Supporting Information for

"Metal membranes with hierarchically organized nanotube arrays"

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Experimentals

Preparation of nanoporous alumina template: Monodomain nanoporous Al_2O_3 templates were prepared by the anodization of nanoindented aluminum as described previously.[1] In brief, mirror finished aluminum plates (typical diam. = 4 cm) were nanoindented by using an imprint stamp consisting of hexagonally arranged Si_3N_4 pyramids (interpit distance = 500 nm and height = 260 nm), and subsequently anodized in an acid electrolyte (V = 195 V, 1 wt. % H_3PO_4, 0 °C). With this electrochemical condition, the microscopically determined pore diameter, pore density, and film growth rate turned out to be 182 nm, 4.6 x 10^8 cm^{-2}, and around 4 mm/h, respectively. After anodization, free-standing alumina templates were obtained by stepwise voltage reduction technique; free-standing templates are recommended because they can be floated on the surface of alumina etching solution (30 wt. % H_3PO_4), enabling facile removal of alumina template after the electrodeposition of metals (see text). We could systematically adjust the pore diameters of the alumina template by isotropic chemical etching using 10 wt. % H_3PO_4 (45 ^oC). At this wet-chemical etching condition, the pore diameter of the template increased at a rate of ~ 4 nm/min.

Fabrication of ferroelectric nanodot arrays: Large-area (1 cm x 1 cm) arrays of ferroelectric $Pb(Zr_{0.40}Ti_{0.60})O_3$ (PZT) nanodots were obtained on Nb-doped $SrTiO_3$ single-crystal substrate with (100)-orientation by pulsed laser deposition (PLD) of PZT layer through an Au nanotube membrane mask. Briefly, the Au membrane comprising a regular array of nanoscale tubes is placed on the substrate and PZT is subsequently deposited by PLD at room temperature from a ceramic target with 10 % PbO excess. After the lift-off process the nanostructures were crystallized by a thermal annealing in air at 600°C for 1 h. In order to check the ferroelectric properties the obtained nanostructures were characterized by piezoresponse scanning probe microscopy. Piezoresponse measurements were performed using an Autoprobe CP-Research (Thermomicroscopes) atomic force microscope in contact mode equipped with a Pt-coated ATEC-EFM (Nanosensors) cantilever. The hysteresis loops were raised at 18.4 kHz using a previously described technique.[2]

