

## Supporting info

Toposelective vapor deposition of hybrid and inorganic materials inside nanocavities by polymeric templating and vapor phase infiltration

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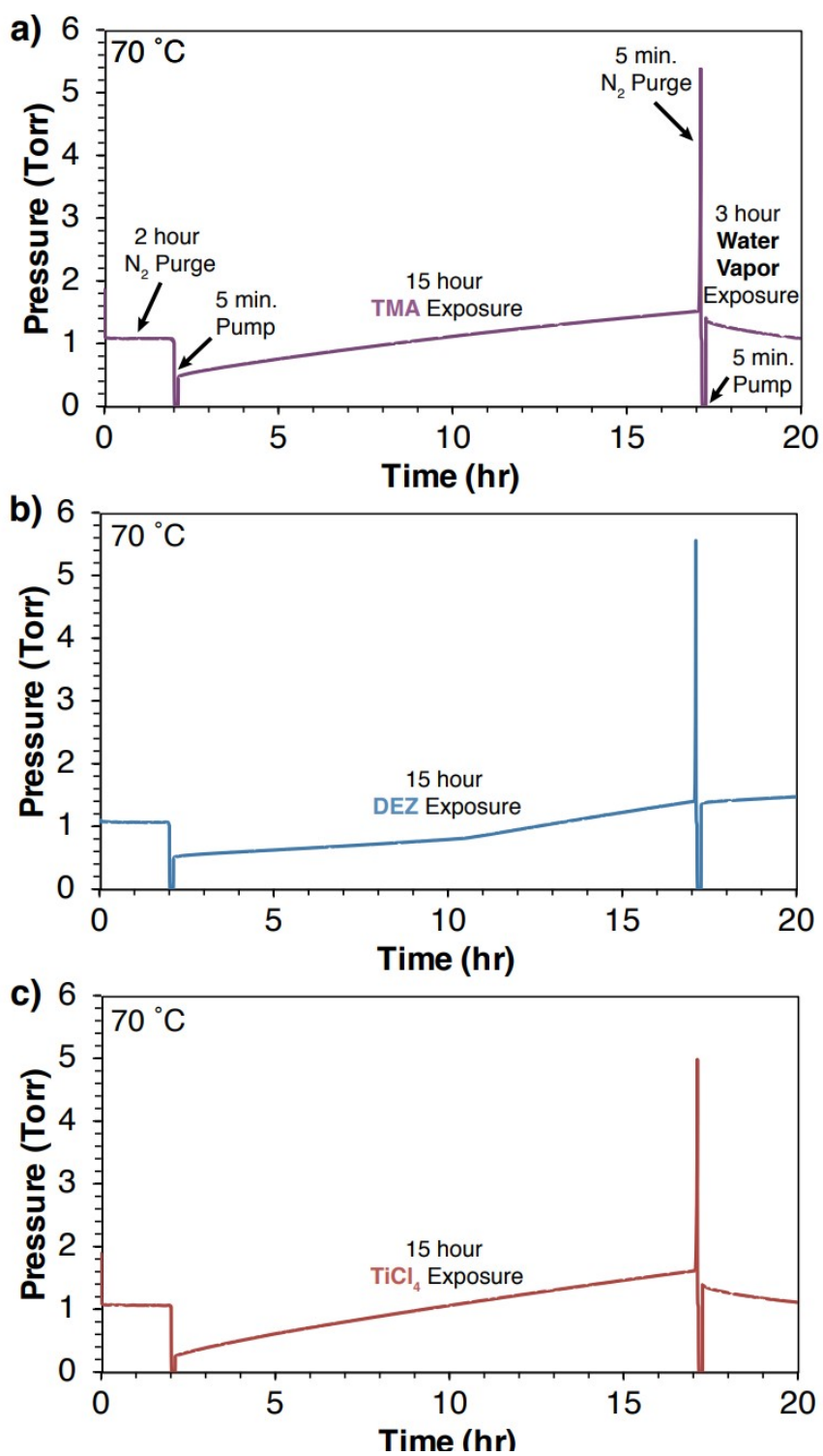
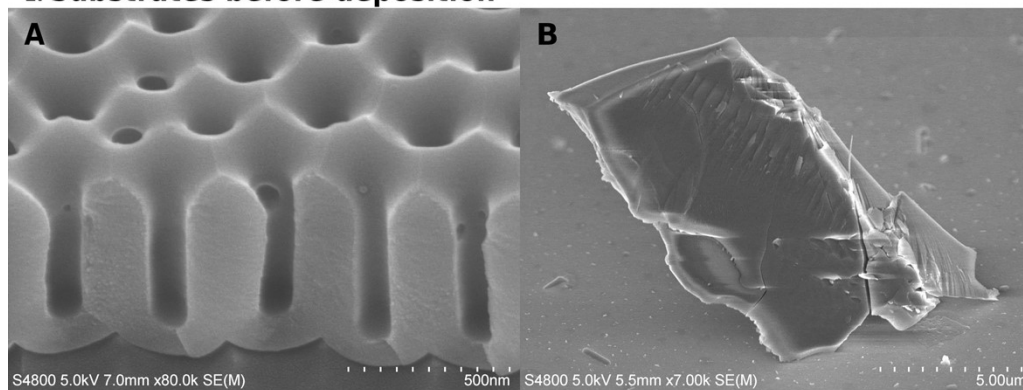
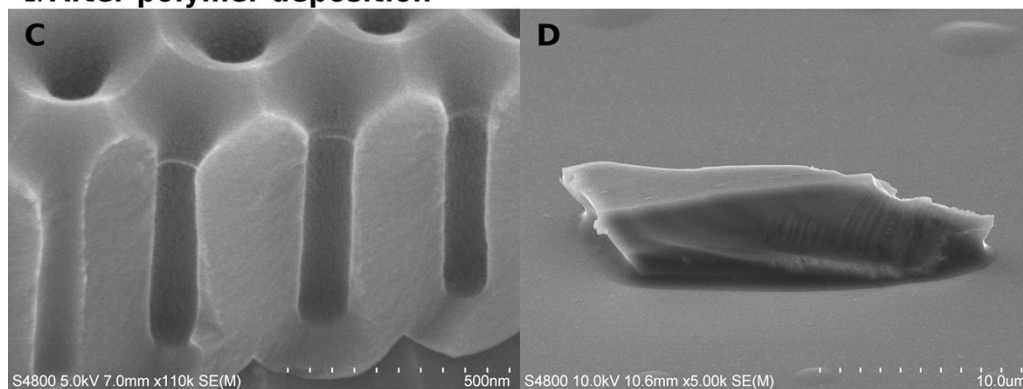


