

# Self-Assembled Fabrication of Vertically Oriented Ta<sub>2</sub>O<sub>5</sub> Nanotube Arrays, and Membranes Thereof, by One-Step Tantalum Anodization

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We report for the first time synthesis of high-aspect-ratio tantalum oxide nanotube arrays via one-step anodization of Ta foil. The use of aqueous electrolytes containing HF:H<sub>2</sub>SO<sub>4</sub> in the volumetric ratios 1:9 and 2:8 results in formation of ordered nanodimpled surfaces with 40–55 nm pore diameters over the potential range 10–20 V. The addition of 5–10% of either ethylene glycol (EG) or dimethyl sulfoxide (DMSO) to the HF and H<sub>2</sub>SO<sub>4</sub> aqueous electrolytes resulted in the formation of Ta oxide nanotube arrays up to ~20 μm thick, either securely anchored to the underlying Ta film or as robust free-standing membranes, as dependent upon the anodization time and applied voltage.

## Introduction

Since the discovery of the chemical inertness of Ta toward aqueous acids by Anders Ekeberg in 1802,<sup>1</sup> who related this inertness to the formation of an oxide layer atop the metal surface, the anodic growth of Ta<sub>2</sub>O<sub>5</sub> films has received considerable interest.<sup>2</sup> Anodization of tantalum has been widely investigated in many electrolyte systems containing mineral acids such as H<sub>2</sub>SO<sub>4</sub>,<sup>3–5</sup> H<sub>3</sub>PO<sub>4</sub>,<sup>3,4,6</sup> and HClO<sub>4</sub>,<sup>7</sup> organic acids such as formic,<sup>8</sup> butyric,<sup>8</sup> oxalic,<sup>6</sup> and citric<sup>9</sup> acids; salt solutions such as Na<sub>2</sub>SO<sub>4</sub>,<sup>10</sup> and oxidizing agents such as H<sub>2</sub>O<sub>2</sub><sup>11</sup> at anodization voltages typically between 100 and 200 V<sup>12</sup> over a wide range of temperatures.<sup>13</sup> The resulting films were found to be amorphous and compact in nature. Double anodization experiments resulted in the formation of similar compact layers of Ta<sub>2</sub>O<sub>5</sub> at lower

voltages, ~40 V.<sup>14</sup> The kinetics of film formation and breakdown in the above-mentioned electrolyte systems have been experimentally<sup>15–18</sup> and theoretically<sup>19,20</sup> well-documented.

Ta<sub>2</sub>O<sub>5</sub> has found many applications including use as a protective coating material,<sup>21</sup> catalyst,<sup>22</sup> capacitor, resistor, and optical device,<sup>23</sup> as well as in biomedical applications.<sup>24,25</sup> The utility of the material has motivated continuing studies to further refine and extend the various synthesis techniques.

One-dimensional (1D) semiconducting nanostructures such as nanotubes and nanowires have attracted extensive attention because of their unique physical properties and potential applications. Therefore, the fabrication of nanotubular Ta<sub>2</sub>O<sub>5</sub> structures of high-aspect-ratio is expected to be promising for many applications.<sup>26–28</sup> That there is considerable interest in the field is indicated by recent reports on the fabrication of several forms of Ta<sub>2</sub>O<sub>5</sub> nanostructures such as nanoporous films,<sup>29,30</sup> nanodots,<sup>31</sup> nanodimples,<sup>32</sup> and hollow spheres.<sup>33</sup> However, the electrochemical fabrication of either Ta<sub>2</sub>O<sub>5</sub> nanorod or nanotube arrays appears not yet to have been

