Anodic Aluminum Oxide Template Assisted Synthesis of Copper Nanowires using a Galvanic Displacement Process for Electrochemical Denitrification

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Supplementary Information

Kinetics of anodization process

A current-time transient, such as shown in Figure S1, was measured during the anodization process performed in 0.3 M oxalic acid at 20 °C with DC voltage of 45 V. At the start of anodization, the current density was high due to the exposure of the fresh electropolished aluminum surface. After that, the current density dropped drastically with time due to the high resistance of the uniformly formed compact oxide layer on the surface. The minimum in the current density was observed after 10 s in the current-time transient curve (shown in the inset of Figure S1) and indicates pore nucleation from the compact layer.

Afterwards, a local maximum is reached in approximately 60 s pointing to pore rearrangement and steady-state anodization was achieved.[1] This is indicative of the equilibrium between oxide formation and dissolution at the pore bottom.

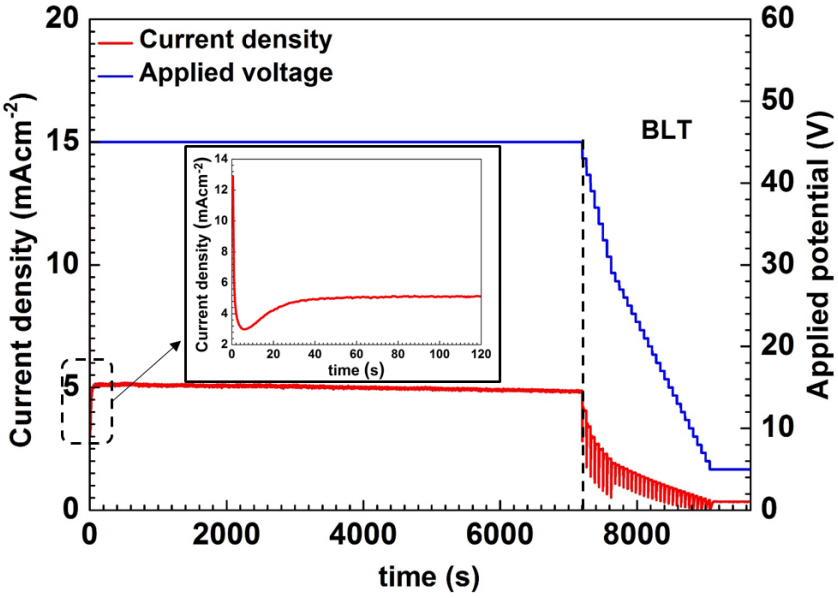

Figure S1: A current-time transient curve recorded during the second step (7200 s) of anodization process and BLT process

To rupture the barrier layer at the bottom, the BLT process was carried out after the end of the second anodization step, which is from 7200 to 9420 s. Current-time transient measured during BLT process is marked in Figure S1 and it corresponds to a non-steady state of anodization favouring dissolution, which causes perforation of the barrier layer at the bottom.

SEM images of AAO template

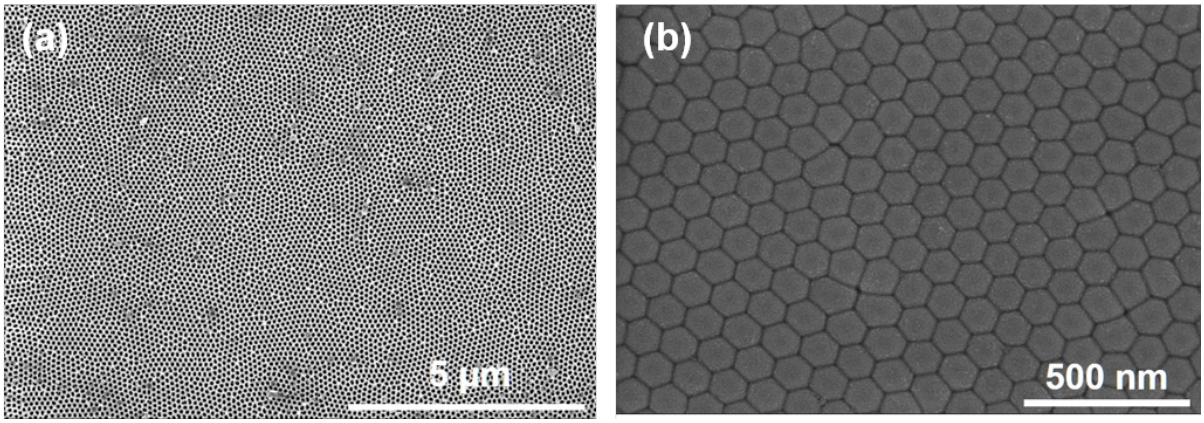

Figure S2: SEM images of as-formed AAO (a) Top-view of AAO at low magnification (b) Bottom-view of as-formed AAO shows the ordered closed barrier layer.

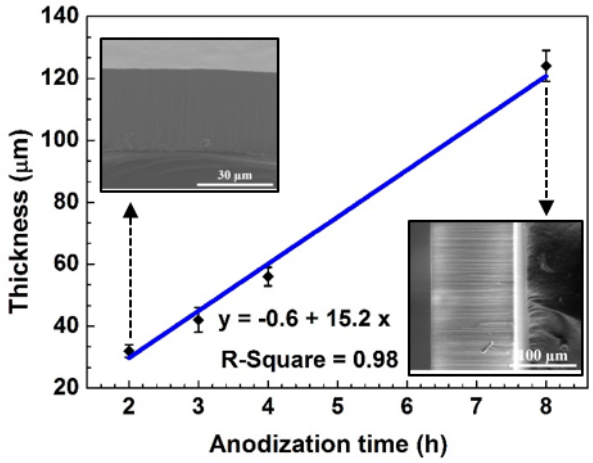

Figure S3: Plot of oxide thickness vs. anodization time showing a linear growth behavior. The growth rate is calculated from the slope and is found to be 15.2 μm h^{-1}. The insets show cross sectional SEM images of the AAO template for 2 and 8 h, where the increase in oxide length is evident. For subsequent NW growth experiments, the anodization time was fixed at 2 h.

