



## ARTICLE

## Supporting Information

## Title:

In situ protein-templated porous protein-hydroxylapatite nanocomposite microspheres for pHdependent sustained anticancer drug release

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Figure S1. DLS spectra of ASM in water (1mg mL<sup>-1</sup>).



Figure S2. FTIR spectra of (A) AS powder; (B) ASM; (C) ASM: DOX= 20:1; (D) ASM: DOX= 2:1; (E) ASM: DOX= 1:5; (F) DOX powder.



**Figure S3.** DOX-derived fluorescence signal from DOX@ASM. The red profile on the right image shows the fluorescence intensity change across a particle.



**Figure S4.** Encapsulation efficiency of silk fibroin microspheres at different adsorption times. The inset is the morphology of silk fibroin microspheres.



**Figure S5.** Morphology of Bcap-37 cells incubated with PBS, DOX@ASM and free DOX with a concentration of 20 μg mL<sup>-1</sup> after 60 h incubation.



**Figure S6.** Morphology and cytotoxicity of C2C12 cells after incubation with DOX@ASM. (A) Morphology of C2C12 cells after 12 h incubation with PBS, DOX@ASM (10  $\mu$ g mL<sup>-1</sup>) and free DOX (10  $\mu$ g mL<sup>-1</sup>) for 3 h, 24 h, and 60 h. (B) The proliferation of C2C12 cells after incubation with PBS, DOX@ASM (10  $\mu$ g mL<sup>-1</sup>) and free DOX (10  $\mu$ g mL<sup>-1</sup>) was determined using MTS assay. \*p < 0.05,\*\*, p < 0.01.