## **Electronic Supplementary Information**

# Biomimetic assembly of multilevel hydroxyapatite using bacterial

# cellulose hydrogel as a reactor

Xun Liu,\*<sup>a,b</sup> Kangxin Li,<sup>a</sup> Chaoqun Wu,<sup>a</sup> Zhaoqian Li,<sup>a</sup> Bo Wu,a Xiaohui Duan,<sup>a</sup> Yong Zhou<sup>c</sup>

and Chonghua Pei\*a

<sup>a.</sup> State Key Laboratory of Environment-friendly Energy Materials, Southwest University of Science and Technology, Mianyang 621010, China.

<sup>b.</sup> Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA.

<sup>c.</sup> Department of Materials Science and Engineering, National Lab of Solid State Microstructure, ERERC, Nanjing University, Nanjing 210093, China.

## Materials and methods

### Chemicals

The raw chemicals used in this experiment, including Na<sub>3</sub>PO<sub>4</sub>, CaCl<sub>2</sub> and CuSO<sub>4</sub>, were all analytically pure. The bacterial cellulose hydrogel (BCH) was food-grade. The Wal-Mart supermarket provided hen eggs. The experimental water was ultrapure (UPT-I-5/10/20T).

### Preparation

Purification of BCH: cut BCH into uniform pieces of about 1 cm<sup>3</sup>, then put them into beaker, continue to add 5% NaOH solution, boil the mixture for 30 minutes, and finally wash BCH with ultrapure water to neutral pH.

Sample preparation: the initial concentration of  $CaCl_2$  solution and  $Na_3PO_4$  solution was 0.2 mol/L. Egg white was added to the two solutions at 1 v/v%. BCH was first soaked in  $CaCl_2$  solution for 24 h, then transferred to  $Na_3PO_4$  solution to continue to soak for another 24h to mineralize it fully. After mineralization, the result was extracted, washed and dried for subsequent tests.

### Characterization

A BX51 polarizing microscope (Olympus Co., Japan) was used to observe the samples' appearance, and a TM-1000 electron microscope produced by Japan Hitachi Company was used to observe their morphology. An X-ray diffractometer (D/max-RB, Rigaku Co., Japan) was used to investigate crystal type, with a Cu Ka radiation source and a step scan of 0.020 from 2.50 to 600 ( $\lambda$ =0.15418 nm, voltage=30 kV, current=20 mA). The Fourier transform infrared spectroscopy (FTIR) test was done using a FT-IR-G988 (Thermo Nicolet Co., America) to determine composition; the scanning range was from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> with an accuracy of 4 cm<sup>-1</sup>. TEM characterization was done using the Libra 200FE 200 kV field emission transmission electron microscopy system produced by Carl Zeiss Smt Pte Ltd (Germany).



Fig. S1 Optical microscope pictures of the filamentous mineralization.



Fig. S2 SEM images of filamentous mineralization prepared without EW.



Fig. S3 HRTEM image of filamentous mineralization prepared with EW.



Fig. S4 TG-DSC curves of filamentous mineralization prepared without EW.



Fig. S5 TG-DSC curves of pure dried EW.



Fig. S6 SEM image of bacterial cellulose



Fig. S7 Chemical structure of bacterial cellulose



Fig. S8 Diagram of the mineralization mechanism for the sample prepared in the CaCl<sub>2</sub> solution.



Fig. S9 Photo of samples mineralized in the  $CaCl_2$  solution.



**Fig. S10** XRD patterns of mineralized samples prepared in the CaCl<sub>2</sub> solution (a) with egg white and (b) without.



Fig. S11 Photo of the sample prepared using agar gel as template (mineralized in the Na<sub>3</sub>PO<sub>4</sub> solution).



Fig. S12 Optical microscope photo of the filamentous mineralization prepared using agar gel as template (mineralized in the Na<sub>3</sub>PO<sub>4</sub> solution).



**Fig. S13** SEM images at different magnifications of the mineralization prepared using phosphorylated BCH as template.



**Fig. S14** SEM images at different magnifications of the mineralization prepared using oxidized BCH as template.



Fig. S15 XRD patterns of the samples prepared using (a) phosphorylated BCH and (b) oxidized BCH as template.