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Electronic Supplementary Information

Tree-like Alumina Nanopores Generated in a Non-steady-state Anodization

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Materials and Methods

Preparation of Ordered Porous Alumina Template

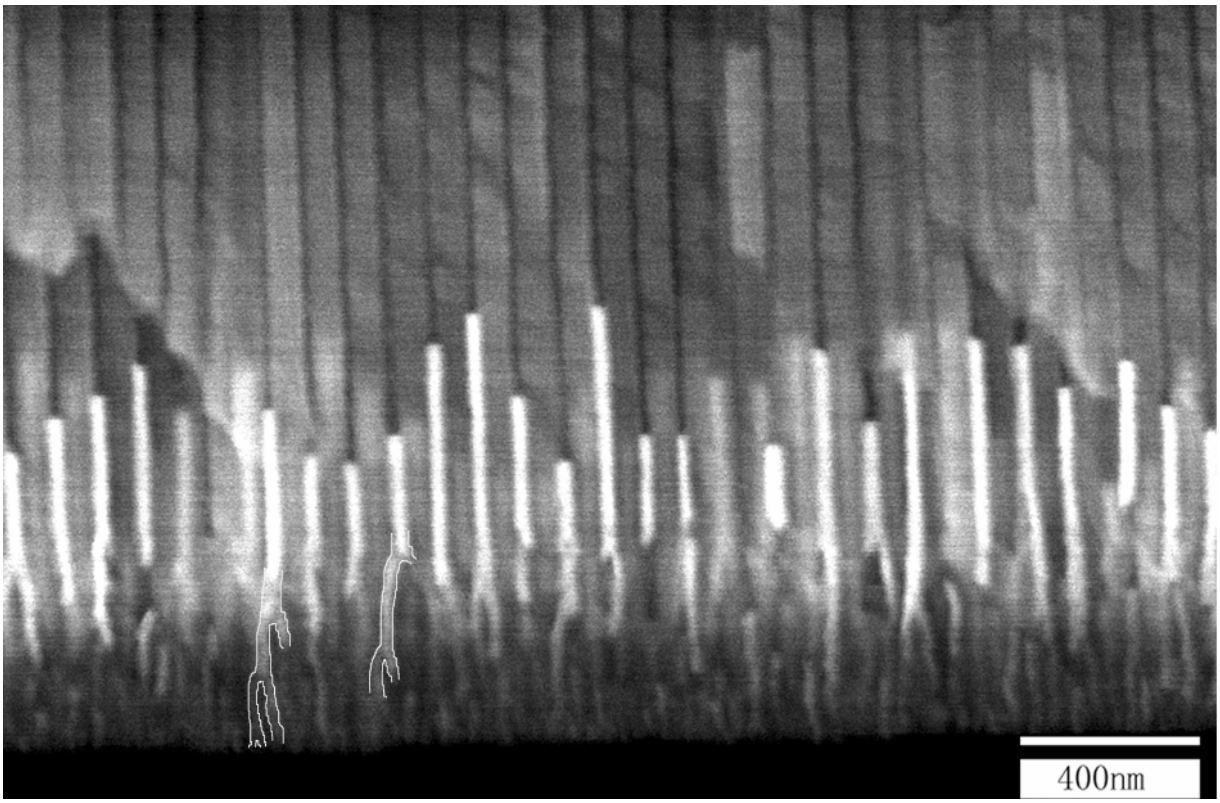
The ordered porous alumina with a pore depth of ~2 μ m were prepared by a well-established procedure[1]. Briefly, the as-received aluminium plates (99.999%) were chemically cleaned by consecutive sonication in acetone, deionized water, isopropanol, deionized water for 5 minutes and annealed at 550 centigrade in an argon atmosphere for 3 hours. The cleaned aluminum substrate was further electrochemically polished in 1:4 solution of $HClO_4$ and ethanol. Then, the cleaned aluminium plates were assembled into an electrochemical cell and anodized in 0.3M oxalic acid solutions at 40 V at 3 centigrade for 12h. The alumina layer was selectively removed by a solution containing 6.8g $CuCl_2 \cdot 2H_2O$, 200ml 37% HCl and 200ml deionized water. The second anodization was conducted again in oxalic acid at 40 V at 4 centigrade for 2 hours. SEM indicated that a pore depth of ~2 μ m was reproducibly obtained.

The Tree-like Nanopores generated in non-steady-state anodization

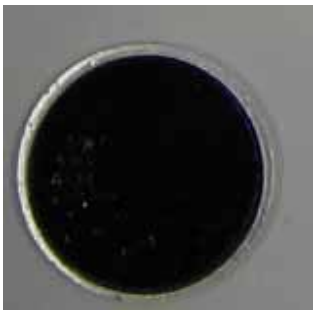
Immediately after second anodization was finished, the cell potential was decreased every 30 second to a value defined by equation: $U=U_0*e^{-t/\tau}$, where U is the anodization potential, U_0 is initial anodization potential, t is time, τ is exponential time constant. The stop potential is 5 V. The non-steady-state anodization was performed in 0.3 M oxalic acid solution at 4 centigrade. It was found that this procedure reproducibly resulted in generation of tree-like nanopores.

