

# Anatase Titanium Dioxide Coated Single Wall Carbon Nanotubes Manufactured by Sonochemical-Hydrothermal Technique

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## ABSTRACT

A novel, cost effective, sonochemical-hydrothermal technique was used for the deposition of nanosized anatase titanium dioxide (TiO<sub>2</sub>) onto single wall carbon nanotubes (SWCNTs). This technique is described and the characterization of the synthesized TiO<sub>2</sub>-SWCNTs is reported. The characterization techniques employed include scanning electron microscopy (SEM), Raman spectroscopy, and X-ray diffraction (XRD). From the characterization the size and morphology of the synthesized TiO<sub>2</sub> nanoparticles (deposited on the SWCNTs) are reported. Furthermore, it is demonstrated that the created TiO<sub>2</sub> nanoparticles are chemically attached to the SWCNTs. Also, an important correlation between calculated TiO<sub>2</sub> crystal size and the red shifts in the lowest Raman TiO<sub>2</sub> (E<sub>g</sub>) predominate peak is reported. The synthesized TiO<sub>2</sub>-SWCNTs have potential for large scale production and application in a variety of new technologies such as clean energy power generation devices, electrical storage devices, photocatalysts, and sensors.

**Keywords:** SWCNT; Sonochemical; Hydrothermal; Nanoparticle; Single Wall Carbon Nanotube; TiO<sub>2</sub>

## 1. Introduction

The benefits of coating nanosized titanium dioxide (TiO<sub>2</sub>) onto the surface of carbon nanotubes (CNTs) is of great scientific interest as nanoparticles often exhibit different physical and chemical properties, as the size of the material becomes smaller and smaller, relative to their bulk material counterparts. This interesting shift in particle properties is largely due to the large surface area and surface to volume ratio of the material, which dominates the contributions made by the small bulk of the material [1]. Some of the unique size-dependent properties of nanomaterials include quantum confinement in semiconductor particles (movement of electrons and holes in semiconductor materials) and transport properties related to phonons and photons [2-5]. Properties also vary as the shapes of the nanomaterials differ [6,7]. It is because of the access to this new realm of physical and chemical properties that substantial research efforts in nanoscience and nanotechnology have been dedicated [8-10].

Titanium dioxide coated carbon nanotubes (TiO<sub>2</sub>-CNTs)

are currently being developed and considered for many applications, where nanoparticle (TiO<sub>2</sub>) are presently used, such as sensors, photovoltaics, and photocatalysts. The beneficial pairing of nanoparticle TiO<sub>2</sub> with CNTs, or more particularly the pairing of TiO<sub>2</sub> with single-wall carbon nanotubes (SWCNTs), is the enhancement of the many unique properties of unmodified nanosized TiO<sub>2</sub>. SWCNTs possess excellent mechanical properties, large surface areas, one dimensional electron transport properties, and allow for surface chemical modifications to control the type of bonds that can be formed with TiO<sub>2</sub>. Additionally, the TiO<sub>2</sub>-SWCNT interface results in a unique quantum effect to provide trap states for electrons. This is an useful technique, known as the Schottky barrier, where there is a space-charge separation region that functions to increase recombination times for electron-hole pairs. [11] Essentially, by this method, the formation of a Schottky barrier results in the TiO<sub>2</sub> having an excess positive charge and the SWCNT having an excessive negative charge. Thus, the nanosized TiO<sub>2</sub> preferentially captures generated free electrons, via redox mechanisms, from the surrounding environment (*i.e.* transfer of

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electrons from electrolyte solution in a solar cell, or the transfer of electrons from the oxidation of an organic species in a photocatalytic oxidation cell). Furthermore, SWCNTs have a large electron-storage capacity of one electron for every 32 carbon atoms [12]. Therefore, they easily accept photon-excited electrons in from  $\text{TiO}_2$ , thus hindering the recombination. For applications that require UV light (such as photovoltaic and photocatalytic) it is proposed that CNTs may also act as a photosensitizer for the  $\text{TiO}_2$  [13]. Since UV light represents only 5% of the total sunlight spectrum, being able to capture a larger portion of the spectrum is advantageous. It has also been reported that the carbon-oxygen-titanium bond extends the light absorption to longer wavelengths, thus also leading the potential improvements in efficiency.

Various methods of synthesizing  $\text{TiO}_2$ -CNTs have been reported. Generally, most of these processes are either time consuming, cumbersome, expensive, lack the control for the deposition  $\text{TiO}_2$ , and/or produce inferior results. A list of some of these processes include sol-gel [14-18], sol [19,20], hydrothermal [21,22], solvothermal [23], electrochemical oxidation [24], electrochemical deposition [25,26], electrophoretic co-deposition of  $\text{TiO}_2$ -CNT films and deposition of  $\text{TiO}_2$  onto CNT [27-29], alternative methods of sonochemical [30,31], chemical vapor deposition [32-36], and heterogeneous coagulation [37-40].

The advantages of using the novel sonochemical-hydrothermal technique to prepare titanium dioxide-coated carbon nanotubes ( $\text{TiO}_2$ -CNTs) include low cost and readily available: 1) manufacturing equipment (sonicator, autoclave, and furnace); and 2) chemical precursors (aqueous titanium(III) sulfate and carbon nanotubes). Additionally, the technique is easy and relatively quick, producing chemically attached, uniformly dispersed,  $\text{TiO}_2$  encapsulated CNTs.

