

Electronic Supplementary Information (ESI)

Large-scale Sparse TiO₂ Nanotube Arrays by Anodization

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Experimental

Prior to anodization, titanium foils with 0.3 mm thick were mechanically polished with polishing-cloth, then successively cleaned by deionized water, acetone and deionized water in an ultrasonic bath, and finally dried ambient air. After the pretreatment, the Ti foils were anodized at 80 V (supplied by a DC power) with a round surface (2 cm diameter) exposed to the electrolyte, using a two-electrode configuration with a piece of round lead plate (2 cm diameter) as the counter electrode. The distance between the anode and the cathode was maintained at 1 cm for all the experiments. The anodization reactor was airproofed with polyethylene membrane and kept in a 25 °C bath in the anodization process. The anodization current was recorded by a multimeter, which was interfaced with a computer. The hydrofluoric acids used in the experiments contain 40 wt.% HF. The surface morphology and the structure of the specimens were characterized by a scanning electron microscopy (Thermal Field Emission Environmental scanning electron microscopy, FEI Quanta 400 FEG) and an X-Ray Diffractometer (Cu-K α , D-MAX 2200 VPC, RIGAKU). The bottom view and side view of the nanotube arrays were obtained from the cracked films after bending the specimens. We counted the nanotube quantity from the scanning electron micrograph (SEM) manually, marking the nanotubes sequentially with the Photoshop software. The tube density equals to the nanotube quantity on a SEM divided by the imaging area of the SEM counted. Each value plotted in Figure 3(b) is the average value of three tube density values counted from three SEM images taken from different locations on a sample, and the error bar is the standard deviation of the values of the tube density.

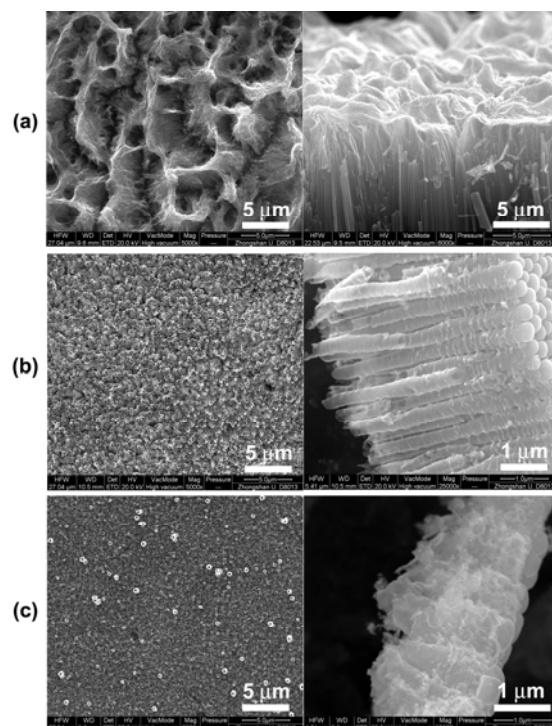


Figure S1 The scanning electron micrograph (SEM) images of the top view (left panel) and side view (right panel) of the S-TNTAs formed at 80 V for 12 h in ethylene glycol (EG) based electrolyte containing 4.0 wt.% HF and (a) 5.0 wt.% water, (b) 15.0 wt.% water and (c) 18.0 wt.% water.

