Supporting Online Material for

Biomimetic Synthesis of Novel Calcium Carbonate Heterogeneous Dendrites

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Experimental section:

1.1 Experiment according Kitano method

In a second set of experiments to study the kinetic process of $CaCO_3$ nucleation, a saturated $Ca(HCO_3)_2$ solution was prepared by bubbling CO_2 gas into a solution (100 mL) containing 1.5 g $CaCO_3$ powder for 90 min to shift a $CaCO_3/Ca(HCO_3)_2$ equilibrium toward the more water-soluble $Ca(HCO_3)_2$. The surplus $CaCO_3$ was filtered off subsequently. And then, CO_2 was bubbled through for another 10 min with/without additives. Finally, the Kitano solution (100 mL) was transformed to a beaker and stirred slightly but constantly. The pH values were measured automatically by computer which was connected to pH meter (PHS-2F). The solution pH increases because CO_2 is constantly removed from the solution. The $CaCO_3$ nucleation is indicated by a sharp pH drop.

1.2 Calculation of the saturation index and carbonate ion concentrations

The calculated supersaturation (S) with respect to an amorphous calcium carbonate (ACC), was expressed as the ratio of ionic activity product to solubility product (*Ksp*). We choose to use the value for hydrate ACC reported by Clarkson et al ($Ksp = 9.1*10^{-7}$). [1]

The solution carbonate concentrations (CO_3^{2-}, HCO_3^- and H_2CO_3) were calculated, based on the total inorganic carbon concentration (C_{total}) and pH measurements,[2] using a simplified carbon mass balance and carbonic dissociation constants (K_1, K_2), as described in Equations (1).

$$[C_{total}] = [HCO_3^-]+[CO_3^{2-}]+[H_2CO_3^*];$$

$$[CO_3^{2-}] = [C_{total}]K_1K_2/([H^+]^2+K_1*[H^+]+K_1K_2); \quad (1)$$

$$K_1 = 4.30*10^{-7},\ K_2 = 5.61*10^{-11}\ (25°C);$$

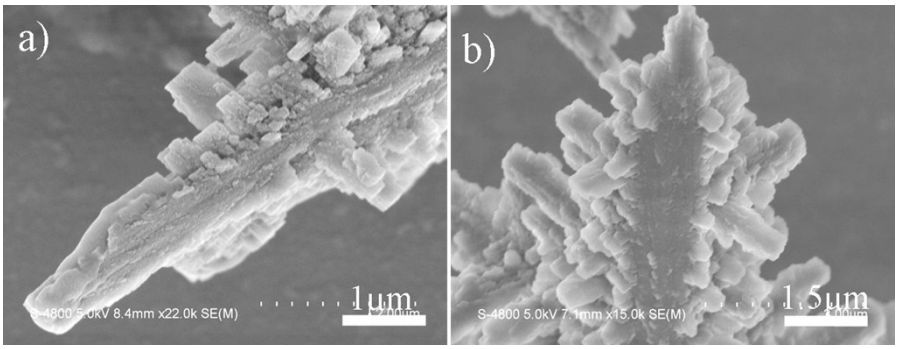

Fig. S1 SEM images of local structures in a dendrite. (a) The tip of trunk is smooth; (b) nanobranches grow along the trunk.

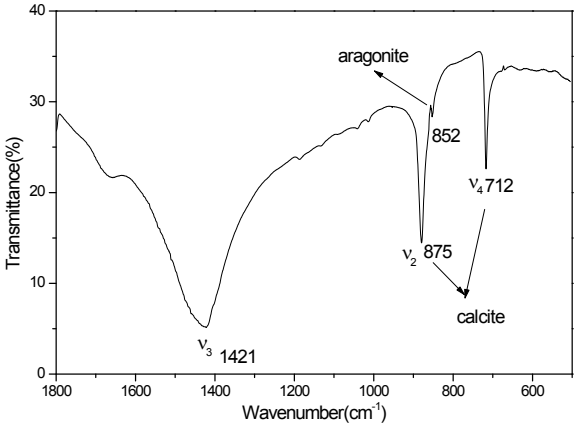

Fig. S2 FT-IR spectrum of $CaCO_3$ dendrites obtained after two weeks. [BSA] : [PSS] = 0.5 : 0.1, (unit: g L^{-1}).

