Electronic Supplementary Information
Controlling the wall thickness and composition of hollow precipitation tubes

László Roszol and Oliver Steinbock*

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

Fax: (+1) 850-644-8281, E-mail: steinbck@chem.fsu.edu

Experimental details

Synthesis

The following chemicals are used without further purification: copper sulfate pentahydrate (Spectrum Chemicals), zinc sulfate heptahydrate (Fisher Scientific), and sodium metasilicate pentahydrate (Fisher Scientific). The solutions are prepared in nanopure water (18 MΩcm; EASYpure UV, Barnstead).

We inject the copper or zinc sulfate solutions into a glass cylinder (diameter 22 mm, height > 10 cm) containing the sodium silicate solution through a glass nozzle (inner diameter 1 mm) using a syringe pump (NE-1600, New Era Pump Systems). The height of the silicate solution in the glass cylinder is about 9 to 10 cm. We introduce the air bubbles into the silicate solution using a stainless steel needle (BD 23G); the tip of the needle is just above the nozzle.

The tubes usually preserve their structure after rinsing and drying, but if prepared in 2.0 M sodium silicate solution for $t = 0$ they collapse during the drying process.

The pH of the 0.5 M $CuSO_4$ and $ZnSO_4$ solutions is 3.3 and 4.6, respectively. The pH of 1 M and 2 M sodium silicate solutions is 13.4 and 13.6, respectively.

Characterization

We characterize the geometry of the tube segments with a calibrated microscope (Intel Play QX3) connected to a computer. The length and the diameter of the segments are measured under 10x and the 60x magnification, respectively. The mass of each tube is determined with a microbalance (CAHN C-32). Scanning electron microscope (SEM) images are recorded on a JEOL JSM-5900 scanning electron microscope with an energy-dispersive X-ray (EDS) attachment operating at 30 kV. The samples are coated with carbon.

Additional SEM images and EDS data

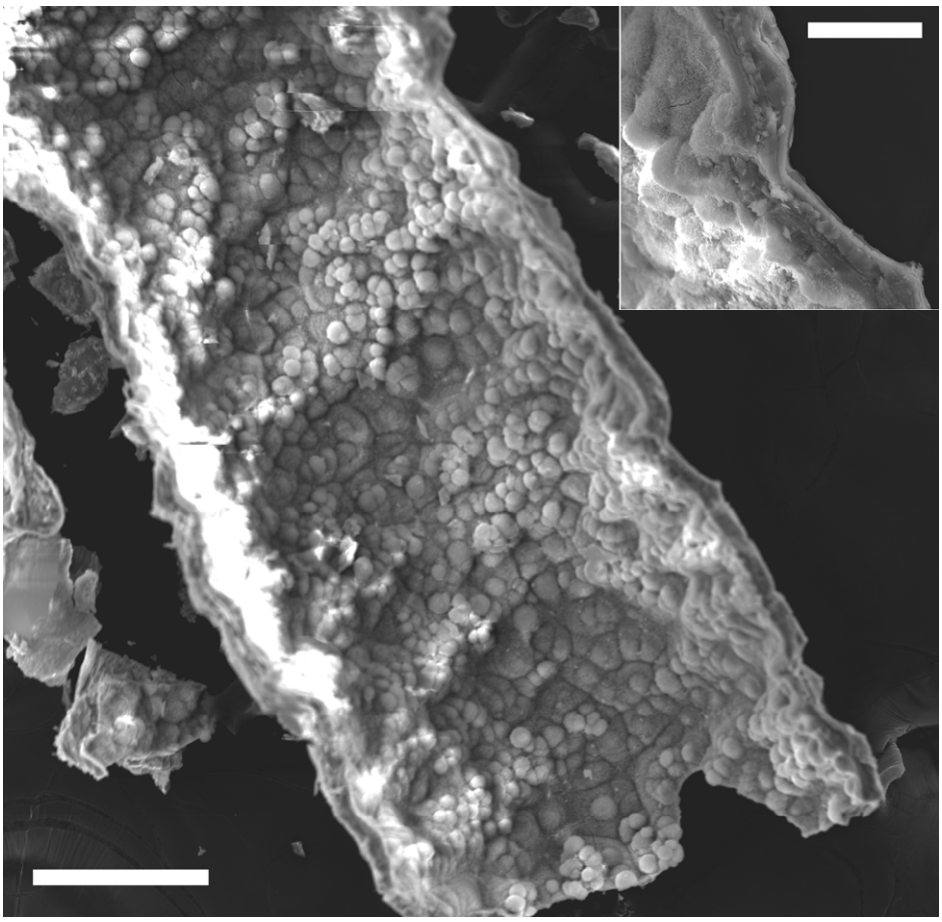

Figure S1. Scanning electron micrograph of the inner surface of a copper-based silica tube; t = 15 min. Inset: a magnified part of the tube wall. The wall thickness is about 28 µm; accurate measurements are not possible due to the rough, nodular surface. The nodules are present only under certain synthesis conditions but this dependence has not been studied further. Nodules have higher sulfur contents (see Figure S2 b) than the inner surface of tubes without nodules. Scale bar: 200 µm; inset: 50 µm.