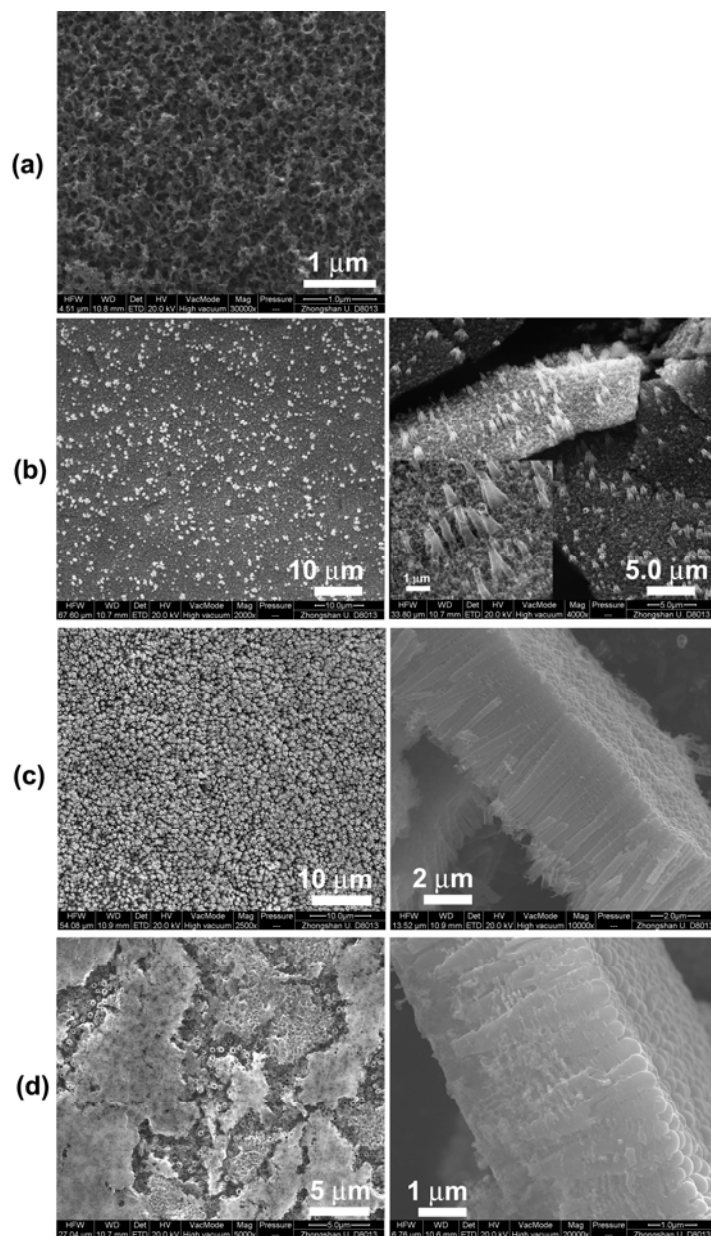


Figure S2 The SEM images of the top view (left panel) and side view (right panel) of the S-TNTAs formed at 80 V for 12 h in EG based electrolyte containing 17.5 wt.% water and (a) 5.0 wt.% HF acid, (b) 4.0 wt.% HF acid, (c) 2.0 wt.% HF acid and (d) 0.5 wt.% HF acid.

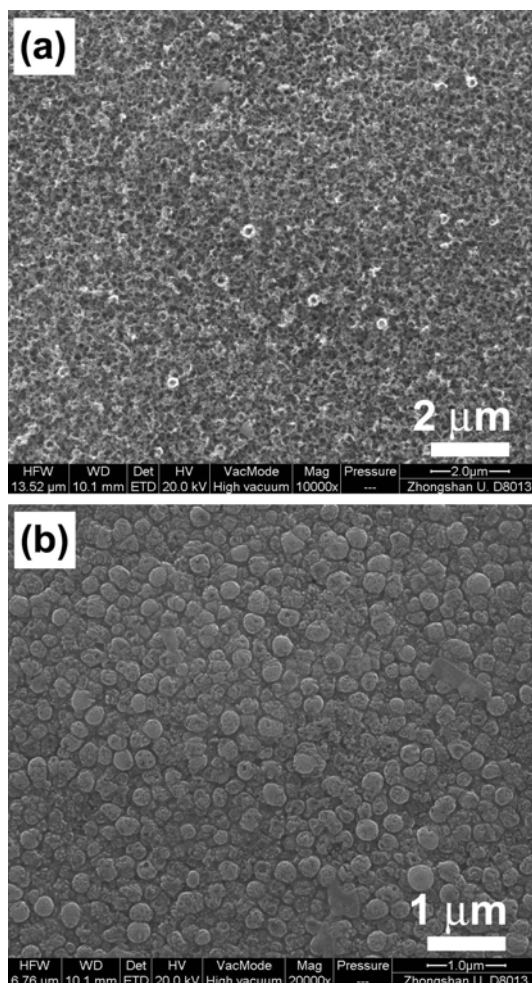


Figure S3 The SEM images of the (a) top view and (b) bottom view of the sponge-like porous oxide (SPO) layer formed at 80 V for 4 h in the so-called “aged electrolyte”, which has been anodized for 12 h. The fresh electrolyte is EG solution containing 3.5 wt.% HF and 17.5 wt.% water.