## 2. Experimental Procedures and Testing Apparatus

### 2.1. Synthesis of $\text{TiO}_2$ -SWCNTs

The synthesis of the  $\text{TiO}_2$ -SWCNTs started by loading 10 mg of SWCNTs into a 50 mL conical bottom polypropylene centrifuge tube. Next, 20 ml of 0.38 M titanium(III) sulfate solution was added. The centrifuge tube with the SWCNTs and solution was then placed in a test tube rack under a sonicator probe horn that is mounted on a ring stand. The sonicator used is a Qsonica ultrasonic cell disruptor, model Q125 by Misonix, equipped with a 1/8" diameter probe and operating at a frequency of 20 kHz. The probe tip was immersed into the solution and a power of 1 W/mL was utilized. Samples were exposed for set amount of times to achieve desired amount

of  $\text{TiO}_2$  deposition. After sonification was complete the tube containing the synthesized  $\text{TiO}_2$ -SWCNT in titanium(III) solution was centrifuged at 3500 RPM for 1 hour. The tube was then removed from the centrifuge and the liquid supernatant was decanted from the  $\text{TiO}_2$ -SWCNTs that were dropped to the bottom of the container. The  $\text{TiO}_2$ -SWCNTs were then washed by adding 20 mL of deionized water and exposing to ultrasound sonication for a duration of 3 minutes at a power of 1 W/mL to re-suspend the  $\text{TiO}_2$ -SWCNTs. The tube was then re-centrifuged at 3500 for 1 h, the liquid decanted and replaced with clean deionized water, and then re-suspended by sonication for 3 minutes at a power of 1 W/mL. This wash procedure was repeated 2 more times. The  $\text{TiO}_2$ -SWCNTs were stored in water in the centrifuge tubes until ready for characterization.

It was determined by Raman analysis that an amorphous form of  $\text{TiO}_2$  was deposited on the surface of the SWCNTs via this sonochemical process. It is of interest to convert amorphous (poorly crystallized) forms of deposited  $\text{TiO}_2$  to their corresponding ordered anatase crystal structure. For this conversion, a hydrothermal calcination process was used. Here, 10 mg of the  $\text{TiO}_2$ -SWCNT reaction product and 10 mL of deionized water were placed in 23 mL Teflon<sup>®</sup> lined, high pressure stainless steel digestion bomb, utilized as an autoclave. The autoclave was loaded into a furnace for 8 h at 250 degrees C to achieve hydrothermal calcination of the  $\text{TiO}_2$ -SWCNT product. Upon completion the finished autoclaved samples were cooled to ambient and stored in the deionized water.

### 2.2. Scanning Electron Microscopy (SEM)

The morphology of pristine SWCNTs and  $\text{TiO}_2$ -SWCNTs (2 h sonication) were characterized by scanning electron microscopy (S 4800 SEM, Hitachi Co., Tokyo, Japan). The pristine SWCNT sample for this analysis was prepared by ultrasonic dispersion in isopropanol followed by deposition onto a conductive porous silver membrane. The  $\text{TiO}_2$ -SWCNTs (stored in water from the synthesis step) were prepared for analysis by homogeneously dispersing in water followed by deposition onto a conductive porous silver membrane. A small sample was cut from this prepared composite and adhered via conductive tape to the microscope stage. Once the sample was staged it was then loaded into the microscope for analysis.

### 2.3. Raman Spectroscopy

Sample spectra were obtained using a Thermo Scientific Nicolet Almega XR Dispersive Raman Spectrometer equipped with an Olympus BX-51 research microscope.

Raman spectra analysis was conducted on samples from 100 to 4000  $\text{cm}^{-1}$  with the laser operating at 532 nm at 100% of 150 mW with the beam going through the microscope equipped with a MPlain 10X BD objective.

## 2.4. X-Ray Diffraction (XRD)

X-ray diffraction (XRD) data was collected by using a Rigaku Miniflex, with  $\text{CuK}\alpha$  radiation of 40 kV/4 mA,  $\lambda = 1.5406 \text{ \AA}$ . For pristine SWCNTs, the sample was prepared by deposition of SWCNTs on a silver membrane filter as described above for the SEM analysis. A small sample was cut from this prepared composite and the scan was ran from  $2\theta = 10^\circ$  to  $40^\circ$ . For the remaining samples ( $\text{TiO}_2$ -SWCNTs), measured as dry powders, preparation consisted filling the powder sample dish and loading into the diffractometer. The collected scans were obtained from a range of  $2\theta = 20^\circ$  to  $75^\circ$ .

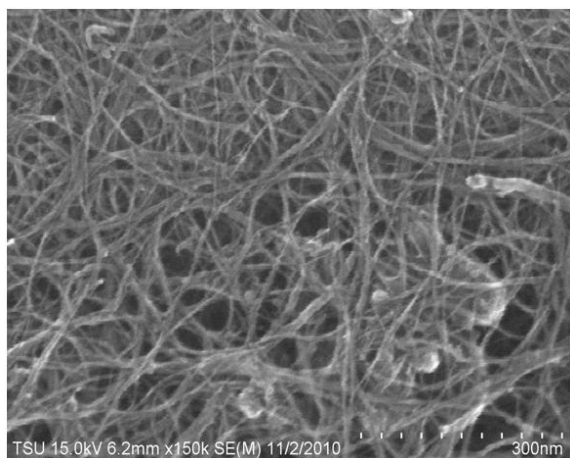
## 3. Results and Discussion

### 3.1. Characterization of Pristine SWCNT

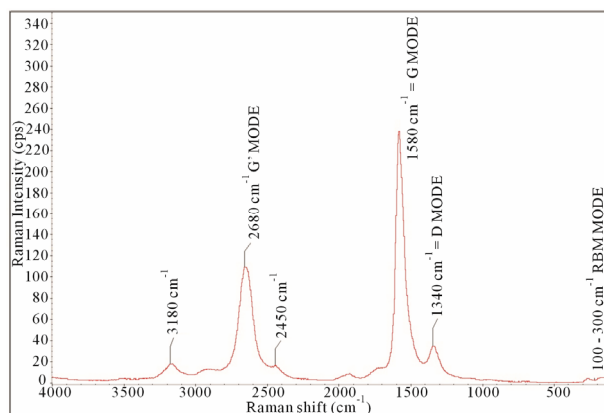
The first point of reference is **Figure 1** that depicts the SEM image of dispersed SWCNTs deposited on a silver membrane filter at 150 k magnification.

From the SEM image it is demonstrated that the SWCNTs show a superstructure that exhibits a high degree of entanglement between the bundles of tubes. This can be accounted for by the report that SWCNTs allow for remarkable Van der Waals interactions due to their smooth, uniform surfaces in close proximities. Thus, the majority of the tubes are bundled via direct van der Waals attractions along their entire lengths [41]. These SEMs are in good agreement with similar reports published in the literature [42-48].

The Raman spectrum for the SWCNTs is shown in **Figure 2**.



