Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Peptoid Nanosheets as Soluble, Two-dimensional Templates for Calcium Carbonate Mineralization

*Joo Myung V. Jun, M. Virginia P. Altoe, Shaul Aloni, Ronald N. Zuckermann**

The Molecular Foundry, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, United States

Corresponding author e-mail : rnzuckermann@lbl.gov

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Synthesis of B28 peptoid nanosheets (S1)

Block 28 peptoid was synthesized as previously described[1, 2] on a Protein Technologies Prelude synthesizer and purified by reverse phase prep HPLC, and characterized by analytical HPLC, MALDI, and LCMS. The final peptoid products were lyophilized from 1:1 (v/v) water and acetonitrile and stored at -80˚C. Lyophilized peptoids were then dissolved in 1:1 (v/v) DMSO: H_2O to make final 2 mM stock solution. Nanosheets were formed in the following solution conditions: 20 µM B28 peptoid, 10 mM Tris, pH 8.0. This was created by mixing 5 µL of the 2 mM peptoid stock solution and 495 µL of 10 mM pH 8.0 Tris buffer in a 4 mL vial. This solution was placed on a vial rocker for up to 3 days (288 cycles) to produce the nanosheets. Sheets were then analyzed and characterized by fluorescence microscopy, SEM, AFM, and XRD.

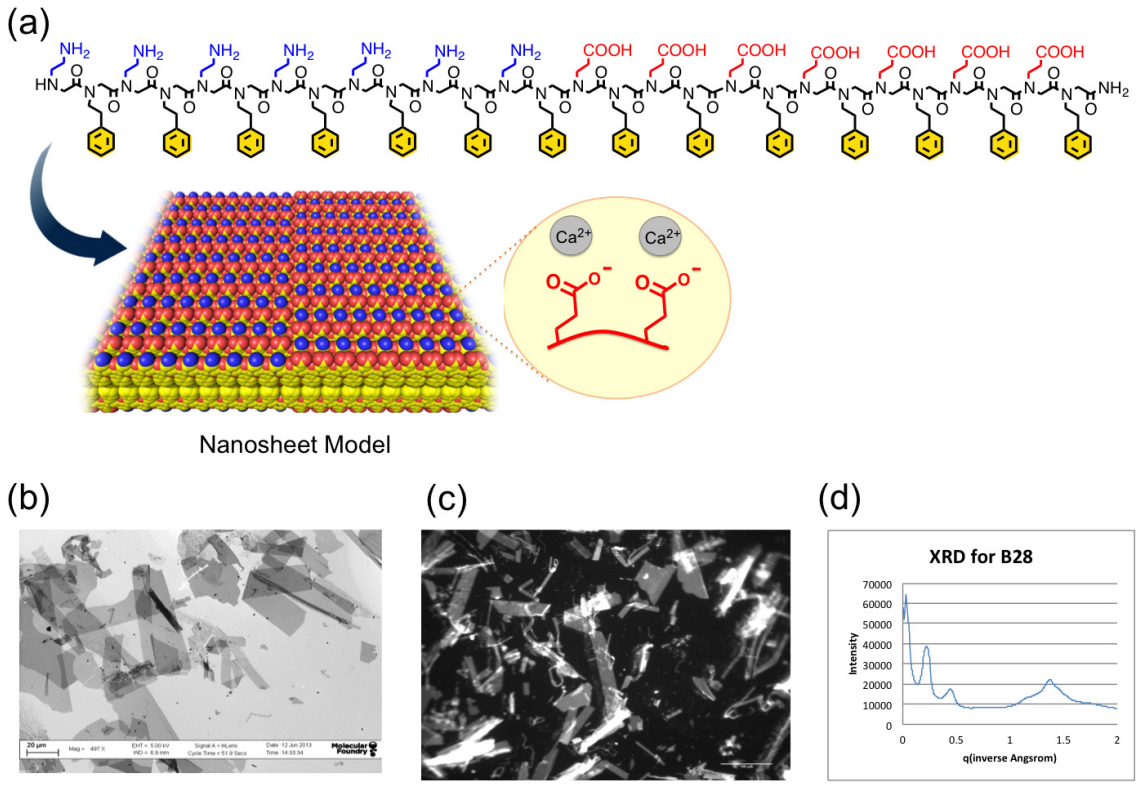

Figure S1. Structure of B28 peptoid nanosheets. (a) Chemical sequence of the block 28 peptoid and a model for the assembled peptoid nanosheets, where the hydrophilic exterior residues are red and blue, and the hydrophobic interior is yellow. (b) SEM images of a population of nanosheets. (c) Fluorescence microscopy image of peptoid stained with Nile red. (d) X-ray powder diffraction pattern of B28 peptoid nanosheets indicating their thickness of ~3 nm.

