Supporting Information

SELF-ASSEMBLED 'FLORAL DUMBBELL' SILICA-CALCIUM CARBONATE

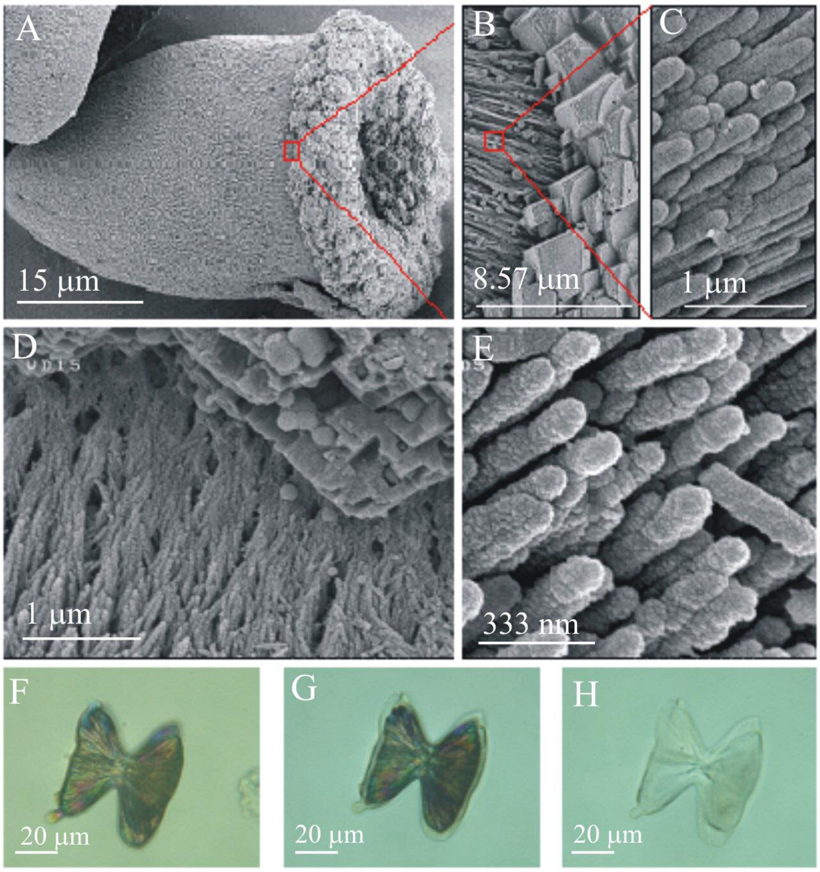

Figure S_1. Self-assembled 'floral dumbbell' silica-calcium carbonate. (A to C) Zoom sequence, showing details of the surface texture. (D and E) High-magnification FESEM images of biomorphs (after alkaline leaching of silica) showing the orientational ordering of aragonite crystallites. (F to H) Optical micrographs of the aggregates, viewed under crossed polarizers, showing the progressive dissolution in dilute hydrochloric acid of aragonite from the carbonate-silica material, leaving a silica 'ghost'. A-E show only half of the complete aggregate.

Figure S_1 shows optical and Field Emission Scanning Electron Microscopy (FESEM) images of biomorphic calcium carbonate-silica composites. Each dumbbell cluster is composed of two conical subunits, 90 μm in length and 30 μm in maximum diameter. The form is reminiscent of the wheat-sheaf forms reported previously[1,2,3], though with important differences. First, most of the carbonate material in the aggregates is aragonite, rather than calcite. For example, Figure S_{1A} presents one conical subunit, in which two different crystalline modifications can be observed. The major component is aragonite (intergrown with amorphous silica, described below), with the usual rod-like habit (400-500 nm in width), accompanied by characteristic calcite rhombohedra lining the outer rims that form last (see Figure S_{1B}). Second, the ordering of the nanoscale aragonite rods is very similar to that observed previously in barium and strontium biomorphs[4]. The walls are composed of radially aligned aragonite-silica rods. The presence of calcite in later stages of growth is likely to be due to a secondary nucleation and not to a phase transition between aragonite and calcite. Indeed, aragonite clusters without calcite rims are occasionally found in the reaction cells.

