in a vibrating sample magnetometer (VSM: LDJ-9600-1) at room temperature. The specific BET surface area and pore size of materials were carried out with an Autosorb-iQ gas sorption analyzer at 77 K. FT-IR spectra were conducted on a Nicolet IS50 FT-IR spectrometer. UV-vis spectra of

DOX were examined on a HeλIOS-γ spectrometer (Thermo Finnigan, USA). Thermogravimetric analysis (TGA) was determined by a STA449F3 thermal analyzer heating from room temperature to 900^{o}C at 5 ^{o}C·min^{-1}. The surface electronic states were investigate by an X-ray photoelectron spectroscopy (XPS: PerKin-Elmer PHI 5000C) at room temperature.

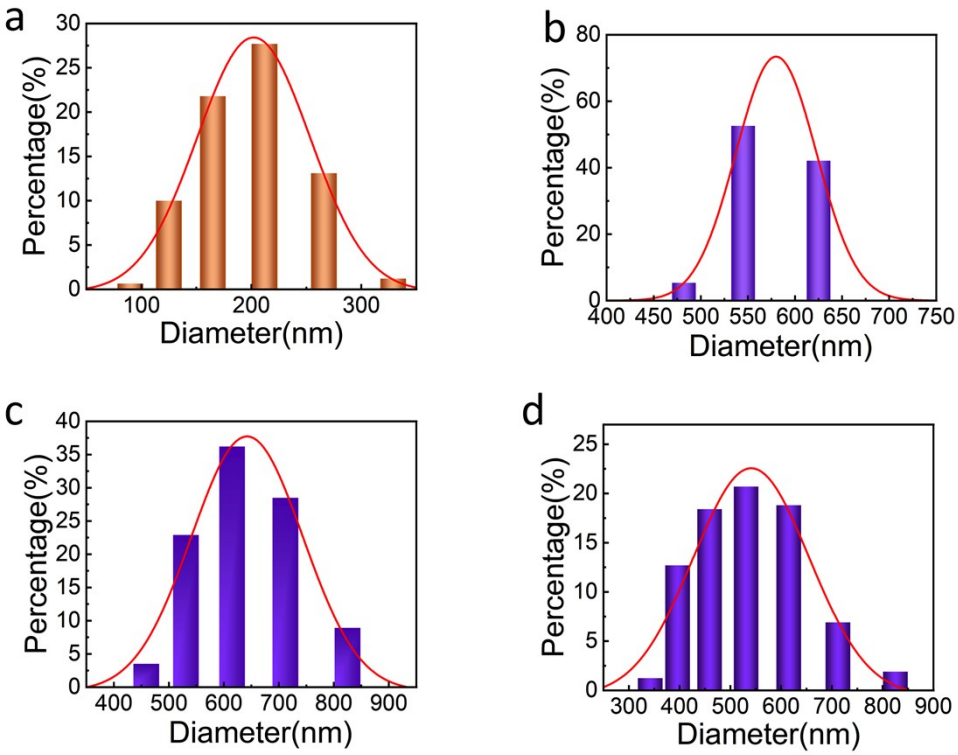

Fig.S1 Size distributions of Fe_3O_4-DA(a), ZIF-67@ZIF-8(b), Fe_3O_4@ZIF-67@ZIF-8(c), and Fe_3O_4@Co/Zn-ZIF(d) nanoparticles determined

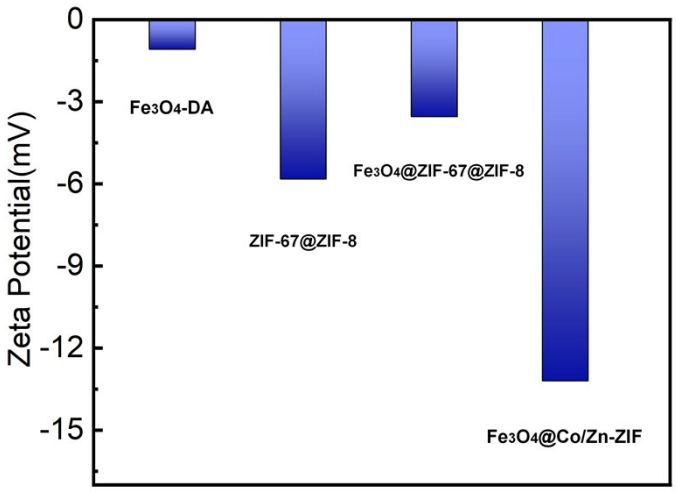

Fig.S2 Zeta potential values of Fe_3O_4-DA, ZIF-67@ZIF-8, Fe_3O_4@ZIF-67@ZIF-8, Fe_3O_4@Co/Zn-ZIF