**Figure 1.** SEM image of pristine SWCNT deposited on a silver membrane filter at 150 k magnification.

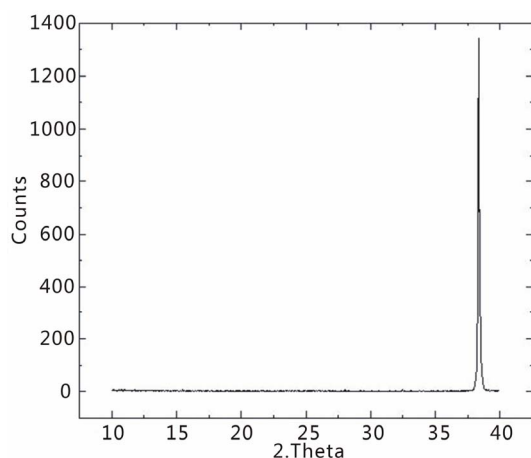


**Figure 2.** Raman spectrum of pristine SWCNTs.

As reported by Eklund, five peaks centered at around 1340  $\text{cm}^{-1}$  (D mode), 1580  $\text{cm}^{-1}$  (G mode), 2450  $\text{cm}^{-1}$ , 2680  $\text{cm}^{-1}$  (G' mode), and 3180  $\text{cm}^{-1}$  are due to SWCNTs [49]. These five peaks are clearly visible and labeled in the spectrum. Here the three predominate modes include the D, G, and G' modes. The D mode (1340  $\text{cm}^{-1}$ ) originates from structural defects and is present in all graphite-like carbons. The G mode (1580  $\text{cm}^{-1}$ ) corresponds to planar vibrations of carbon. The position of the G band confirms that the sample is mainly composed of single wall carbon nanotubes [49]. The G' mode (2680  $\text{cm}^{-1}$ ) is the second overtone of the D mode, which makes the name misleading. It is given because it is usually the second strongest mode in graphite. It is reported that the diameter of the SWCNT influences the position of the G' mode, thus a rough estimate of tube diameter can be deduced (this information is not reported in this study) [50]. Two additional modes worth noting include the radial breathing mode and the bundling mode. The radial breathing mode is the result of the expansion and contraction that occurs across the radial cross section in the nanotubes, typically occurring in the 100 to 350  $\text{cm}^{-1}$  range [51,52]. A special form of the radial breathing mode, the bundling mode, is reported to originate from the collective vibration in a bundle of SWCNTs [53]. It is apparent from **Figure 2** that there is a percentage of the SWCNTs that are bundled.

XRD was performed for SWCNTs deposited on a silver membrane filter as shown in **Figure 3**.

A single peak centered at  $2\theta = 38.36^\circ$  is identified as silver from the membrane filter support and agrees with published literature [54]. There are no peaks for SWCNTs because crystal plains are non-existent. It is worth noting, from the lack of MWCNT spectral lines, that the CNTs evaluated are confirmed to be of single wall configuration [55-57]. MWCNTs are reported to have a peak at  $2\theta = 26.06^\circ$ , corresponding to the inter-planar spacing of 0.342 nm between the tubes [58]. This



**Figure 3.** XRD spectrum of SWCNTs deposited on a silver membrane filter.

spectrum is used for comparison against  $\text{TiO}_2$ -SWCNTs spectra.

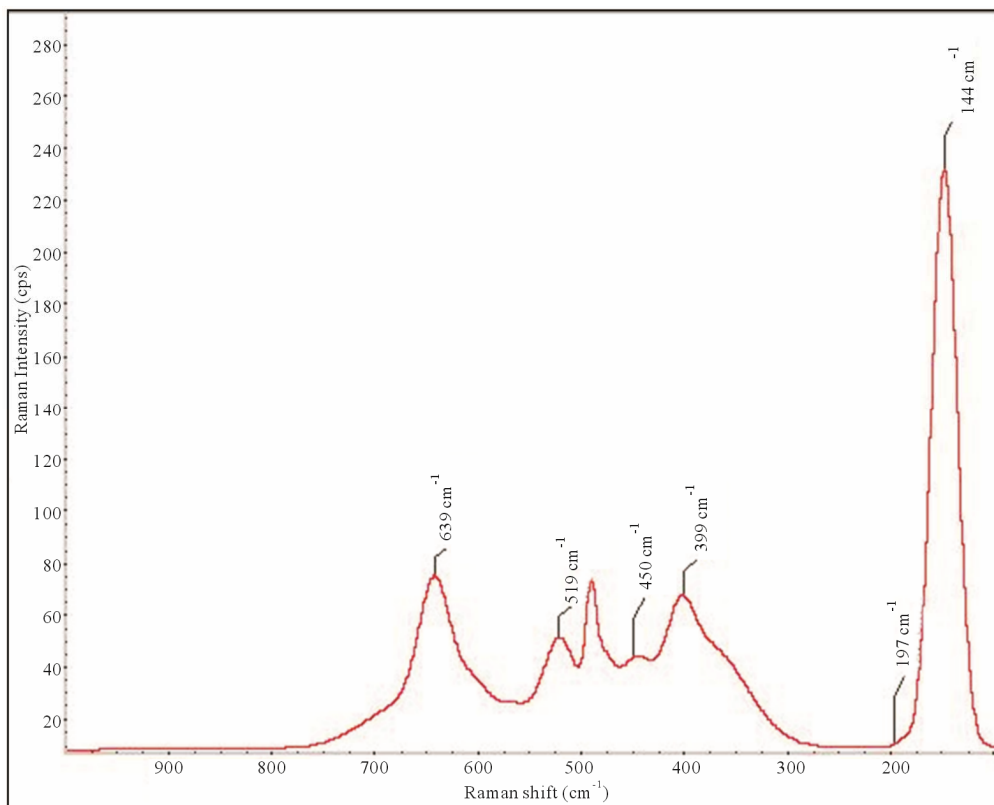
### 3.2. Characterization of P25

The Raman spectra for P25 (a commercially produced nanosized  $\text{TiO}_2$  from Evonik) is shown in **Figure 4**.