Figure S1: Experimental details about long-pulse VPI.

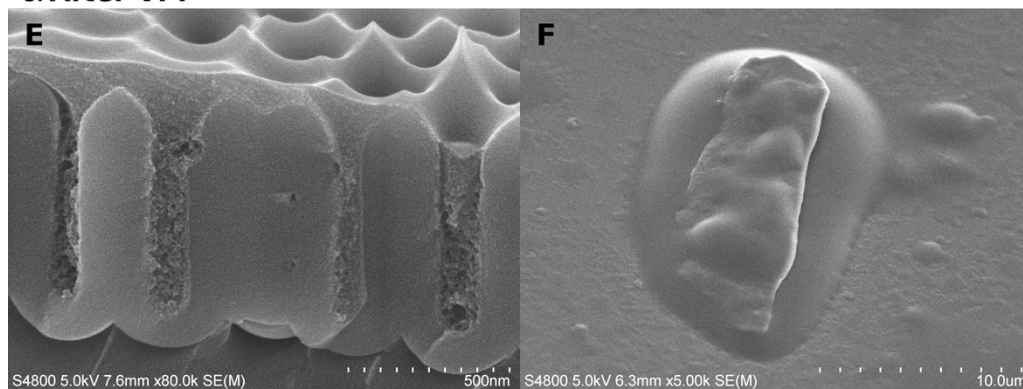
### 1. Substrates before deposition



### 2. After polymer deposition



### 3. After VPI



### 4. After calcination at 450 C

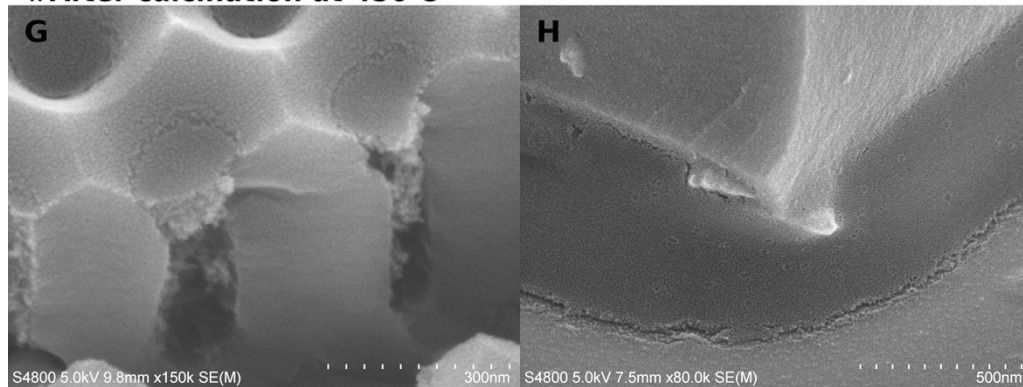


Figure S2: Tilted-view SEM images of AAO and glass substrates during different stages of the workflow. First row: empty pores and no filling below particles. Second row: Polymer