

Supporting Information

For

Controlled Growth of Novel Hyper-branched Nanostructures in Nanoporous Alumina Membrane

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Experimental

The AAO templates were prepared with a modified two-step anodization process similar to the one found in reference [1-3]. The high purity aluminum sheets (99.999 % metal basis, Sigma-Aldrich) were first cleaned and degreased with ultrasonic cleaning in acetone for 20 minutes, and annealed in nitrogen at 500 °C for 2h, and then electropolished in a 1:3 volume mixture of perchloric acid (70 %, ACS reagent, Sigma-Aldrich) and ethanol (>99.5 %, ACS Reagent, Sigma-Aldrich) at a current density of 100 mA/cm² and a temperature of 1 °C for 1 min. The aluminum is mirror like at the end of electropolishing. In the first anodization step, the electropolished aluminum sheet was anodized in a 0.3 M oxalic acid (10 % w/v, Ricca Chemical Company) solution at 40 V and at 1 °C for 36 h. The surface area for the anodized Al sheet is 1cm by 3 cm. This preliminary oxidization layer creates dimples in the Al substrate that results in ordered pores during the second anodization. This AAO layer is removed by immersing the sample in a solution of 6 wt. % phosphoric acid (85 wt. % in H₂O, Aldrich) and 1.8 wt. % chromic acid (10% w/v, LabChem Inc.) until the AAO was totally etched and a shiny aluminum surface was obtained. The second anodization was first carried out at 40 V and at 1 °C for about 18 min under the same conditions as the first anodization step. As to produce the branch tier structures, the sample was first anodized in the 0.3 M oxalic acid solution at 28.3 V and at 1°C for 20 minutes, stopped and then changed to current control process. Gradually increased anodization current to 3.8 mA and anodized the sample at 3.8 mA for 10 min. Then took out the sample from the electrolyte and dried it in air for 10 to 15 min. Additional tiered pore structures was obtained by repeatedly running sample at 28.3 V and 3.8 mA current, respectively. To form the multi-branches at terminals of the trunk, the final anodization was run at different current: 1.8 mA for 2 minute, 0.30 mA for 33 minutes and 0.004 mA for 25 minutes, respectively.

After the second anodization, the barrier layer was chemically etched by immersing the sample into a 5 wt. % phosphoric acid at RT for 10 min. This process also etches the

pore walls and results in larger pore diameters [3]. The silver nanowires were electrodeposited into the pores of AAO by AC electrodeposition with peak-to-peak modulation currents of ± 20 mA and delay time of 3 ms. The electrolyte was aqueous solution composed of AgNO_3 (>99%, ACS Reagent, Sigma-Aldrich) 2 g/L and boric acid (99.5%, ACS Reagent, Sigma-Aldrich) 20 g/L. The electrolyte was buffered to pH=2.5 with H_2SO_4 solution. After electrodeposition, the AAO template with silver nanowires was detached from the aluminum substrate with solution of saturated HgCl_2 (99.999%, Aldrich). 1.0 M NaOH solution was used to dissolve the AAO template and free the silver nanowires.

The samples were characterized with Field Emission Scanning Electron Microscopy (Jeol JSM 6330). UV-Vis spectra were taken with a Varian Cary 50 conc UV-Visible spectrophotometer (Varian Australia Pty. Ltd.). The x-ray diffraction spectrum of Ag/AAO membrane was collected using a Bruker HiStar X-Ray Diffractometer.