The six Raman active modes,  $A_{1g} + 2B_{1g} + 3E_g$ , for anatase  $\text{TiO}_2$  that have been reported in the literature are

detected at  $144\text{ cm}^{-1}$  ( $E_g$ ),  $197\text{ cm}^{-1}$  ( $E_g$ ),  $399\text{ cm}^{-1}$  ( $B_{1g}$ ),  $513\text{ cm}^{-1}$  ( $A_{1g}$ ),  $519\text{ cm}^{-1}$  ( $B_{1g}$ ), and  $639\text{ cm}^{-1}$  ( $E_g$ ), [59] and the peaks at  $250$ ,  $450$ , and  $620\text{ cm}^{-1}$  are due to the Ti-O-Ti bond of rutile spectrum [60]. The characteristic bands for brookite (not found in this study) are reported at  $128$ ,  $135$ ,  $153$ ,  $172$ ,  $195$ ,  $214$ ,  $247$ ,  $288$ ,  $322$ ,  $366$ ,  $396$ ,  $412$ ,  $454$ ,  $461$ ,  $502$ ,  $545$ ,  $585$ , and  $636\text{ cm}^{-1}$  [61]. In the spectra for P25, five anatase crystal peaks were detected at  $144\text{ cm}^{-1}$ ,  $197\text{ cm}^{-1}$ ,  $399\text{ cm}^{-1}$  ( $B_{1g}$ ), and  $639\text{ cm}^{-1}$ . One rutile peak can be seen at  $450\text{ cm}^{-1}$ . The positions and intensities of the Raman active modes correspond well with the percent of anatase phase of  $\text{TiO}_2$  relative to the percent of rutile. The spectrum agrees with the P25 spectrum published by Parussulo. [62] The full width at half maximum (FWHM) of the strongest peak ( $144\text{ cm}^{-1}$ ) is  $27.0\text{ cm}^{-1}$  correlating to the manufactures reported  $21\text{ nm}$  crystallite size.

XRD of P25 nanoparticle was ran from  $2\theta = 20^\circ$  to  $75^\circ$ . Anatase  $\text{TiO}_2$  has diffraction peaks at  $2\theta = 25.18^\circ$  (strongest peak),  $37.78^\circ$ ,  $48.00^\circ$ ,  $53.89^\circ$ ,  $54.99^\circ$ ,  $62.57^\circ$ ,  $68.68^\circ$ ,  $70.15^\circ$ , and  $75.01^\circ$ , corresponding to the reflections from  $101$ ,  $004$ ,  $200$ ,  $105$ ,  $211$ ,  $204$ ,  $116$ ,  $220$ , and  $215$  crystal planes [63]. The strongest peaks for rutile and brookite are at  $2\theta = 27.5^\circ$  for the  $110$  crystal plane and  $2\theta = 30.8^\circ$  for the  $121$  crystal plane of rutile and brookite respectively. [64] The spectrum is shown in **Figure 5**.



**Figure 4.** Raman spectrum for P25.

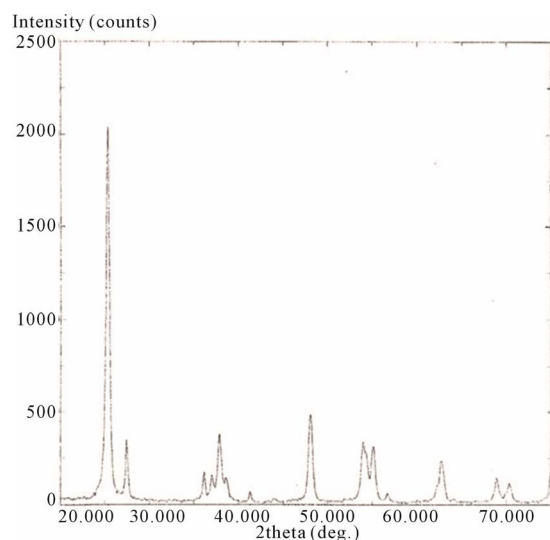


Figure 5. XRD spectrum of P25.

Here, the spectrum shows predominately anatase  $\text{TiO}_2$  with the necessary diffraction peaks at  $2\theta = 25.18^\circ$  (strongest peak),  $37.78^\circ$ ,  $48.00^\circ$ ,  $53.89^\circ$ ,  $54.99^\circ$ ,  $62.57^\circ$ ,  $68.68^\circ$ ,  $70.15^\circ$ , and  $75.01^\circ$ . The remaining peaks are due to the rutile structure. The integrated intensities of the strongest peak of both anatase ( $I_{a,101}$  at  $25.4^\circ$ ) and rutile ( $I_{r,110}$  at  $27.5^\circ$ ) were used to calculate the percentage of rutile and anatase according to the formulas:  $W_r(\%) = I_r / (0.8844I_a + I_r) \times 100$  and  $W_a(\%) = 100 - W_r(\%)$  [65]. The values indicate a composition of 78.8 % anatase and 21.2% rutile. Additionally, the average crystal diameter was calculated from the largest peak by the Scherrer's equation which is  $B = K\lambda / \beta \cos\theta$  where  $B$  is the crystalline size, in nm;  $\lambda$  is the wavelength for the radiation used, which is  $1.54056\text{\AA}$  for Cu;  $\beta$  is the full width at half maximum intensity (FWHM);  $\theta$  is the angle for the XRD maximum peak and the shape factor,  $K$  is 0.93 [66]. This value is 20.3 nm and agrees well with the published value of 21 nm.

### 3.3. Characterization of Sonochemical Synthesized $\text{TiO}_2$ -SWCNTs

This portion of the study was conducted in order to characterize and determine a profile for increasing sonication exposure times for the deposition of  $\text{TiO}_2$  onto SWCNTs. Sonochemical deposition times of 10 minute, 20 minute, 30 minute, and 2 h were performed and investigated.

Figure 6 shows the SEM for  $\text{TiO}_2$  deposited on SWCNT at a deposition time of 2 hours.

From the micrograph microscopy image it is clear that the entangled superstructure and, clearly demonstrates the nanosized  $\text{TiO}_2$  that has been successfully decorated on the SWCNTs. It is noted that homogeneous deposition of

both agglomerates of small  $\text{TiO}_2$  particles and isolated grains appear to be deposited on the SWCNTs. This is in agreement with findings reported by Yao [67].