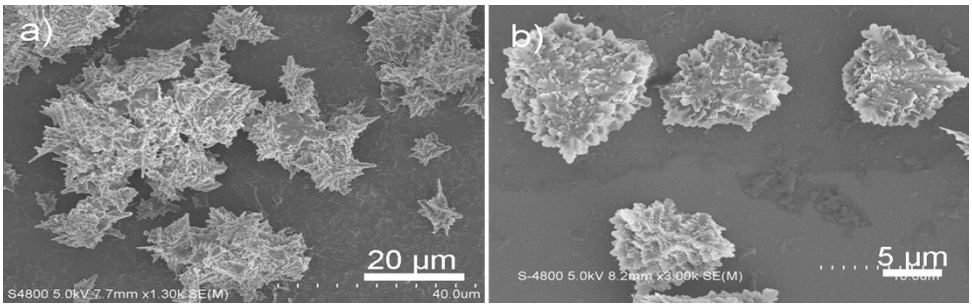

Fig. S3 SEM images for $CaCO_3$ dendrites after 8 days. (a) [BSA] : [PSS] = 0.5 : 0.1, at 25°C; (c) [BSA] : [PSS] = 0.5: 0.3. (Unit: g L^{-1})

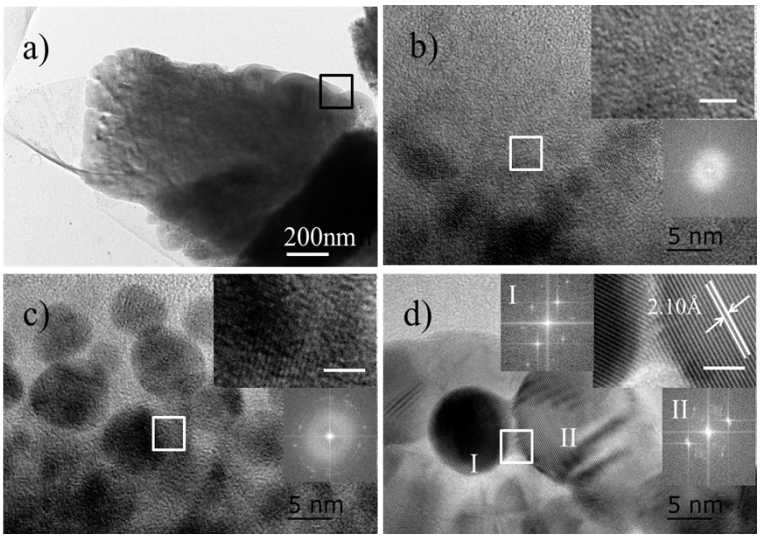

Fig. S4 Crystallization process of ACC into aragonite particles under the high-energy electron beam irradiation. (b, c, d) crystallization in the square nanoregion at different time: (b) 0 s; (c) 30 s; (d) 60 s. Insets are corresponding magnified images and FFT patterns taken from where square or uppercase roman numerals indicate. (Inset scale bar: 2 nm)

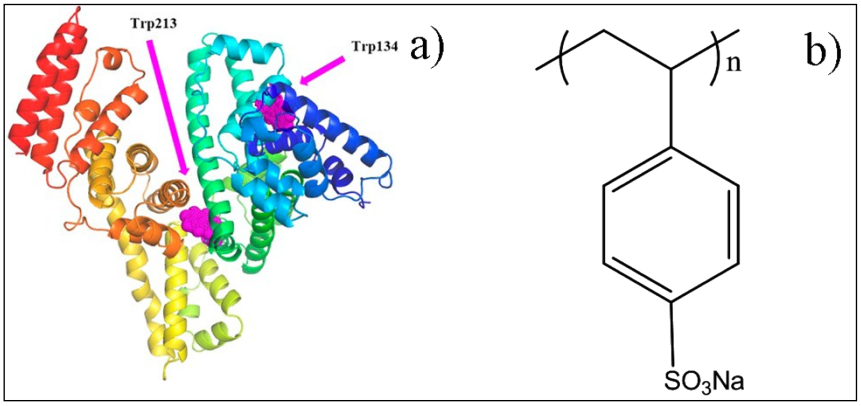

Fig. S5 The molecular structure of BSA (a) and PSS (b).