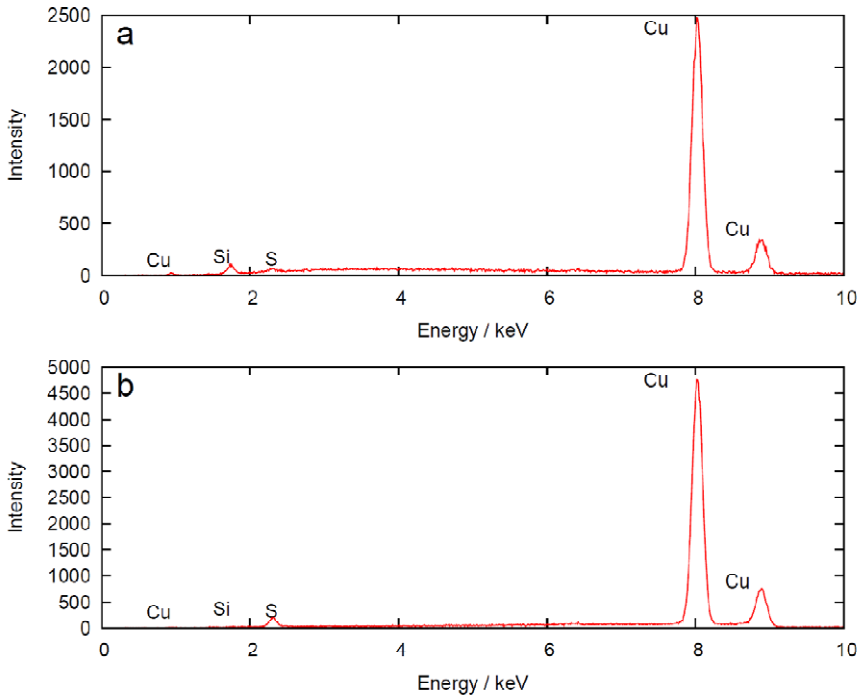

Figure S2. EDS spectra of the tube in Fig. S1. (a) Outside surface; [Cu] = 96.9 wt.%, [Si] = 2.5 wt.%, and [S] = 0.6 wt.%. (b) Inside surface; [Cu] = 98.0 wt.%, [Si] = 0.0 wt.%, and [S] = 2.0 wt.%.

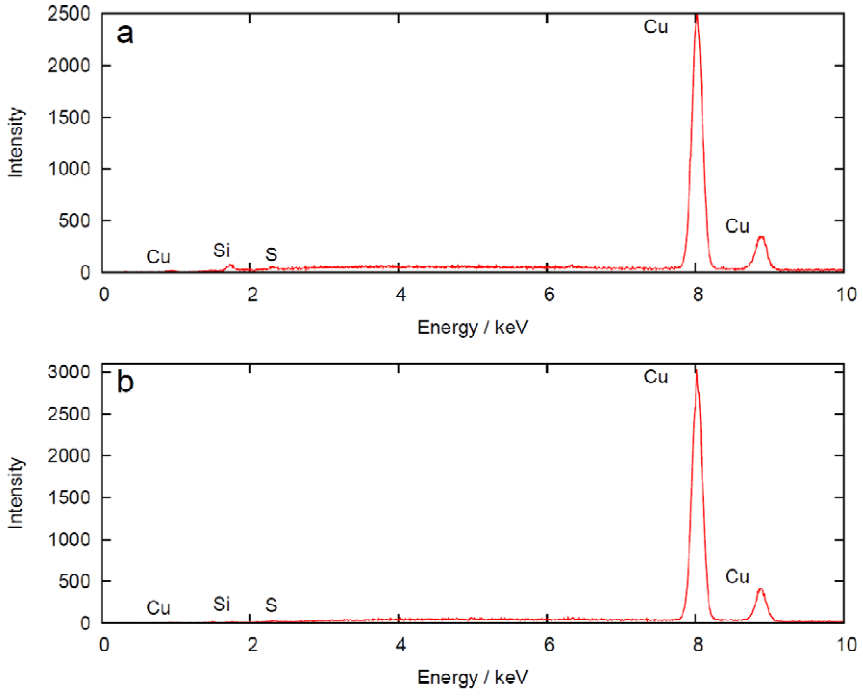

Figure S3. EDS spectra of the copper-based silica tube in Fig. 2b. (a) Outer layer of the wall; [Cu] = 98 wt.%, [Si] = 1.5 wt.%, and [S] = 0.4 wt.%. (b) Inner layer of the wall; [Cu] = 99.7 wt.%, [Si] = 0.1 wt.%, and [S] = 0.2 wt.%.