Figures 7-10 depict the Raman spectrum of the manu-

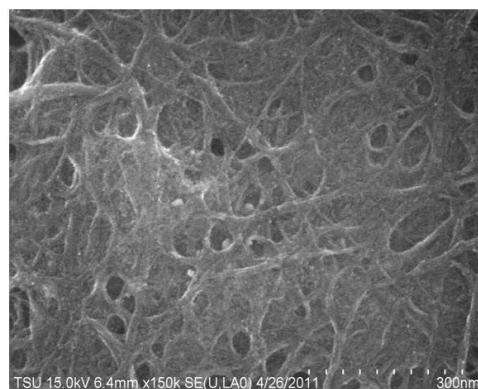


Figure 6. SEM image of 2 h sonochemical deposition of  $\text{TiO}_2$  on SWCNT at 150 k magnification.

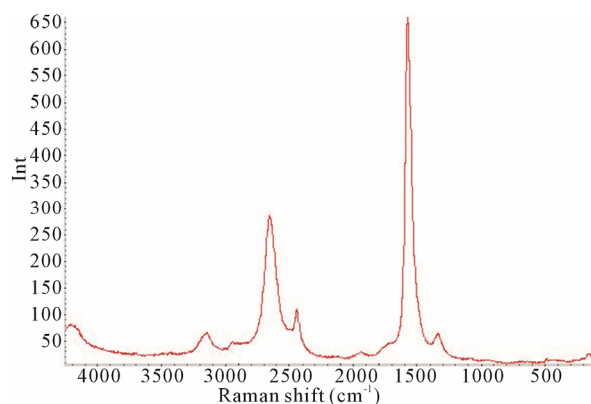


Figure 7. Raman spectrum of the synthesized  $\text{TiO}_2$ -SWCNTs at deposition time of 10 minute exposure to sonication with no hydrothermal treatment (Y-axis is Raman intensity, CPS).

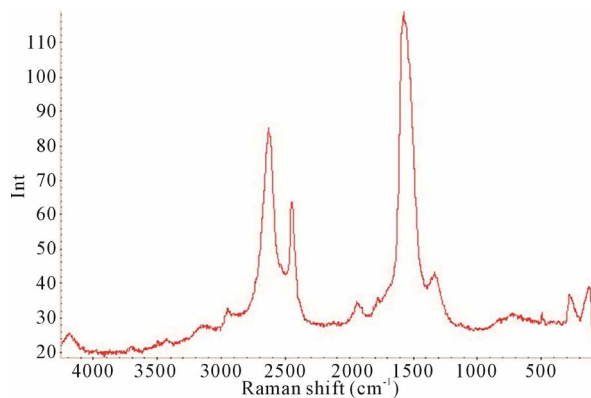
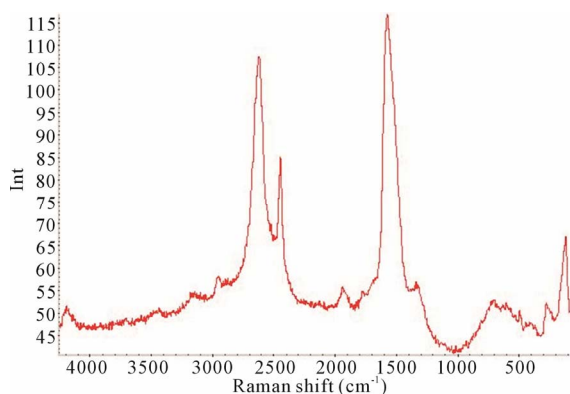
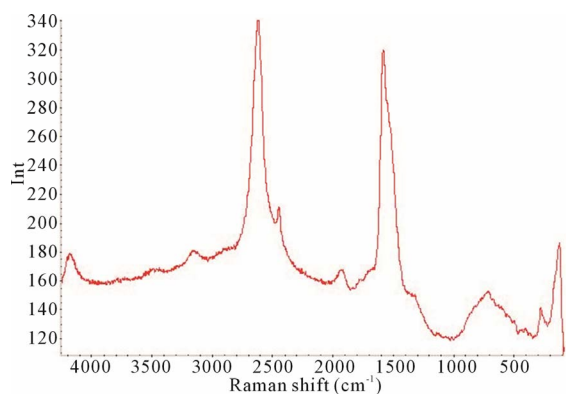


Figure 8. Raman spectrum of the synthesized  $\text{TiO}_2$ -SWCNTs at deposition time of 20 minute exposure to sonication with no hydrothermal treatment (Y-axis is Raman intensity, CPS).



**Figure 9.** Raman spectrum of the synthesized  $\text{TiO}_2$ -SWCNTs at deposition time of 30 minute exposure to sonication with no hydrothermal treatment (Y-axis is Raman intensity, CPS).



**Figure 10.** Raman spectrum of the synthesized  $\text{TiO}_2$ -SWCNTs at deposition time of 2 h exposure to sonication with no hydrothermal treatment (Y-axis is Raman intensity, CPS).

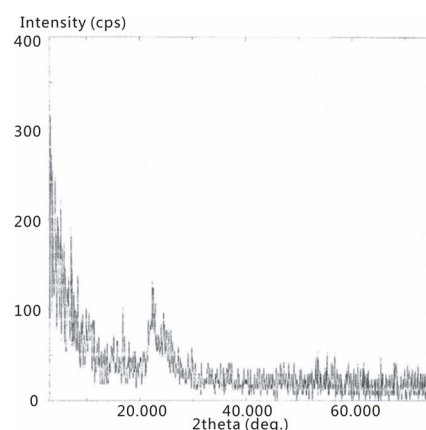
factured  $\text{TiO}_2$ -SWCNTs from  $90\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ , at deposition times of 10 minute, 20 minute, 30 minute, and 2 h exposures to sonication.

All the Raman spectra reveal the SWCNTs peaks but are absence of crystalline  $\text{TiO}_2$ , as noted by comparison with **Figure 4**. In the  $\text{TiO}_2$  portion of the spectrums, below  $650\text{ cm}^{-1}$ , the absence of the crystalline  $\text{TiO}_2$  confirms the amorphous characteristic of the deposited material. It is apparent that amorphous  $\text{TiO}_2$  was predominant in all the samples. This is further confirmed by **Figure 11** where the XRD of the 2 h sample is presented.

