

**Patterning of periodic high-aspect-ratio nanopores in anatase
titanium dioxide from titanium fluoride hydrolysis**

Supporting Information

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Experimental Procedure

The starting porous template was made from strips of high purity aluminum foil (99.97%). Those strips were mechanically ground with increasingly smaller grit size silicon carbide sanding discs and chemo-mechanically polished with a slurry of Al₂O₃ powder and 10% H₂O₂. The aluminum was degreased in a 5% NaOH solution at 60 °C for 30 second and rinsed with water. The aluminum was electropolished in a 5:1 ethanol/perchloric acid (70%) mixture at 10V in an ice bath to produce a mirror finish.

In order to obtain monodisperse pore dimensions in the aluminum oxide anodizations that last hours^{1,2} are necessary without sophisticated equipment.³ Monodispersity is important to accurately study the effect pore dimensions have on the carrier mobility, absorption, and power conversion efficiency of hybrid photovoltaic devices in future studies. The hexagonal array of cylindrical pores was produced by the three step anodization process. The polished aluminum was anodized in 0.3 M oxalic acid for 10 min at 30 V and 22 °C. The porous aluminum oxide formed by this anodization was stripped by a mixture of 0.4M H₃PO₄ and 0.2 M CrO₃ for 15 min at 60 °C. A 3 hour long anodization was then performed to form the hexagonally packed pore structure. The oxide was stripped again under the same conditions for 20 min. A final anodization was performed to create the organized template and to determine the final depth of the pores. The pores were widened and cleared of excess oxide in 1M H₃PO₄ for 10 min and then rinsed with water and allowed to dry for at least 12 hours.

The dry porous aluminum oxide template was filled with the thermoplastic polymer poly(methyl methacrylate) (PMMA). A 4 wt.% solution of PMMA (M_w: 350kg, T_g: 122 °C) in chlorobenzene was spin-cast onto the template for 60 s at 1000 RPM. The aluminum strip was then cut into 1 cm x 1 cm pieces using a wire saw at 2500 RPM and a slurry of glycerol, water, SiC powder (240 grit) in a 4:1:1 volume ratio. The pieces were thoroughly rinsed with water to remove any residual slurry and then blown clean with a N₂ stream. The PMMA was heat infiltrated into the pores at 200 °C in a vacuum oven for 30 min. A 2 mm thick layer of poly(dimethylsiloxane) (20:1 Elastomer/Curing Agent) (PDMS) was drop-cast onto the PMMA film and then cured for in an oven for 1 hour at 60 °C. A small clean 1 cm² square glass slide and a small amount of PDMS was place onto the cured PDMS and cured for an additional hour.

The patterned TiO₂ was created by a solution deposition method from TiF₄. A mass of 1.5g of TiF₄ was added to 270 mL of H₂O (purified by Millipore system) and stirred for 20 min. The pH of the solution was adjusted to 1.80 by adding 0.15 M NH₃. Cetyltrimethylammonium bromide (CTAB) was added and the solution was stirred for 1 hour.

The aluminum and aluminum oxide were dissolved in order to free the PMMA fingers from the template and to maintain the high-aspect-ratio fingers. A 1.4 wt% solution of iron(III) chloride in 4M HCl was used at 65 °C to dissolve the aluminum. The samples were dipped in water to removed excess acid and then placed in a 10 wt.% NaOH solution for 30 min to remove the oxide. The samples were lightly rinsed with water and immediately placed into the TiF₄ solution without allowing it to dry. Samples were held at an angle to prevent particles from falling onto the pattern and bubbles from being trapped on the samples. The TiF₄ solution was slowly heated to 60 °C over 2 hours. Titania was deposited for 4 hours at this temperature. The samples were gently rinsed with water and allowed to dry in a high humidity environment for 12 hours.

A precursor to titanium dioxide was used to bind the bottom of the formed pattern to the fluorine-doped tin oxide (FTO) substrate. The TiO₂ precursor was a mixture of Ti(OEt)₄, trifluoroacetic acid, HCl_(aq), and ethanol in a 0.975 : 0.5 : 0.175 : 3.15 volume ratio. A few drops of

the binder was placed onto the back of the pattern and then embossed onto the FTO. Before the binder dried the sandwiched pattern was pressed on a laboratory press and placed in a 90 °C oven for 1 hour. The PDMS was peeled from the FTO and the PMMA was dissolved in acetone. The resulting pattern was sintered at 450 °C for 6 hours with a 1 °C/min temperature ramp.

Collapsed PMMA Fingers

An AFM topography image was taken of dried PMMA fingers and is shown in Figure S1. The fingers collapsed upon drying and formed aggregated structures. These structures do not separate after being rehydrated.