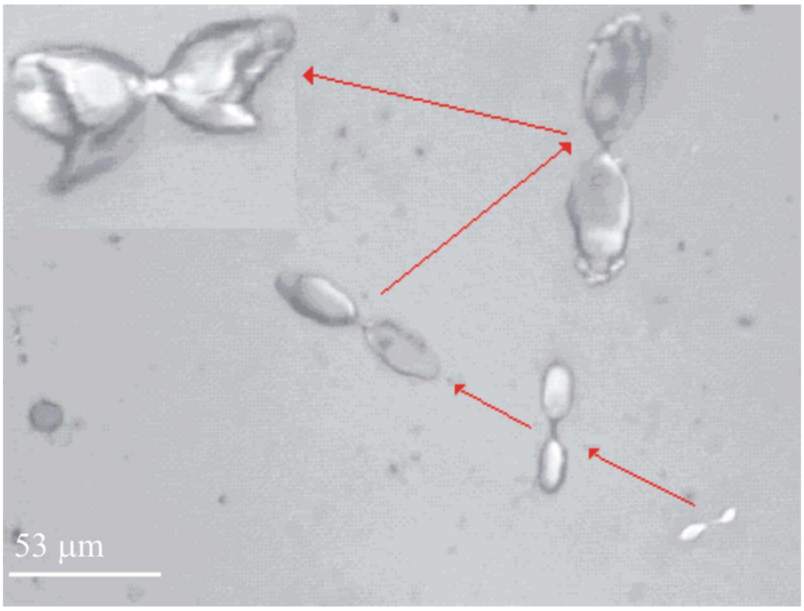

Figure S_2. Optical micrograph of silica-calcium carbonate aggregates, viewed between crossed polarizers, which shows the growing sequence of a floral dumbbell structure.

Figure S_2 shows the sequence of shapes of biomorphic floral dumbbell composites. Initially, a perfect dumbbell cluster forms which is composed of needle-like crystals. With time, the cluster appears to grow more in length than in width and finally develops into a ‘floral dumbbell’, composed of two open conical subunits. This growth behaviour might be related to the mutual orientation of the crystallites that intergrow with amorphous silica.