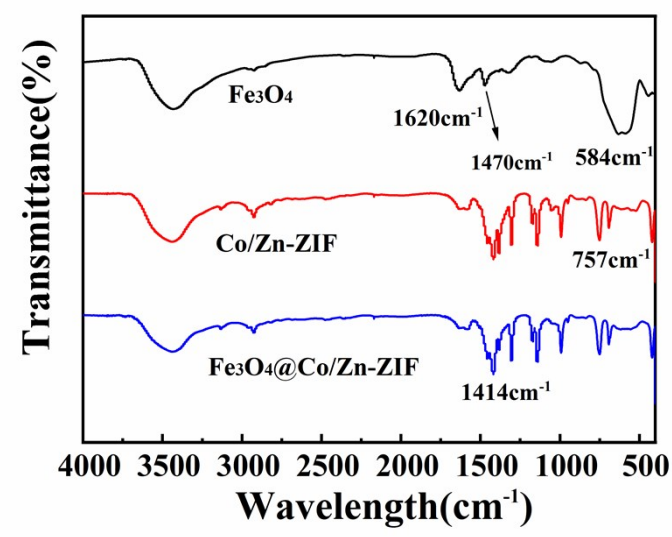

Fig.S3 FT-IR spectra of Fe_3O_4, Co/Zn-ZIF and Fe_3O_4@Co/Zn-ZIF

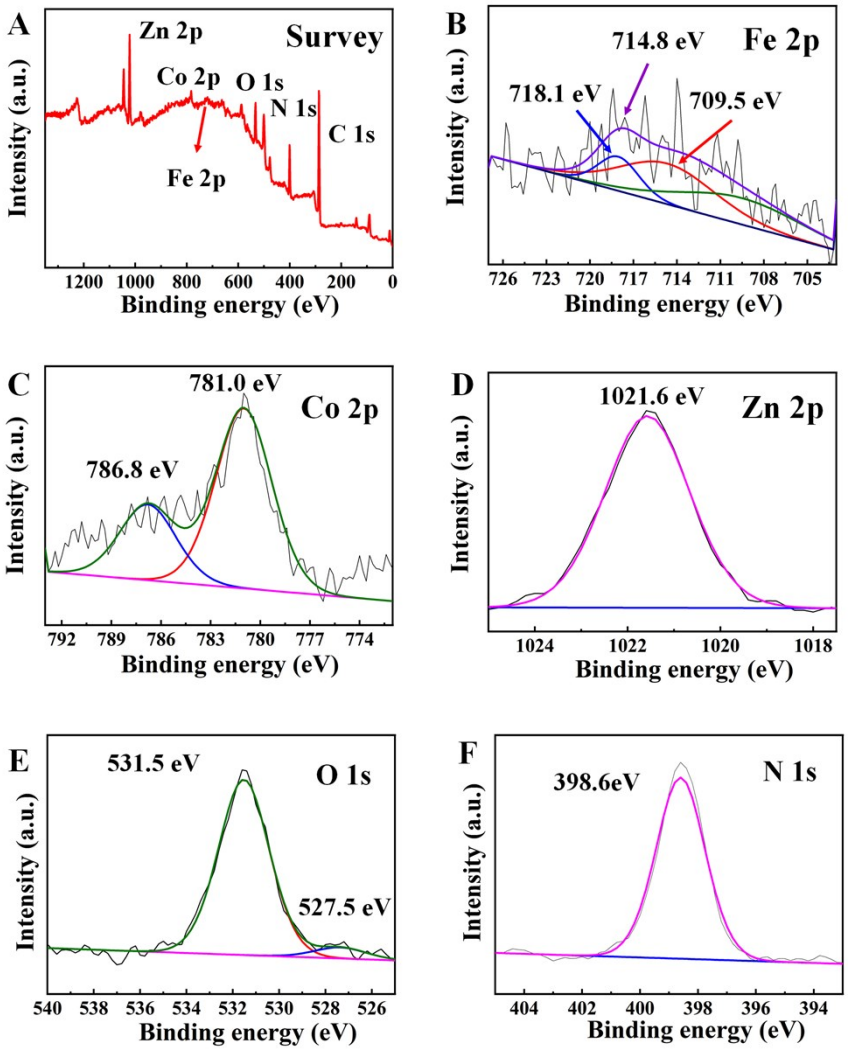

Fig.S4 XPS of Fe_3O_4@Co/Zn-ZIF: (A) survey XPS spectra; (B) Fe 2p3/2; (C) Co 2p3/2; (D) Zn 2p3/2; (E) O1s; (F) N1s

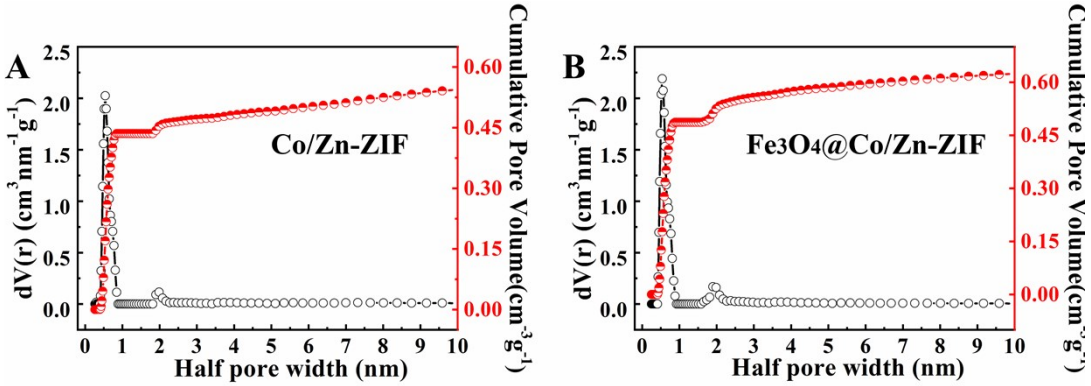

Fig.S5 DFT pore size distribution of Co/Zn-ZIF and Fe_3O_4@Co/Zn-ZIF