Table S1 detected $[Ca_{free}]^{2+}$ after mixed with various additives ($[CaCl_2]$ = 1g/L).

Different additives	Ca^{2+}+BSA(0.5g/L)	Ca^{2+}+PSS(0.1g/L)	Ca^{2+}+BSA(0.5g/L)+PSS(0.1g/L)
$[Ca_{free}]^{2+}$ (g/L)	0.998	0.983	0.940

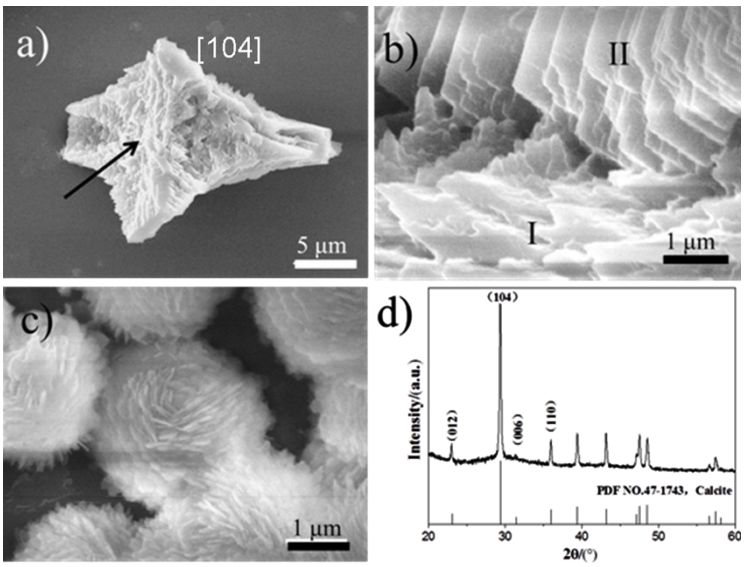

Fig. S6 SEM (a) and magnified images (b) of calcite samples obtained in the pure BSA mineral solution; (c) SEM image of calcite followers synthesized in the mineral solution controlled by PSS; (d) the corresponding XRD pattern of sample in (c). [BSA]=0.5g L^{-1}, [PSS] = 0.1g L^{-1}

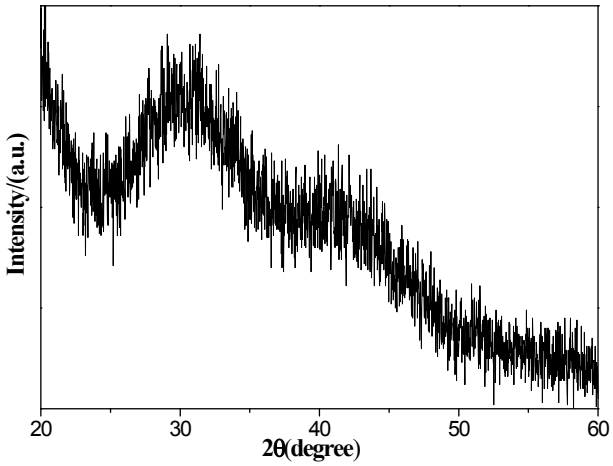

Fig. S7 XRD pattern of mineral films after 3 days.