has been deposited in the pores and below the particles. Third row: Polymer has been turned into a swollen hybrid material by VPI. Fourth row: the hybrid material was turned into inorganic depositions by calcination. The cross-sections were prepared by bending the surface right before sputtering and SEM imaging.

### Long-pulse Ti-VPI: top-down EDS mapping

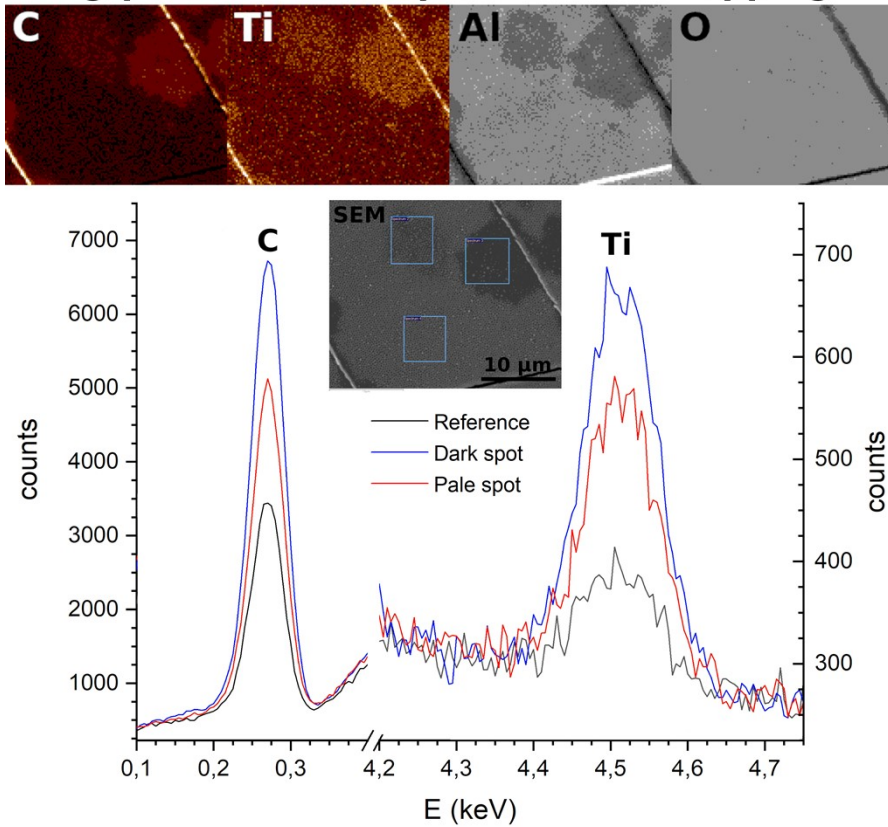
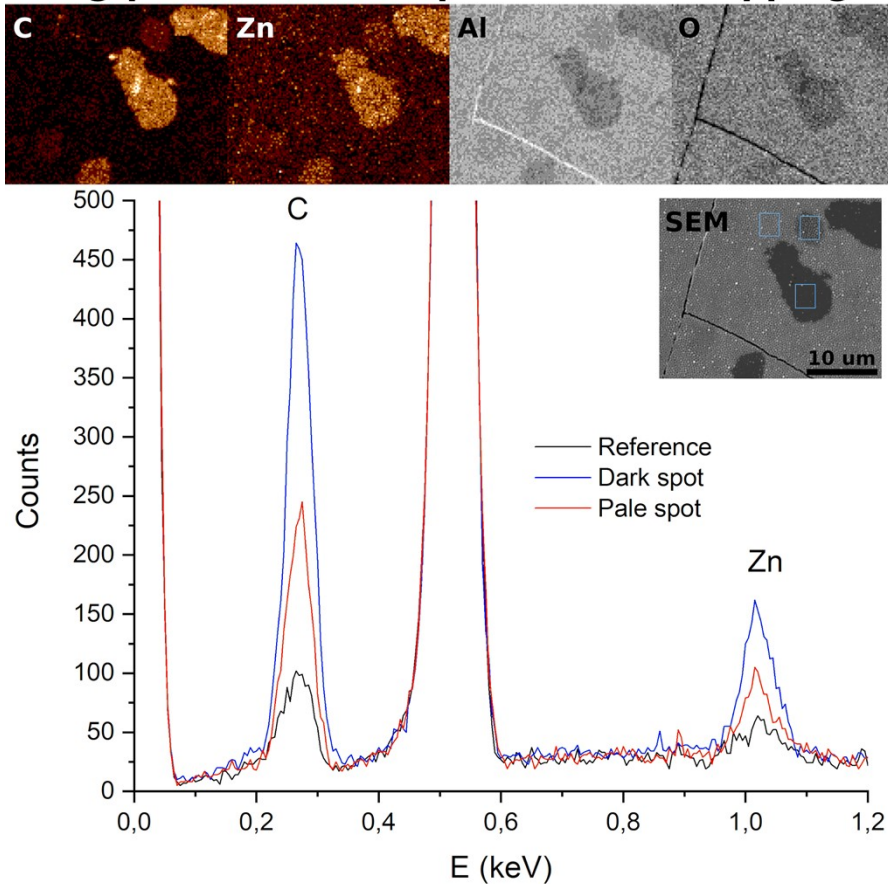