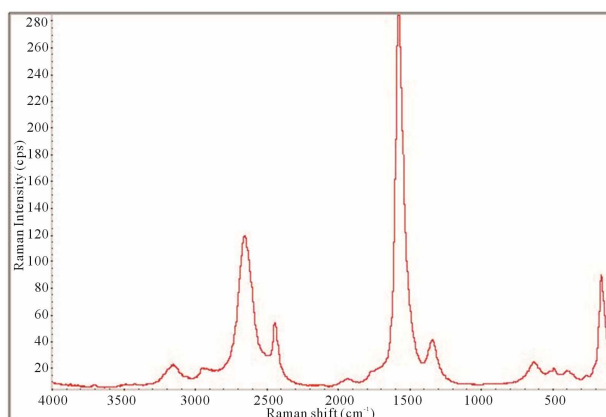
Here the spectrum shows no discernible peaks that would be expected for a crystalline material, as noted by comparison with the XRD spectrum for P25 as seen in **Figure 5**.

### 3.4. Characterization of Hydrothermal Treated $\text{TiO}_2$ -SWCNTs

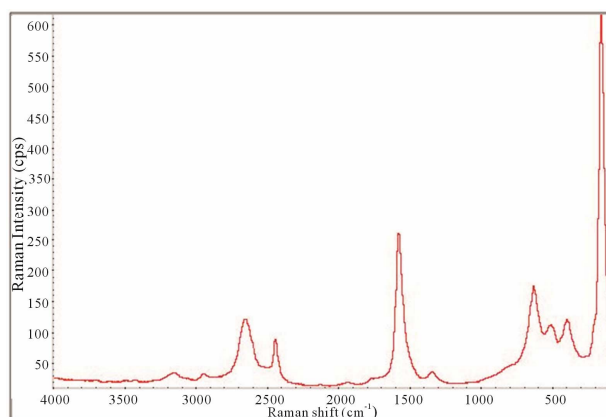
**Figures 12-15** depict the Raman spectrum of the synthesized  $\text{TiO}_2$ -SWCNTs from  $90\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ , at



**Figure 11.** XRD spectra of the synthesized  $\text{TiO}_2$ -SWCNTs at deposition time of 2 h exposure to sonication, with no hydrothermal treatment.

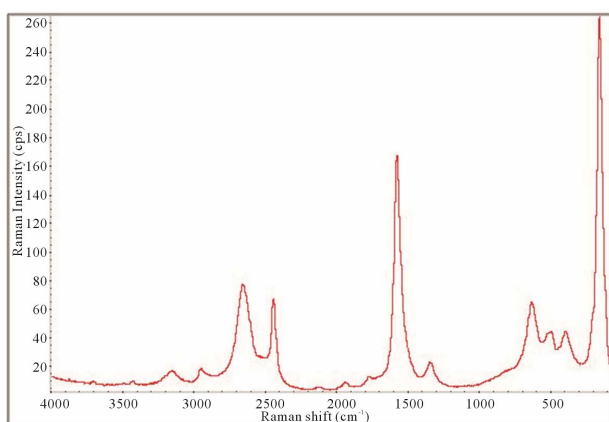


**Figure 12.** Raman spectrum of the synthesized  $\text{TiO}_2$ -SWCNTs at deposition time of 10 minute exposure to sonication with hydrothermal calcination treatment.

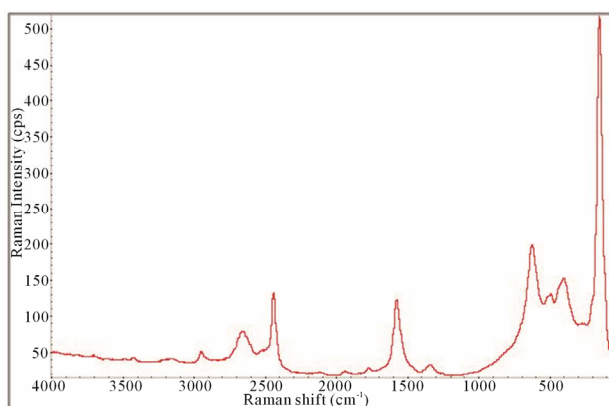


**Figure 13.** Raman spectrum of the synthesized  $\text{TiO}_2$ -SWCNTs at deposition time of 20 minute exposure to sonication with hydrothermal calcination treatment.

deposition times of 10 minute, 20 minute, 30 minute, and 2 h exposures to sonication, followed by hydrothermal



**Figure 14.** Raman spectrum of the synthesized TiO<sub>2</sub>-SWCNTs at deposition time of 30 minute exposure to sonication with hydrothermal calcination treatment.

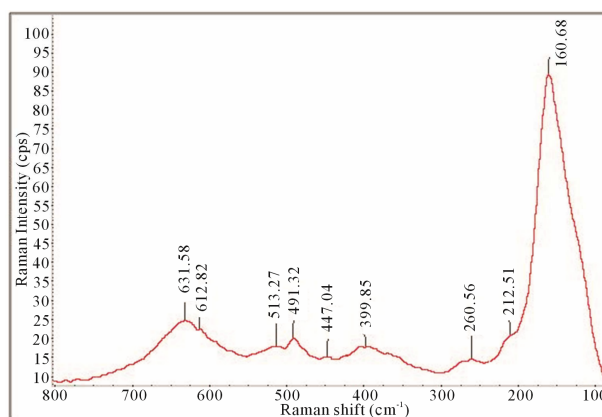


**Figure 15.** Raman spectrum of the synthesized TiO<sub>2</sub>-SWCNTs at deposition time of 2 h exposure to sonication with hydrothermal calcination treatment.

calcination treatment.