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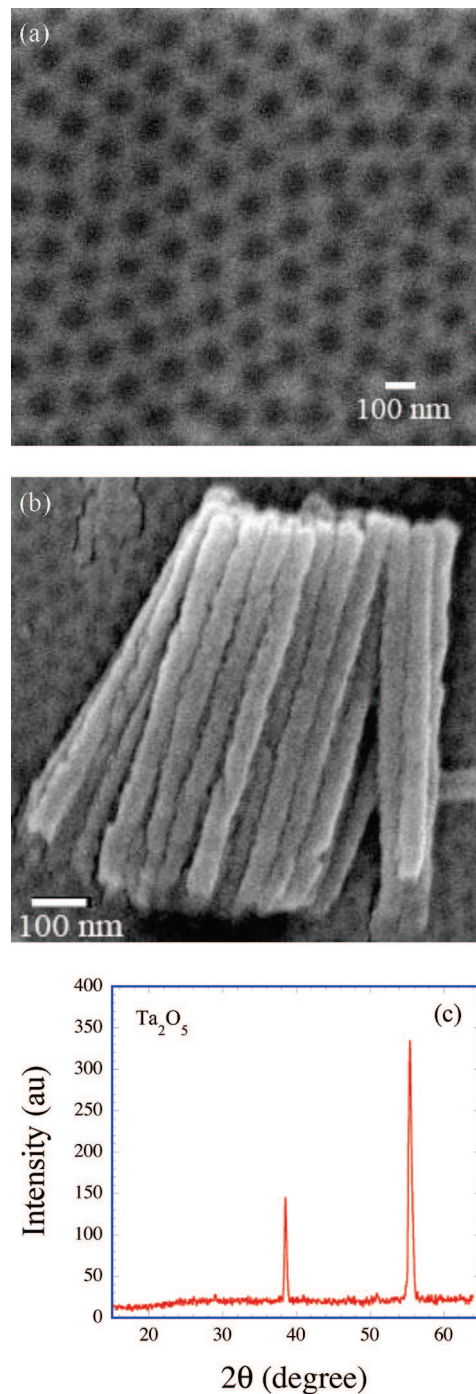
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reported. Herein, we report for the first time the fabrication of highly ordered vertically oriented nanotube arrays and robust nanotubular membranes of Ta oxide by one-step anodization of Ta foil in electrolytes containing concentrated HF and H<sub>2</sub>SO<sub>4</sub> with either ethylene glycol (EG) or dimethyl sulfoxide (DMSO).

Pure tantalum foil (99.9% purity, 0.25 mm thick) was purchased from Sigma Aldrich. Prior to anodization, samples were sonicated in acetone for 20 min followed by a deionized water rinse and then dried in a nitrogen stream. The anodization was performed using a two-electrode cell with tantalum foil as the working electrode and platinum foil as the counter electrode, under constant applied voltage at room temperature (approximately 22 °C). The distance between the two electrodes was kept at approximately 3 cm. Ta-foil sample sizes were 1 cm × 2 cm, with 1 cm × 1 cm immersed in the electrolyte. Electrolytes containing concentrated HF (48%) and H<sub>2</sub>SO<sub>4</sub> (98%) in the volumetric ratios 1:9 and 2:8 were studied. The effect of some additives such as H<sub>3</sub>PO<sub>4</sub> (0.05–0.1M), ethylene glycol (5–10 vol %) and dimethyl sulfoxide (5–10 vol %) were also examined. The time-dependent anodization currents were recorded using a computer controlled Keithley 2000 multimeter. Anodized sample morphology was examined using a JEOL JSM-6300 field-emission scanning electron microscope (FESEM). Crystalline phases were detected and identified by a glancing angle X-ray diffractometer (GAXRD) on a Philips X'pert MRD PRO X-ray diffractometer (Almelo, The Netherlands).

With stirred mixtures of concentrated HF and H<sub>2</sub>SO<sub>4</sub>, we were able to achieve nanodimpled tantala surfaces, pore diameters 40–55 nm, over the voltage range 10–20 V. Figure 1a shows an illustrative FESEM image of Ta surfaces anodized at 15 V for 10 min in an aqueous electrolyte of HF + H<sub>2</sub>SO<sub>4</sub> in the volumetric ratio 2:8. Close-packed hexagonal spacing of the pores is achieved, with the pore diameter increasing from ≈ 40 to 55 nm with increasing HF concentration (1:9 to 2:8 ratio). It is necessary to stir the electrolyte during anodization to obtain a patterned surface, otherwise a smooth surface is obtained.<sup>32</sup> In an approach analogous to that reported by Allam and co-workers,<sup>34</sup> we investigated the effect of the addition of H<sub>3</sub>PO<sub>4</sub> as a buffering medium in the concentration range 0.05–0.1 M by which we observed the formation of nanowire/nanorod arrays up to 1300 nm in length. Figure 1b shows a nanowire/rod bundle, from a mechanically fractured sample, obtained using a 1:9 vol. ratio of HF + H<sub>2</sub>SO<sub>4</sub> with 0.1 M H<sub>3</sub>PO<sub>4</sub> at 15 V. The as-anodized fabricated nanorod arrays are amorphous, subsequently crystallized by a high temperature anneal.



