Electronic Supplementary Material (ESI) for Soft Matter.

Polyelectrolyte Complex Films Influence the Formation of Polycrystalline Micro-Structures

Elias Nakouzi, Hadi Fares, Joseph B. Schlenoff, and Oliver Steinbock*

Supplementary Information

Prior to processing, the as-formed multilayers can have many undesired characteristics for surface and bulk studies. For example, immersion in salt solutions can slowly change a PSS-capped film into a PDADMA-capped film as excess polycations diffuse to the surface. Moreover, the use of relatively high salt concentrations (here 1 M NaCl) is desirable to create thicker films, but significantly increases the surface roughness of the resulting multilayers (approximately 80 nm roughness for a 550 nm 40-layer film). Accordingly, the ionic content of the surrounding solution can have a drastic impact on the film structure and chemistry, which renders the films unsuitable for crystallization experiments. To circumvent these problems, we process the multilayers using a recently reported method, wherein the prepared multilayers are cycled between solutions of 2 M NaCl for 30 min, and 10 mM PSS in 1 M NaCl for 5 min. The salt ions promote polymer diffusion which eliminates the discrete layering and smooths the surface, while the additional polyanions compensate the excess PDADMA and reduce the ionic content within the films. In a final processing step known as "overcompensation", an excess amount of PDADMA or PSS can then be added to the films in a controlled fashion. At equilibrium, this addition of polyelectrolytes produces films with 35% excess of either ammonium (PDADMA) or sulfonate (PSS) groups throughout the film. Figure 2 in the main manuscript text shows infrared spectroscopy measurements of the PDADMA-dominated, PSS-dominated, and stoichiometric films. With PSS exhibiting slower diffusion, the addition requires more salt and time to reach overcompensation equilibrium.

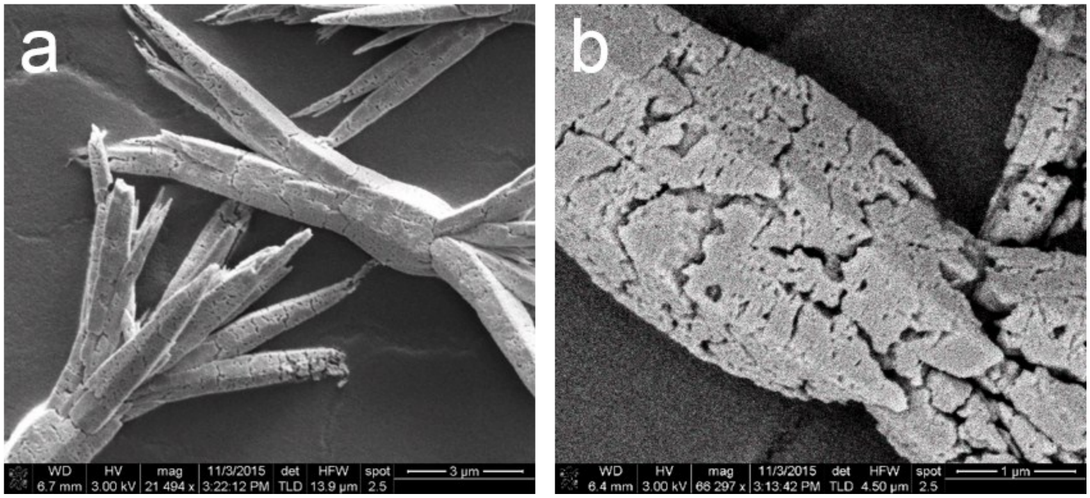

Figure S1. Classical barium carbonate crystals obtained by crystallization of $BaCO_3$ on the polymeric films in the absence of silicate. Similar structures were obtained using the three distinct polymer substrates. We observe the expected witherite habits with some defects in the crystals.