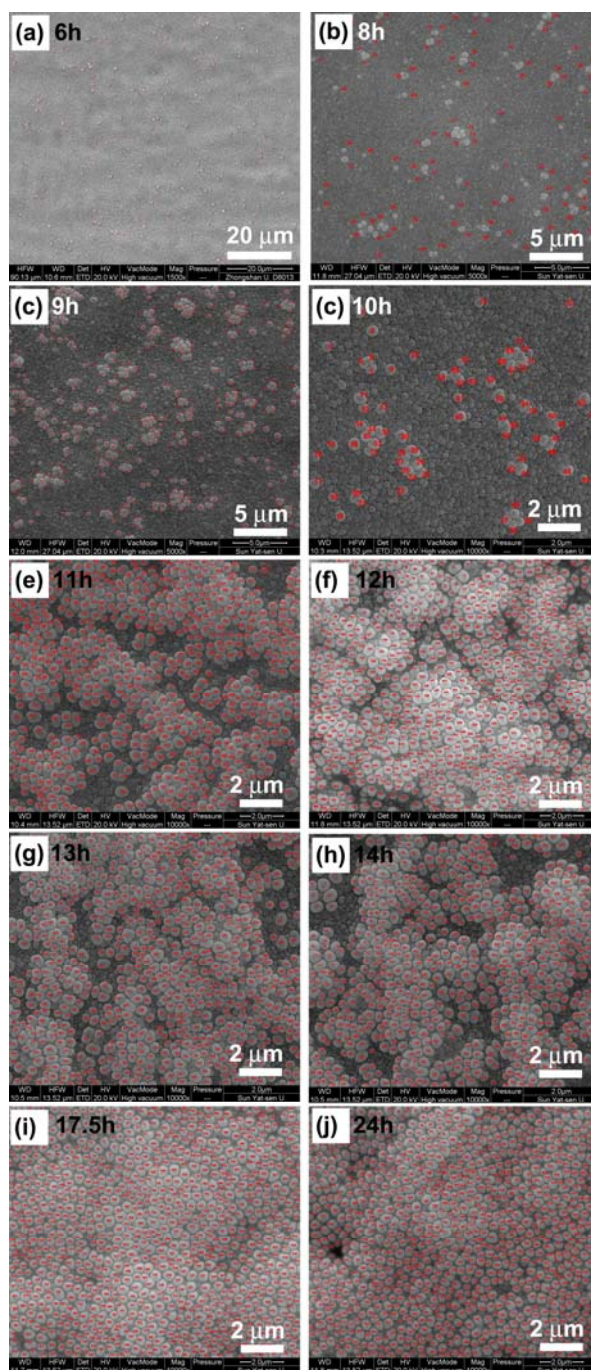


Figure S4 The statistic results of the tube density from the bottom views of SEM images of samples formed by anodization for (a) 6 h, (b) 8 h, (c) 9 h, (d) 10 h, (e) 11 h, (f) 12 h, (g) 13 h, (h) 14 h, (i) 17.5 h and (j) 24 h at 80 V in EG based electrolytes containing 3.5 wt.% HF and 17.5 wt.% water.

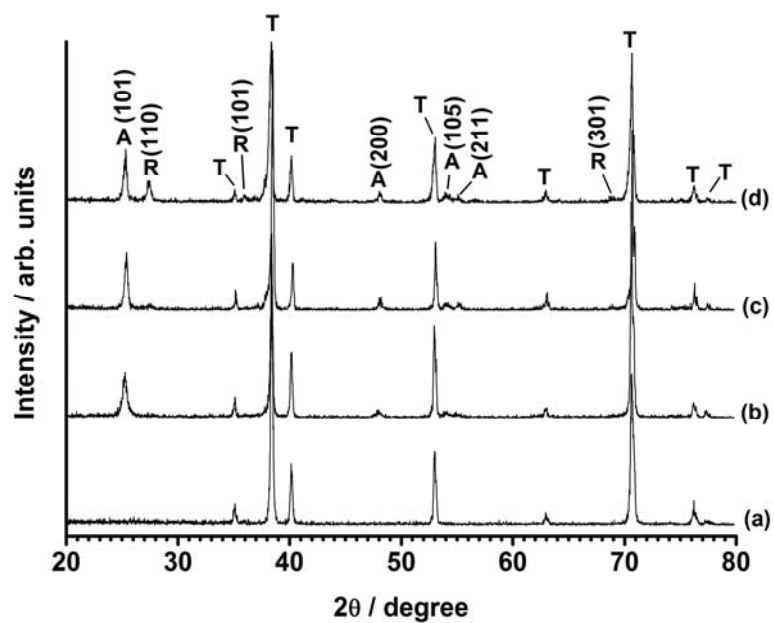


Figure S5 X-ray diffraction patterns of the S-TNTAs samples annealed in a muffle furnace in the air ambient for 2 h at the temperature of (a) no annealing, (b) 350 °C, (c) 450 °C and (d) 550 °C. The S-TNTAs samples are formed at 80 V in EG based electrolytes containing 4.0 wt.% HF and 17.5 wt.% water. A, R, and T represent anatase, rutile, and titanium, respectively.