Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

Ionic Liquid Mediated Auto-Templating Assembly of $CaCO_3$-Chitosan Hybrid Nanoboxes and Nanoframes

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Experimental Procedures: For the synthesis of $CaCO_3$-chitosan nanostructures, calcium chloride dehydrate (99+%), 1-butyl-3-methylimidazolium chloride (≥ 98%), medium molecular weight chitosan, and sodium carbonate (≥ 99%) were purchased from Sigma Aldrich. All chemicals were used as received. 4.01 g [BMIM][Cl], 0.029 g $CaCl_2$, and 0.02 g chitosan were put inside a vial and melted at 100°C. The mixture was sonicated with a sonication probe (Misonix XL-2000) for 2 min to dissolve the $CaCl_2$ and chitosan solid. After the solids dissolved in solution, 0.2 mL of 1M Na_2CO_3 solution was dispensed into the vial. The solution was sonicated for 1 min with the sonication probe at a temperature of 100°C. Lastly, the sample was dialyzed using dialysis membrane (Spectrum Laboratories MWCO: 12,000 - 14,000 daltons).

Analysis Methods: Nanostructures were viewed with transmission electron microscope (FEI Tecnai G2 F20 FE-TEM), and scanning electron microscope (JEOL JSM-7500F). Samples for scanning electron microscopy were coated with 4 nm of Pt/Pd. Analysis of nanostructure crystal structure was performed using x-ray diffraction (Bruker-AXS D8 Advanced Bragg-Brentano). After dialysis the samples were filtered, dried overnight, and powderized with mortar and pestle. The samples were scanned from 20 to 70° (2θ). Cu anode was used with $\lambda = 1.54$ angstroms. The voltage was set at 40 kV, and the current was set to 40 mA. Samples were scanned at a rate of

1°/min with a step size of 0.015°. The diffraction pattern from a nanoframe were obtained with transmission electron microscope (JEOL JEM-2010). Thermal gravimetric analysis was performed using TGA Q50 instrument. After dialysis was completed, the samples were filtered, dried overnight, and powderized. Samples were scanned from 25 to 1000˚C at a rate of 15˚C/min.

Fourier Transform Infrared Spectroscopy (FTIR): In order to determine whether chitosan chemically bonded with $CaCO_3$, FTIR spectroscopy was performed (Bruker Alpha-P). $CaCO_3$ prepared in water yielded peaks at similar wavelengths to those of $CaCO_3$ prepared in [BMIM][Cl] (Fig. S1 and S2). The three peaks located from 700-1400 cm^{-1} can be attributed to the C-O bonding of $CaCO_3$. The weak peak at about 1790 cm^{-1} is due to the C=O bonding of $CaCO_3$. FTIR was also performed on the $CaCO_3$-chitosan hybrid (Fig. S3). The peaks from 600-1400 cm^{-1} can be attributed to the C-O, C-C, and C-N bonding of chitosan and $CaCO_3$. Peaks from 1640-1800 cm^{-1} arise from the C=O bonding of $CaCO_3$. Lastly, peaks from 2500-3320 cm^{-1} are due to the C-H, N-H, and O-H bonds in chitosan. A significant peak shift is observed for the 1388.45 cm^{-1} peak in the Fig. S1 and 1393.69 cm^{-1} peak in Fig. S2 to the 1404.56 cm^{-1} peak in Fig. S3. This may be caused by the absorption of chitosan to $CaCO_3$ surface.

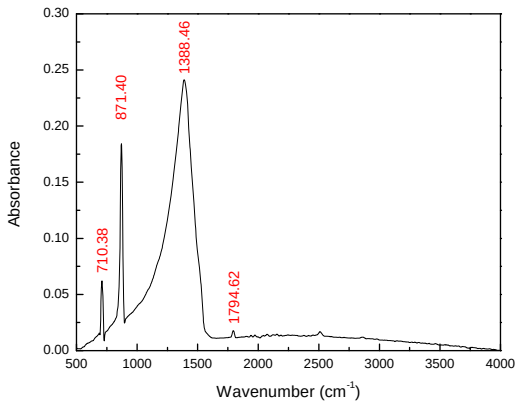

Fig. S1 FTIR spectra of $CaCO_3$ prepared in water.

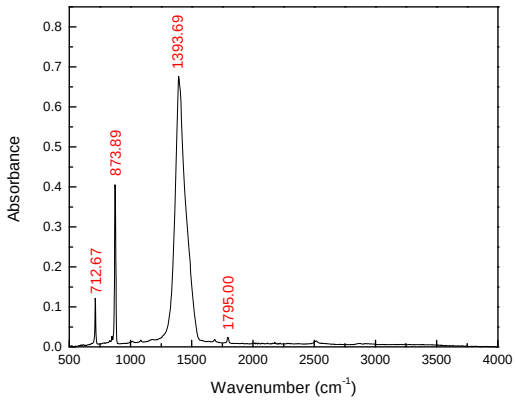

Fig. S2 FTIR spectra of $CaCO_3$ prepared in ionic liquid [BMIM][Cl].