Mineralization of peptoid nanosheets (agarose method) and sample preparation (S2)

$(NH_4)_2CO_3$ (99.999% trace metal basis) and anhydrous $CaCl_2$ (≥97%) were purchased from Sigma-Aldrich and were used as received. In order to support the nanosheets, a flat section of Agarose gel (certified molecular biology grade, Bio-Rad) (2% w/v) was prepared. 100 μL of a nanosheet solution, and 300 μL MilliQ water were combined and filtered twice in a 100 kD centrifugal filter (Amicon Ultra/Millipore, 0.5 mL size) at 5000 rpm x 3 min, yielding 100 μL of peptoid nanosheet solution. 10 μL of the filtered nanosheet solution was applied to the 2% agarose gel (4 x 10 x 10 mm) and the solution was allowed to settle for 1 hr. The gel containing the nanosheets was placed into 24-well plate, followed by the addition of 600 μL of 10 mM $CaCl_2$ solution that is just enough to cover the surface of the gel. The 24-well plate was sealed with an adhesive plastic cover, and 15 holes were punctured using a 20 gauge syringe needle to allow slow diffusion. 500 mg of $(NH_4)_2CO_3$ in a 20 mL scintillation vial was kept completely open during mineralization process to serve as the CO_2 source. A sealable chamber with two levels was used as a desiccator, where the 24-well plate was placed on the second floor and $(NH_4)_2CO_3$ on the first floor as shown in Figure S2d. In order to prepare the sample for imaging, PELCO® silicon nitride support films (15 nm with 9 each 0.1 x 0.1 mm windows) from Ted Pella were plasma cleaned for 3 minutes before use. After 30 min to 3 hr of mineralization, the gel was transferred onto a Kimwipe for 30 sec, and then placed onto a glass slide to dry for 10 min until no solution was visible on the gel. Once nanosheets were settled on to the gel, 10 μL of a 50% EtOH solution was added to wash out the residual $CaCl_2$ that might be sitting on top of the sheets without dissolving the mineralization layer on the sheet. Once the gel was dried for additional 10 min, the nanosheets were transferred (via adsorption) to a clean Si_3N_4 substrate by placing the substrate on top of the gel for 2 minutes, and then removing the gel. The substrate was dried under vacuum and then imaged via SEM, AFM, and TEM. All analysis was done on a single silicon nitride grid for each sample: 0 min, 30 min, 2 hr, and 3 hr mineralized sample. SEM was imaged with Inlense 5 Kev, and AFM analysis was done in Veeco with TAP 150AL-G tips.

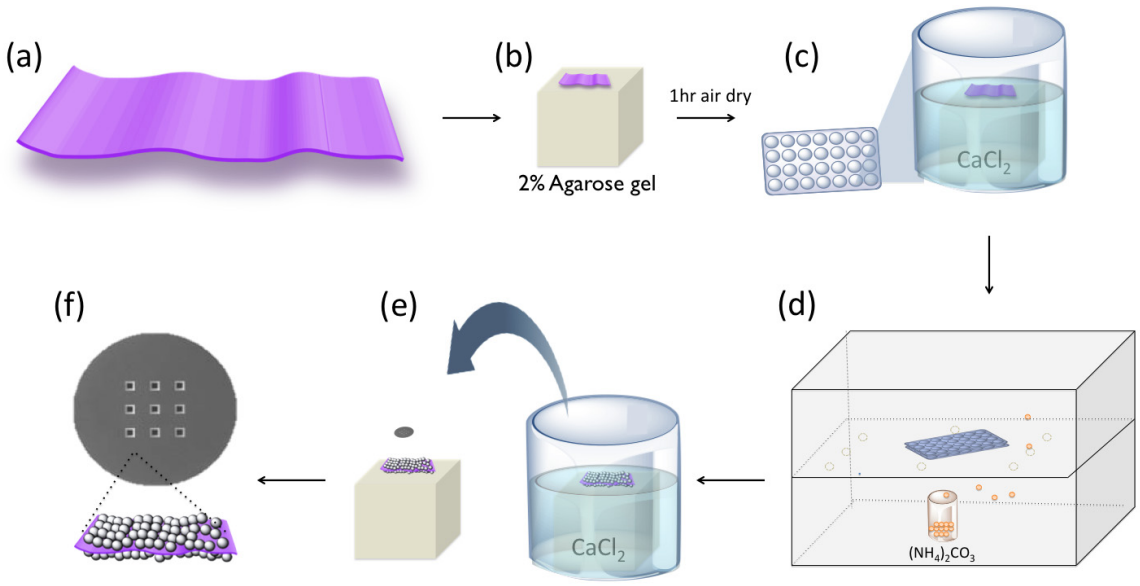

Figure S2. Agarose-supported nanosheet mineralization and analysis scheme.(a) Dialyzed, free-floating nanosheets are produced in aqueous solution, and are (b) deposited on the surface of an agarose gel. (c) The gel is placed into 24-well plate and submerged into a $CaCl_2$ solution. (d) The nanosheet/calcium solution is placed in a sealed chamber along with an ammonium carbonate CO_2 source. (e) The mineralized sheets are transferred onto a TEM grid. (f) Si_3N_4 substrate with mineralized nanosheets.