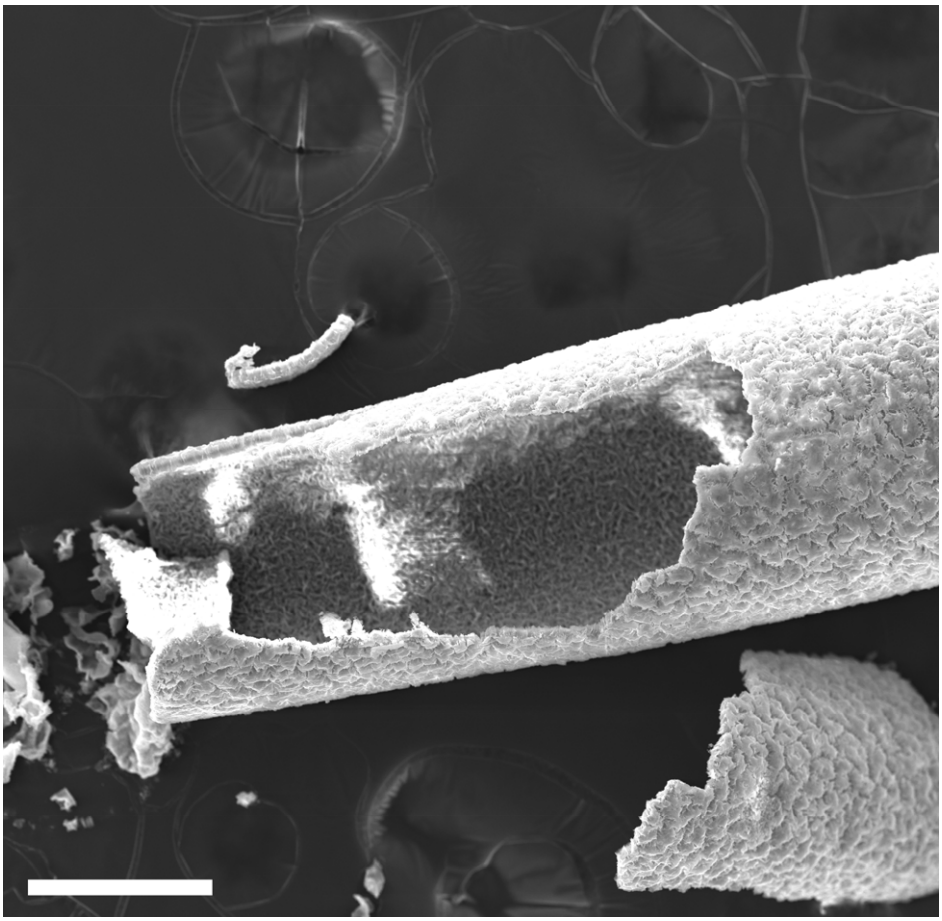

Figure S4. Scanning electron micrograph of a zinc-based silica tube produced in 1.0 M silicate solution by injection of 0.5 M zinc sulfate solution; t = 30 min. Scale bar: 200 μm.

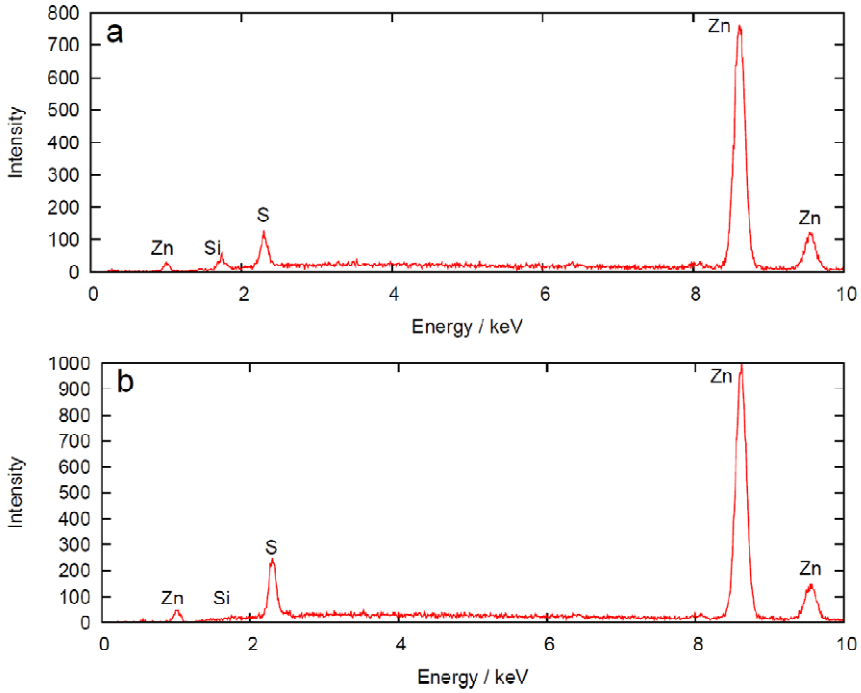

Figure S5. EDS spectra of the tube in Fig. S4. (a) Outer part of the wall; [Zn] = 90.4 wt.%, [Si] = 2.7 wt.% and [S] = 5.8 wt.%. (b) Inner part of the wall; [Zn] = 88.4 wt.%, [Si] = 0.2 wt.%, and [S] = 10.4 wt.%.