

Supplementary Information

Ultraviolet Sensing Using TiO₂ Nanotube Integrated High Resolution Planar Microwave Resonator Device

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TiO₂ Membrane Preparation and Characterization

Titanium foils with 0.79 mm thickness (99.7%; Sigma Aldrich) were degreased by sonication in methanol and deionized water (DI) and then dried in a flowing stream of nitrogen gas. A conventional two-electrode electrochemical cell was used for anodization of TiO₂ nanotubes with dimensions of 1 × 4 cm and 0.5 × 4 cm for anode and cathode respectively. A reference TiO₂ nanotube array sample was formed by anodizing Ti foil in an electrolyte consisting of 0.1 M ammonium fluoride and 5% vol. DI water in ethylene glycol (EG) at 60 V. In comparison, a TiO₂ nanotube membrane was anodized with an electrolyte consisting of 1.5 M lactic acid, 0.1 M ammonium fluoride, and 5% vol. DI water in EG to improve the rate of anodization and thus obtain longer nanotubes in shorter time. In mechanical terms, the factor that determines the growth rate in a classic high field anodization process is a high driving voltage that is established across the growing oxide without causing local dielectric breakdown events such as burning [1,2]. Among all the other factors, the threshold voltage for 'burning' depends on the electrolyte's ionic species such as citric acid, malonic acid, oxalic acid, and lactic acid. These weak organic acids shift the threshold voltage to a higher value which leads to more rapid anodization process [3, 4]. Furthermore, the incorporation of carbon into the walls of the nanotubes due to anodization in

organic electrolytes decreases the permittivity and increases the critical breakdown field [5]. Unlike the TiO₂ anodization reference electrolyte, the 1.5 M lactic acid electrolyte needed adjustments such as cooling down the electrochemical cell with ice due to the high cell currents resulting from the use of a high anodization voltage. After a few experimental anodization processes, the anodization process with an initial applied voltage of 120 V for three minutes followed by 100 V for 1 hour in a glass beaker cell gave the best results in terms of TiO₂ nanotube formation, thickness and anodization current control. The as-prepared TiO₂ nanotubes on foil were then annealed in air at 500° C for 2 hours. The TiO₂ nanotubes on foil were then anodized for a second time in a regular electrolyte to form an amorphous thin layer of TiO₂ under the anatase TiO₂ nanotube layer. The difference between the TiO₂ NT phases caused a tension between the two layers and as a result, a free standing TiO₂ nanotube membrane with a thickness of 19 μm was formed. When compared to the regular EG-based electrolyte, the lactic acid based electrolyte more than doubled the growth rate of TiO₂ nanotubes. A regular electrolyte produced TiO₂ NT films with a thickness of 19 μm in about 2.5 hours but the lactic acid recipe produced the same length of TiO₂ NTs in 1 hour.