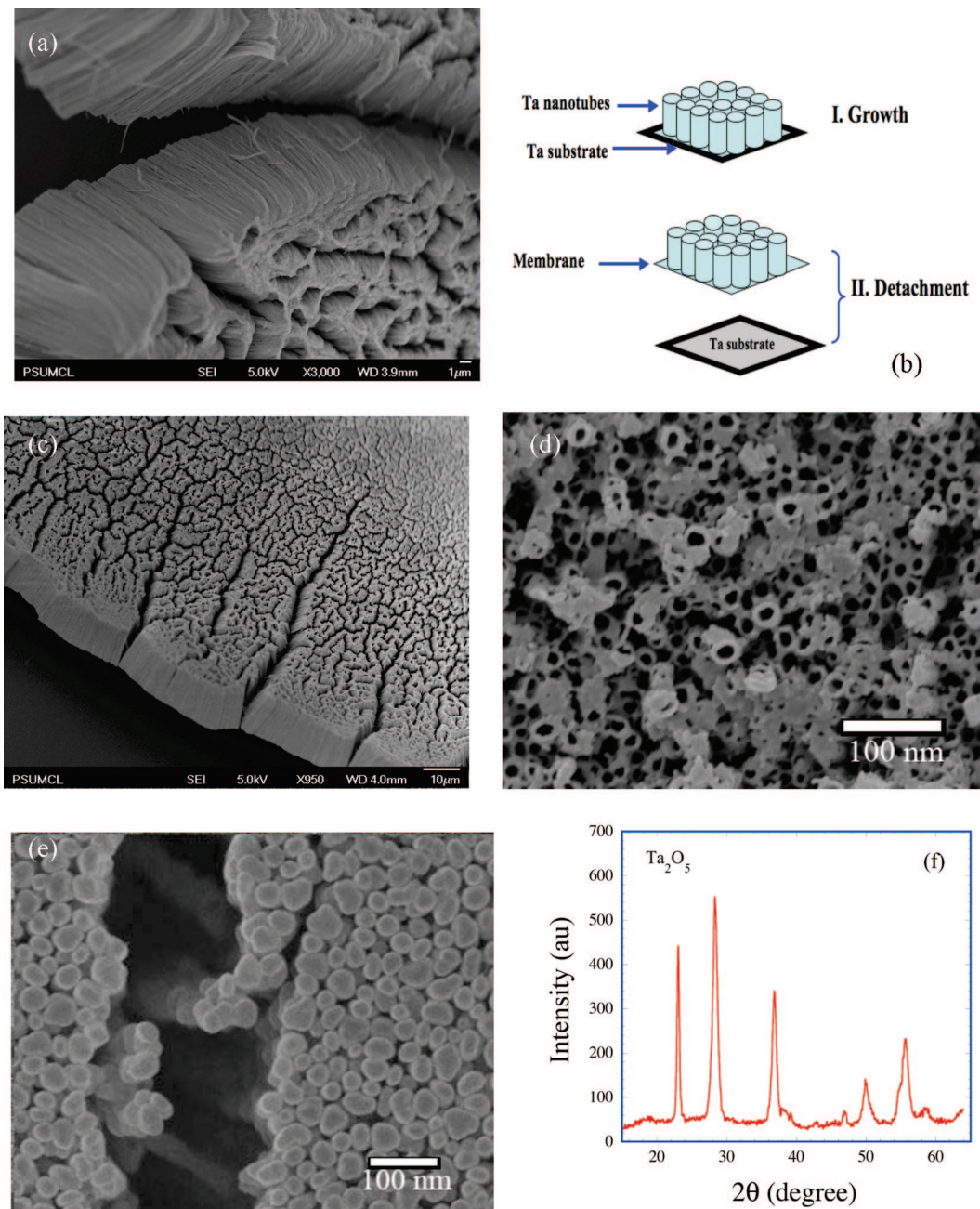
**Figure 1.** Illustrative FESEM micrograph of tantala film topology obtained upon anodizing Ta in (a) a stirred aqueous electrolyte containing HF + H<sub>2</sub>SO<sub>4</sub> (2:8 vol. ratio, 15 V); (b) HF + H<sub>2</sub>SO<sub>4</sub> (1:9) + 0.1 M H<sub>3</sub>PO<sub>4</sub> (15 V, cross-sectional view of mechanically fractured sample) independently of electrolyte stirring; (c) 2° glancing angle X-ray diffraction (GAXRD) pattern of sample (b) after annealing at 400 °C for 3 h in oxygen (up/down ramp rate of 1 °C/min).

