Electronic Supplementary Material (ESI) for ChemComm.

Biomorph Growth in Single-Phase Solutions: Expanding the Structure Spectrum and pH Range

Elias Nakouzi, Pamela Knoll, and Oliver Steinbock*

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390, USA

Experimental Methods

Biomorphs are synthesized in initially homogeneous solutions of [$BaCl_2$] = 5 mM, [Na_2SiO_3] = 8.4 mM, and [Na_2CO_3] = 0.001–1 mM. All stock solutions are prepared with ultrapure water (Barnstead EASYpure UV). Before initializing the reaction, we purge the barium and silicate solutions with N_2 gas to minimize traces of pre-dissolved CO_2. We then mix the solutions and adjust the pH to the desired value by adding a few drops of 1 M HCl or NaOH. The pH is measured using a Fisher Scientific, Accumet AB250 pH meter. The reaction solution is subsequently transferred to a Petri dish (Greiner Bio-One, 3.5 cm diameter, 1.0 cm height) and mixed with the required microvolume of 0.1 M sodium carbonate. The total solution volume of 10 mL fills the reaction container completely. Accordingly, the liquid-air interface is reduced to a small bubble at the solution surface. We seal the container tightly with multiple layers of Parafilm and place it in an N_2-purged storage chamber kept at room temperature. Within a few hours, the crystal aggregates begin to form.

Optical microscopy images are acquired using a Nikon Elements Ti inverted microscope equipped with a Photometrics Coolsnap HQ2 camera. For the high resolution images, we use a JEOL 7401F Field Emission Scanning Electron Microscope (FE-SEM) operating at 10-20 kV. The Powder X-ray Diffraction (PXRD) measurements are conducted using a PANalytical X'pert PRO diffractometer operating at the Cu Kα emission line. We collect data for a 2θ range of 10° to 80° at a scan speed of 0.02 deg/s. Finally, the infrared (IR) spectra are obtained using a PerkinElmer Spectra 100 instrument working in attenuated total reflectance mode.

Supporting Data

As described in the manuscript, the biomorphs in the single-phase system can reach millimeter lengthscales. Figures S1 (a) and (b) show examples of convex funnels that grew for more than ten days. Moreover, the biomorphs can form complex wavy patterns and thin-walled assemblies (Fig. S1c-f). Closer inspection of these structures shows that they consist of nanosized building blocks that are characteristic of biomorphs (Fig. S1g).