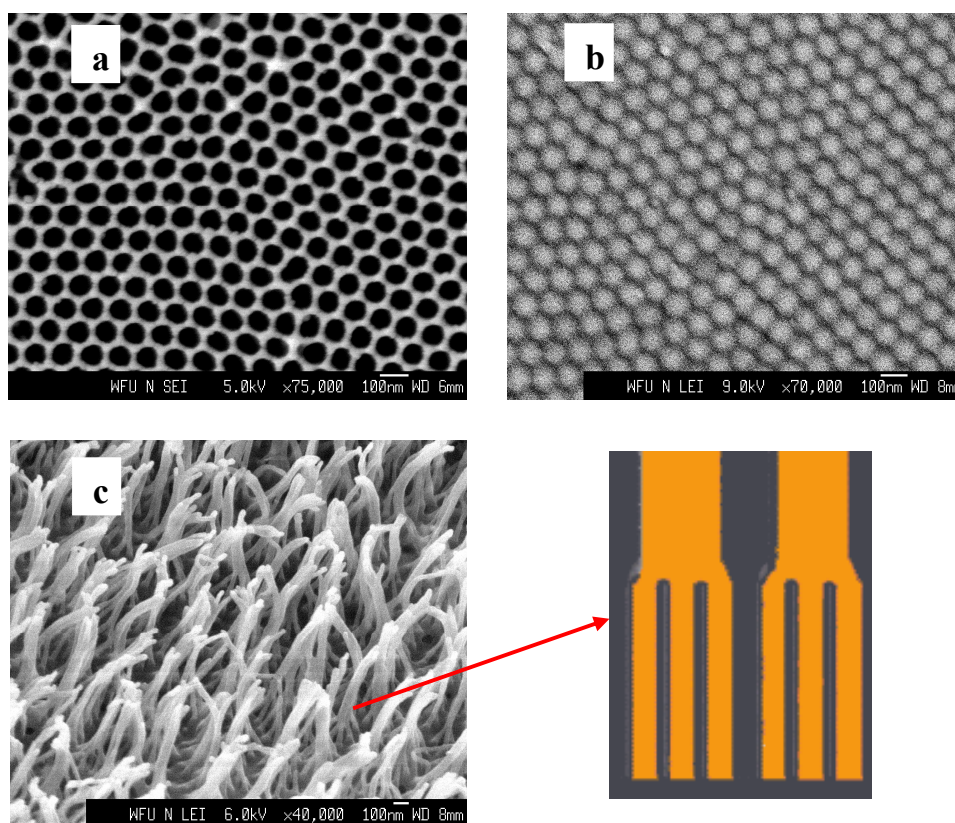


Figure S1: SEM images of the top view of the AAO nanochannels array (a), the top view of the AAO nanochannels array after filled with Ag nanoparticles (b), and the freestanding branched nanowires which have a linear stem exhibiting multi-branches at terminal(c).

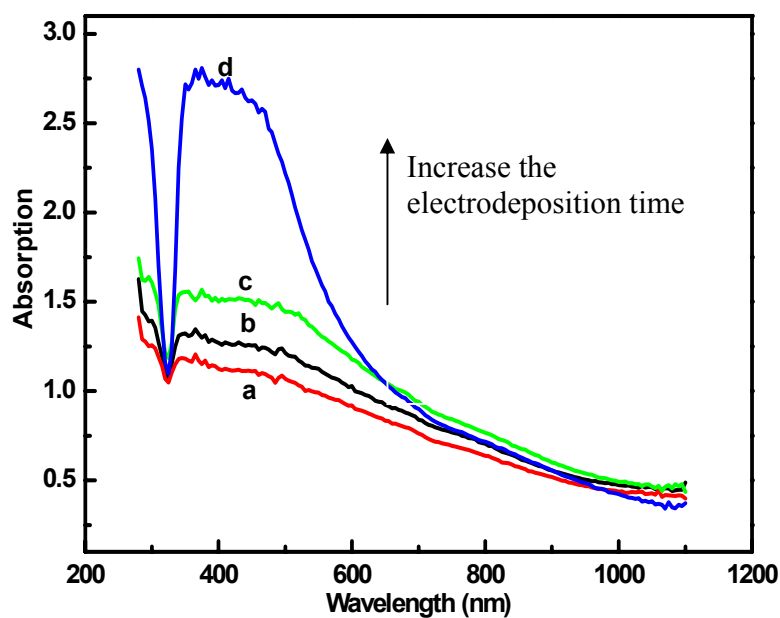


Figure S2 UV-Vis absorption spectra of straight Ag nanowires with different electrodeposition time: (a) 20 s; (b) 50s; (c) 2 min and (d) 20 min.

References

- [1] H. Masuda, K. Fukuda, *Science*, 1995, 268: 1466–1468
- [2] W. Lee, K. Schwirn, M. Steinhart, E. Pippe, R. Scholz and U. Gösele, *Nature Nanotechnology*, 2008, 3, 234 – 239.
- [3] O. Jessensky, F. Müller, and U. Gösele, *Appl. Phys. Lett.*, 1998, 72(10): 1173-1174.