EDX SPECTRA OF ‘CORALLINE’ SELF ORGANISED SILICA-CALCIUM CARBONATE BIOMORPHS

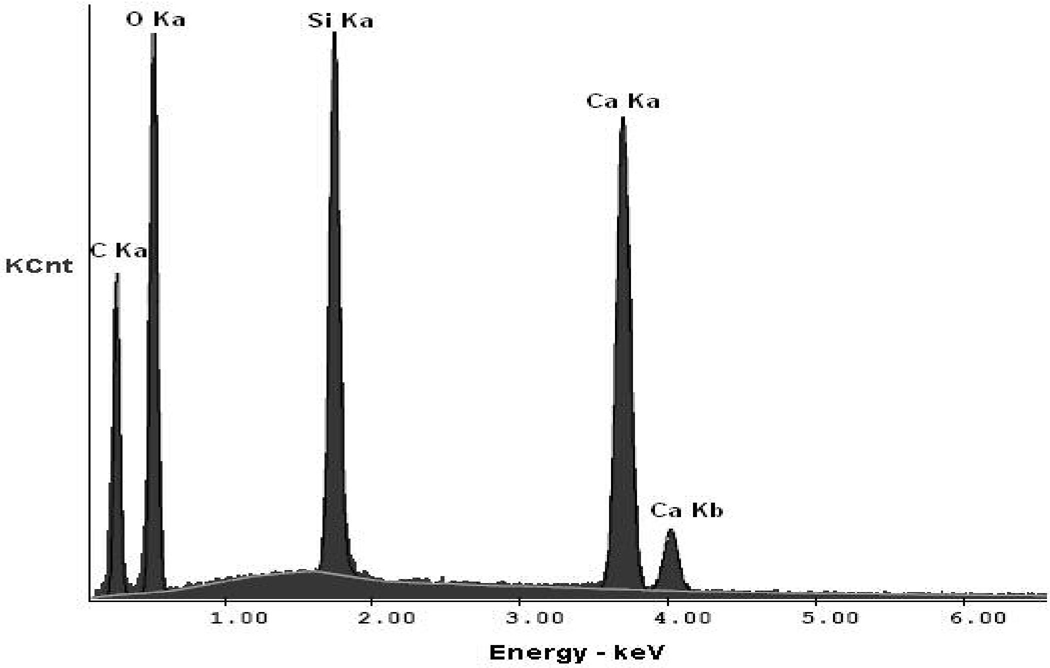

Figure S_3. EDX spectrum of self organised silica-calcium carbonate biomorphs.

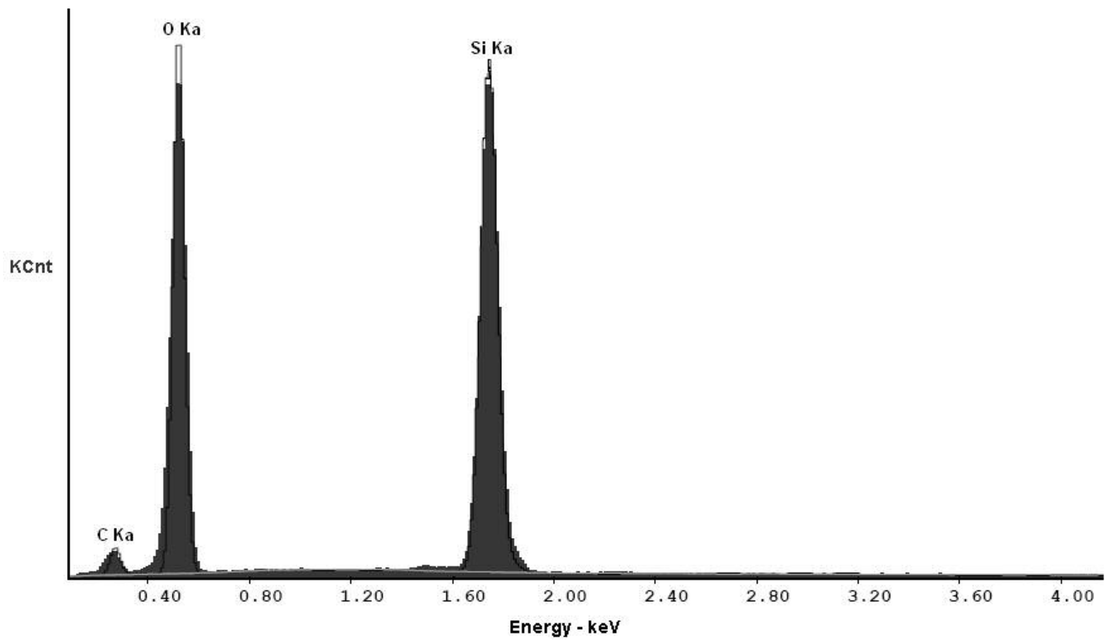

Figure S4. EDX spectrum of a hollow silica skin left after immersion of the 'coralline' silica-calcium carbonate biomorphs in 0.1M HCl.

(1) Dominguez Bella, S.; Garcia Ruiz, J. M. *J. Mat. Sci.* **1987**, *22 (9)*, 3095

(2) Garcia-Ruiz, J. M. *J. Cryst. Growth* **1985,** *73 (2)*, 251.

(3) Dominguez Bella, S.; Garcia Ruiz, J. M. *J. Cryst. Growth* **1986**, *79 (1-3)*, 236.

(4) Terada, T.; Yamabi S.; Imai H. *J. Cryst. Growth* **2003**, *353*, 435.