Figure 1c shows the XRD of a sample annealed at 400 °C for 3 h in oxygen with an up/down ramp rate of 1 °C/min, with the peaks indicating formation of Ta<sub>2</sub>O<sub>5</sub>.

On the basis of our previous efforts using polar organic electrolytes for Ti anodization, see for example,<sup>35–38</sup> we investigated the effect of adding relatively low concentrations of either ethylene glycol (EG) or dimethyl sulfoxide (DMSO) to aqueous electrolytes containing mixtures of HF and H<sub>2</sub>SO<sub>4</sub>. We have achieved tantala nanotube arrays in electrolytes

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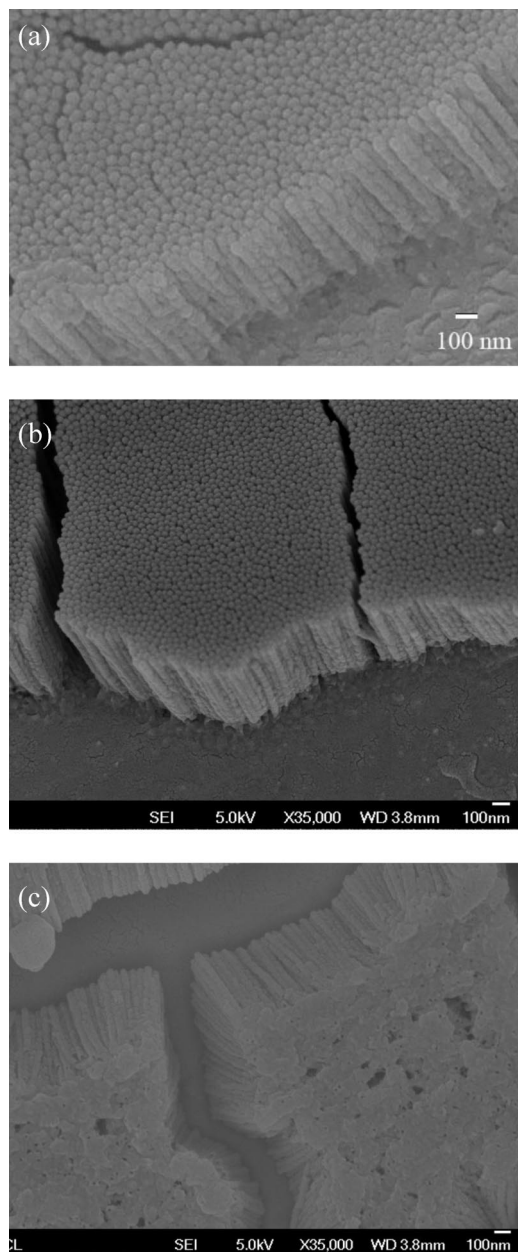


**Figure 2.** Illustrative FESEM images of surfaces obtained upon anodizing Ta in aqueous electrolytes containing HF + H<sub>2</sub>SO<sub>4</sub> (1:9) + 5% dimethyl sulfoxide at (a) 15 V sample mechanically fractured for viewing; (b) schematic illustration of the growth and detachment of the tantalum nanotube array membrane from the Ta substrate; (c) cross-sectional FESEM image of 20 V free-standing membrane; (d) 20 V, top surface of resulting self-standing membrane; (e) bottom of membrane obtained at 20 V; and (f) 2° glancing angle X-ray diffraction (GAXRD) pattern of a membrane sample annealed at 300 °C for 1 h in oxygen (ramp rate 1 °C/min).

containing concentrated HF and H<sub>2</sub>SO<sub>4</sub> in the volumetric ratio 1:9 in the presence of 5–10 vol % of either EG or DMSO over the voltage range 10–20 V. Anodization of Ta foil at 10, 12 and 15 V in electrolytes containing HF, H<sub>2</sub>SO<sub>4</sub>, and 5% DMSO for 20 min results in the formation of vertically oriented nanotube arrays of lengths 2.3, 7.5, and 11.1 μm, respectively. Figure 2a is a FESEM image of a mechanically fractured nanotube array sample obtained at 15 V. Anodization at 20 V, even for durations as short as a few minutes, results in tantalum oxide nanotube array membrane formation, see Figure 2b; these membranes, dried in nitrogen, remain flat. Figure 2c–e shows cross-sectional and back-side images of a tantalum nanotube array membrane.

