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A microscopy study of the effect of annealing temperature on the morphological and structural properties of titanium dioxide nanotubes fabricated on functional substrates

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Abstract

It is well known that the morphology and crystalline phase composition of TiO2 in titanium dioxide nanotubes (TNTs) is of considerable importance because it governs the efficiency of many photon assisted chemical and physical reactions in dye sensitized solar cells (DSSC). The efficiency of DSSC employing TNTs is dependent on the stability of the photochemistry reactions which can be optimized by controlled development of either Anatase or Rutile phases of TiO2. Moreover, the microstructure such nano tube pore diameter, tube length and the stability of nanotubes also play a significant role in dye absorption, efficient percolation of the redox electrolyte and vectorial transport of photon generated electrons. In this work TiO2 nanotubes have been fabricated on FTO glass substrates by electrochemical anodization of Ti metal film on FTO glass substrates (functional substrates) deposited by RF sputtering. The fabricated TNT on functional substrates (FS) were thermally treated at different temperatures. The fabricated, thermally treated TNTs-FS were subjected morphological evaluation using scanning electron microscopy (SEM) and morphological-structural evaluation using high resolution transmission microscopy (HRTEM. Our Results have shown that TNTs prepared on FTO glass substrates demonstrated remarkable morphological and structural stability as compared TNTs on metal substrates annealed at the same temperatures

Keywords: Titanium Dioxide Nanotubes, Functional Substrates, Heat Treatment, Sem Microscopy, Transmission Microscopy

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Introduction

In the past decades, considerable efforts have been devoted to development of high efficient solar cell devices that use low cost and non-toxic materials. Among these technologies, DSSCs are deemed as the most promising candidates, which commonly use mesoporous titanium dioxide thin films to make photo-anodes, in particular 3-D networks of nanoparticles (TNPs) [1]. However, the random connections in mesoporous TNPs unavoidably bring about interfacial charge recombination of the electron-hole pairs and simultaneously led to low efficiency solar devices. Highly ordered TNTs may stimulate the performance DSSCs due to vectorial charge transport and large surface area for maximum dye loading [2]. 1-D and highly ordered TNTs offers an excellent electrical channel for vectorial charge transfer, thus enhance separation of the photo induced electron-hole pairs, which reduces charge recombination and maximizes photo absorption. TNTs arrays with highly ordered and vertically orientated nanotubular structures provide a large internal surface area and also introduce a free electron traveling path to reduce carrier charge recombination possibilities [3]. Nevertheless, the nature (opaque) of the metal substrate to which TNTs are grown hinders the application of TiO2 based material in solar cells or electrochromic devices. Hence, TNTs grown on transparent conductive substrate are of particular interest for high photo-current conversion. There is a need for Ti film layers deposited on functional substrate that can transmit visible light towards the active layer [4]. To enhance vectorial charge transfer activity TNTs arrays, various strategies have been employed such as the improvement of the surface morphology, crystal structure, surface area [5-9] and doping with non-metals or metals [10-15]. In this study, we synthesized anodic TNT films on functional substrates in fluoride containing glycerol electrolyte solution. This work is dedicated to microscopic evaluation of the effect of annealing temperature on the morphology of TNTs fabricated on fluorine doped tin oxide (FTO) glass substrate (FS). The morphological changes due to change in annealing at different temperatures has been first examined using SEM and more extensively interrogated at higher magnification using high resolution (HRTEM).

Experimental details

This section presents the detailed experimental procedures used in the fabrication and characterization of titanium dioxide nanotubes (TNTs) on functional substrates (FS) substrates.

Deposition of Ti film on FTO glass substrate

Ti films (Titanium target of 99.99%) were sputter coated on FTO using RF sputtering system technique. Prior to RF sputtering, the fluorine doped tin oxide (FTO) glass substrates were ultrasonically cleaned using acetone, ethanol and DI water for 15 minutes, respectively. Then the vacuum chamber was pumped down until the base pressure was5×10^{-4} Pa. The sputtering chamber pressure was kept at 1.5 Pa during the deposition in argon atmosphere. An RF power of 120 W and substrate temperature of 200 °C was maintained during the depositions to ensure better adhesion between the substrate and titanium film. RF sputtering was done for 4 hours at deposition rate of 0.70 Å/s. to obtain a Titanium thin film of about 10 μm (thickness).

Preparation of TNTs by electro-anodization

TNTs were synthesized via anodization in a two electrode setup home-made Teflon cell. Ti film coated FTO glass substrate was used as the working electrode (anode), while Pt foil was employed as the counter electrode (cathode) Figure 1, shows the actual photograph of the experimental set up used in this study.

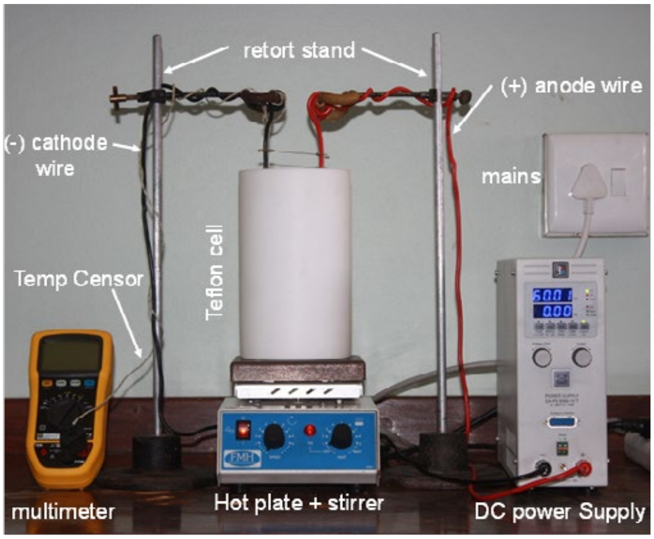

Figure 1: Shows the actual photograph of the electro-anodization system used in the study.