Figure S3. EDS elemental maps of long-pulse VPI experiments on AAO in top-down view. Dark and pale spots refer to areas where the polymer has stayed inside the pores (pale) or slightly overgrown the pore mouths (dark). The analyzed areas are marked in the SEM images with squares. Elemental maps and SEM images are as insets.

### Long-pulse Zn-VPI: top-down EDS mapping



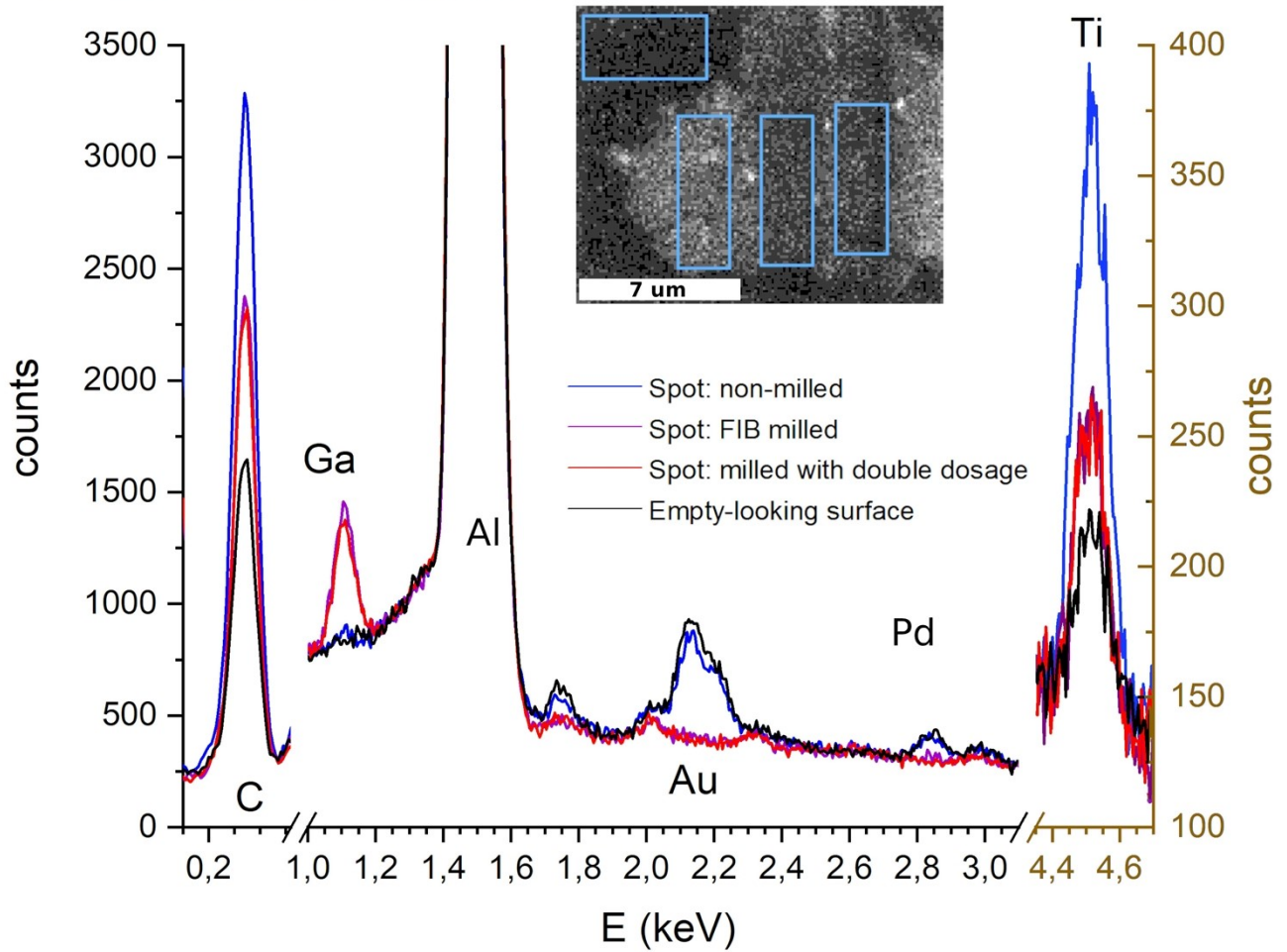
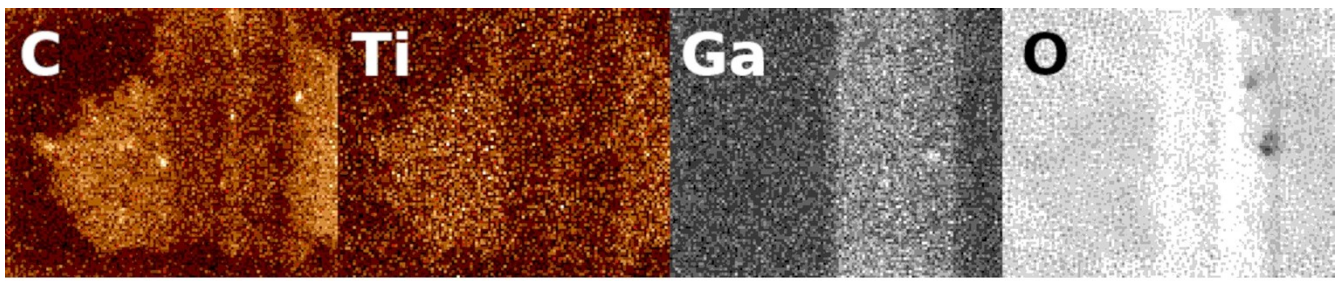


Figure S4. EDS elemental mapping of long-pulse  $\text{TiO}_x$ -VPI on AAO samples after focused ion milling with two dosages. Elemental maps and SEM image with analyzed areas marked as insets.

