

Postsynthetic processing of copper hydroxide-silica tubes†

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Cite this: *Chem. Commun.*, 2013, **49**, 5736

Received 27th February 2013,
Accepted 25th March 2013

DOI: 10.1039/c3cc41516c

www.rsc.org/chemcomm

Using reaction conditions far from equilibrium, we produce hollow tubes of silica-supported $\text{Cu}(\text{OH})_2$. The samples are then processed postsynthetically without compromising the macroscopic tubular structure. We specifically induce an amorphous–crystalline transition and demonstrate the sequential conversion of $\text{Cu}(\text{OH})_2$ to CuO , Cu_2O , and metallic copper using thermal treatment and wet chemistry.

Living systems are capable of exploiting non-equilibrium reaction conditions for the production of a wide spectrum of hierarchically ordered materials.¹ In these materials, the desired design features can span from the molecular level all the way into the macroscopic world. The adaption of this approach to non-biological processes, however, remains a big challenge for modern science and engineering.² One of the few known examples capable of accomplishing this feat is a class of reaction–diffusion–advection systems in which inorganic, tubular structures form *via* precipitation reactions.³ The archetype of this reaction class is the so-called “chemical garden” experiment^{4,5} in which, within seconds or minutes, salt crystals (not group I) react in an aqueous silicate solutions to produce macroscopic precipitation tubes. Recent studies have shown that this process can be controlled by flow injection^{6–8} and other techniques.^{9–11} In addition, it is now known that the resulting materials can be powerful catalysts¹² or reveal other features such as superparamagnetism¹³ and photoluminescence.¹⁴

Research in this area of “chemobrionics”¹⁵ is only at the beginning but it will likely yield an arsenal of diverse tools allowing chemists to create non-trivial macroscopic shapes and hierarchically ordered materials using controlled self-organization. Despite the great potential of this approach, it is likely that the resulting materials will require postsynthetic processing. In this study, we explore such a methodology for the example of silica-supported copper hydroxide tubes.

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† Electronic supplementary information (ESI) available: Experimental details and additional SEM images. See DOI: 10.1039/c3cc41516c

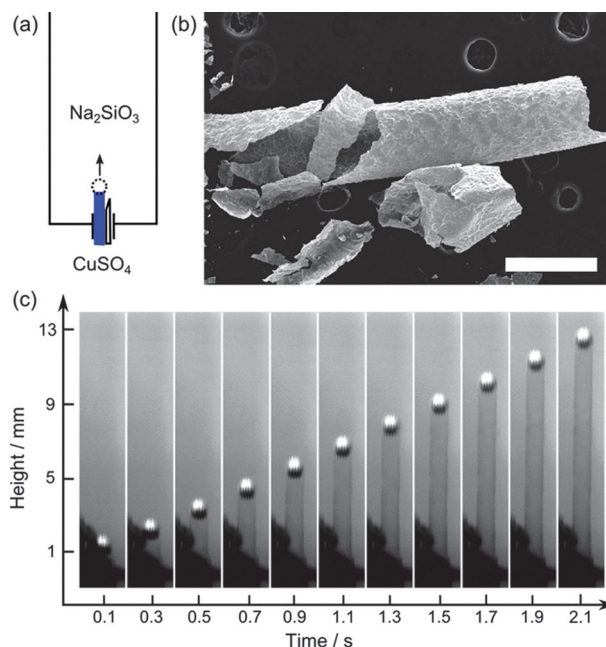


Fig. 1 (a) Sketch of the experimental setup. (b) SEM image of a tube processed by heating to 900 °C (red tube). Scale bar: 0.5 mm. (c) Sequence of video images illustrating the steady growth of a tube in the reactor shown in (a). Notice that the air bubble (bright disk) is pinned to the main growth zone at the upper rim of the tube. The diameter of the tube is about 0.5 mm.

We prepare the latter structures using a flow injection technique first described in ref. 6. It involves the hydrodynamic delivery of copper sulfate solution (0.5 M) into a large reservoir of sodium silicate solution (1.0 M) (see Fig. 1). The injection of the lighter copper solution occurs in an upward direction through a simple glass nozzle and is carried out at a constant pump rate (here 4 mL h⁻¹). In addition, we employ a bubble-guidance method in which a small air bubble is injected into the flow. The bubble subsequently pins to the reaction zone at the top of the forming tube *via* interfacial tension.⁷ This growth process results in single, straight tubes with diameters only slightly smaller than those of the bubble. The vertical growth velocity (v) is constant in time and proportional to the flow rate

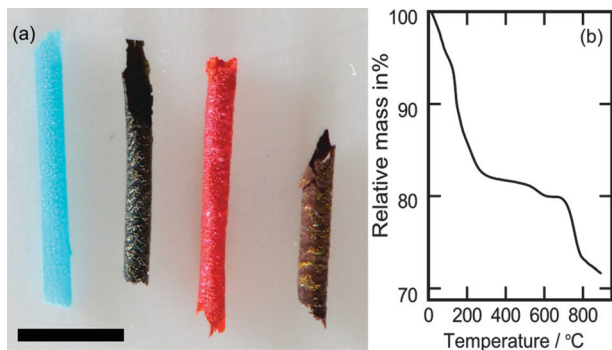


Fig. 2 (a) Representative examples of the original tube (left) and three distinct postsynthetic stages. From left to right, the different colors are indicative of $\text{Cu}(\text{OH})_2$ (blue), CuO (black), Cu_2O (red), and metallic copper (brown). Scale bar: 2 mm. (b) TGA trace obtained for initially blue tubes. The relative mass is the measured mass divided by the initial mass.