Anodization was performed in the glycerol based electrolyte solution (96.5 wt% glycerol, 0.5 wt% NH4F and 0.35 wt% DI water) at 60 V for 72 hours. TNTs formed were rinsed with ethanol and DI water, and then dried in air stream. Finally, TNTs were subjected to thermal treatment at 350 °C, 450 °C, 550 °C and 650 °C to obtain TiO_2 phase distribution.

Sample Characterization

Field Emission Scanning Electron Microscope (FE-SEM) Zeiss Auriga SEM equipped with EDS with SmartSEM software was used to study morphological properties of nanotubular TiO2 with an accelerating voltage of 30 KV at different magnifications. In order to evaluate the thickness and cross sectional morphology of nanotubular TiO2. For cross sectional and surface analysis the samples were frozen in liquid nitrogen and fractured whilst frozen. The fractured sample was then mounted onto a sample holder with the fractured side facing up after gold coating. For surface morphology the samples were mounted directly onto a sample stub and sputter coated. For HRTEM analysis sample preparation proceed: TiO2 nanotubes were mechanically detached from the surface of the functional substrate (FTO glass substrate) suspended in ethanol and deposited onto Carbon coated Cu grids. After preparation the samples were analysed in a TEM to determine the morphological-structural properties of titanium dioxide nanotubes. For TEM and STEM analysis a Philips CM microscope operating at an acc voltage of 100kV was used. HRTEM images were obtained using a PHILIPS CM 300 UT operating at an acc voltage of 300kV.

Results and Discussions

Scanning Electron Microscopy (SEM)

Anodization of titanium occurs as a result of the competition between oxide formation and chemical dissolution of the oxide by fluoride ions [16, 17]. The main reaction at anode is titanium oxidation which results in the formation of titanium oxide proceeds as follows.

$$\text{(1) } Ti \rightarrow Ti^{4+} + 4e-$$

$$\text{(2) } Ti^{4+} + 2H_2O \rightarrow TiO_2 + 4H^+$$

Subsequently, pores are formed due to localized chemical dissolution of the oxide by fluoride ions and this result in the formation of a water soluble complex titanium hexa-fluoride ($[TiF_6]^{2-}$). Titanium hexa-fluoride formation proceeds according to equation 3:

$$\text{(3) } TiO_2 + 4H^+ + 6F^- \rightarrow [TiF_6]^{2-} + 2H_2O$$

The competition between the formation of titanium oxide and chemical

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dissolution by fluoride species is known to result in nanotubular structures [18]. Nonetheless, water oxidation also takes place as anodic side reaction, leading to oxygen evolution as per reaction 4:

$$(4)\ 2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Water oxidation reaction is considered to be responsible for the peeling off and inhomogeneity of the TiO2 film. In most scenarios this reaction is negligible such as in an electrolyte with low water content, such as organic electrolyte, in particular glycerol electrolyte employed in this study [16]. In the presence of such a low water content fluoride electrolyte, titanium oxidation (as per reaction 2) prove to be superior [16].

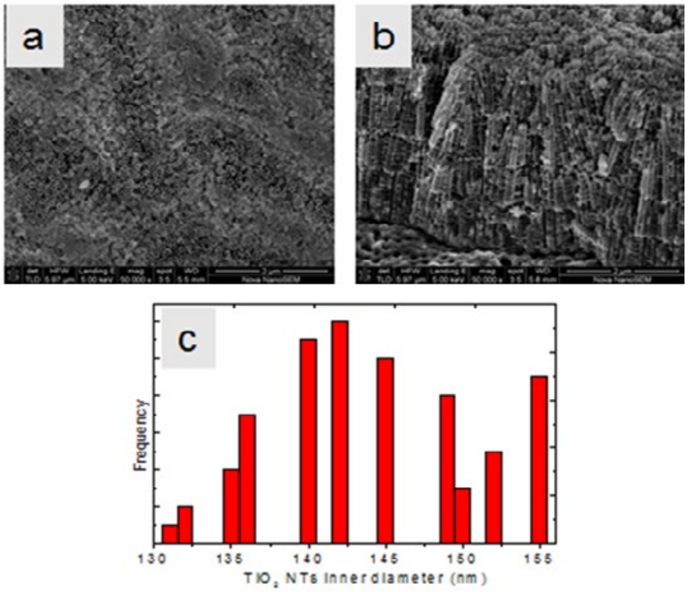

Figure 2: SEM micrographs of TNTs on FTO glass substrate annealed at 350 °C
(a) surface SEM images of TNTs
(b) cross sectional SEM images
(c) Histogram showing pore size distribution, respectively.

In this study the TNTs produced remained attached to the functional substrate, hence reaction 4 is negligible. SEM analysis presented here Figure 2-5 have shown that the prepared TNTs remained intact to the FTO glass substrate. However, prolonged periods of continuous anodization (96 hours) resulted in intense formation of oxygen bubbles. It has been reported in circumstances where reaction 4 is dominant. The presence of oxygen bubbles results in delamination of TNTs layer and a colour change in the electrolyte [16], which was observed during prolonged periods of anodization (96 hours). Hence it was ideal to limit the period of anodization to 72 hours for production of TNT arrays with good adhesion to the surface of functional substrate.

