

# Self-Standing Crystalline TiO<sub>2</sub> Nanotubes/CNTs Heterojunction Membrane: Synthesis and Characterization

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**ABSTRACT:** In the present study, we report for the first time synthesis of TiO<sub>2</sub> nanotubes/CNTs heterojunction membrane. Chemical vapor deposition (CVD) of CNTs at 650 °C in a mixture of H<sub>2</sub>/He atmosphere led to in situ detachment of the anodically fabricated TiO<sub>2</sub> nanotube layers from the Ti substrate underneath. Morphological and structural evolution of TiO<sub>2</sub> nanotubes after CNTs deposition were investigated by field-emission scanning electron microscopy (FESEM), glancing angle X-ray diffraction (GAXRD), and X-ray photoelectron spectroscopy (XPS) analyses.

**KEYWORDS:** TiO<sub>2</sub> nanotubes, CNTs, heterojunction, anodization, CVD

## INTRODUCTION

One dimensional nanostructures such as nanotubes exhibit unique properties because of their special geometry, high surface area and high aspect ratio paving the way for transferring ions, electrons, photons, gases, and fluids.<sup>1–6</sup> Although the electrical and mechanical properties of carbon nanotubes (CNTs) combined with their flexible nature<sup>7</sup> open a wide variety of applications in different areas, the photoactivity of TiO<sub>2</sub> nanotubes (TNTs) makes them promising candidates for use in solar cells,<sup>8</sup> water splitting,<sup>9</sup> sensors,<sup>10</sup> tissue engineering,<sup>11</sup> and drug delivery.<sup>12</sup> Among different synthesis methods, particular interest has been given to the anodic growth of TiO<sub>2</sub> nanotubes on Ti foil as it leads to the formation of an array of closely packed vertically aligned tubes.<sup>6</sup> However, in many applications, the use and performance of this material are limited by the fact that the nanotube layers are attached to the metallic Ti substrate.<sup>13</sup> For instance, although the application of anodically grown TiO<sub>2</sub>/Ti nanotubes in dye-sensitized solar cells (DSSCs) showed exciting results,<sup>13</sup> the use of crystallized freestanding TNT array membrane in dye-sensitized solar cells (DSSCs) showed a roughly 100% increase in the conversion efficiency compared to those grown on a Ti substrate.<sup>14</sup> Also, the employment of TNT arrays grown on Ti foil (usually opaque) in DSSCs applications requires back-side illumination (from the transparent cathode side) which is not an optimal approach for power conversion efficiency.<sup>14</sup> Therefore, several procedures are currently being used to detach TNT arrays from the Ti substrate through e.g. ultrasonication,<sup>15</sup> the selective dissolution of the supporting Ti substrate,<sup>16</sup> a reduction of anodization voltage at the end of the anodization process<sup>17</sup> and the application of a large voltage pulse for a short time.<sup>18</sup> Although recent reports demonstrate successful fabrication of relatively large surface area TNTs membranes,<sup>14</sup> they still suffer from low photoconversion efficiency due to the wide band gap of pure TiO<sub>2</sub> and most importantly the charge carrier recombination problems. Therefore, considerable efforts have been taken involving dye sensitizing, doping, and decoration of TiO<sub>2</sub> nanotubes by lower band gap nanoparticles and quantum dots.<sup>6</sup> However, except for solar cell application, dye

sensitizing is not applicable in most applications. Also, doping of TiO<sub>2</sub> nanotubes deteriorates the charge transfer properties by increasing defects as sites for electron–hole recombination.<sup>19</sup> Therefore, many efforts have been conducted to improve the electron transfer rate and reduce recombination percentage. By taking the benefits of flexible conductive carbon nanotubes, one can promote separation of photogenerated charge carriers and enhance electron transfer through the combination of CNT with TiO<sub>2</sub> nanotubes where the later play a crucial role in the vectorial charge transfer of carriers.<sup>10,19–23</sup> To this end, there are several reports in the literature on the synthesis of TiO<sub>2</sub> NTs/CNTs composites using the CVD technique.<sup>24,25</sup> Although synthesis and application of TiO<sub>2</sub> nanotubes<sup>14,17,26</sup> as well as carbon nanotubes (CNTs) membranes<sup>27</sup> were reported separately, to the best of our knowledge, there is no report in literature on the fabrication of heterojunction membrane of both TiO<sub>2</sub> NTs and CNTs. In the present study, in situ crystalline TiO<sub>2</sub> NTs/CNTs membrane was synthesized by CVD of CNTs on anodically grown TiO<sub>2</sub> nanotube arrays. The morphological and structural evolution of TiO<sub>2</sub> nanotube layers were investigated by SEM, EDX as well as XPS. We believe our work is important because it is expected to open a new perspective for advanced applications of the material in various applications such as solar energy conversion by taking the benefits of both TiO<sub>2</sub> NTs and CNTs.