All the Raman spectra displayed the necessary peaks for anatase TiO<sub>2</sub> crystals and SWCNTs showing they are both present in the samples. This is illustrated by comparison with the spectrum obtained for P25 as shown in **Figure 4**. **Figures 12-15** also allude to a trend where the peaks appear more robust and defined as the length of deposition time increases. It appears that exclusively anatase was made in all the samples with the exception of the 10 minute specimen. For the 10 minute sample rutile TiO<sub>2</sub> appears to also be present along with the anatase. A clearer illustration is portrayed in **Figure 16** where is of interest to note the anatase peaks at 160.68 cm<sup>-1</sup> (E<sub>g</sub>), 212.51 cm<sup>-1</sup> (E<sub>g</sub>), 399.85 cm<sup>-1</sup> (B<sub>1g</sub>), 513.27 cm<sup>-1</sup> (A<sub>1g</sub>), and 631.58 cm<sup>-1</sup> (E<sub>g</sub>) and vaguely depicted rutile peaks at 260.56 cm<sup>-1</sup>, 447.04 cm<sup>-1</sup>, and 612.82 cm<sup>-1</sup>. The strongest, well resolved 160.68 cm<sup>-1</sup> (E<sub>g</sub>) mode is due to the external vibrations of the anatase structure, indicating that long-range order was formed [68].

This is also the case for the other measured TiO<sub>2</sub>-SWCNT

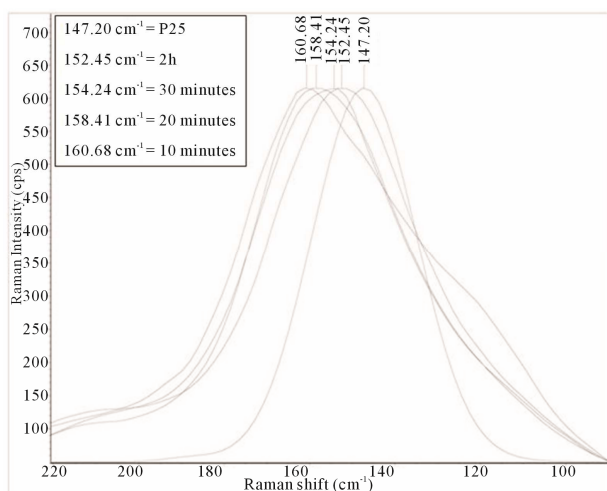


**Figure 16.** Raman spectrum of 90 cm<sup>-1</sup> to 800 cm<sup>-1</sup> for synthesized TiO<sub>2</sub>-SWCNTs at deposition time of 10 minute exposure to sonication with hydrothermal calcination treatment.

samples.

All the samples show spectral peaks that are broadened and/or shifted with respect to P25, with the 10 minute sample showing the largest shift. For the 10 minute sample, the largest shift differences are noted at the highest and lowest E<sub>g</sub> mode. The highest mode has blue shifted (peak at 631.58 cm<sup>-1</sup>) while the lowest mode (E<sub>g</sub>) has red shifted by approximately  $\Delta 16$  cm<sup>-1</sup> (from 147.20 cm<sup>-1</sup> for P25 anatase to 160.68 cm<sup>-1</sup>). A similar shift was reported by Bersani *et al.* who attributed it to phonon confinement caused by the decrease in the crystal size of the anatase TiO<sub>2</sub> [69]. These shifts are apparent in nanoparticles that have a diameter smaller than 15 nm and are indicative of reduction of crystal sizes [70]. For comparison, **Figure 17** show an overlay of the observed red shift, for the lowest mode (E<sub>g</sub>), for the samples evaluated.

Here the compiled Raman spectrum from 90 cm<sup>-1</sup> to 220 cm<sup>-1</sup> for the synthesized TiO<sub>2</sub>-SWCNTs at deposition times of 10 minute, 20 minute, 30 minute, and 2 h exposures to sonication with hydrothermal calcination treatment is shown. The spectrum is normalized for the large TiO<sub>2</sub> (E<sub>g</sub>) peaks clustered around 147 cm<sup>-1</sup> to 161 cm<sup>-1</sup> with the spectrum of p25 added for reference. With the grain size of P25 equal to a measured 20.4 nm, it is clear that the samples have relatively smaller sized TiO<sub>2</sub> particles. The decrease in size trend corresponds to a decrease in sonication exposure time. In addition to the shift in peaks, an increase in band asymmetry and broadening are observed as the length of sonification time decreases. The broadening of the peaks is reported to result from strain gradients in systems where TiO<sub>2</sub> is being chemically anchored to CNTs. These strain effects can extend several nm into materials [71]. To illustrate the relative broadening of the peaks, a measure of full



**Figure 17.** Compiled Raman spectrum illustrating the observed red shift, for the lowest mode (E.g.), for the samples evaluated.

width at half maximum (FWHM) for the samples at the lowest E<sub>g</sub> mode is: 10 minute = 49.1 cm<sup>-1</sup>, 20 minute = 41.8 cm<sup>-1</sup>, 30 minute = 41.2 cm<sup>-1</sup>, 2 h = 39.2 cm<sup>-1</sup>, P25 = 25.4 cm<sup>-1</sup>.

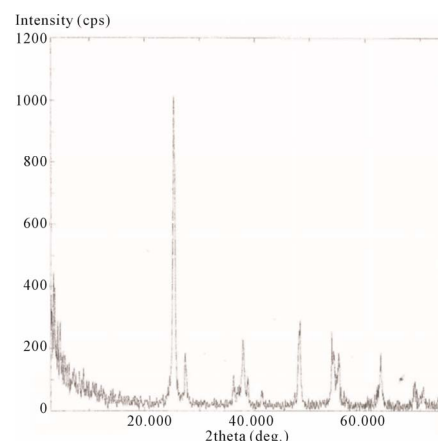
The XRD spectra for the hydrothermally treated samples, including 10 minute, 20 minute, 30 minute, and 2 h are presented in **Figures 18-21**.

Here the scans were ran from  $2\theta = 20^\circ$  to  $75^\circ$ . The spectrums show the characteristics of predominately anatase TiO<sub>2</sub> with diffraction peaks at  $2\theta = 25.18^\circ$  (strongest peak),  $37.78^\circ$ ,  $48.00^\circ$ ,  $53.89^\circ$ ,  $54.99^\circ$ ,  $62.57^\circ$ ,  $68.68^\circ$ ,  $70.15^\circ$ , and  $75.01^\circ$ . The average crystal diameter for each sample was calculated from the largest peak by the Scherrer's equation as described previously. These values are reported in **Table 1**.

