Electronic Supplementary Information

Biomimetic assembly of multilevel hydroxyapatite using bacterial cellulose hydrogel as a reactor

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Materials and methods

Chemicals

The raw chemicals used in this experiment, including Na3PO4, CaCl2 and CuSO4, 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 cm3, 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 CaCl2 solution and Na3PO4 solution was 0.2 mol/L. Egg white was added to the two solutions at 1 v/v%. BCH was first soaked in CaCl2 solution for 24 h, then transferred to Na3PO4 solution to continue to soak for another 24 h 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 (λ=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⁻¹ to 400 cm⁻¹ with an accuracy of 4 cm⁻¹. 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$_2$ solution.

Fig. S9 Photo of samples mineralized in the CaCl$_2$ solution.
**Fig. S10** XRD patterns of mineralized samples prepared in the CaCl$_2$ solution (a) with egg white and (b) without.

**Fig. S11** Photo of the sample prepared using agar gel as template (mineralized in the Na$_3$PO$_4$ solution).
Fig. S12  Optical microscope photo of the filamentous mineralization prepared using agar gel as template (mineralized in the Na$_3$PO$_4$ 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.