

Metal-organic frameworks shaped into one-dimensional nanostructures via templated electrodeposition*

A. W. Maijenburg^{1,#}, L. Movsesyan^{1,2}, C. Trautmann^{1,2}, and M.E. Toimil-Molares^{1,#}

¹Materials Research, GSI, Darmstadt, Germany; ²Technische Universität Darmstadt, Darmstadt, Germany

Metal-organic frameworks (MOFs) are a relatively new class of hybrid materials, which consist of metal ions or clusters as the secondary building unit and organic linkers connecting the metallic building units via coordination bonds of moderate strength [1]. Thereby, MOFs combine the robustness and crystallinity of inorganic materials with the flexibility of organic molecules. This opens up the possibility for MOFs to be used in a wide range of applications ranging from gas storage and gas separation to sensors and photocatalysis [1-3].

In this study, MOF nanowires were made via electrodeposition inside etched ion-track membranes in order to precisely control the size, shape and location of the resulting MOF crystals. By controlled oxidation of Cu nanowires in a solution containing 1,3,5-benzenetricarboxylate (BTC) molecules, we synthesised nanowires of the well-known MOF $\text{Cu}_3(\text{BTC})_2$, which consists of Cu^{2+} ions as the metallic core linked together by BTC ligands. To the best of our knowledge, this is the first time that templated electrodeposition was used for the synthesis of one-dimensional MOF nanostructures.

Polycarbonate (PC) foils with a thickness of 30 μm were irradiated with Au ions of a total energy of 2 GeV and a fluence of 10^8 ions/ cm^2 at the UNILAC linear accelerator of GSI. After irradiation, the ion tracks were transformed to nanoscale pores by chemical etching, which resulted in PC membranes with cylindrical pores with a diameter of ~ 80, 130, 210 and 260 nm. After etching, one side of the PC membranes was coated with ~125 nm of Au using an Edwards S150B sputter coater. Next, the mechanical stability of this Au layer was enhanced by electrodeposition of a thicker Au layer using a commercial gold plating solution (AuSF, METAKEM) at -0.7 V vs. a Au counter electrode in a two electrode setup for 2 h.

Cu nanowires were electrodeposited inside the PC membranes from an aqueous solution containing 1.0 M CuSO_4 and 0.2 M H_2SO_4 at a temperature of 60 °C and a potential of -0.1 V vs. a Cu counter electrode for 8 min. The as-deposited Cu nanowires were transferred to $\text{Cu}_3(\text{BTC})_2$ using a 50/50 vol% ethanol/water solution containing 5.8 mM BTC and 6.42 M tributylmethylammonium methyl sulfate (MTBS) at a temperature of 55 °C and a potential of 2.5 V vs. a Cu counter electrode for 30 min.

Figure 1 shows XRD patterns of the $\text{Cu}_3(\text{BTC})_2$ nanowires with different diameters made in this study. For the

thickest nanowires, most of the peaks associated with $\text{Cu}_3(\text{BTC})_2$ are visible [2], but as the diameter is decreased, also less reflections are visible in the XRD pattern. The Cu peak is assigned to incomplete conversion of the as-formed Cu nanowires to $\text{Cu}_3(\text{BTC})_2$. More interestingly, we also observed a peak associated with Cu_2O , which we relate to be the intermediate product from the conversion of Cu to $\text{Cu}_3(\text{BTC})_2$, indicating that the conversion takes place via a two-step oxidation reaction.

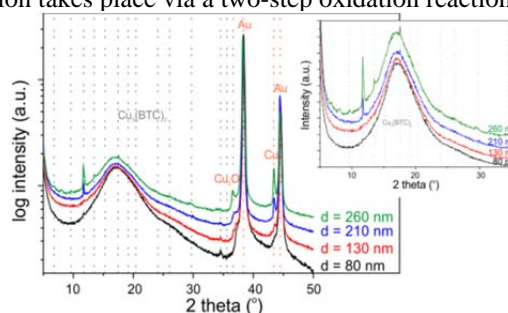


Figure 1: XRD patterns of $\text{Cu}_3(\text{BTC})_2$ MOF nanowires with different diameter. The grey dotted lines denote reflections identified to originate from $\text{Cu}_3(\text{BTC})_2$ [2]. Inset: Zoom in at a linear scale of the area of interest.

Figure 2 presents selected SEM images of the formed MOF nanowires with a diameter of ~260 nm, which show a smooth surface indicating optimized growth conditions. More interestingly, the nanowires are not completely converted yet and a sharp interface between the bright Cu and the darker $\text{Cu}_3(\text{BTC})_2$ segments is observed. This allows us to conclude that the conversion proceeds linearly from the top to the bottom of the nanowire.

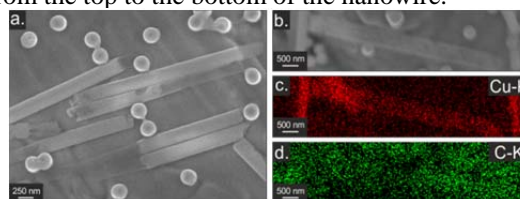


Figure 2: (a,b) SEM images of $\text{Cu}_3(\text{BTC})_2$ MOF nanowires with a diameter of 260 nm, and (c,d) EDX maps indicating the distribution of Cu (c) and C (d) in the nanowires shown in (b).

References

- [1] M.A. Nasalevich et al., *CrystEngComm* 16 (2014) 4919.
- [2] B. van de Voorde et al., *Journal of Materials Chemistry C* 1 (2013) 7716.
- [3] R. Ameloot et al., *Chemistry of Materials* 21 (2009) 2580.

* Work supported by Humboldt Research Fellowship for postdoctoral researchers.

w.maijenburg@gsi.de, m.e.toimilmolares@gsi.de