Atomic Force Microscopy analysis of mineralized nanosheets (S3)

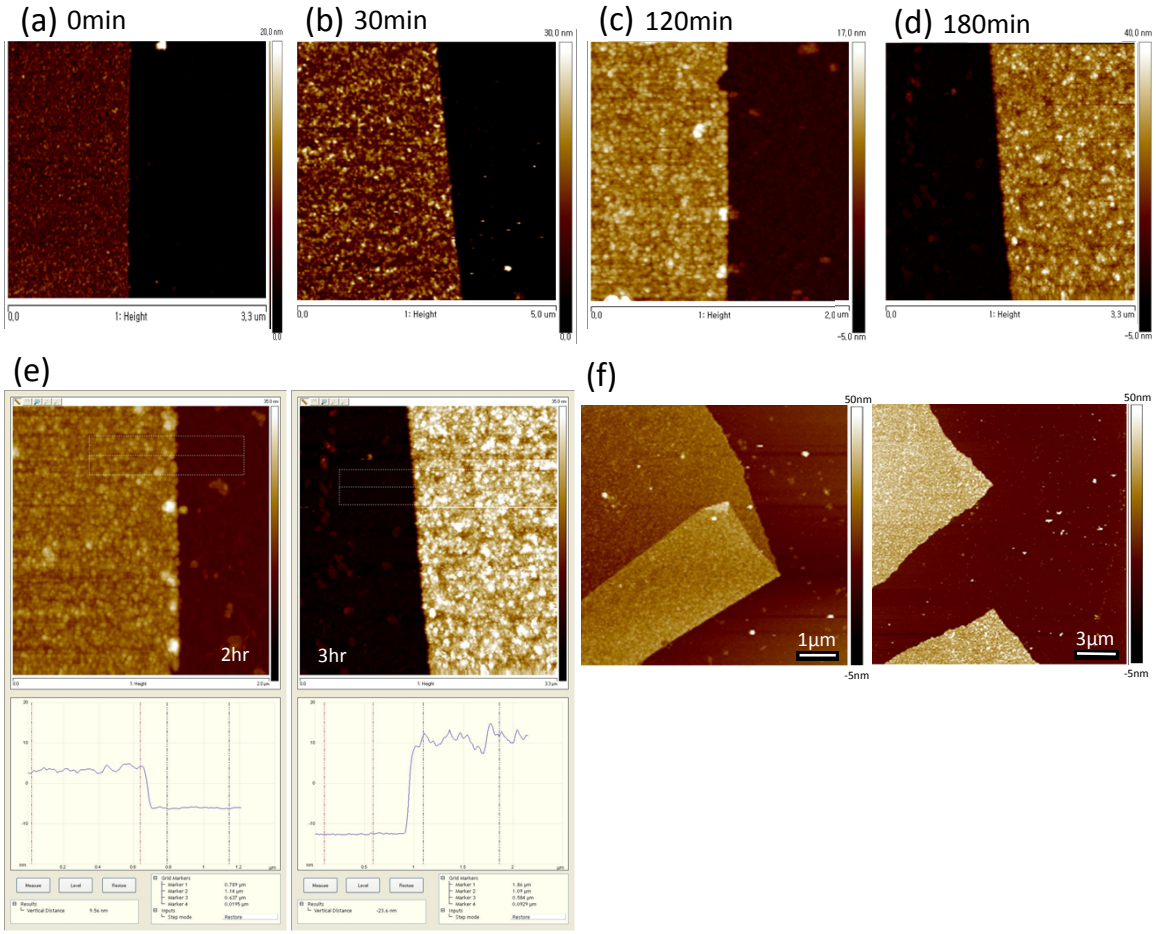

Figure S3. AFM images of peptoid nanosheets during the course of mineralization. (a-d) Normalized to different height scale (bar on the right) to show more prominent features of the mineralized nanosheets. (e) Thickness was measured by averaging over the square area. Changes in both the height and roughness can be observed over the course of mineral growth. (f) Zoomed out images of mineralized nanosheets.