Figure 2 (a) presents the SEM micrographs of the surface morphology of the TNTs prepared on functional substrates and annealed at 350 °C. SEM micrographs in Figure 2 have revealed a regular & well orientated nanotubular layers. Additionally, Figure 2 has revealed that the surface of the TNTs annealed at 350 °C are covered by an oxide barrier layer. The presence of the oxide barrier layer can be attributed to the continuous chemical etching of TiO2 in the presence of fluoride ions [21–23]. Moreover, the presence of the oxide barrier layer can be attributed to incomplete dissolution during chemical etching from reaction (2), hence, the as formed TNTs are not completely separated from each other [24, 25]. Furthermore, the cross sectional SEM images of TNTs grown on FTO glass substrate in Figure 2 (b) reveal that TNTs formed have periodic rings representing TNTs with rough walls. The presence of rough tube walls is due to current oscillations [12, 26], which also beneficial for DSSC application as the presence of rough tube was has been reported to increase the available surface area for efficient adsorption dye [9, 10]. The histogram in Figure 2 (c) has revealed that the fabricated titanium dioxide nanotubes have pore size diameter range 130 nm–155 nm with a modal pore diameter of 142.14 nm. Table 1 presents measured pore diameters of the TNTs-FS annealed at different temperatures. For the sake of comparison and clarity, Table 1 has also presented the measured pore diameters for the TNTs prepared on metal substrates [26].

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Annealing Temperature (°C)	Pore Size Range (nm)		Modal pore diameter (nm)	
	TNT-Ti (Foil)	TNTs-FS	TNT-Ti(Foil)	TNTs-FS
350	20-70	130-155	34.56	142.14
450	45-100	150-170	56.52	163.35
550	30-65	90-140	42.50	103.48
650	15-55	85-105	31.05	85.05

Table 1: Surface parameters of TNTs-Ti (foil) as compared to TNTs-FS as function of annealing temperature [26].

Table 1, has clearly revealed that TNTs prepared on functional substrates and annealed at 350 °C, have an improved modal pore size diameter of 142.14 nm as compared to TNTs grown on titanium metal foil with modal pore diameter range 34.56 nm [26]. This, implies that TNTs prepared on functional substrates are better electrode materials candidates for DSSC solar cell application. As the large pore size diameter is accompanied by a larger surface area for efficient dye absorption and redox electrolyte percolation for efficient generation of electron hole. These results are in mutual agreement with confocal Raman large area scan previous reports that revealed the presence of well crystallized Anatase TNTs phase on the surface of the TNTs annealed at 350 °C, which is favoured in DSSC application [27].

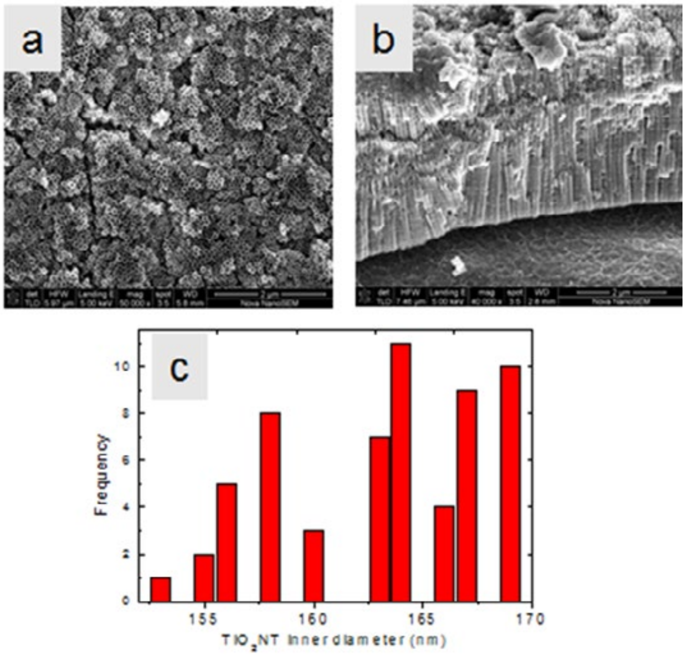

Figure 3:SEM micrographs of TNTs on FTO glass substrate annealed at 450 °C
(a) surface SEM images of TNTs
(b) cross sectional SEM images Histogram showing pore size distribution, respectively.

Figure 3, has revealed that further increase in annealing temperature to 450 °C has resulted in the formation of an improved surface morphology of the TNTs prepared on functional substrates as shown in Figure 3(a). From the SEM images alone it is not possible to whether establish the increase annealing temperature to 450 °C resulted in formation of an improved surface morphology it due to formation of a well crystallized Anatase phase of TiO_2. However, it well known that Anatase phase of TiO_2 is stable dominant phase at 450 °C. Furthermore, these results are in mutual agreement with our previous report [27] where Raman spectroscopy large area scan revealed the presence of a well crystallized Anatase phase of TiO_2 with Raman vibrational mode at 158.95 cm^{-1} (Eg), 210.01 cm^{-1} (Eg), 399.54 cm^{-1} (B1g), 519.09 cm^{-1} (A_{1g}) and 636.79 cm^{-1} (Eg).) for the samples annealed at 450 °C. Since the Anatase phase of TiO2 phase is preferred in charge-separating devices such as DSSC the fabricated TNTs-FS and annealed are ideal electrode materials2 [32]. Additionally, the histogram in Figure 3(c) and Table 1, has revealed that the TNTs annealed at 450 °C have a larger pore diameter sizes in the range 150 nm- 170 nm and a modal

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pore size diameter of 163.35 nm compared to the TNTs annealed at 350 °C. Additionally, Table 1 has revealed that the TNTs prepared on functional substrates and annealed at 450°C have superior modal pore size diameters of 163.35 as compared to the TNTs prepared on metal substrates with a modal pore size diameter of 56.52 nm. Yet again, the TNTs fabricated on functional substrates have outshined the TNTs fabricated on Ti (foil) [10]. Accordingly, the increased pore diameter also results in increased surface area for maximum dye loading, thus increase in photo induced electrons [13]. Simultaneously allowing efficient penetration for redox electrolyte for efficient regeneration of the dye sensitizer during photo sensitization. These observations further cement the fact that the TNTs prepared in this work are ideal electrode materials for preparing DSSCs.