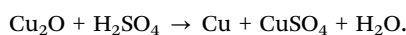
(Q) of the injected reactant. It obeys $v = Q/(\pi R^2)$, where R is the radius of the tube.⁷

After this initial preparation, the tube is extracted from the solution, rinsed in distilled water three times, and allowed to dry under ambient conditions. Subsequently we heat the dried tubes in an argon atmosphere to 900 °C and simultaneously perform a thermogravimetric analysis (TGA). During the heating process the tubes undergo striking color changes. Initially their color is light blue; then after heating to 550 °C it is black, and finally at 900 °C crimson-red (Fig. 2a, first three samples from left to right). We note that upon heating to 550 °C and subsequent cooling to room temperature, most of the tubes preserve their tubular structure, but for heating to 900 °C tubes can break or lose their tubular shape.

The representative TGA curve in Fig. 2b reveals a transition at around 140 °C and continuous water loss up to 400–450 °C. At higher temperatures, we observe a smaller mass loss at around 600 °C and a pronounced one around 750 °C. The transitions at 140 °C and 750 °C correspond to the reactions of $\text{Cu}(\text{OH})_2$ to CuO ¹⁶ and CuO to Cu_2O , respectively, although the transition temperatures are slightly lower than the reported values.¹⁷ This small difference might be caused by a dependence of the transition temperature on the ramp rate which in our experiment was slower (2 °C min^{-1}) than in ref. 17.

The highly reproducible mass loss at around 600 °C is probably caused by the conversion of copper silicate to copper(II) oxide.¹⁸ Attempts to directly identify copper silicate in our samples failed so far, possibly because our measurements were hampered by the small amount of sample available.

In addition to heat induced compositional changes, we also investigated a chemical modification of the red, silica-supported Cu_2O tubes in sulfuric acid (0.1 M). These reaction conditions are known¹⁹ to reduce Cu_2O powder to metallic copper particles according to the disproportionation reaction:



In our experiments, we expose the tubes to a large volume of sulfuric acid for 2 hours, then rinse three times in water, and dry the product in air at room temperature. The color of the

resulting samples is brown (Fig. 2a). Furthermore, we observe that the tubular shape is always preserved during the acid treatment. The products, however, are rather fragile and many tubes break into several fragments during drying. To overcome this problem, we employ a slightly different method in which the wall thickness of the original silica- $\text{Cu}(\text{OH})_2$ structure is increased by a prolonged injection of copper sulfate solution.²⁰ The duration of this secondary, radial growth phase should be around 30 min or more to ensure a sufficient increase in tube stability. The brown (rightmost) sample in Fig. 2a is a representative example of a tube obtained under this slightly modified protocol. All subsequent analyses, however, are performed for samples obtained without prolonged injection.

Scanning electron microscopy (SEM) characterizations of the surface morphology of the tubes at different postsynthetic stages reveal qualitative differences (see the SEM images in ESI†). The most notable variation is found for the outer surface of the brown tubes that feature a porous network structure underneath a cracked top layer. The typical length of these pores is around 500 nm. Further analysis using powder X-ray diffraction (XRD) yields the XRD patterns shown in Fig. 3. The blue silica-copper hydroxide tubes do not show any measurable crystallinity (Fig. 3a). The broad feature in the region around 23° (present in all the XRD patterns and labeled by an asterisk) is assigned to amorphous silica. The XRD pattern of each of the black, red, and brown tubes shows clear diffraction peaks that allow for a reliable assignment. The diffraction peaks are labeled by their corresponding Miller indices. We find that the XRD patterns of the black tube and the red tube (Fig. 3b and c, respectively) are in good agreement with the published patterns of copper(II) oxide (JCPDS No. 048-1548) and copper(I) oxide (JCPDS No. 078-2076), respectively. The XRD pattern of the brown tube (Fig. 3d) consists of three peaks ($2\theta = 43.3, 50.4, 74.1^\circ$) that are