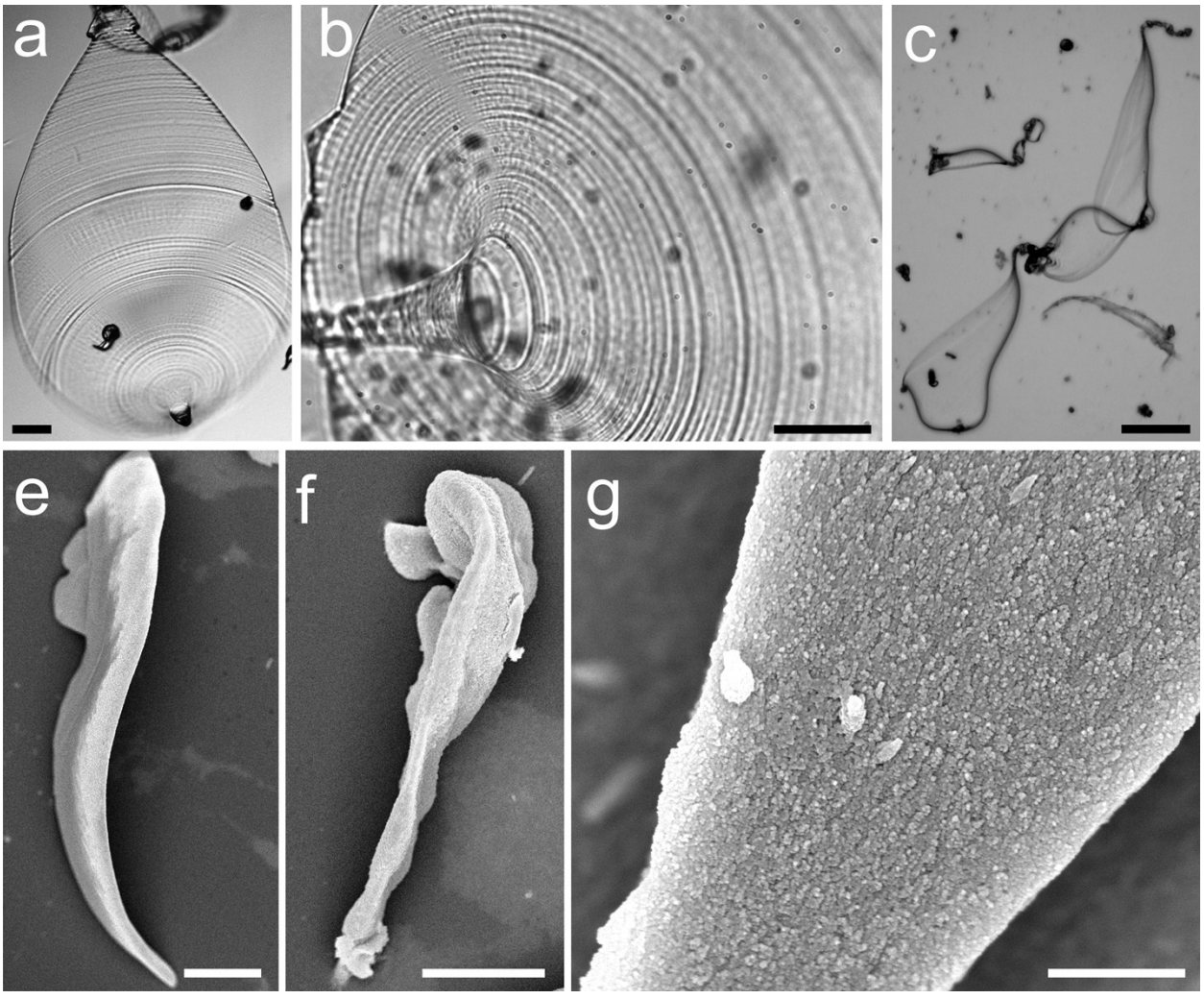

Fig. S1 (a-c) Optical micrographs and (d-f) SEM images of the thin-walled biomorphs. Scale bars represent: (a, b) 100 µm, (c) 10 µm, and (e) 1 µm.

Figure S2 plots the IR spectrum of biomorphs that form at pH > 12. The peaks at 1111, 956, and 800 cm^{-1} as well as the shoulder around 1150 cm^{-1} clearly indicate the presence of silica. This result is particularly interesting since silica is highly soluble at these reaction conditions (see manuscript).

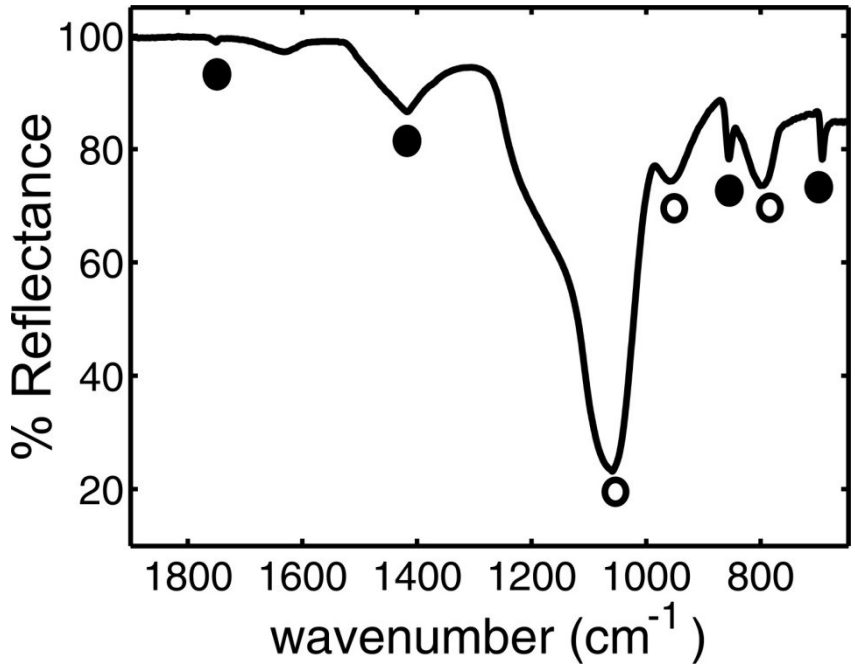

Fig. S2 IR spectrum of biomorphs formed at pH > 12. Filled and open circles indicate the characteristic barium carbonate and silica peaks, respectively.

Image Analysis

We analyze SEM images to obtain detailed information on the dominant local orientation within the nanorod aggregates. This method is based on the two-dimensional autocorrelation function of the gray-level image. More specifically, we compute the correlation decay as the image is shifted by Δx in x-direction and Δy in y-direction with respect to the original image. This analysis is carried out for non-overlapping boxes of 100×100 pixels and yields local autocorrelation maps $c(\Delta x,\Delta y)$. The correlation is always maximal for $(\Delta x,\Delta y)=(0,0)$ and decays in all directions but persists longer if the image is shifted in the direction of the nanorods. To determine this direction, we fit an ellipse to the $c = 0.2$ contour and find the length of its short (i.e., semiminor) and long (semimajor) axes, which we denote as s and l, respectively. The long

axis indicates the dominant nanorod orientation that in Fig. 3d is represented by the individual vectors. The vector lengths are proportional to the eccentricity of the ellipse $(1-s^2/l^2)^{1/2}$, which we use as a semi-quantitative measure of the persistence of the correlation. In addition, we perform an *ad hoc* assignment of the biomorph's growth direction that is reflected in the arrow head positions. Notice that the entire analysis is based on surface data projected onto the image plane. Accordingly, we do not resolve out-of-plane variations in the nanorod alignments if the sample surface is perfectly parallel to the image plane.