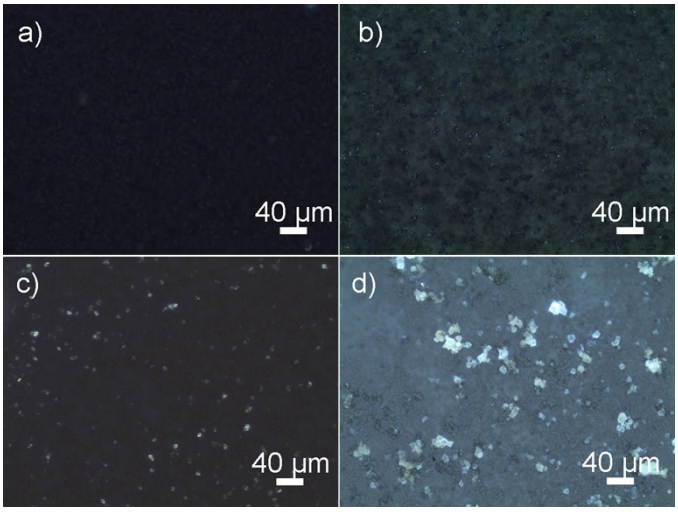

Fig. S8 POM image of mineral films at different stage: (a) 1-2 day; (b) 4 day; (c) 6 day; (d) 8 day.

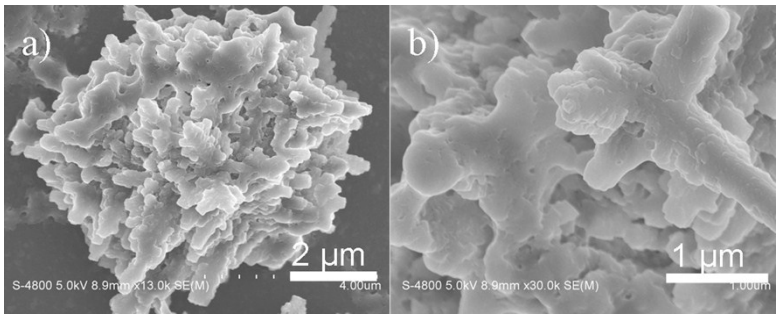

Fig. S9 Different magnification SEM images of dendrite after 7 days. A smooth coating was observed on the surface of calcite scaffoldings.

Table S2 Viscosity of mineral solution at different reaction time (mPa • S)

	[BSA]/[PSS]=0.5/0.1（25°C）	[BSA]/[PSS]=0.5/0.1;（10°C）	[BSA]/[PSS]=0.5/0.3;（25°C）
0	3.21	3.33	3.61
0.5 d	2.83	3.09	3.14
1 d	2.92	3.19	3.25
1.5 d	3.25	3.33	3.36
2 d	2.64	2.83	2.93
2.5 d	2.37	2.78	2.84
3d	2.31	2.36	2.79

Viscosity of pure water is1.38 mPa • S. The viscosity of early mineral solution matches up to 50% glycol solution at 25°C

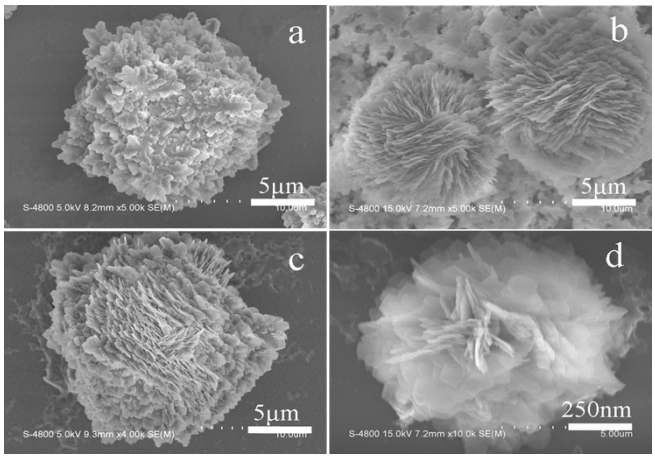

Fig. S10 SEM images of products obtained with different concentrations of BSA and PSS at 25 °C. (a) 0.5: 0.3; (b) 0.5: 0.5; (c) 0.3: 0.1; (d) 0.1: 0.1 (g L^{-1}). [$CaCl_2$]=1 M