Our observations from SEM micrographs of TNTs grown on functional substrates (FTO glass) triumphs when compared to TNTs grown metal substrate (Ti foil). These observations conclude that FTO glass is the better substrate for fabrication of high ordered TNTs for better application in DSSCs. In addition, It can also be observed from the cross sectional SEM micrographs Figure 3 (b) that the TNTs tube walls were smoother after the TNTs were subjected to thermal treatment at 450 °C as compared to TNTs annealed at 350 °C. The presence of smooth tube might have a dual effect (1) reduction of the available surface area for dye loading and (2) might result in an enhanced path ways for photo induced electrons from one point to another along the TNTs [30, 31]. These results are in mutual agreement with confocal Raman depth profiling revealing that the length of the nanotubes consisted of Anatase phase of TiO2 with Raman vibration modes at 160.01 cm^{-1} (E_g), 210.78 cm^{-1} (E_g), 393.18 cm^{-1} (B_{1g}), 515.87 cm^{-1} (A_{1g} or B_{2g}), 637.79 cm-1 (E_g) all belonging to a greatly improved crystallinity of Anatase TNT phase. Anatase phase being the favoured phase of TiO2 due to its high photocatalytic activities compared to rutile phase of TiO_2 [31]. A thin portion of the compact oxide layer on top of the TNTs was also observed from the cross sectional SEM micrographs shown here in Figure 3(b). The barrier oxide layer might be attributed to incomplete etching of the first oxide layer formed [24, 25]. The top barrier oxide layer can be alleviated by post treatment of the TNTs such as ultra-sonication in dilute HF solution [33]. However, having this kind of the nanoporous top layer does not fully affect the properties of the TNTs as long as the tubes end remains open for dye penetration [34]. Therefore, the elimination of the thin top layer by ultra-sonication has no significant influence on the properties of the photo electrode [34].

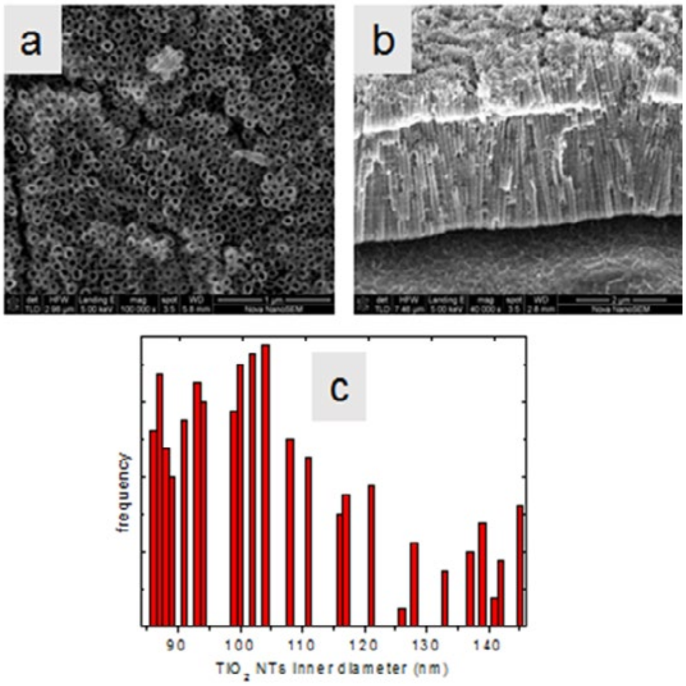

Figure 4: SEM micrographs of TNTs on FTO glass substrate annealed at 550 °C
(a) surface SEM images of TNTs
(b) cross sectional SEM images
(c) Histogram showing pore size distribution, respectively

Further increase in sample annealing temperature led to highly ordered and even smoother TNTs walls as shown in cross sectional view SEM images in Figure 4. (b). The well inter-connected TNTs with uniform pore diameters are grown on the 5 hours sputtered titanium film. The histogram in Figure 4 (c) show inner diameters of the TNTs in the range between 85 nm – 145 nm. The walls of the TNTs at 550 °C are greatly improved compared to TNTs at 450 °C. Furthermore, the surface morphology of the TNTs on FTO glass substrate annealed at 550 °C is shown here in Figure 4 (a), it is clearly evident that the increase in annealing temperature resulted in slight or no change in surface morphology of TNTs. These observations are in contradiction to Lupiwana et al., [26] who observed a significant change in surface morphology for the TNTs on metal foil annealed at 550 °C. Lupiwana et al., [26] reported the presence of raptured, collapsing and deformed TNTs surface morphology metal substrate at a similar annealing temperature [26]. It is interesting to note from SEM micrographs in Figure 4 (a) and Figure 4 (b) that the TNTs grown functional glass substrate and annealed at 550 °C remained intact and did not show any signs of deformation, collapse and rupture of the morphology. However from the SEM micrographs alone it's not possible to establish

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whether the failure of these TNTs prepared on functional substrates is related to the phase transformation.

However, our previous Raman measurements have indicated the presence of Raman vibrational modes at 156.51 cm-1 (Eg), 206.36 cm-1 (Eg), 401.97 cm-1 (B1g), 520.30 cm-1 (A1g) and 638.79 cm-1 (Eg) all belonging to a well crystallized Anatase phase of TiO2. In lieu of these Raman observations we can safely conclude that the TNTs prepared on functional substrates are more stable and ideal electrode materials for DSSC solar cell applications [27].