Table S1 BET surface areas and DFT pore size distribution of Co/Zn-ZIF and Fe_3O_4@Co/Zn-ZIF

Catalysts	BET surface areas (m^2/g)	Total pore volume (cm^3/g)	Average pore size (nm)
Co/Zn-ZIF	1588	0.747	1.04
Fe_3O_4@Co/Zn-ZIF	1397	0.705	1.49

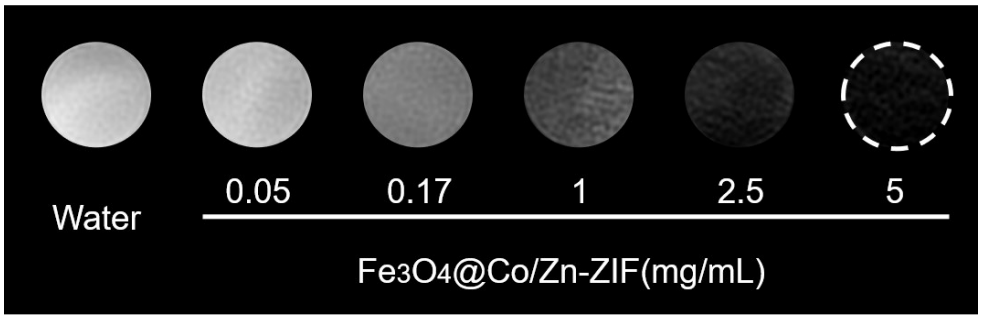

Fig.S6 In vitro T_2-weighted MR images of Fe_3O_4@Co/Zn-ZIF with different concentrations.