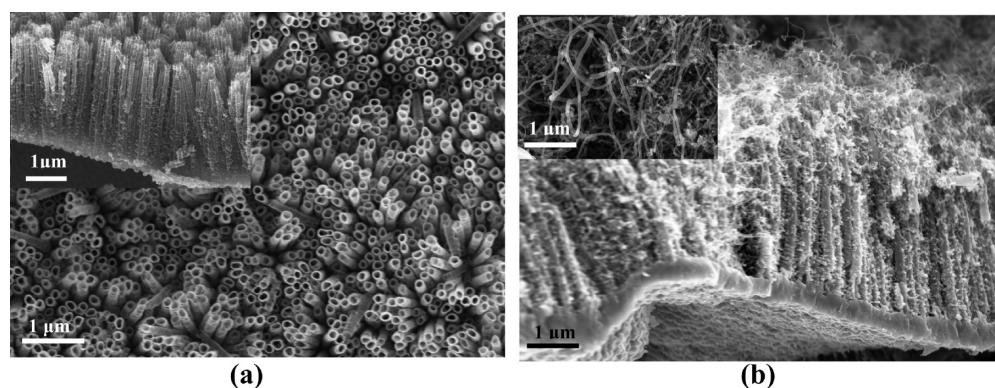
## EXPERIMENTAL SECTION

Prior to anodization, pure titanium foil samples (2.0 × 1.0 cm × 0.25 mm) were ultrasonically cleaned with ethanol followed by a deionized (D.I.) water rinse. The anodization was performed in a two-electrode electrochemical cell with the titanium foil as the working electrode and platinum foil as the counter electrode at room temperature (approximately 22 °C) at 20 V for 20 h in a formamide-based electrolyte containing 0.2 wt % NH<sub>4</sub>F and 5 vol %

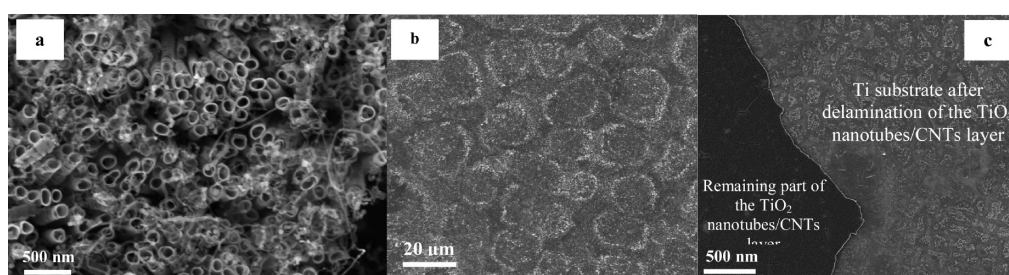
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**Figure 1.** FESEM image of top view and cross sectional view of anodically grown  $\text{TiO}_2$  nanotubes on Ti foil (a) before and (b) after chemical vapor deposition of CNTs at  $680^\circ\text{C}$ .



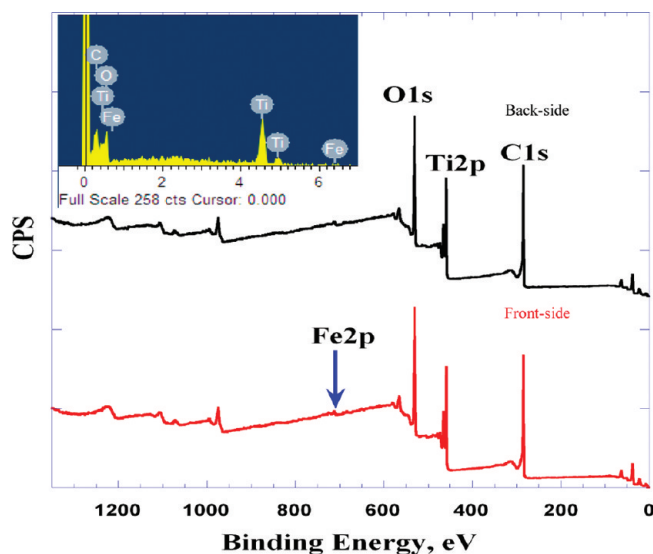
**Figure 2.** FESEM image of (a) top-view and (b) bottom-view of in situ formed  $\text{TiO}_2$  nanotubes membrane covered by CNTs grown at  $650^\circ\text{C}$ , and (c) accompanied top view SEM image of Ti substrate underneath and a remaining part of  $\text{TiO}_2$  nanotube/CNT layer.

