Supporting Information

Fabrication of heparinized hierarchically hollow hydroxyapatite microspheres as bone substitute for controlled growth factors delivery

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^b Key Laboratory of Natural Medicine and Immuno-Engineering of Henan Province, Henan University, Kaifeng, 475004, P.R. China. E-mail: sjiahua@henu.edu.cn; Tel: +86-378-2864665; Fax: +86-378-2864665.

^c School of Material and Chemical Engineering, Zhengzhou University of Light Industry, 5 Dongfeng Road, Zhengzhou, 450002, P.R. China. E-mail: cfh_ciac@yahoo.com.cn; Tel: +86-371-63556510; Fax: +86-371-63556510. $(10-x-y/2)CaCO_3 + (6-y)Na_2HPO_4 \longrightarrow Ca_{10-x-y/2}(HPO_4)_x(PO_4)_{6-x-y}(CO_3)_y(OH)_{2-x-y}(PO_4)_x(PO_4)_{6-x-y}(PO_4)_y(PO_4)_{6-x-y}(PO_4)_y(PO_4)_{6-x-y}(PO_4)_y(PO_4)_y(PO_4)_{6-x-y}(PO_4)_y$

 $+ (4-x-y/2)CO_2 + (6-y)Na_2CO_3 + (2-y/2)H_2O$

Equation S1. The chemical reaction equation of hydroxylcarbonte apatite.

(1)



Figure S1. TEM images of pure $CaCO_3$ particles after soaking in emulsion solution for 24 h.



Figure S2. EDX spectra of HHAMs-HP converted from CCPs-HP by treatment with emulsion solution for 24 h.



Figure S3. TEM (a) and fluorescence (b) images of $CaCO_3$ particles with FITC-labeled heparin after soaking in emulsion solution for 24 h.



Figure S4. CD spectra acquired at 20 °C of bFGF.