Conversion of ACC to CaO via TEM electron beam irradiation (S4)

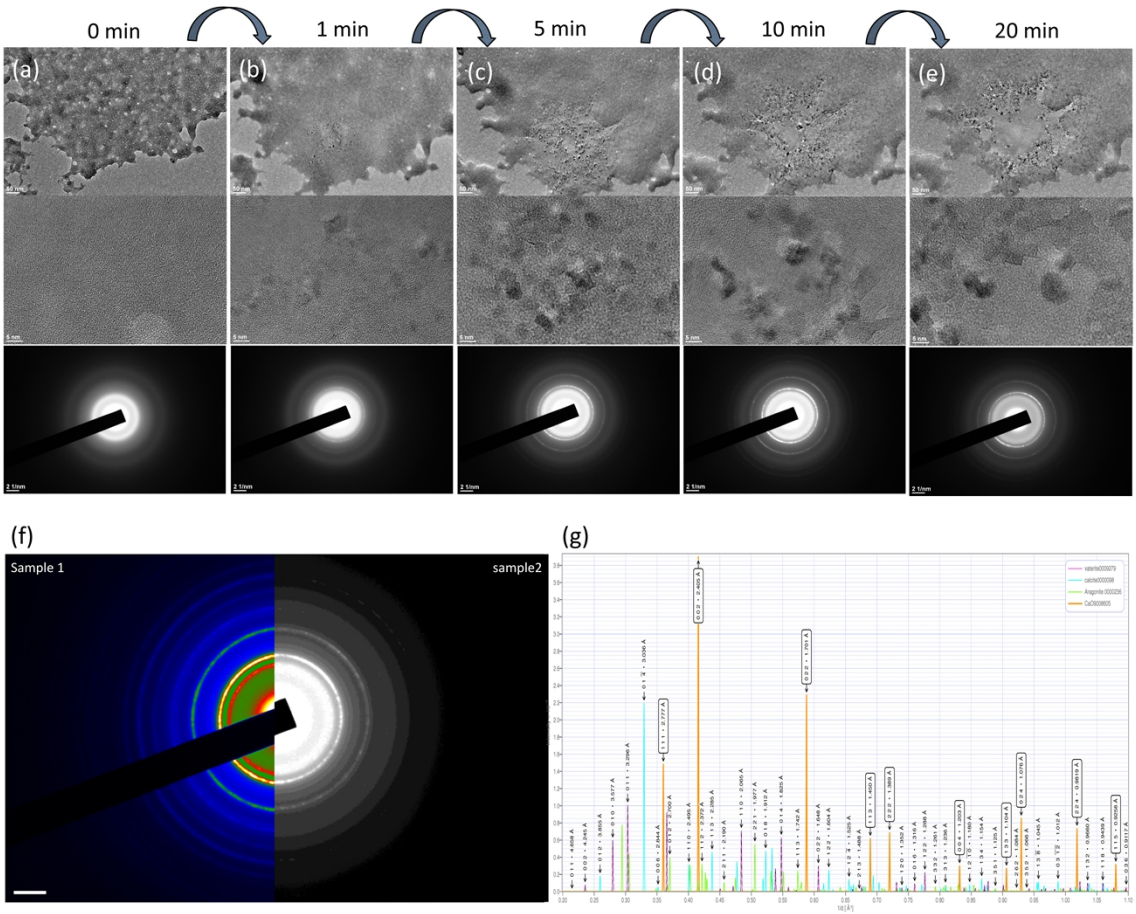

Figure S4. Change in diffraction pattern from amorphous to crystalline, induced by exposure of intense electron-beam irradiation (200 kV, ~10^7 electron/nm^2/s) in the TEM. Each panel represents 30 kX (top row), 400 kX (middle row), and diffraction ring (bottom row) of image after (a) 0 minute, (b) 1 minute, (c) 5 minute, (d) 10 minute, and (e) 20 minute exposure (f) Two samples were examined to determine the d-spacing after 20 minute exposure. (g) The crystals formed after 20minues of e-beam irradiation resulted in decomposition of $CaCO_3$ into CaO, confirmed by comparison of all anhydrous calcium carbonate and CaO phases.

References:

1. K. T. Nam, S. A. Shelby, P. H. Choi, A. B. Marciel, R. Chen, L. Tan, T. K. Chu, R. A. Mesch, B.-C. Lee, M. D. Connolly, C. Kisielowski and R. N. Zuckermann, *Nat. Mater.*, **2010**, *9*, 454-460.
2. B. Sanii, R. Kudirka, A. Cho, N. Venkateswaran, G. K. Olivier, A. M. Olson, H. Tran, R. M. Harada, L. Tan and R. N. Zuckermann, *J. Am. Chem. Soc.*, **2011**, *133*, 20808-20815.