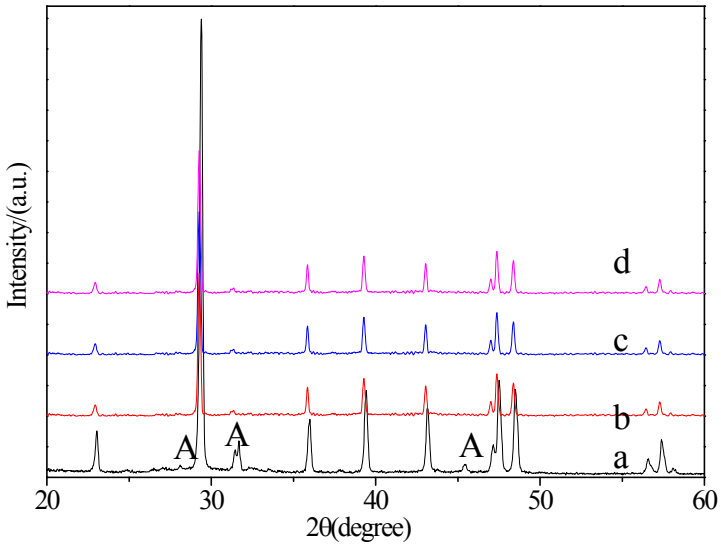

Fig. S11 XRD pattern of samples obtained at different concentrations of BSA and PSS after 8 days. (a) 0.5: 0.3; (b) 0.5: 0.5; (c) 0.3: 0.1; (d) 0.1: 0.1 (unit g L^{-1}). A is the aragonite phase.

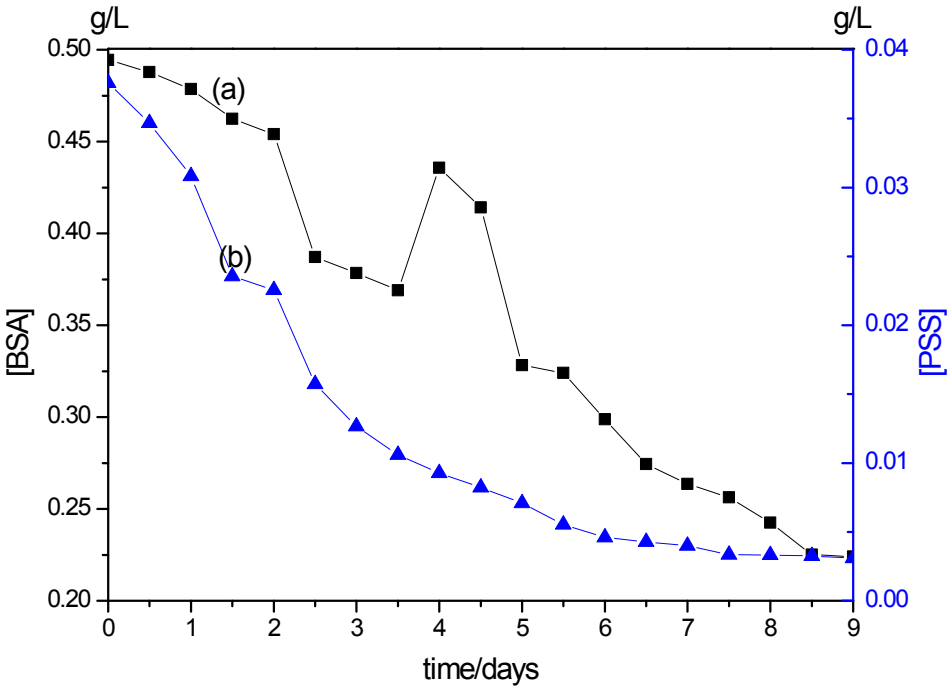

Fig. S12 Time-resolved concentrations of different additives during the mineralization process.

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1 J. R. Clarkson, C. T. Price and J. J. Adams, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 243
2 H. L. Bohn, B. McNeal, G. O'Connor, Soil Chemistry, John Wiley Sons, New York, 1985, 16.