$\text{H}_2\text{O}$ . Agilent E3612A DC power supply was used for potentiostatic anodization. After anodization, the samples were rinsed thoroughly with deionized water and then dried under a stream of nitrogen. Multiwall carbon nanotubes were grown by chemical vapor deposition on the previously grown titania nanotubes in a simplified hot-wall reactor at ambient pressure. In this process, the metal catalyst ferrocene was dissolved in a liquid hydrocarbon, Xylene, to form a feed solution with different ratios. This solution was delivered by a syringe pump to an injection tube and dispersed into a stream of hydrogen and helium. This vapor was transported into a hot quartz tube reactor at  $650^\circ\text{C}$  and  $680^\circ\text{C}$ . The morphology and structure of the fabricated samples were examined using a Zeiss SEM Ultra60 field-emission scanning electron microscope (FESEM), X-ray photoelectron spectroscopy (XPS) experiment using a Thermo Scientific K-alpha XPS with an Al anode. The crystalline phases were detected and identified by a glancing angle X-ray diffractometer (GAXRD) on an X'pert PRO MRD with Copper source.

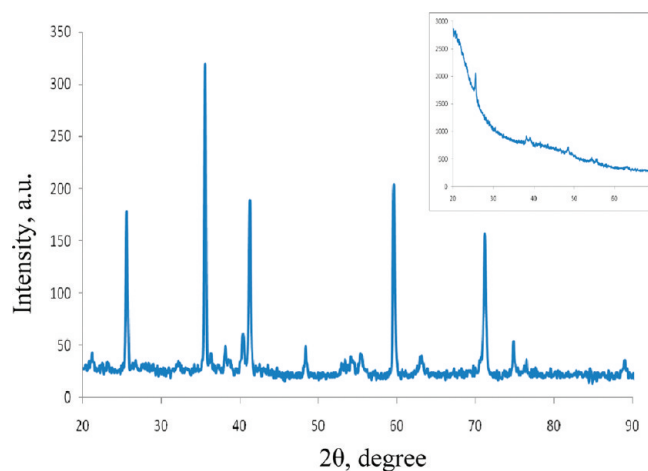
## RESULTS AND DISCUSSION

Figure 1a shows FESEM images of the anodically grown self-organized  $\text{TiO}_2$  nanotubes via the anodization of Ti foil in a formamide based electrolyte. Note that close-packed nanotube arrays  $\sim 3\ \mu\text{m}$  long are formed. Figure 1b shows FESEM top and cross-sectional view images of  $\text{TiO}_2$  nanotubes after the CVD of CNTs on their surfaces at  $680^\circ\text{C}$  for 90 min. The CNTs are fully covering the  $\text{TiO}_2$  nanotube surface, see inset image. Cross-sectional view of  $\text{TiO}_2$  NTs/CNTs heterojunction shows that the  $\text{TiO}_2$  nanotubes retained their structure and length ( $\sim 3\ \mu\text{m}$ ) even after the CNT growth at  $680^\circ\text{C}$ . Although it was shown that short  $\text{TiO}_2$  nanotubes with lengths of  $400\ \text{nm}$ <sup>28</sup> and  $320\ \text{nm}$ <sup>10</sup> are not stable at annealing