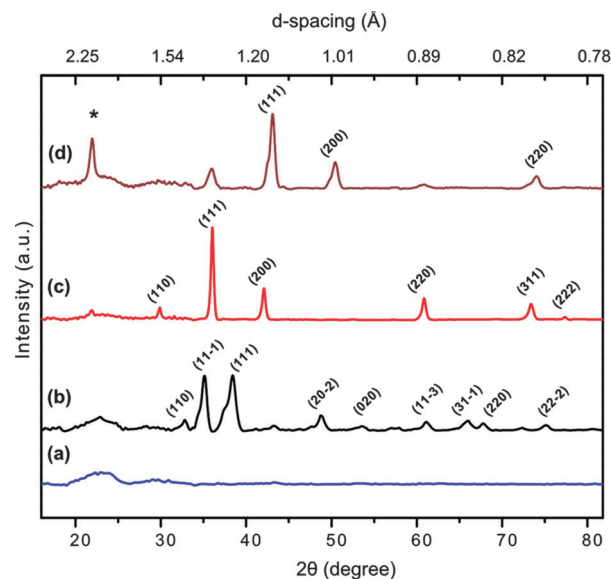


Fig. 3 XRD patterns for (a) blue, (b) black, (c) red, and (d) brown tubes. The Miller indices show the characteristic peaks of CuO (b), Cu_2O (c), and Cu (d). The asterisk denotes the position of a broad hump that is typical for amorphous silica (visible in all patterns).

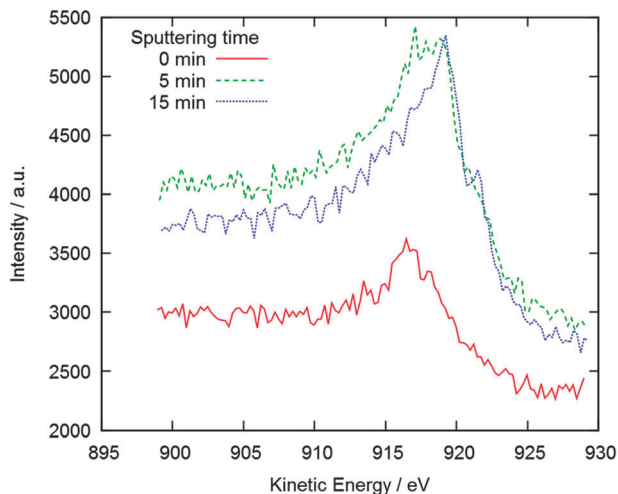


Fig. 4 L3VV Auger kinetic energy of the brown tubes. Sputtering the sample shifts the intensity maximum from 916.6 eV (solid, red curve) to 919.3 eV (dotted, blue curve).

characteristic for copper metal (JCPDS No. 089-2838). In addition, we observe a peak at $2\theta = 36.4^\circ$ that strongly suggests the presence of some residual copper(I) oxide.

The composition of the brown tubes is evaluated further using X-ray photoelectron spectroscopy (XPS). In the binding energy, we observe a Cu 2p doublet with peaks at 932.5 eV and 952.4 eV (Cu 2p_{3/2} and Cu 2p_{1/2}, respectively). This finding suggests that the sample contains Cu⁰ or Cu¹⁺ but it excludes Cu²⁺ because its Cu 2p_{3/2} peak occurs at 933.5 eV.²¹ To differentiate between Cu⁰ and Cu¹⁺, we measure the L3VV Auger kinetic energy. The corresponding solid, red line in Fig. 4 reveals a single broad maximum at 916.6 eV that indicates the presence Cu¹⁺ and absence of Cu⁰ because the Cu⁰ peak is expected at around 918.5 eV.²¹

The latter result seemingly contradicts our XRD assignments. However, after sputtering the sample for 5 min with argon ions at 2 kV, Auger energy measurements reveal an increase in energies (green, dashed curve in Fig. 4), which after 15 min of sputtering yield a signal maximum at 919.3 eV (blue, dotted curve in Fig. 4). These results suggest that the surface of the initial sample is covered by Cu₂O which is removed in the sputtering process to expose metallic copper. We note that prior to the Auger measurement, the samples are exposed to air for about one day. It is hence likely that the oxide surface layer formed by oxidation of metallic copper during this time interval.

Earlier studies on the oxidation of thin copper films revealed^{22,23} that the process occurs sequentially through Cu₂O and that measurable amounts of CuO are formed only after 1–13 days of air exposure. The latter feature combined with the small exposure times in our study is, hence, consistent with the presence of surface-bound Cu₂O and the absence of CuO.

In conclusion, we have demonstrated the postsynthetic processing of silica-supported Cu(OH)₂ tubes by physical and chemical means. This processing induces sequential oxidation

of Cu(OH)₂ down to metallic particles. It is remarkable that the self-organized tubular structure of the samples is essentially conserved during these changes. This finding is even more surprising if we consider that (i) the initial structure is layered with the Cu(OH)₂ and silica dominating the interior and exterior parts of the tube wall,²⁴ respectively and (ii) the less pronounced changes in the silica phase occur at only very high temperatures. We believe that this study demonstrates the versatility that may arise if unconventional methods from the realms of self-organization research and systems chemistry are combined with conventional chemical approaches. Furthermore, we note that the thermal treatment induced a crystalline transition, however, the silica remained amorphous. In our specific case, this transition resulted in Cu₂O which is a widely studied semiconductor.

This work was supported by the National Science Foundation (Grant No. 1005861). We thank Dr Eric Lochner for assistance with the XPS measurements.

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