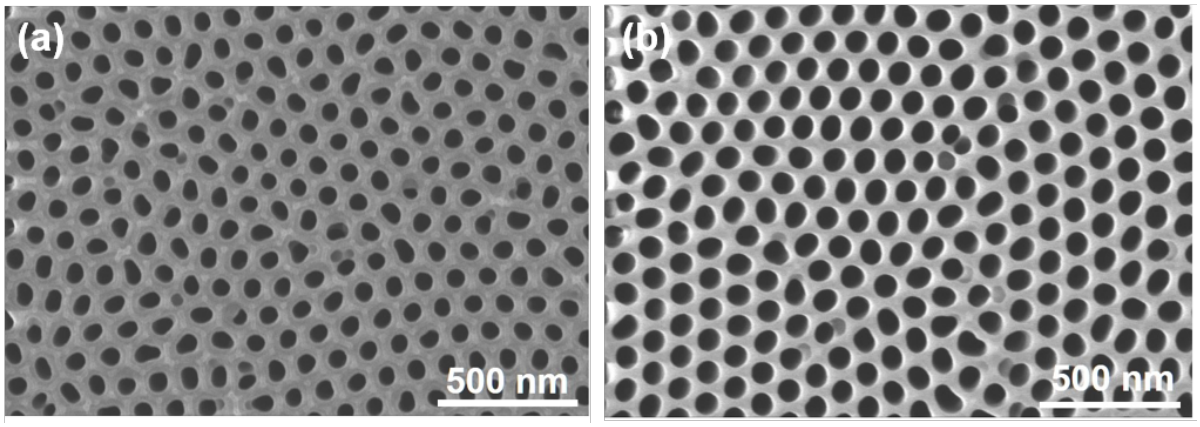

Figure S4: (a) Top view of the AAO after the two-step anodization process b) Top view of the AAO after BLT and after etching in 5 wt. % H_3PO_4 for 45 min. The pore size is increased during this process. The AAO features are compared in Table 1.

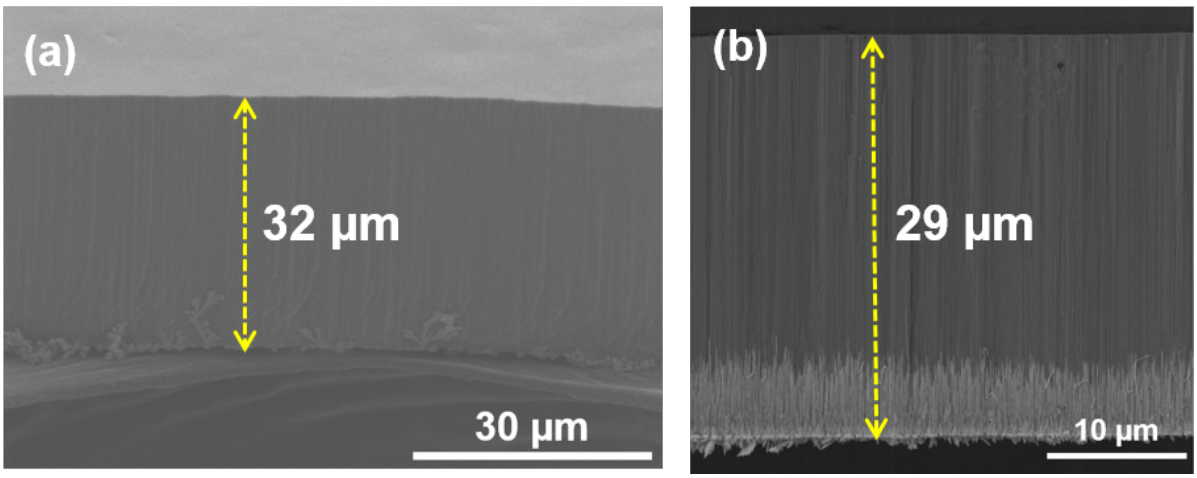

Figure S5: SEM images of alumina template (a) Before copper deposition (b) After copper deposition. In highly acidic conditions of the electrolyte, some amount of alumina also dissolved and the difference in height is approximately 3 µm.

Table S1: Comparison of geometrical features of as-formed AAO and after etching. The data is obtained by analyzing SEM images, such as those shown in Figure S3, using Image J. The etching process does not change the interpore distance but only widens the pores, as seen by an increase in diameter and a reduction in wall thickness. The template after etching is ready for NW deposition.

AAO dimensional features	**As-formed (nm)**	**After BLT + etching (nm)**
Pore diameter (Dp)	66 ± 6	78 ± 10
Interpore distance (Dc)	115 ± 12	115 ± 13
Wall thickness (Dw)	24 ± 7	14 ± 5
Porosity (%)	28.4	42.7

References

(1) Sulka, G. D.; Stepniowski, W. J. Structural Features of Self-Organized Nanopore Arrays Formed by Anodization of Aluminum in Oxalic Acid at Relatively High Temperatures. *Electrochim. Acta* **2009**, *54*, 3683-3691.