Postsynthetic processing of copper hydroxide-silica tube

Electronic Supplementary Information

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Experimental details

Our study uses the following chemicals: copper sulfate pentahydrate (Spectrum Chemical), sodium meta-silicate pentahydrate (Fisher Scientific), and 0.2 N sulfuric acid (Fisher Scientific). All solutions are prepared using nano-pure water (18 M Ω cm).

The CuSO₄ solution is injected into the sodium silicate solution through a glass nozzle (inner diameter: 1 mm). The injection of the slightly acidic copper sulfate solution into the alkaline silicate solution results in the co-precipitation of copper hydroxide and silica. Tubular precipitate forms at the interface of the two solutions, around the injected jet. At the beginning of the tube formation, we pin an air bubble to the tip of the growing structure by injecting air into the flow CuSO₄ solution. This injection is carried out using a syringe and a stainless steel needle (BD, 22G) that terminates within the aforementioned glass nozzle.

Heating the tubes to 550 $^{\circ}$ C does not cause any damage to the tubes, but if we heat them to 900 $^{\circ}$ C, we observe that some tubes break; about half of them preserve their tubular shape. Probably the sintering of the silica causes the observed damage.

We believe that the produced materials (CuO, Cu_2O , and metallic Cu) are stable because after a few months their color has not changed.

Scanning electron microscopy (SEM) is carried out with a JEOL JSM-5900 scanning electron microscope. The samples are coated with gold.

X-ray photoelectron spectroscopy (XPS) is carried out with a Physical Electronics 5100 Series XPS using an unmonochromated Al K α source. The pass energy is 44.75 eV. We sputter the sample with Ar⁺ at 2 kV over a 2 cm square raster area at a 1.5 μ A stage current. The sample was broken into small pieces for the measurement; most probably we could measure not only the outer surface of the tubular sample, but also the inner surface.

We use a TA Instruments Q50 TGA for thermogravimetric analyses (TGA). The samples are held on a Pt pan. The initial mass of the samples is at least 2 mg.

Powder X-ray diffraction (XRD) is carried out with a Rigaku DMAX 300 Ultima 3 diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å).

Additional experimental results

The SEM images (Figure S1) show that the macroscopic surface morphology of the tubes does not change noticeably during the post-synthetic processing; however, microscopic changes can be discerned on the outer surface (Figure S2). Heating the tubes to 550 $^{\circ}$ C (transition from blue to black) does not change the surface (Figure S2a and S2b), but heating to 900 $^{\circ}$ C removes cracks from the surface (Figure S2c). One can speculate that the latter effect is caused by the sintering of silica.

Figure S2d shows the effect of exposing the red tubes to sulfuric acid. The acid and/or the resulting reaction enlarge the pores in the wall. This change could also explain the increased fragility of the brown tubes.



Fig. S1 SEM images of the (a) blue, (b) black, (c) red, and (d) brown tubes. Scale bars: 0.5 mm.



Fig. S2 SEM images of the outer surface of (a) blue, (b) black, (c) red, and (d) brown tubes. Scale bars: 10 μm.