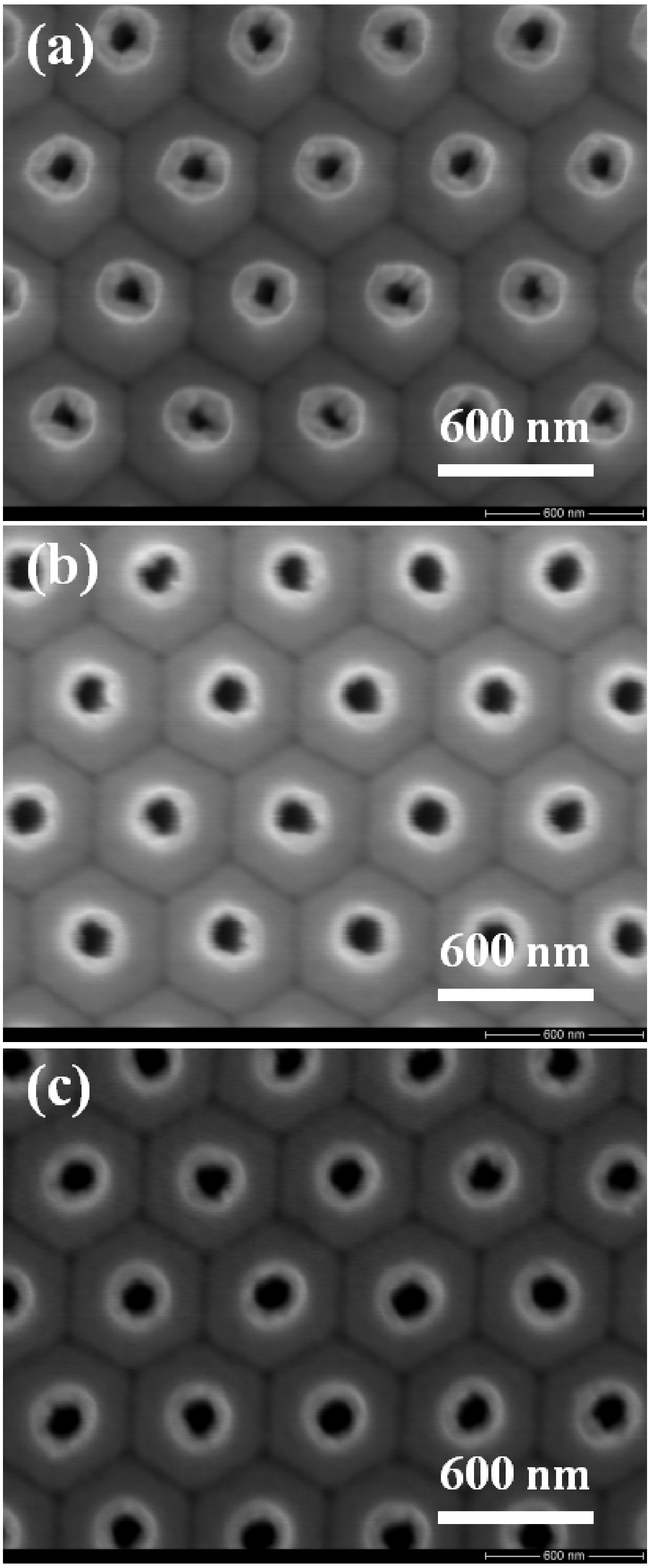

Figure S1. SEM images of Au nanotube membranes replicated from nanoporous Al_2O_3 membrane (D_P = 245 nm, D_{Int} = 500 nm), showing the effect of electrodeposition time on the inner-tube diameter of the metal nanotubes. The electrodepositions were performed at 1.4 mA/cm^2 for (a) 90 sec, (b) 60 sec, and (c) 50 sec.

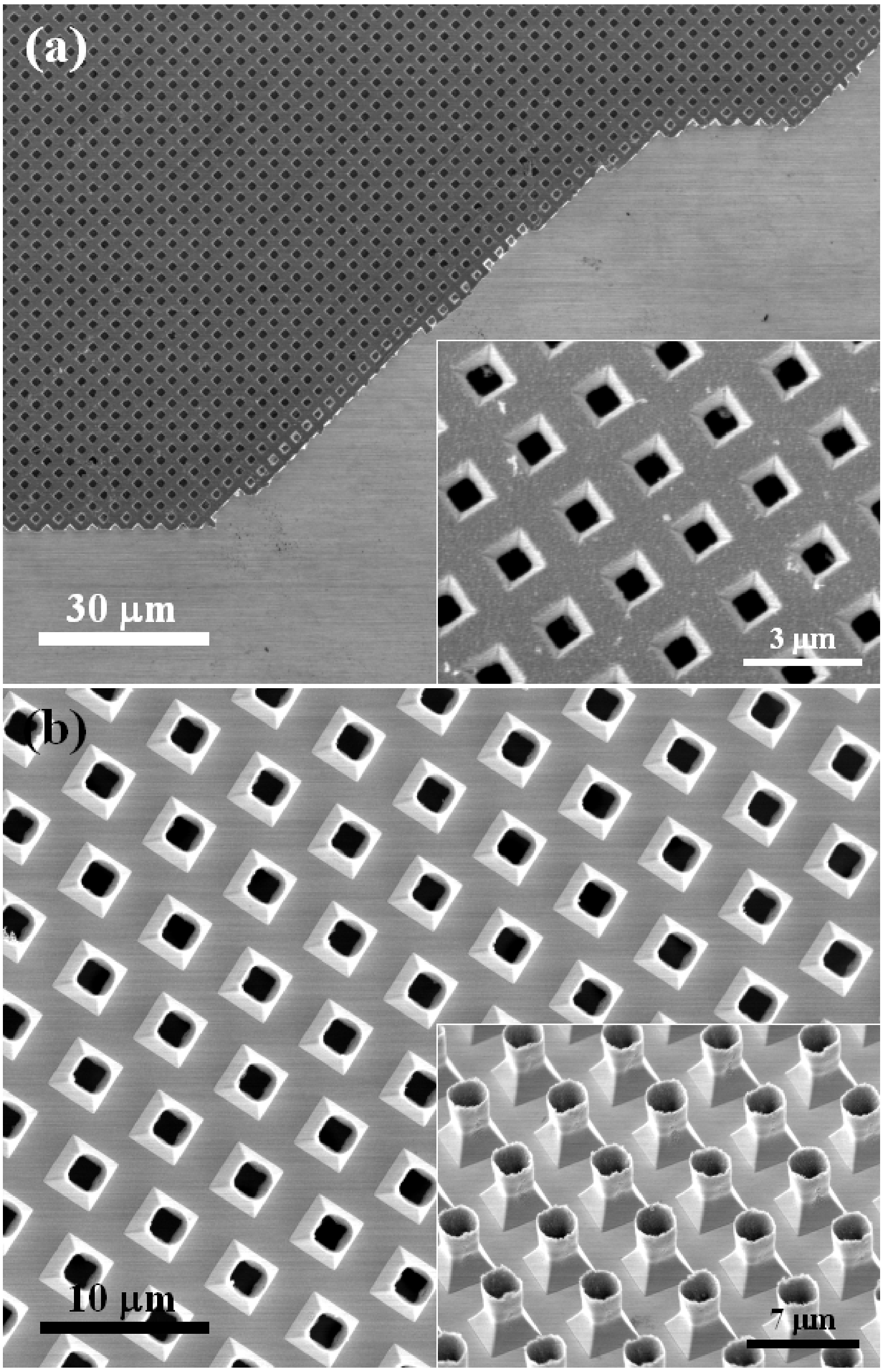

Figure S2. (a) Front and (b) back surface SEM images of Au membranes replicated from patterned Si substrates with different 2-D arrangements of etch pits; square array for (a) and hexagonal array for (b). The high magnification views of each micrograph are presented as inset.