This could be attributed to the absence to metal substrate, which normally catalyses the transformation of Anatase to Rutile at such temperatures. Perhaps the nature of the underlying substrate (Fluorine doped tin oxide) inhibits the transformation of Anatase to Rutile. It has been also been reported that the exact temperature of Anatase to Rutile transformation depends on source (1) preparatory history, and (2) to be dependent on the interface with the titanium metal substrate. Since in this study we employed a completely different substrate, we would like to believe the stability of the fabricated TNTs is due to the nature of the substrates, which has inhibited the conversion of Anatase to Rutile. The histogram in Table 1 has also indicated larger modal pore diameter (103.48 nm) and pore size range (90-140 nm) for the TNTs prepared on function substrates. As compared to the TNTs prepared on metal substrate with modal pore diameter (42.50 nm) and pore size range of (30-65 nm). Hence, the TNTs prepared on functional substrate are more superior for DSSC solar cell application. These observations further prove that our method of fabrication of TNTs on functional substrates is more superior to the previous reported methods [26. 2. 3].

In order to further examine the effect annealing temperature on the surface morphology of TNTs prepared on FTO glass substrates we further increased the annealing temperature to 650 °C. Figure 5, Shows the SEM micrographs of TNTs prepared on functional substrate and annealed at annealed at 650 °C.

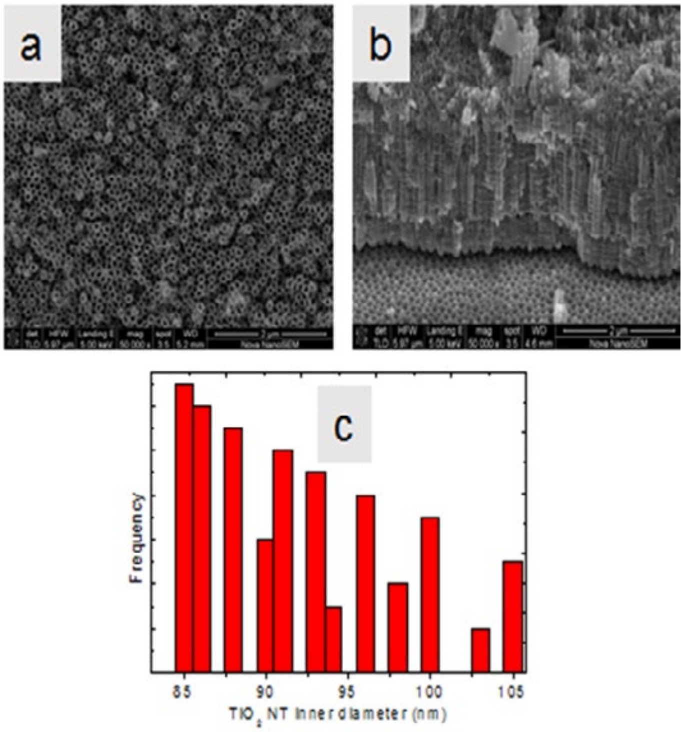

Figure 5: SEM micrographs of TNTs on FTO glass substrate annealed at 650 °C
(a) surface SEM images of TNTs
(b) cross sectional SEM images
(c) Histogram showing pore size distribution, respectively.

It is clearly, evident from Figure 5 (a) that TNTs begin to feel the effect of annealing temperature as the TNTs partially collapse, with some oxide rings which build up the nanotubes beginning to sinter together. These observations are in contrast to previous reports which have reported complete loss of TNTs surface morphology, more particularly for the TNTs prepared on titanium metal substrates. Jaroenwaraluck et-al [7] reported that an increase in annealing temperature to 600 °C resulted complete loss of TNTs. More recently Lupiwana et al [26] reported that the TNTs prepared on metal substrate completely rupture and deformed at annealing temperatures of 550 °C and 650 °C, which is attributed to the substrate effect [26]. In previous studies, Grimes and co-workers et-al [36] explained the collapse as the consequence of rutile protrusions from interface metal/metal oxide into the anodic film following oxidation of the substrate at 580 °C and higher temperature, which is commonly known as the "substrate effect". The fact that the TNTs prepared in this study remained intact suggest that presence of the FTO glass substrate inhibits the transformation of Anatase to Rutile.

The histogram in Figure 5 (c) and Table 1 has revealed that TNTs prepared on functional substrates and annealed at 650 °C have modal

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pore diameter of 85.05 nm and pore size range 85 nm–105 nm, which is smaller than the TNTs annealed at 350 °C, 450 °C and 550 °C. These observations further provide evidence of earlier observations that the TNTs partially collapse and deform with increases in annealing temperature. However, the prepared TNTs and annealed a 650 °C are still more superior as compared to TNTs prepared on metal substrate that have been reported to have a smaller pore diameters as illustrated here in Table 1. SEM micrographs in Figure 5 (b) revealed the presence of a barrier oxide layer covering the top of the TNTs on FTO glass substrate. Thin oxide top layer on TNTs grown on functional substrates is resistive to chemical dissolution and all attempts to remove it in dilute acid solution failed and diluted HF damages TNTs layers easily and even detach them from the substrate [18]. Kanta et al., [33] in contrast reported that the top barrier oxide layer can be alleviated by post treatment of the TNTs such as ultra-sonication in dilute HF solution. The oxide layer on top of the TNTs might be due to incomplete etching of the first oxide layer formed in reaction (2) [16]. In spite the thin barrier layer on top of the TNTs, our TNTs are of particular high quality and of interest as electrode materials for DSSCs. In conclusion the SEM surface morphology analysis has revealed remarkable properties for the TNTs prepared on functional substrates as compared those reported in literature [1-3]. However, it was important to observe that the stability of the TNTs up 650 °C as this allows investigation of their performances in DSSC where Anatase is the preferred phase.