Without disturbing their flatness, we crystallized the initially amorphous membranes via a 300 °C 1 h anneal in a pure oxygen environment, with glancing angle X-ray diffraction patterns (GAXRD) of a resulting sample shown in Figure 2f.

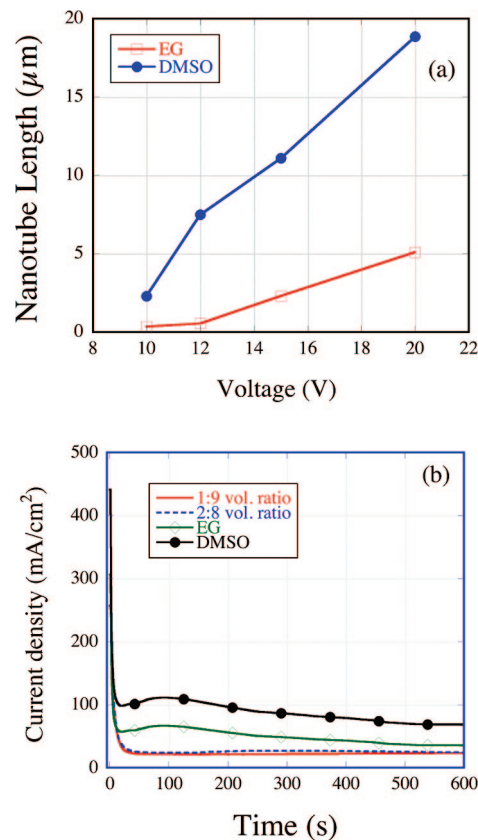
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**Figure 3.** FESEM image of tantalum surfaces achieved using an electrolyte containing HF + H<sub>2</sub>SO<sub>4</sub> (1:9) + 5 vol % ethylene glycol at: (a) 10, (b) 12, and (c) 15 V.

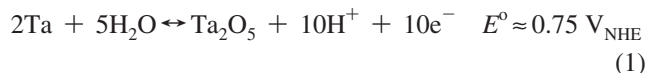
Figure 3a–c shows well-developed nanorod/nanotube arrays, with thicknesses up to 5.1  $\mu\text{m}$ , obtained by anodizing tantalum in aqueous electrolytes containing 1:9 HF+H<sub>2</sub>SO<sub>4</sub> and 5 vol % EG for 20 min at, respectively, 10, 12, and 15 V. Note that the resulting architectures at 10 and 12 V (images a and b in Figure 3) seem closer to that of rods than tubes. However, inspection of the structures obtained at 15 V shows that the surface, although coated with a thin layer of precipitate debris, has characteristic openings on the surface indicating nanotubular morphology. Anodization at 20 V for durations of 25 min or longer resulted in the detachment of the formed Ta oxide nanotube arrays in membrane form.<sup>39</sup>

The thickness of the nanotube/nanorod films are found to increase with increasing anodization voltage; Figure 4a shows the length of the resulting nanotubes as a function of



**Figure 4.** (a) Variation of nanotube length as a function of anodization voltage for samples fabricated in the presence of ethylene glycol (EG) and dimethyl sulfoxide (DMSO). (b) Anodization current–time response of Ta samples anodized in different electrolytes, either HF + H<sub>2</sub>SO<sub>4</sub> (1:9) + 5% EG, or HF + H<sub>2</sub>SO<sub>4</sub> (1:9) + 5% DMSO. Anodization time in all cases is 20 min.

