Supplementary Information for:

Acid Polysaccharide-Induced Amorphous Calcium Carbonate (ACC) Films: A Colloidal Nanoparticles Self-Organization Process

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S1 Synthesis and Chemical structure of maleic chitosan

Synthesis of Maleic Chitosan:

The synthesis of maleic chitosan was carried out using a novel approach developed in our own group (Provisional U.S. patent filed). The starting material, chitosan (Sigma product) has 75% degree of deacetylation, with Brookfield viscosity 20.0-200cps (1% acetic acid). Briefly, 1.0 g methanesulfonic chitosan salts were dissolved in 100ml DMSO solvent under stirring at room temperature. Solid maleic anhydride of 6-fold in molar ratio was then added to the solution, and the reaction mixture was stirred under N₂ at 60 °C for 24 hrs. The resulting product in the solution was precipitated out by acetone, filtered, washed with copious amounts of acetone, and dried. Methanesulfonic (or tolunesulfonic) anions in the product were then removed from the chitosan salts by adding 0.1M NaHCO₃ solution. Finally the solution was dialyzed against deionized water (MW cut off 12,000) and lyophilized to yield 69% of the products. Degree of Substitution of Maleic chitosan=1.2, with N-2 and O-6 substitution 0.75 and 0.45, respectively. Molecular weight (Mₙ) =56,000.

Chemical structure of maleic chitosan:

![Chemical Structure of Maleic Chitosan](image)

Figure S1. Chemical Structure of Maleic Chitosan
S2 Additional Optical and cross-polarized optical microscopy images of 40min ACC sample.

Figure S2. Optical and cross-polarized optical microscopy images of 40min ACC sample. (a) Optical microscopy image, (b) cross-polarized optical microscopy with the first-order red \( \lambda \)-plate inserted.

S3 TEM image of the 40min sample

Figure S3. TEM micrograph of 40 min samples showing that the 40min sample obtained is always very thick for TEM observation.