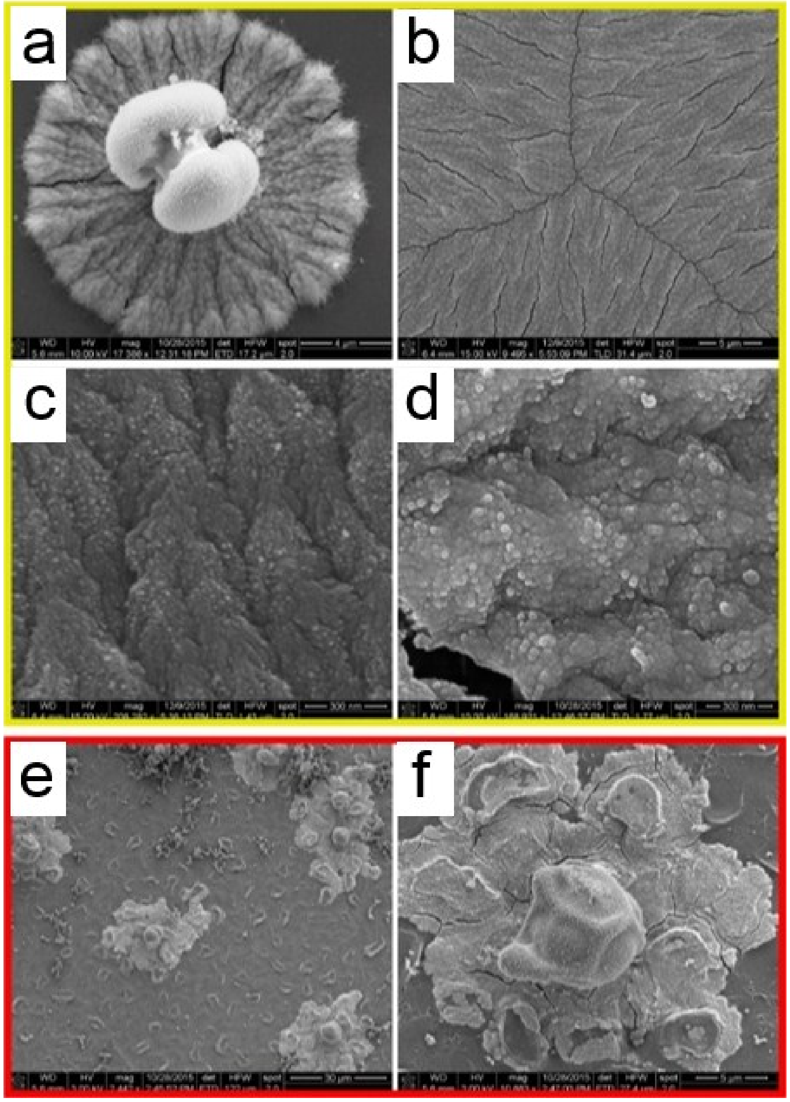

Figure S2. Silica carbonate biomorphs grown on (a-d) stoichiometric, and (e,f) PSS-dominated films.

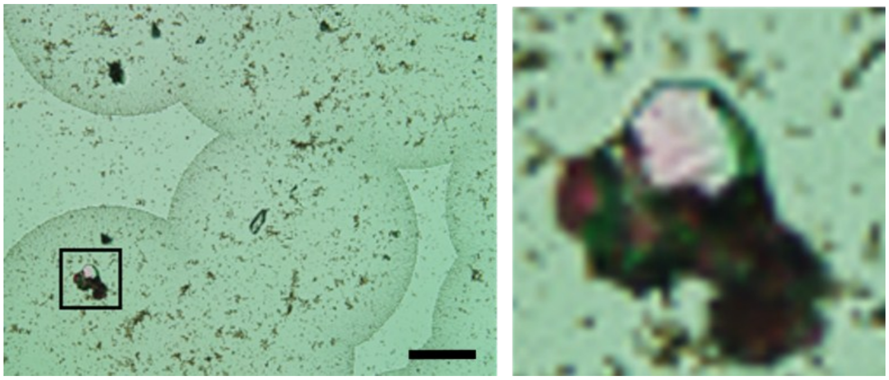

Figure S3. Optical image of biomorph films grown for several days on stoichiometric substrates and viewed between two crossed polarizers. The nanoparticle films do not show gradients in extinction patterns, unlike typical biomorph sheets (see enlarged black box). Scale bar: 100 µm.