## **Supporting Information**

## Biodegradable MnFe-hydroxide Nanocapsules to enable Multi-

## therapeutics Delivery and Hypoxia-Modulated Tumor Treatment

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Figure S1. SEM image of solid  $SiO_2$  nanoparticles as hard template.



Figure S2. TEM images of the nanoparticles synthesized when only using (a) Mn<sup>2+</sup> or (b) Fe<sup>3+</sup> precursor.



**Figure S3**. TEM images of SiO<sub>2</sub>@MnFe(OH)<sub>x</sub> nanoparticles after incubating in NH<sub>3</sub>·H<sub>2</sub>O solution with various concentrations: (a)~(c) 0.25 M, (d)~(f) 0.5 M, (g)~(i) 1.5 M at 120 °C for 24h.



**Figure S4**. XRD pattern of H-MnFe(OH)<sub>x</sub> nanocapsules.



**Figure S5**. (a) FTIR spectrum and (b) TGA-DSC curve of H-MnFe(OH)<sub>x</sub> nanocapsules.



**Figure S6**. HRTEM image of H-MnFe(OH)<sub>x</sub> nanocapsules.



**Figure S7**. Digital photographs and corresponding size distribution of  $H-MnFe(OH)_x$  in water, PBS, normal saline (NS) and cell culture medium (DMEM) at 0 and 24 h.



**Figure S8**. LC and EE of (b) DOX and (c) ICG into H-MnFe(OH)x with various mass ratios *via* individual loading.



**Figure S9**. (a) UV–vis–NIR spectra and (b) the standard curve of DOX at different concentrations. (c) UV–vis–NIR spectra and (d) the standard curve of ICG solutions at different concentrations.



**Figure S10**. Elemental mapping for DOX&ICG/ H-MnFe(OH)<sub>x</sub>. Scale bar (20 nm).



**Figure S11**. DOX release from DOX&ICG/ H-MnFe(OH)<sub>x</sub> in PBS at pH = 7.4, and pH = 6.5 with 808 nm irradiation (0.69 W cm<sup>-2</sup>).



**Figure S12.** Temperature photographs of DOX&ICG/ H-MnFe(OH)<sub>x</sub> at various concentrations under NIR irradiation for 0-5 min (808 nm, 0.69 Wcm<sup>-2</sup>).



**Figure S13**. UV–vis–NIR absorption spectra of DPBF upon 808 nm laser irradiation (0.69 W cm<sup>-2</sup>).



Figure S14. The viability of 4T1 cells incubated with various concentrations of  $Fe^{3+}$  or  $Mn^{2+}$ .



**Figure S15**. Fluorescence images of 4T1 cells stained with calcein-AM (green, live cells) and propidium iodide (red, dead cells) after treated with ICG/SiO<sub>2</sub> and ICG/LDH samples upon NIR irradiation in N<sub>2</sub> or O<sub>2</sub> atmospheres. Scale bar = 50  $\mu$ m.



**Figure S16**. Digital photographs of the mice on day 1, 8 and 15 after various treatments.