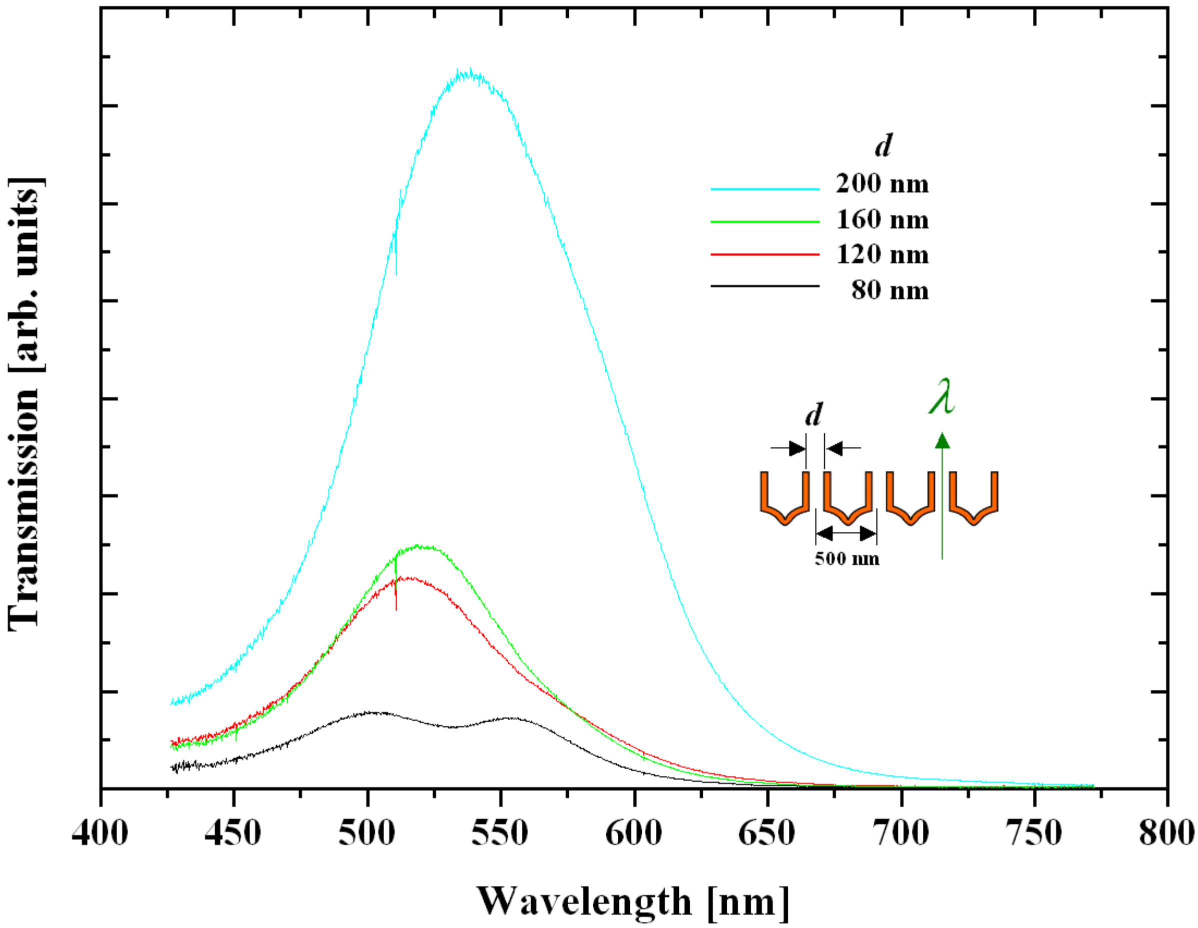

Figure S3. The evolution of transmission spectra of Au nanotube membranes as a function of inner tube diameter (*d*). The Au nanotube membranes were fixed on glass plates. The inset shows the measurement configuration.

Reference

(1) Choi, J.; Nielsch, K.; Reiche, M.; Wehrspohn, R. B.; Gösele, U. *J. Vac. Sci. Technol. B* **2003**, *21*, 763.

(2) Harnagea, C.; Pignolet, A.; Alexe, M. *Integr. Ferroelectr.* **2001**, *38*, 667