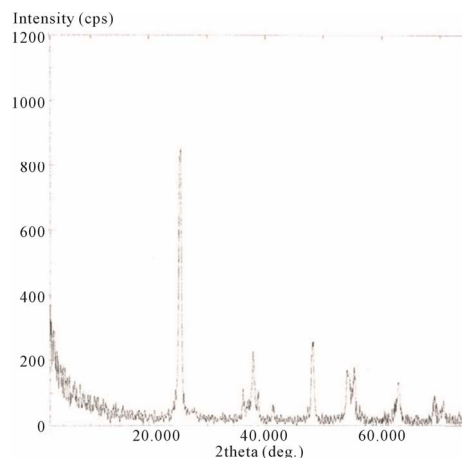
It is clear from the data that the size of TiO<sub>2</sub> decreases as the length of deposition time is reduced. The size of the deposited TiO<sub>2</sub> versus the observed Raman red op-shift, for the lowest mode (E<sub>g</sub>), for the samples evaluated, is also depicted in **Table 1**. Here a significant correlation is realized where the decreasing crystal size of deposited TiO<sub>2</sub> is linked to the observed Raman red shift for the lowest E<sub>g</sub> mode measured for the TiO<sub>2</sub>.

#### 4. Summary and Conclusions

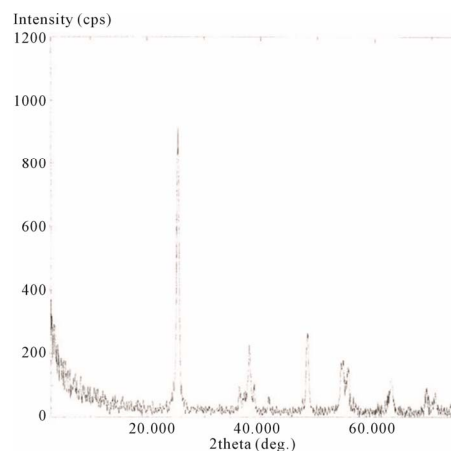
In this report a novel sonochemical technique and subsequent hydrothermal annealing process, utilized to synthesize crystalline anatase TiO<sub>2</sub>-SWCNTs was disclosed. This method is low cost and uses readily available equipment and chemical precursors. Additionally, the process is easy and relatively quick, producing chemically attached, uniformly dispersed, TiO<sub>2</sub> encapsulated CNTs. These main advantages of the sonochemical-hydrothermal technique generally provide a superior



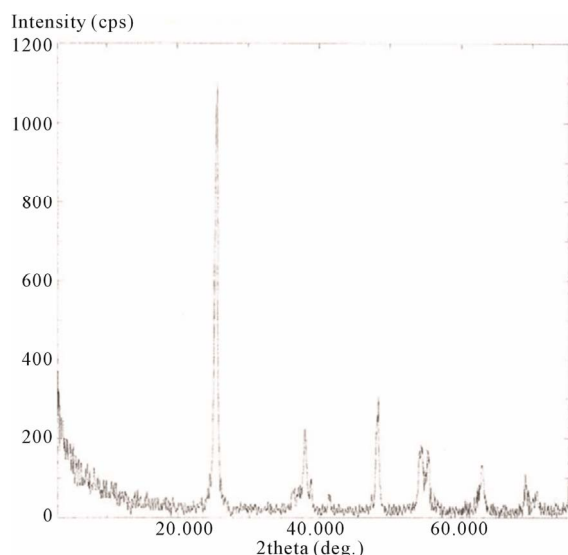
**Figure 18.** XRD spectrum of calcinated (hydrothermally treated) TiO<sub>2</sub> on SWCNTs—10 minute sonication exposure sample.



**Figure 19.** XRD spectrum of calcinated (hydrothermally treated) TiO<sub>2</sub> on SWCNTs—20 minute sonication exposure sample.



**Figure 20.** XRD spectrum of calcinated (hydrothermally treated) TiO<sub>2</sub> on SWCNTs—30 minute sonication exposure sample.



**Figure 21.** XRD spectrum of calcinated (hydrothermally treated) TiO<sub>2</sub> on SWCNTs—2 h sonication exposure sample.

**Table 1.** TiO<sub>2</sub> calculated particle size and specific surface area as determined from XRD correlated with lowest TiO<sub>2</sub> E.g. Raman peak.

| Sample     | Size of TiO <sub>2</sub> (XRD) | TiO <sub>2</sub> (E.g.) Peak (Raman) |
|------------|--------------------------------|--------------------------------------|
| 10 minutes | 8.4 nm                         | 160.68 cm <sup>-1</sup>              |
| 10 minutes | 9.2 nm                         | 158.41 cm <sup>-1</sup>              |
| 10 minutes | 13.2 nm                        | 154.24 cm <sup>-1</sup>              |
| 2 h        | 15.0 nm                        | 152.45 cm <sup>-1</sup>              |
| P25        | 20.3 nm                        | 147.20 cm <sup>-1</sup>              |

synthetic route as compared with other processes that are either time consuming, cumbersome, expensive, lack the control for the deposition TiO<sub>2</sub>, and/or produce inferior results. The TiO<sub>2</sub>-SWCNTs were characterized by scanning electron microscopy, Raman spectroscopy, and X-ray diffraction. From the characterization the size, ranging from 8.4 to 20.3 nm, anatase and rutile morphology of the synthesized TiO<sub>2</sub> nanoparticles were reported. Furthermore, it was postulated that the created TiO<sub>2</sub> nanoparticles are chemically attach to SWCNTs. This is supported by the Raman spectra where in addition to the observed red shift in lowest TiO<sub>2</sub> E.g. Raman peak, an increase in band asymmetry and broadening are also observed. An important correlation between calculated TiO<sub>2</sub> crystal size and the red shifts in the lowest Raman TiO<sub>2</sub> (E.g.) predominate peak was reported. The synthesized TiO<sub>2</sub>-SWCNTs have potential for application in a variety of new technologies such as clean energy power generation devices, electrical storage devices, photocatalysts, and sensors.

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