Fabrication of Gold Nanotrees by Pulsed Electrodeposition

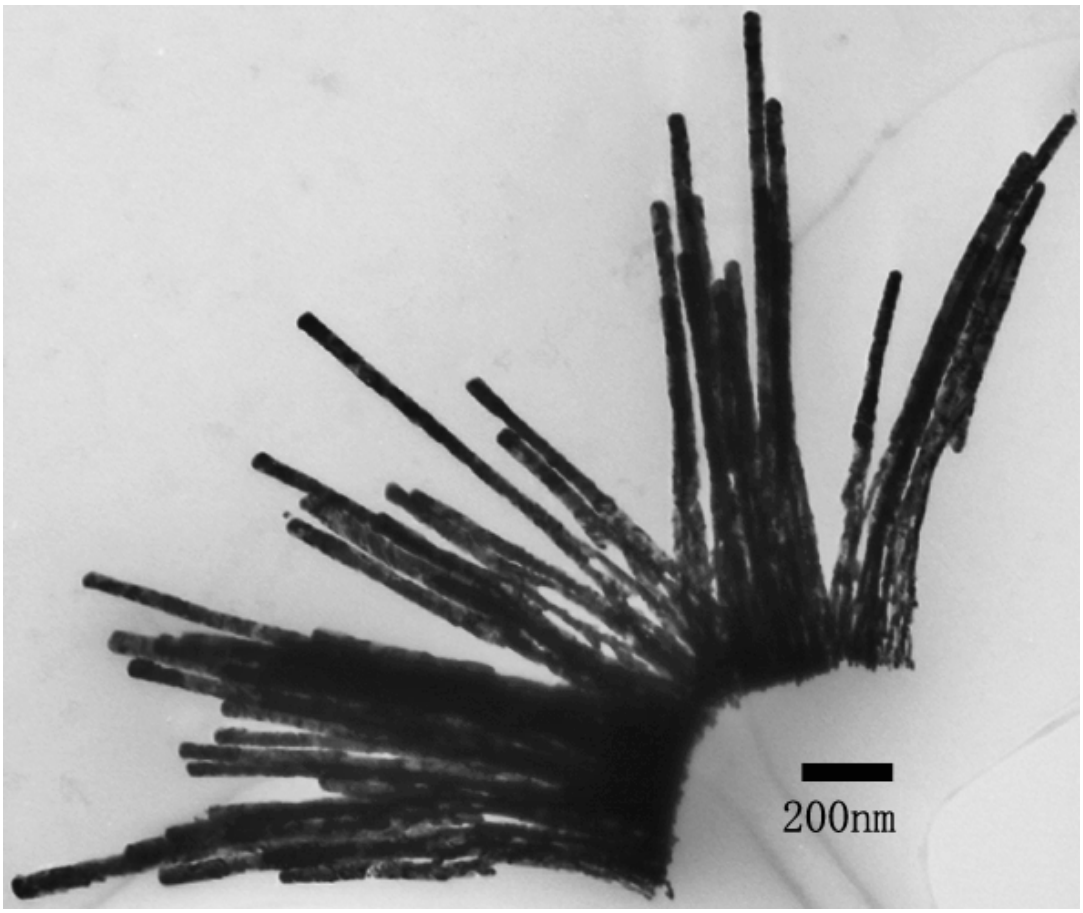
After anodization potential was decreased to 5V, oxalic acid was exchanged with a highly concentrated gold electroplating solution which was prepared according to previous report [2]. The deposition condition has been described previously [3]. To fabricate gold nanotree arrays, alimnium was selectively removed by a solution containing 6.8 g copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), 200ml 37% HCl and 200 ml deionised water, which resulted in an alimina membrane embedded with gold nanotree arrays. To release as-fabricated gold nanotrees, alimina was further removed by 30 wt.-% aqueous KOH at room temperature.



S1 SEM micrograph of cross-sectional gold impregnated nanoporous alumina films, showing a tree-like nanogold exist in the alumina matrix.



S2 Photograph of an aluminium/alumina disc with tree-like pores after electrodeposion of gold, showing uniformity of gold infiltration.



S3 A TEM micrograph of the Gold nanotree assemblies in a sector-like way. It indicates strong interactions among the gold branches.

References

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3. K. Nielsch, F. Muller, A. P. Li, U. Gösele, *Adv. Mater.* 2000 12, 582-586.