temperatures  $>580^\circ\text{C}$ , in the present study, nanotubes with  $\sim 3\ \mu\text{m}$  length survived at  $680^\circ\text{C}$ . Very recently, Allam and Elsayed<sup>29</sup> reported that the tubular structure of  $7\ \mu\text{m}$  long  $\text{TiO}_2$  nanotube does not collapse even upon annealing at temperatures  $>600^\circ\text{C}$ . Accordingly, the tube length seems to be a crucial factor determining the thermal stability. A more precise examination of  $\text{TiO}_2$  NTs/CNTs shows delamination of free-standing nanotube layers from Ti substrate. Figure 1b shows  $\text{TiO}_2$  NTs layers detached from the Ti substrate underneath after the CVD of CNTs at  $680^\circ\text{C}$ . This process led to in situ formation of free-standing  $\text{TiO}_2$  NTs/CNTs heterojunction structure. Although, in most cases, delamination of  $\text{TiO}_2$  nanotube layer from the Ti substrate is not desired, herein we used the delamination during the CVD process to fabricate a free-standing membrane. Chemical reaction of Ti substrate with hydrogen during the CVD of CNTs and thermal stresses developed between oxide barrier layer and Ti substrate due to the mismatch between coefficient of thermal expansion of oxide layer and Ti substrate during heating/cooling can be considered as the main reasons for delamination.<sup>30</sup> Although delamination occurred at  $680^\circ\text{C}$ , the high CVD temperature and relatively long deposition time led to distortion of Ti substrate and full coverage of  $\text{TiO}_2$  nanotubes with CNTs that can decrease the exposed active surface area of  $\text{TiO}_2$  nanotubes and consequently diminishes its photoconversion efficiency. Additionally, the membrane was not completely detached from the surface. When the deposition temperature decreased to  $650^\circ\text{C}$  (roughly minimum temperature needed to grow CNTs) and the amount of ferrocene as well as deposition time decreased to  $0.001\ \text{g/mL}$  and 40 min, respectively, a reasonable decrease in the amount of CNTs on the  $\text{TiO}_2$  nanotube surface was obtained. Figure 2a shows a top-view image of in situ formed  $\text{TiO}_2$  nanotubes/CNTs membrane completely separated from Ti substrate. As seen, not only the CNTs but



**Figure 3.** XPS analysis of front and back side of in situ formed membrane of  $\text{TiO}_2$  nanotubes covered by CNTs grown at  $650^\circ\text{C}$  and accompanied EDX analysis of front-side of the membrane.



**Figure 4.** (a) X-ray diffraction pattern of  $\text{TiO}_2$  nanotubes/CNTs attached to the Ti substrate underneath and (b) glancing angle X-ray diffraction pattern of the detached  $\text{TiO}_2$  NTs/CNTs membrane.

also the  $\text{TiO}_2$  nanotubes can obviously be observed. Under this condition, a high surface area of  $\text{TiO}_2$  nanotubes can absorb sunlight, while CNTs can accelerate transfer of photogenerated electrons, leading to reduction of electron–hole recombination.<sup>10</sup> Interestingly, although Pang et al.<sup>10</sup> reported collapse and sintering of short  $\text{TiO}_2$  nanotubes during CVD of CNTs at  $700^\circ\text{C}$ , they reported a remarkably enhanced conductivity and electron transfer due to the CNTs-embedded in  $\text{TiO}_2$  substrate. Herein, an optimum combination of  $\text{TiO}_2$  nanotubes and CNTs is expected to lead to even higher photoconversion efficiency, reduced electron–hole recombination, and facile electron transfer.<sup>19–23</sup>

Figure 2b shows the back view of the in situ formed  $\text{TiO}_2$  NTs/CNTs membrane. Figure 2c shows the Ti substrate after delamination of the membrane layer. Note that the back side of the obtained membrane is a replica of the Ti substrate. FESEM examination of the formed membrane shows the presence of some scattered nanoparticles. Figure 3 shows the EDX analysis

of those nanoparticles indicating the presence of iron. The source of iron is the ferrocene that is used for catalytic nucleation of CNTs. To have a better insight on the  $\text{TiO}_2$ /CNTs membrane composition, XPS analysis was conducted on front and back sides of the in situ formed membrane. As seen in Figure 3, although the iron exists on the front-side of  $\text{TiO}_2$ NTs/CNTs membrane, no iron was detected on the backside, confirming the growth of CNTs on  $\text{TiO}_2$  nanotubes. Another very important point to consider is the crystalline nature of the membrane. Although many efforts have been previously done to separate  $\text{TiO}_2$  NTS layer from the Ti substrate, the obtained membranes are always amorphous which limits their application in many fields. To crystallize those amorphous membranes, they have to be annealed at high temperatures for long time which usually led to deterioration of their structure. However, in the present study we were able to crystallize the membrane during its fabrication in a mixture of hydrogen and helium gases (Figure 4). Note that the diffraction peak at  $2\theta \approx 25^\circ$  can be assigned to anatase (101)<sup>29</sup> with no observed reflection for rutile. This adds to the value of the fabricated membrane as anatase is the most photoactive polymorph of titania.<sup>29</sup> Note also that Mahajan et al.<sup>31</sup> reported higher photocurrent of annealed  $\text{TiO}_2$  NTs in hydrogen than those annealed in an oxygen atmosphere.

The results of the present study are promising for development of heterojunction membrane composed of  $\text{TiO}_2$  nanotubes and CNTs. The newly generated heterojunction membranes are expected to be used for dye-sensitized solar cells, water splitting, water purification and desalination, sensors, biofilters, and a wider range of other applications.

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