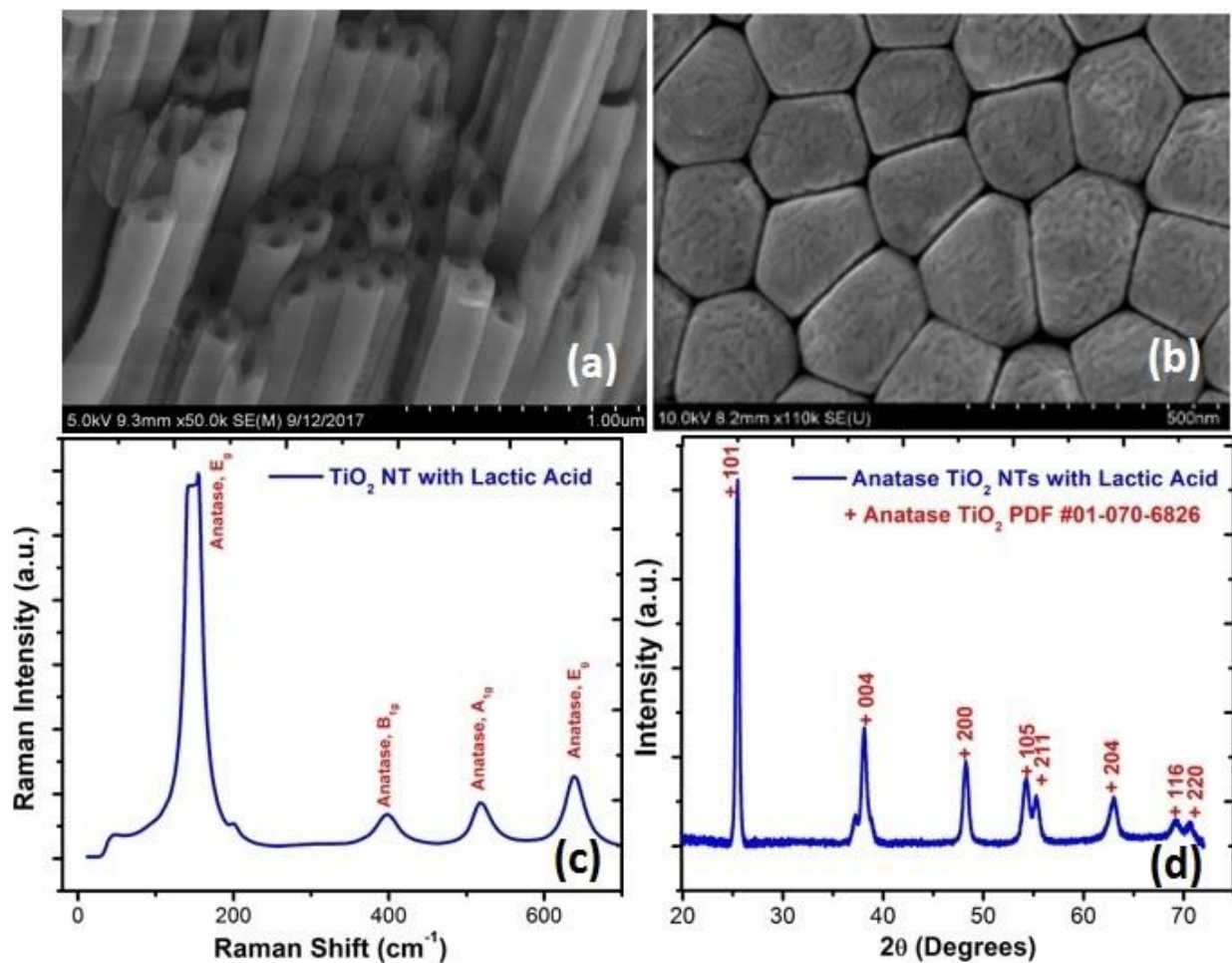


Figure S1 (a) FESEM image of a cross section of a grown TiO₂ nanotube layer. (b) The barrier layer of TiO₂ NTs anodized with a lactic acid electrolyte. The wrinkles on the barrier layer provide indirect confirmation of the high surface area of the TiO₂ NTs (c) The Raman Spectroscopy plot of TiO₂ NTs. (d) The X-ray diffractogram of TiO₂ NTs indicating the presence of anatase phase.

A field emission scanning electron microscope (Hitachi S-4800 FESEM) was used to image the nanotube arrays. X-ray diffraction (Bruker D8 X-Ray Diffractometer) was used to identify the phase of the crystalline TiO₂ NTA and to provide information on unit cell dimensions. The Raman Spectroscopy (Nicolet Omega XR Raman Microscope) was used to study the chemical composition and the bond signature of the TiO₂ NTA. (Figure S1).

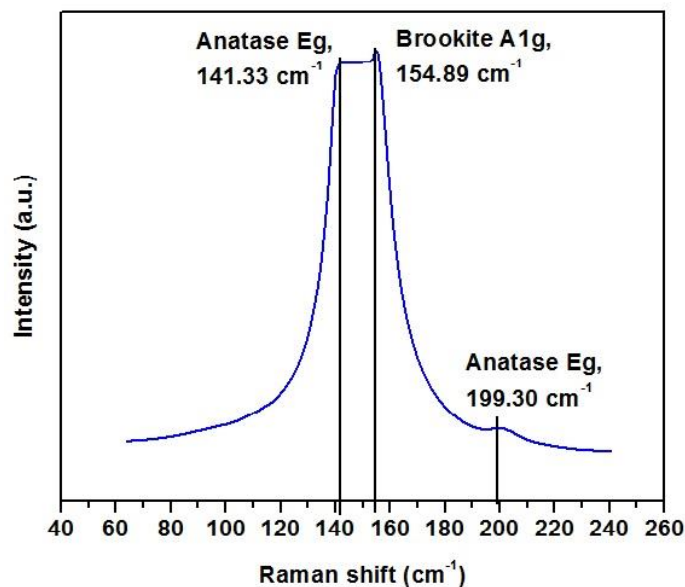


Figure S2. Zoomed in view of Raman spectrum between 60 cm^{-1} and 240 cm^{-1}

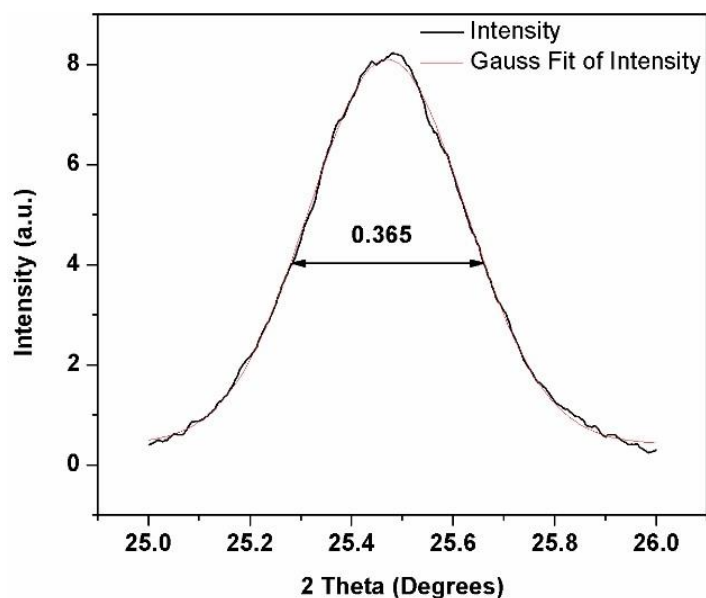


Figure S3. Zoomed in view of the anatase (101) XRD peak of the TiO_2 nanotube arrays

The Raman mode at 154.89 cm^{-1} (Fig. S2) can be due to the anatase E_g mode that is caused by small (less than 4 nm) crystallite size of anatase [6]. However, that is ruled out, based on our Scherer analysis, see the Fig. S2 (FWHM for anatase (101) peak), for which crystallite size is 28 nm. The peak at 154.89 cm^{-1} can also be due to presence of brookite A_{1g} [7]. By ruling out anatase E_g because of large crystallite size, we attribute the Raman mode at 154.89 cm^{-1} to brookite A_{1g} .

References:

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