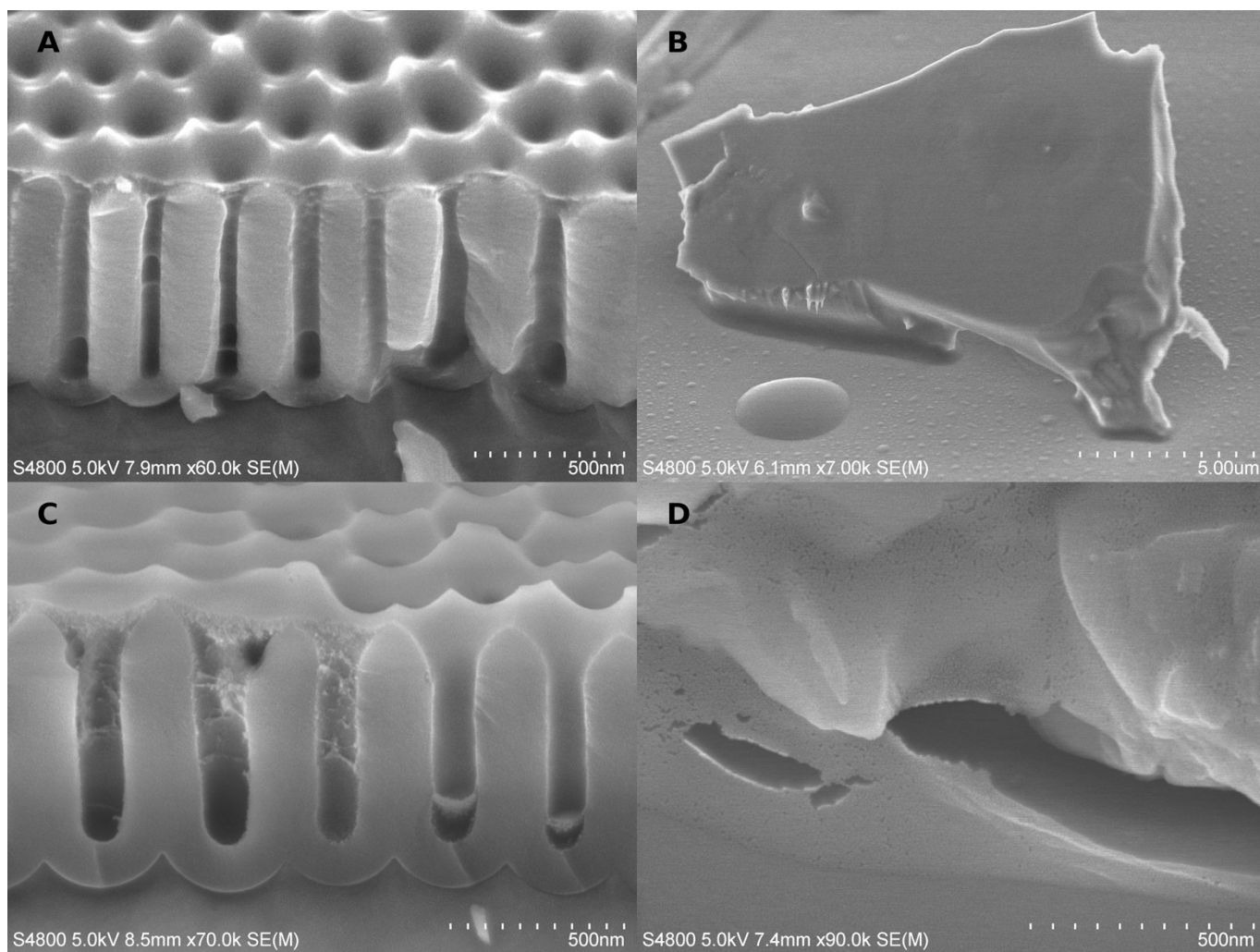


Figure S5. SEM images of short-pulse  $\text{AlO}_x$ -VPI samples with infiltration temperature of 60 °C. Hybrid material on A) AAO and B) glass. C) Slightly overfilled and two underfilled pores on AAO and D) a cracked thin film on a glass sample after calcination at 450 °C.