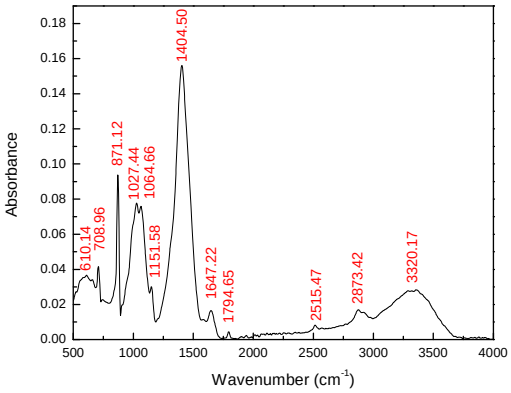

Fig. S3 FTIR spectra of $CaCO_3$-chitosan hybrid prepared in ionic liquid [BMIM][Cl].

SEM of pure $CaCO_3$: SEM images were taken of pure $CaCO_3$ made in water and in [BMIM]Cl medium (Fig. S4). These samples were prepared in the same manner as the $CaCO_3$-chitosan hybrid nanostructures. The $CaCO_3$ formed was spread upon carbon tape and coated with 4 nm of Pt/Pd. It was found that the dimensions of the pure $CaCO_3$ in water and [BMIM][Cl] are 4.79 ± 1.70 x 3.94 ± 1.52 μm and 340 ± 144 x 273 ± 116 nm respectively.

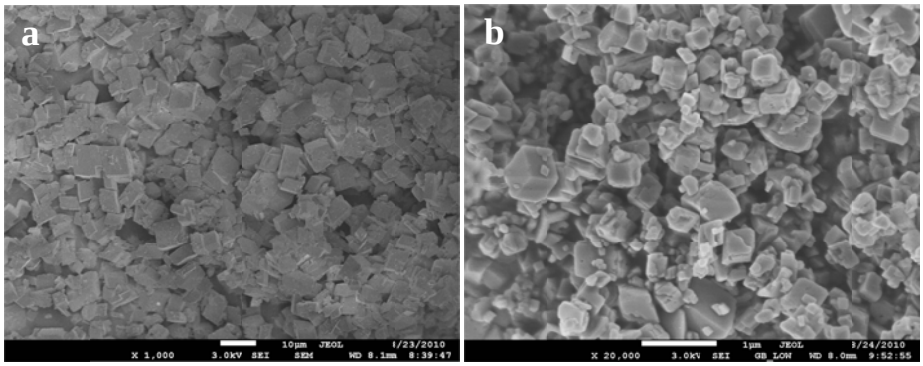

Fig. S4 SEM image of $CaCO_3$ prepared in (a) water and (b) ionic liquid [BMIM][Cl].

SEM image of solid $CaCO_3$ before dialysis: SEM image of solid $CaCO_3$-chitosan hybrid nanostructure was taken before dialysis was performed. The sample was spin coated on a silicon wafer and coated with 4 nm of Pd/Pt. The image is not very sharp because [BMIM][Cl] was not completely removed by the spin coater and residual [BMIM][Cl] caused the sample to charge.

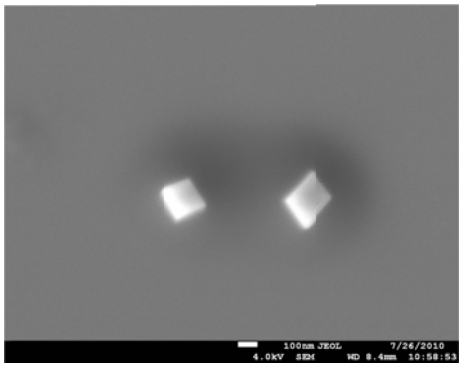

Fig. S5 SEM image of solid $CaCO_3$-chitosan hybrid nanostructure before dialysis.

Thermal Gravimetric Analysis: $CaCO_3$-chitosan samples were dialyzed for 24 and 90 h. 8.15 mg of 24 h sample and 16.06 mg of 90 h sample were used in the analysis. It can be seen in Fig. S6,7 that chitosan decomposed around 300˚C while calcite decomposed at about 750˚C. Weight loss from 50 to 150˚C was attributed to water loss in the samples. There was about 7 wt% water in both samples. In the 24 h sample there was 55 wt% $CaCO_3$ and 38 wt% chitosan. For the 90 h sample there was 59 wt% $CaCO_3$ and 34 wt% chitosan.