High Resolution Transmission Electron Microscopy

HRTEM analysis presented here Figures 6-9 reveal the surface morphological and structural properties of TNTs-FS annealed at different temperatures. Figure 6 has revealed that the TNTs-FS annealed at 350 °C have a oval shape with circular openings. Moreover, the histogram in Figure 6(b) has revealed pore size range of 130 nm–152 nm and with a modal pore size diameter of 130 nm. These observation are in mutual agreement with our SEM micrographs (Figure 2) that have revealed a pore diameter sizes diameters measured 103.48 nm and with a pore size range 130-155 nm for the TNTs-FS annealed at 350 °C. Moreover the HRTEM micrographs have revealed straight nanotube walls for the TNTs-FS annealed this is in mutual agreement with our SEM observations.

It has been reported that the three most common polymorphs of titanium dioxide have

The following lattice parameters: Anatase (a=3.784 Å, c= 9.514Å, α=β=γ=90 PDF 78-2486) with d spacing of (101) plane of 3.52 Å [10], Rutile (a=4. 593 Å, c=2.958 Å α=β=γ=90° PDF #89-8304) with a d-spacing of 3.25 Å) [11], Brookite (a=9.174 Å, b=5.449 Å, c=5. 138 Å, α=β=γ=90° PDF 76-1934) with d-spacing of 3.51 Å [12]. Figure 6 has revealed that the TNT-FS annealed at 350 °C have a d-spacing's of 0.351 nm which corresponds to the (101) plane of Anatase TiO_2. This implies that the fabricated TNTs-FS from the morphological point have multi porous net-work structure and from the structural point view are crystallized in the Anatase phase of TiO_2. These observations further cement the fact that the TNTs prepared in this work are ideal electrode materials for preparing DSSCs.

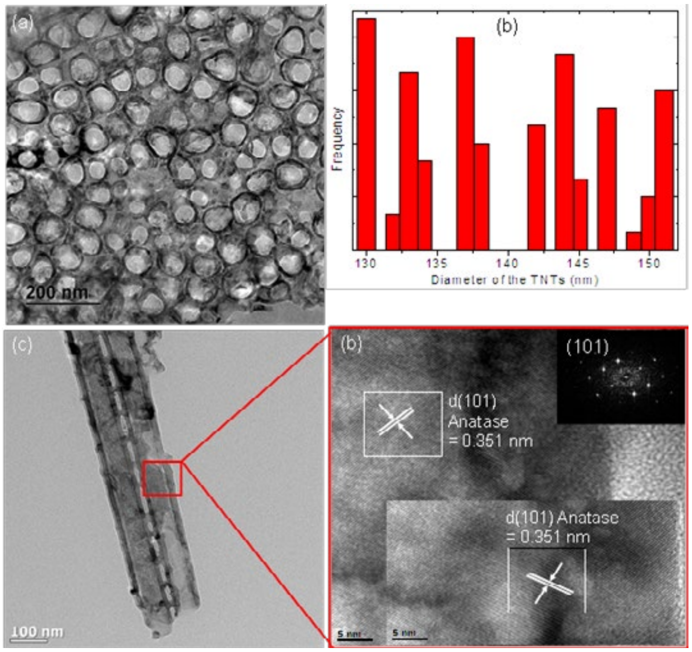

Figure 6:HRTEM images of TNTs annealed at 350 °C
(a) surface images
(b) Histogram showing pore size distribution
(c) cross sectional view showing TNTs walls
(d) individual TNT walls.

To further cross examine the effect of annealing on the surface morphology and crystallinity of titanium dioxide nanotubes on functional substrates. Figure 7, presents the HRTEM images of TNTs-FS annealed at 450 °C Figure 7 has revealed that increase in annealing temperature to 450 °C has resulted in the formation of an improved surface morphology of the TNTs prepared on functional substrates as shown in Figure 4.2(a). The openings of the TNTs observed in Figure 4.6(a) are wider and spherical contrasted to oval openings in Figure 6 (a) at 350 °C. Additionally, the histogram in Figure 7 (b) has revealed that the TNTs-FS annealed at 450 °C have an improved pore diameter sizes in the range 145 nm-165 nm and a modal pore size diameter of 163.1 nm when compared to the TNTs annealed at 350 °C. These observations are in mutual agreement with SEM (Figure 2 (b)) with pore diameter sizes in the range 150 nm-170 nm and a modal pore size diameter of 163.35 nm has been observed. This implies that increase in annealing temperature has resulted in a significant improvement in the surface morphology of titanium dioxide prepared on functional substrates. The fabricated TNT-FS present better electrode materials for application in DSSCs mainly due to increase surface area which will result in improved dye loading which in turn may result in increased number of photon generated electrode. Moreover, the improved surface area can led to improved circulation of the redox electrolyte for efficient regeneration of electron hole by the redox couple.