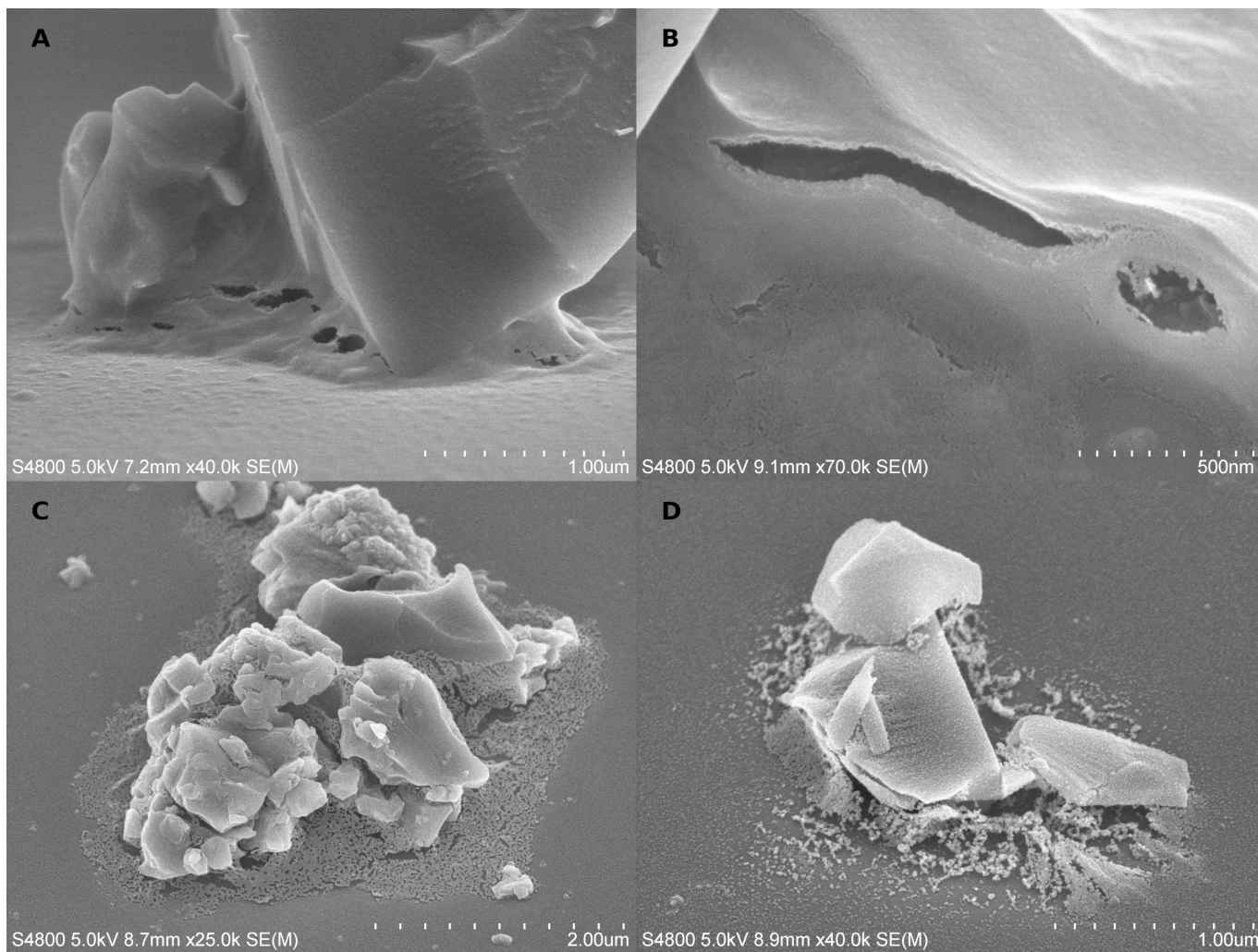


Figure S6. Long-pulse-VPI experiments on the glass substrate with  $O_2$  present in the atmosphere during CT-piCVD. A, B) alumina VPI, when the polymer was deposited with 20%  $O_2$  in the carrier gas, C) titania with 4%  $O_2$  during CT-piCVD, and D) zinc oxide with 4%  $O_2$  during CT-piCVD. The samples were calcined at 450 °C in air.