Supplemental Information

Mechanism of anodic electrodeposition of calcium alginate

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1. Time dependent voltage variation during the electrodeposition

All the electrodepositions were performed using a DC power supply (Keithley 2400 sourcemeter) at controlled constant current densities. To further examine the electrode potential change during the electrodeposition, we record voltage variation during the deposition period at the current density of 4 A/m^2. In our setup, the deposition solution is in direct contact with the anode and cathode which are connected with the "+" and "–" terminals of the sourcemeter (Figure S1 inset). A constant electric current (4 μA) is forced on the electrodes (active electrode area: 1×1 mm^2) with the anode at a higher electric potential and the cathode grounded (potential zero point). Figure S1 shows the electric potential of the anode (or the voltage between electrodes) recorded as a function of deposition time. The voltage increases quickly in the first 20 sec and reach a steady phase of increase for the rest of the deposition.

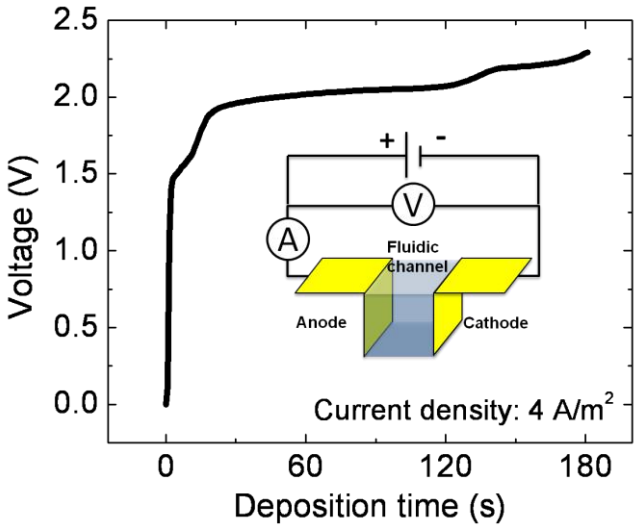

Figure S1. Time dependent electrode potential (voltage) variation during the calcium-alginate electrodeposition at constant current density of $4A/m^2$ (cathode is grounded). Inset, a schematic diagram showing the setup and configuration of the electrical measurement.

2. $CaCO_3$ particle size and distribution

In this section the size and distribution of the $CaCO_3$ particle used in deposition are assessed by both the optical microscopy and the particle analyzer. The calcium carbonate particle was purchased from Sigma-Aldrich ($CaCO_3$ powder, part # 310034). The purity of the $CaCO_3$ is 98% according to the manufacturer. The deposition solutions were prepared by suspending $CaCO_3$ powder (0-0.5%) into sodium alginate solutions (1%) with constant stirring for 12 hrs. The following two techniques were employed to examine the final size and distribution of the $CaCO_3$ microparticles in the deposition solution:

(1) Optical microscopy

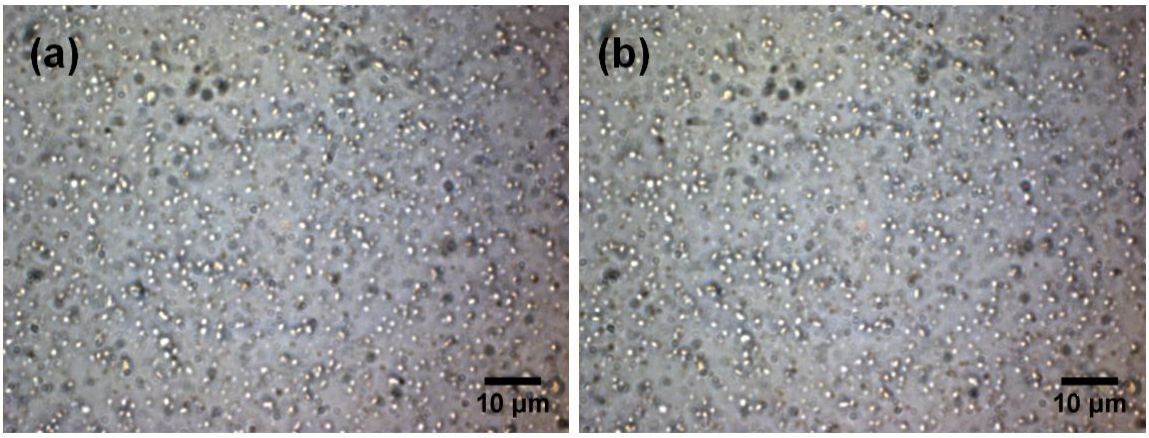

Figure S2. Optical micrographs of the deposition solution (1% Alginate + 0.25% $CaCO_3$ particles) dripped on the glass slide. The Semi-transparent circles are the $CaCO_3$ particles and black circles are the dust on the lens. Images (a) and (b) were taken with a time separation of 1 sec.

Initial examination using optical microscopy indicates evenly distributed $CaCO_3$ particles in the deposition solution with a typical diameter of 1-2 µm. The solution was dripped on a glass slide and covered with a cover slip. Some of the darker circles are the dust on the microscope lens. Only the semi-transparent circles are $CaCO_3$ particles. Figures S2 a and b show two optical micrographs taken with a time separation of 1 sec. Since the $CaCO_3$ particles were moving in the

solution, we can easily tell from these two images that the immobilized dark circles are the dust on the lens and the mobile semi-transparent circles are $CaCO_3$ particles.