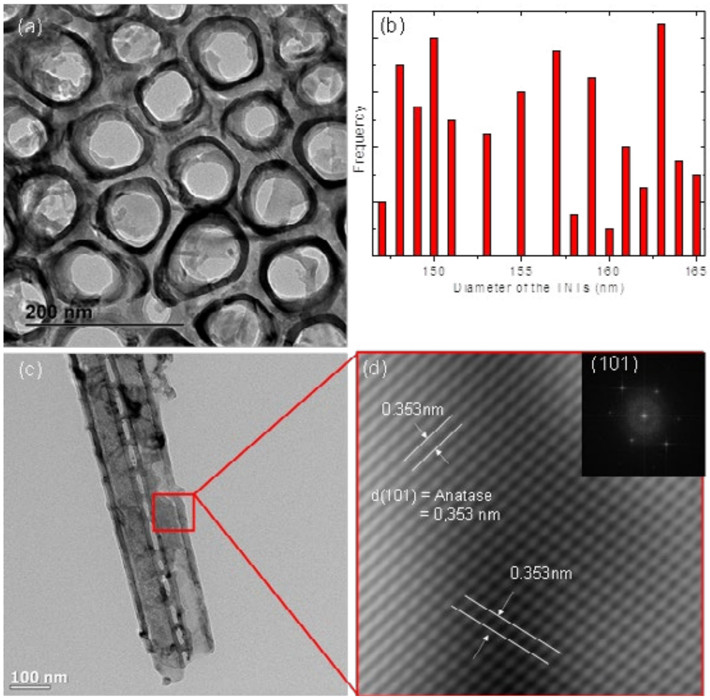

Figure 7: HRTEM images of TNTs annealed at 450 °C
(a) surface images
(b) Histogram showing pore size distribution
(c) cross sectional view showing TNTs walls
(d) individual TNT walls.

The higher magnification HRTEM clearly reveals that TNTs-FS annealed at 450 °C have a slightly larger d-spacing compared to the normal Anatase spacing of 0.352 nm. The d-spacing found in this sample is about 0.353 nm shown here Figure 7(b) which also corresponds to the (101) plane of Anatase TiO2. Moreover the insert in Figure 7(d) of the fast Fourier transform (FFT) of the images, synonymous to the selected area electron diffraction, has revealed that that only the main diffraction (reflection) plane of Miller indices (101) in TiO2 [17] is responsible for diffraction pattern.

To further cross examine the effect of annealing temperature on the surface morphology and crystallinity of titanium dioxide nanotubes fabricated functional substrates. Figure 8, present the HRTEM images of TNTs-FS annealed at annealed at 550 °C. It is clearly evident from Figure 8, that increase in annealing temperature resulted in an improved surface and inner morphology (walls of the TNTs) of TNTs-FS The histogram in Figure 8(b) has revealed a pore size diameter in the range between 115 nm–140 nm with modal pore size diameter of 132 nm these results have been summarized here in Table 2. This observation is in mutual agreement with SEM observations where we observed modal pore diameter 103.48 nm and pore size range 90 nm–140 nm for the TNT-FS annealed at 550 °C. This observation further support our SEM observation were annealed at 550 °C remained intact and did not show any signs of deformation, collapse and rupture of the morphology as shown in Figure 4. This observation is in contrast to previous observation reported [1, 2, 5] where increase annealing temperature resulted in rupture and deformation of TNTs on metal

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substrates. Moreover, The higher magnification HRTEM clearly reveals that TNTs-FS annealed at 550 °C have a d-spacing of 0.353 nm shown here Figure 8(b) which also corresponds to the (101) plane of Anatase TiO2.[1]. TNTs-FS annealed at 550 °C have retained an Anatase and a good surface morphology this implies the presence of the FTO glass substrate inhibits the Anatase to Rutile transformation. This is beneficial for DSSC solar cell applications. As fabricated TNTs –FS and annealed 550 °C retained more dye due to the improved surface morphology and also allow efficient percolation of redox couple for maximum electron-hole pair generation. More are like to show high photo-conversion due to the presence of Anatase phase of TiO2. In light of these HRTEM observations we can safely conclude that the TNTs prepared on functional substrates in this work are more stable and ideal electrode materials for DSSC solar cell applications [27].

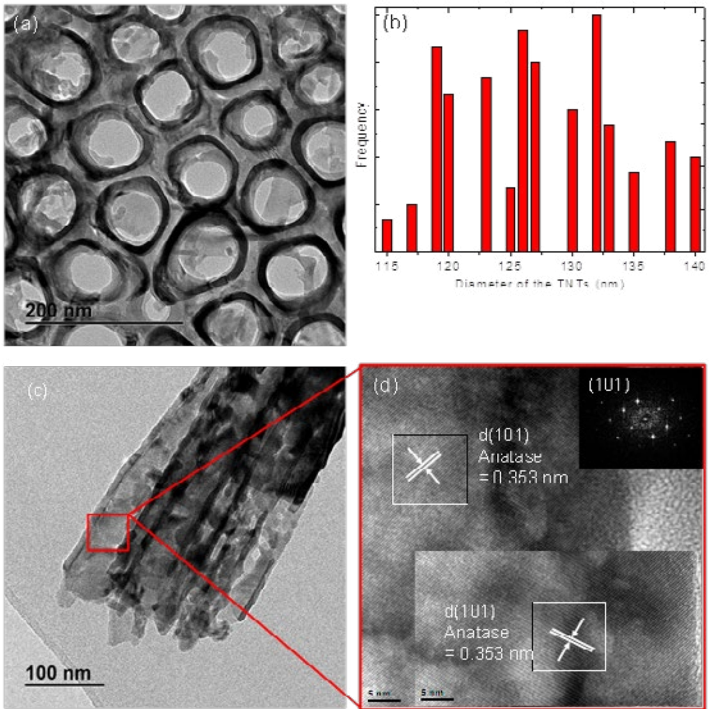

Figure 8: HRTEM images of TNTs annealed at 550 °C
(a) surface images
(b) Histogram showing pore size distribution
(c) & (d) cross sectional view showing TNTs walls.