anodization potential using electrolytes of either HF + H<sub>2</sub>SO<sub>4</sub> (1:9) + 5% EG, or HF + H<sub>2</sub>SO<sub>4</sub> (1:9) + 5% DMSO, with an anodization period of 20 min. Using our described one-step synthesis route Ta<sub>2</sub>O<sub>5</sub> nanotube membranes up to  $\sim 19 \mu\text{m}$  in length have been achieved. The anodization current–time response of samples anodized in electrolytes containing either EG or DMSO, Figure 4b, shows a characteristic shape including the classic dip-rise-gradual fall seen when nanotube arrays are achieved via anodization of Ti in aqueous HCl<sup>34</sup> or HF<sup>40</sup> solutions. Similar to Ti,<sup>34</sup> initially a compact oxide layer is formed through hydrolysis of tantalum:



This oxide layer leads to a dramatic decrease in the anodization current due to its poor electrical conductivity. Note that the current decreased drastically (Figure 4b) in a few seconds from an initial value of about 450 mA to about 50 mA in EG containing electrolytes and 100 mA in DMSO containing electrolytes. After that, Ta<sub>2</sub>O<sub>5</sub> starts to dissolve forming pores, leading to the observed slight increase in current with time. Under sufficient applied voltage magnitude the electric field will be strong enough to migrate the tantalum ions leaving behind voids in the interpore areas,

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which in turn will separate one pore from one another, leading to the formation of discrete tubes oriented vertically to the substrate.

Per detachment of the anodic film, we believe that this may be associated with fluoride ions incorporated into the anodic film. It was shown, during anodization of tantalum, that the inward mobility of fluoride ions is almost twice that of O<sup>2-</sup> ions,<sup>41</sup> leading to the formation of a thin layer of TaF<sub>5</sub> that separates the tantalum substrate from the growing anodic oxide film. This fluoride layer was shown to weaken the adherence of the resultant anodic film.<sup>41</sup>

### Conclusions

We report on the formation of various Ta<sub>2</sub>O<sub>5</sub> nanoarchitectures via potentiostatic anodization of Ta in aqueous electrolytes containing HF and H<sub>2</sub>SO<sub>4</sub> along with low concentrations of either ethylene glycol (EG) or dimethyl sulfoxide (DMSO). Our study showed that the formation of Ta<sub>2</sub>O<sub>5</sub> structures depends on the applied potential as well as the electrolyte composition. Nanodimpled tantalum surfaces, pore diameters 40–55 nm, were obtained upon anodizing Ta at 10–20 V in stirred electrolytes containing mixtures of HF (48%) and H<sub>2</sub>SO<sub>4</sub> (98%) in the volumetric ratios 1:9 and 2:8, with the pore diameter increasing with the amount of HF in the mixture. The addition of H<sub>3</sub>PO<sub>4</sub> as a buffering medium in the concentration range 0.05–0.1 M enables the fabrication of Ta<sub>2</sub>O<sub>5</sub> nanorods up to 1300 nm in length. High-aspect-ratio vertically oriented, Ta<sub>2</sub>O<sub>5</sub> nanotube array films and membranes were obtained upon the addition of 5–10 vol% of either EG or DMSO to electrolyte mixture containing HF and H<sub>2</sub>SO<sub>4</sub> (1:9). Upon anodizing Ta in aqueous electrolytes containing 5% EG, the resulting architectures at 10 and 12 V are closer to that of rods than tubes. However,

anodization at higher voltages, e.g. 15 V, resulted in nanotube formation. The addition of 5% DMSO to the HF and H<sub>2</sub>SO<sub>4</sub> (1:9) electrolyte enables fabrication of high-aspect-ratio nanotube arrays at anodization potentials ranging from 10 to 20 V, with the length of the nanotubes increasing with potential. Self-standing, mechanically robust nanotubular membranes up to 19  $\mu$ m in thickness are obtained at anodization voltages of 20 V. Stirring of the electrolyte was found to have no effect on nanotube array formation. On the contrary, we found that stirring led to faster detachment of the formed nanotube membranes at shorter lengths.

Considering the great utility of the vertically oriented nanotube array architecture in applications including water photoelectrolysis,<sup>42,43</sup> heterojunction solar cells,<sup>44</sup> drug delivery,<sup>45</sup> and gas sensing,<sup>46</sup> with recent review papers on the topic available,<sup>47,48</sup> the subject calls for more systematic studies at various concentrations of HF and H<sub>2</sub>SO<sub>4</sub> in the presence of other organic additives at different anodization potentials to gain more insight into the prevailing mechanisms.

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