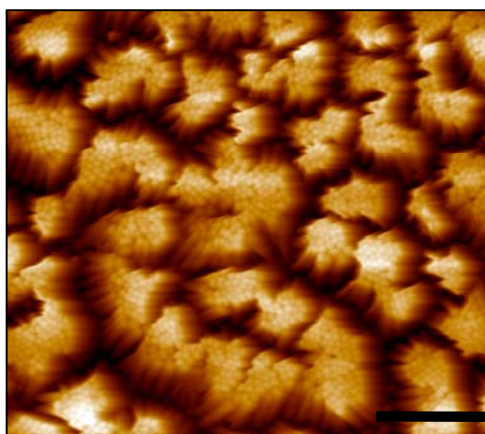


Figure S1: AFM topography image of collapsed PMMA fingers. The scale bar is 1 μm . The topography scale bar is in nm.

The PMMA fingers shown in Figure S1 do not accurately represent the PMMA used to make the patterned TiO_2 reported in the communication. Those PMMA fingers were never allowed to dry and thus the finger aggregation was prevented. When the fingers are dried like those shown in Figure S1 they do not become separated upon rehydration. The dried fingers were used just as the wet fingers were used to create the TiO_2 pattern and resulting structure is shown in Figure S2.

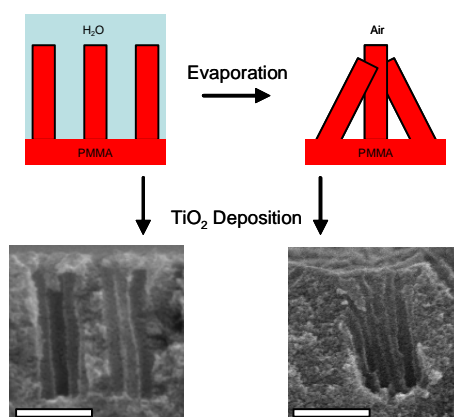


Figure S2: Diagram depicting separated and collapsed PMMA fingers and SEM of resulting TiO_2 patterns. Scale bars are 200 nm.

X-Ray Diffraction

X-ray diffraction (XRD) data was collected by using grazing incidence X-ray diffraction on the patterned thin films of titanium dioxide on FTO. The spectrum is shown in Figure S3. The major peak at 25.4° is indicative of anatase titania. The peaks fit the XRD spectrum of anatase titania formed from TiF_4 . Titania produced through TiF_4 hydrolysis typically grows on the 001 face of the crystal leading to an enhanced signal in the XRD. This characteristic increase of intensity of the 004 peak was not observed because of an overlapping FTO peak. The remaining peaks and some overlapping peaks are assigned to the underlying FTO layer.

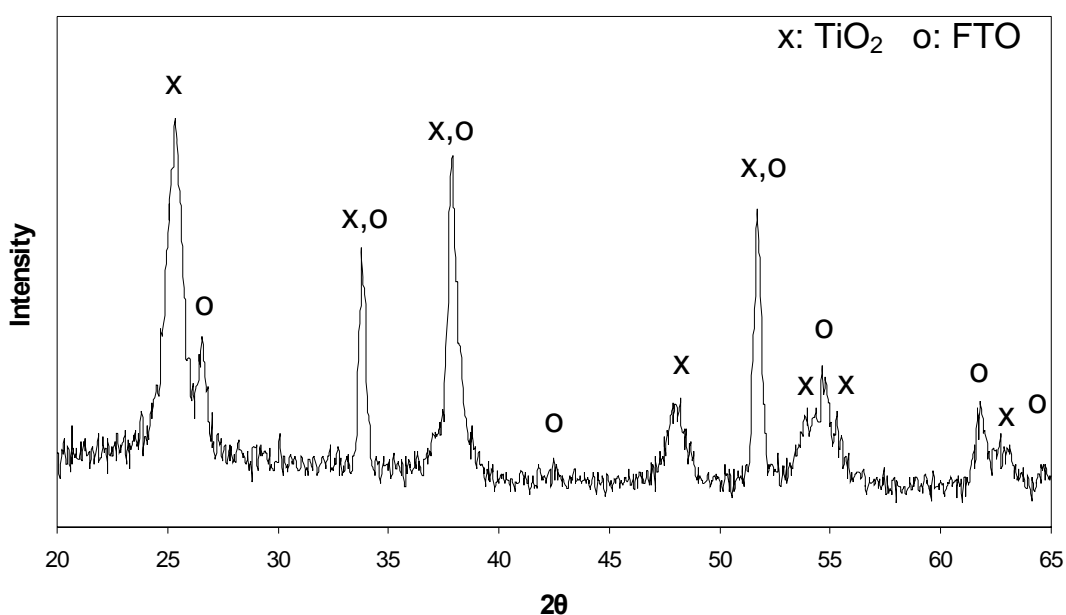


Figure S3: XRD pattern of nanostructured TiO_2 on FTO. The peaks indicative of anatase TiO_2 are labeled with an “x” and those from the underlying FTO layer are labeled with an “o”.

1. A. P. Li, F. Muller, A. Birner, K. Nielsch and U. Gosele, *J. Appl. Phys.*, 1998, **84**, 6023-6026.
2. F. Y. Li, L. Zhang and R. M. Metzger, *Chem. Mat.*, 1998, **10**, 2470-2480.
3. J. Choi, K. Nielsch, M. Reiche, R. B. Wehrspohn and U. Gosele, *J. Vac. Sci. Technol. B*, 2003, **21**, 763-766.