Further increase in annealed temperature to 650 °C resulted in significant change in surface morphology of TNTs-FS as evidenced here in Figure 9. This is in contrast to previous observation where at this temperature significant change in the surface morphology has been reported [1, 888].

It is clearly visible from HRTEM images in Figure 9(a) that a slight or no change in the morphology of the TNTs. The histogram in Figure 9(b) has revealed a slightly smaller pore size diameter in the range between 85 nm–110 nm with a modal pore size diameter of 102.3 nm as compared to the TNT-FS annealed at 350-550°C. While TNTs on metal substrates showed raptured and collapsed TNTs at 550 °C and 650 °C [26]. Comparing TNTs-FS and TNTs-Ti (Foil), it is evident that substrates to which TNTs are grown respond differently to temperature changes. Those prepared on functional substrates showing desirable characteristics after being subjected to thermal treatment. These observations further conclude that TNTs grown on FTO glass substrate are of particular interest to DSSCs. Their transparency, structural and morphology stability may be beneficial for DSSC application.

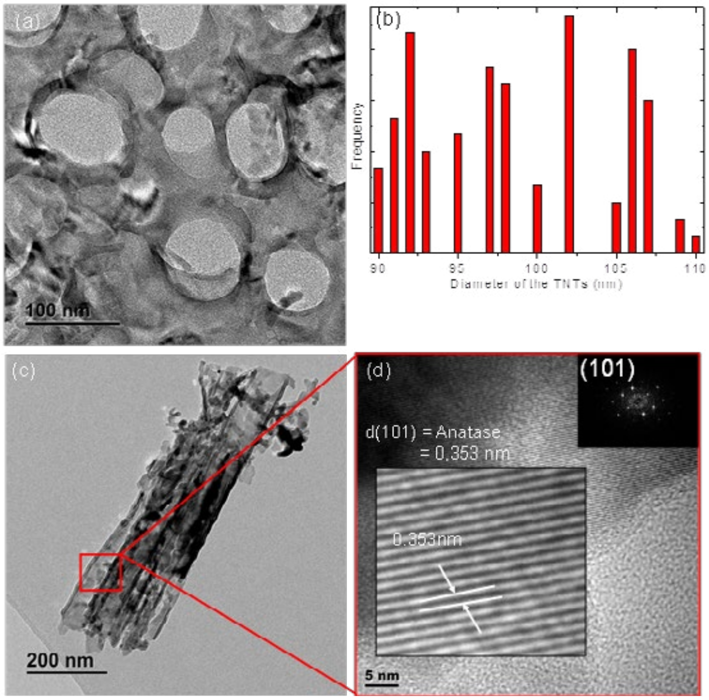

Figure 9 HRTEM images of TNTs annealed at 650 °C
(a) surface images
(b) Histogram showing pore size distribution
(c) cross sectional view showing TNTs walls
(d) individual TNT walls

HRTEM image in Figure 9 (d) revealed that the lattice fringes with lattice spacing of 0.353 nm between two neighbouring lattice fringes, corresponding to the (101) lattice plane of Anatase of TiO_2. Hence it can be concluded that increase annealing temperatures did not show a significant change in the crystallinity and surface morphologies of TNTs-FS. This further proves that TNTs prepared on functional substrates are ideal substrates material for solar cell applications.

Annealing Temperature (°C)	Pore Size Range (nm)		Modal pore diameter (nm)	
	TNT-FS HRTEM	TNTs-FS SEM	TNT-FS HRTEM	TNTs-FS SEM
350	130-152	130-155	130	142.14
450	145-165	150-170	163.1	163.35
550	115-140	90-140	132	103.48
650	85-110	85-105	102.3	85.05

Table 2: Surface parameters of TNTs-FS as function of annealing temperature comparison between HRTEM and SEM measurements.

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Conclusion

In this work Titanium dioxide nanotubes have been fabricated by electro-anodization of titanium thin films on fluorine doped tin oxide glass substrates (functional substrates). In comparison with literature reports on the morphological and structural properties of titanium dioxide grown on titanium foils our SEM analysis has revealed that the morphology of the annealed TNTs on Functional substrate is superior to the morphology of the TNTs on titanium foils over 350 -650 °C temperature range. SEM analysis has revealed that the TNT-FS had larger modal pore size diameters of 142.14 nm, 163.35 nm, 103.48 nm and 85.05 nm for the samples annealed at 350 °C, 450 °C, 550 °C, and 650 °C respectively. As compared to modal pore sizes of 34.56 nm, 56.52 nm, 42.50 nm and 31.05 nm for the TNT-FS annealed at 350 °C, 450 °C, 550 °C, and 650 °C respectively. This observation and the fact that the fabricate TNTs-FS did not show any evidence of partially collapse, rupture and deformation nanotube structures cements the fact that the TNT fabricated in this work are ideal electrode materials for development of DSSCs. The observed increased pore diameter also results in increased surface area for maximum dye loading, thus increase the number of photon generated electrons which obviously led to an improved solar cell performance. Simultaneously the improved architecture also enhances percolation for redox electrolyte for efficient regeneration of electron holes which consequently limits recombination and led to an improved solar cell performance.

HRTEM analysis has also revealed that the surface morphology of the TNTs-FS remained stable and intact over the investigated temperature range.

The higher magnification HRTEM clearly reveals that TNTs-FS annealed in this work had a d-spacing's of either 0.351 nm or 0.353 nm which belongs to the (101) lattice plane of Anatase TiO2. In fact all the TNTs-FS prepared in this work retained an Anatase phase of TiO2. In conclusion we can safely say that the TNTs prepared on functional substrates in this work are more stable and ideal electrode materials for DSSC solar cell applications.

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