(2) Malvern Zetasizer ZS90 particle analyzer

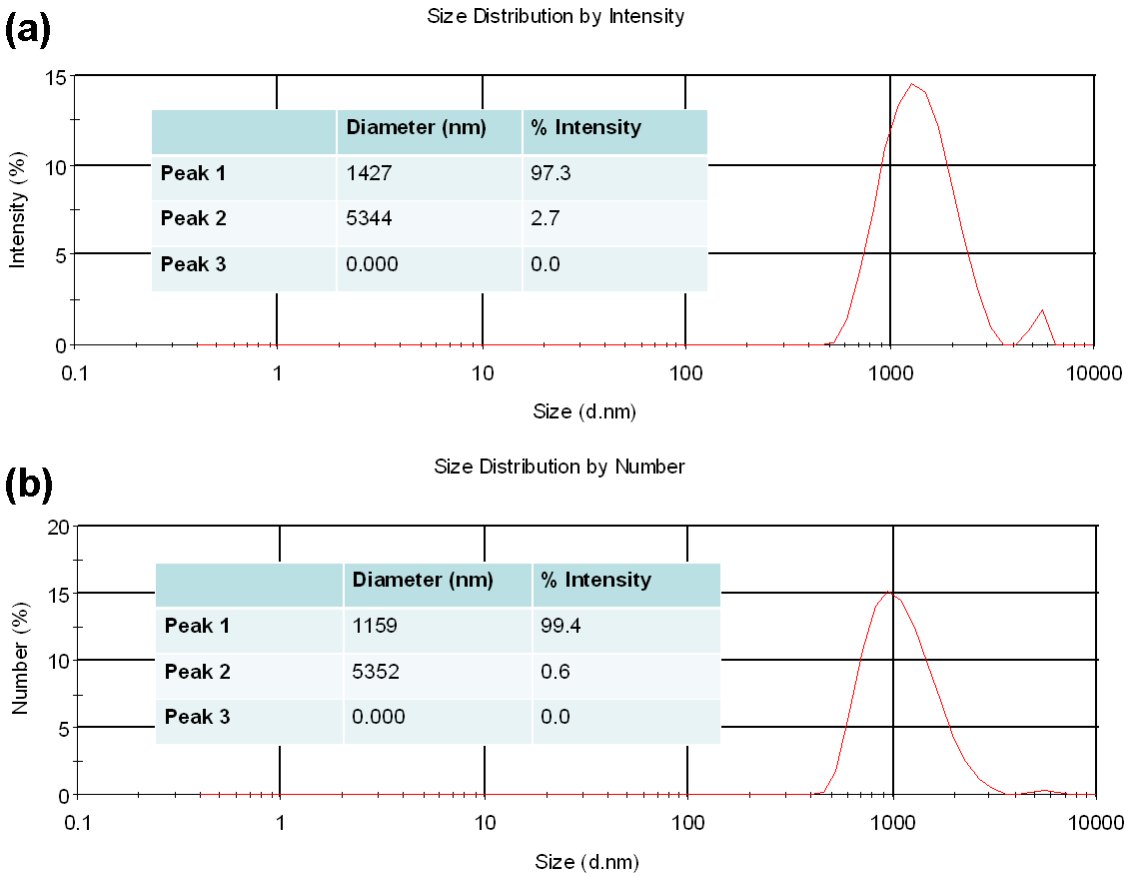

Figure S3. Size and distribution analysis by (a) intensity and (b) number of the $CaCO_3$ particles suspended in solution (concentration: 0.25%, w/v).

Additional examination with a particle analyzer indicates that a majority (over 97%) of the $CaCO_3$ particles have a diameter around 1.16-1.43 μm. A small portion (less than 3%) of the particles has a little bit larger diameter (5.35-5.34 μm). The size distribution measurements based on both intensity (Figure S3 a) and number (Figure S3 b) yield the similar results. 0.25% (w/v) $CaCO_3$ particle suspension solution is used in this set of measurements.

3. Assignment of the Raman Bands of $CaCO_3$, calcium alginate, and alginic acid

Table T1 Assignment of the Raman Bands of $CaCO_3$, calcium alginate, and alginic acid.

	Assignment		
Peak position (cm^{-1})	$CaCO_3$	Ca Alginate	Alginic Acid
1749	asymmetric stretching ν_3 bands vibration [1]		
1734			C=O stretch [2]
1617		ν_{asym} COO^- [2]	
1437	E_g mode of vibrations of CO_3^{2-} ions [3-9]		
1419-1407		ν_{sym} COO^- [2]	ν_{sym} COO^- [2]
1346		δ C-H [10-12]	δ C-H [10-12]
1299		δ C-H [10-12]	δ C-H [10-12]
1241		ν C-O [13-15]	ν C-O [13-15]
1125-1122		C-C str, C-O-C glycosidic link; ring breath, sym [10, 13, 14, 16-18]	C-C str, C-O-C glycosidic link; ring breath, sym [10, 13, 14, 16-18]
1092-1090		C-C str, C-O-C glycosidic link; ring breath, sym [10, 12-14, 16-18]	C-C str, C-O-C glycosidic link; ring breath, sym [10, 12-14, 16-18]
1087	A_{1g} (internal) mode of vibrations of CO_3^{2-} ions [3-9, 19]		
1075		C-O-H bend, C-H bend	C-O-H bend, C-H bend
1069-1063		C-O, C-C str	C-O, C-C str
957-949		δ C-C-H, δ C-O-H [13, 14, 20]	δ C-C-H, δ C-O-H [13, 14, 20]
887-882		ν C-C-H, δ C-O-H, ν_{sym} C-O-C(1,4 glycosidic link) [10, 12, 17]	ν C-C-H, δ C-O-H, ν_{sym} C-O-C(1,4 glycosidic link) [10, 12, 17]
814-806		δ C-O-H, skeletal(ν C-C, ν C-O, δ C-C-H, δ C-C-O [13, 14, 20]	δ C-O-H, skeletal(ν C-C, ν C-O, δ C-C-H, δ C-C-O [13, 14, 20]
735		Ring breathing[13, 14]	Ring breathing[13, 14]
713	E_g (internal) mode of vibrations in CO_3^{2-} ions [3-9, 19]		
674		ν_{sym} C-O-C (glycosidic linkage), ν_{sym} skeletal [13, 14, 21, 22]	ν_{sym} C-O-C (glycosidic linkage), ν_{sym} skeletal [13, 14, 21, 22]
443		δ C-C-C, δ C-O-C [14, 21, 22]	δ C-C-C, δ C-O-C [14, 21, 22]
283	E_g external vibrations of CO_3^{2-} ions [3-9, 19]		

ν = In-plane stretch, δ = deformation mode

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