Electronic Supplementary Material (ESI) for Chemical Communications


# Supporting Information

## Custom-tailoring ordered taper-nanopore AAO membrane by combined nanosphere self-assembling, imprinting, anodizing and etching

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### Experimental details

Silica nanospheres with average diameter ~280 nm are synthesized by modified Stöber method. 1.9 ml of tetraethoxysilane is dropwise added into ethanol solution (100 ml) containing 0.5 M ammonia and 17 M deioned water at room temperature, which is stirred for 12 h at a constant speed of 700 r $min^{-1}$. The as-prepared silica nanospheres are washed with ethanol by repeating the process of centrifugation at a speed of 4000 r $min^{-1}$ for 20 min and ultrasonic dispersion at least five times to remove impurities. These nanospheres are dispersed in a mixture of ethanol and water (V:V=1:1) to form 0.95 M suspension. 1 μL of suspension is dropped onto a clean glass tilted at 8º angle at relative humidity of 40%~50% at room temperature, which produces a hexagonally close-packing silica nanosphere monolayer. The highly pure (99.999%) Al disks with diameters of 2.5 cm were degreased by ultrasonic cleaning in acetone, ethanol and water for 10 min, respectively. Then, the samples were electropolished in a mixture of perchloric acid and ethanol (V/V = 1:4) for 8 min (20 V, 1 ºC). After drying out using nitrogen air flow, the samples are gently placed on the surface of silica nanospheres and patterned into a layer of hexagonally non-close-packed nanopits by keeping the pressure of 102 kN $cm^{-2}$ for 2 s. The electrochemical cell is equipped with a circulation cooling system to effectively remove the reaction heat. Here, the anode is the Al foil and the cathode is the platinum electrode. These nanopits can induce the in-situ and vertical growth of taper-nanopores under 5-step cyclic anodizing in 0.29 M $H_3PO_4$ aqueous solution (5 ºC) at 150 V for 50~200 s and etching in 0.43 M $H_3PO_4$ aqueous solution (30 ºC) for 5~25 min. All SEM images were taken using thermal field emission scanning electronic microscopy (Quanta 400 FEG, FEI) at 20 KV.

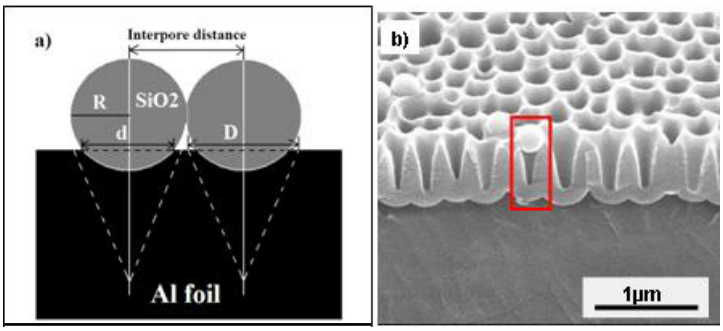


**Figure S1.** a) Schematic illustration of silica nanospheres imprinted on the surface of Al foil, showing a geometrical relationship between the nanospheres and the patterned nanopits. b) The SEM side-view of taper-nanopores. A small number of silica nanospheres embedded into the nanopore can be observed. This was caused by the downward growth of nanopores and the pore-widening induced capture effect. Only if a simple anodizing pre-patterning process is added, we can easily obtain the patterned Al foils and alumina taper-pores without any absorbed nanospheres.

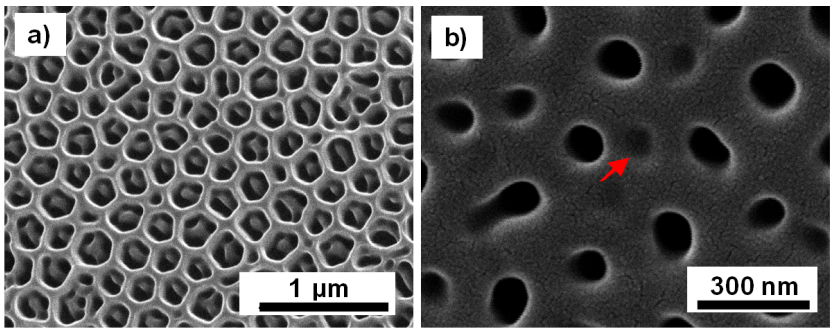


**Figure S2.** SEM top-views of porous anodic alumina achieved at different voltages: a) 80 V; b) 180 V. The pre-patterned Al foils are treated by five-step cyclic anodizing 100 s in 0.29 M $H_3PO_4$ solution and etching 10 min in 0.43 M $H_3PO_4$ solution. The lower anodizing voltage leads to denser branched pores while the higher anodizing voltage results in looser dislocated nanopores, as indicated by the red arrow.

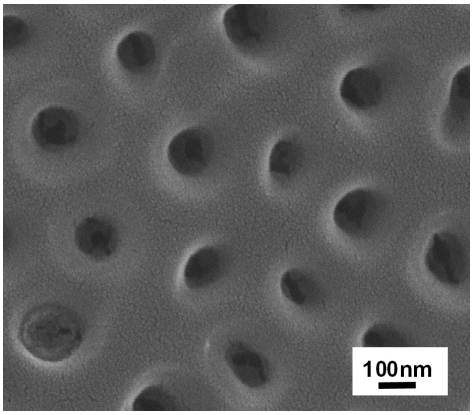


**Figure S3.** SEM top-view of a nanoporous AAO membrane, which was achieved by five-step cyclic treatment of anodizing 100 s in 0.29 M $H_3PO_4$ aqueous solution and etching 5 min in 0.43 M $H_3PO_4$ aqueous solution. Clearly, so short etching time is insufficient to produce regular taper-nanopores.