In this paper the synthesis of self-organized Titania nanotubes (TNTs) by a facile potentiostatic anodization in a glycerol-based electrolyte is reported. The optimized TNTs were subsequently reduced through a cathodic reduction process to enhance its capacitive performance. FESEM and XRD were used to characterize the morphology and crystal structure of the synthesized samples. XPS analysis confirmed the reduction of Ti$^{4+}$ to Ti$^{3+}$ ions in the reduced Titania nanotubes (R-TNTs). The tube diameter and separation between the tubes were greatly influenced by the applied voltage. TNTs synthesized at voltage of 30 V for 60 min exhibited 86 nm and 1.1 µm of tube diameter and length, respectively and showed high specific capacitance of 0.33 mF cm$^{-2}$ at current density of 0.02 mA cm$^{-2}$. After reduction at 5 V for 30 s, the specific capacitance increased by about seven times (2.28 mF cm$^{-2}$) at 0.5 mA cm$^{-2}$ and recorded about 86% capacitance retention after 1000 continuous cycling at 0.2 mA cm$^{-2}$, as compared to TNTs, retained about 61% at 0.01 mA cm$^{-2}$. The charge transfer resistance drastically reduced from 6.2 Ω for TNTs to 0.55 Ω for R-TNTs, indicating an improvement in the transfer of electrons and ions across the electrode–electrolyte interface.

Keywords: anodization; titania nanotubes; glycerol; electrochemical capacitance; morphology; cathodic reduction

1. Introduction

Despite a monumental effort made by governments and policy makers around the world to address energy and environmental issues, the global energy crisis still remains humanity’s concern, owing to the rapidly growing population and sustainability issues associated with fossil fuel reserves. Thus, the increased demand for environmentally-friendly, good-performance and renewable energy storage devices [1,2]. Storage systems, based on electrochemical reactions such as batteries and supercapacitors for renewable energy technologies, have tremendous advantages due to their high quality in energy storage and delivering on demand and in load levelling of the electrical grid [3]. Supercapacitors are important energy storage devices due to their high-power density, longer life cycle, and have bridged the performance gap between traditional dielectric capacitors and batteries/fuel cells in terms of power and energy densities [4]. They are categorized into two main classes, namely, electrochemical double layer capacitors (EDLCs) in which the charge separation takes place at the interface between electrode
and electrolyte and pseudo-capacitors, which is due to the fast Faradaic redox reactions that take place at the surface of active electrode materials [5]. The performance of the supercapacitors depends tremendously on the physicochemical behaviors of their electrode materials. Therefore, it is very important to synthesize excellent electrode material for high performance supercapacitors [6].

A considerably high research interest is focused on ultrathin films because of their tremendous usefulness in the field of optical, medical, electrical and mechanical. In this direction, many efforts have been employed in constructing functional materials with well-designed control of chemical compositions, surface properties, and sizes in one, two and three-dimensional nanostructure [7]. Nanostructured materials with these exceptional properties cannot be found in the bulk phase and have already led to a breakthrough in different fields of science and technology. For instance, one-dimensional (1D) nanostructures such as nanotubes, nanowires, nanorods, and nanobelts, that was started by the discovery of carbon nanotubes by Iijima et al. in 1991 [8]. Within these nanostructure materials, TNTs have attracted attention in energy storage due to their ability to offer high surface areas and greatly enhanced electron transfer pathways in comparison to non-oriented structures, which can lead to a higher charge propagation in active materials. Among all the methods used for the synthesis of TNTs, electrochemical anodization is the most promising method as it offers suitably grown directly-connected nanotubes on the titanium substrate that can be used directly without any binder as a supercapacitor electrode [9]. The attraction of this preparation method is because of its simplicity, cost effectiveness and flexibility in controlling the surface morphological parameters of anodized TNTs which are highly affected by anodizing conditions [10].

Considerable research has been focused on the investigation of the morphology of TNTs under different anodizing conditions such as water content and fluoride concentration in the electrolyte [11–16], anodizing potential [10,12,15,17], anodizing time [13–15,18,19], and temperature [10,20]. For example, Endut et al. [19] observed the transformation of the pits of the oxide layer into larger and deeper pores within 10 to 30 min of the anodization time because of the integration of the smaller with the larger pores. Meanwhile, Kapusta-Kolodziej et al. [20] have revealed that the tube length, pore diameter, cell diameter and porosity of formed TNTs layers increased gradually with increasing the temperature of the electrolyte from 10 to 40 °C.

However, TNTs are characterized by a very low specific capacitance because of its semiconductor nature and poor electrical conductivity [21]. Therefore, some studies have used thermal treatment under hydrogen [22] or argon atmosphere [23] to improve the capacitive performance of TNTs by introducing oxygen vacancies to TNTs lattice. However, these approaches involved intensive controlled conditions such as high temperature and long reaction time. In view of this, several studies have been conducted to reduce TNTs prepared by either one step [9] or two step [24,25] anodization at constant voltage and time in ethylene glycol and in a mixture of glycerin and K2Cr2O7 [26] via the electrochemical modification method, namely the cathodic reduction process. This simple, fast and cost effective method was reported to convert about 22% of Ti4+ ions in TNTs’ surface regions into Ti3+ ions, as evidenced by the XPS peak of Ti3+ 2p3/2 [24].

The viscosity of the electrolyte can affect the movement of ions during anodization process as a result of relatively low chemical dissolution and fluoride ions transmission, and thus, the formed TNTs in glycerol, which are more viscous than ethylene glycol by about two orders of magnitude, will be more homogeneous, compact and uniform [12,13].

This study aimed to compare the morphology and capacitive performance of TNTs and R-TNTs under varying applied voltage and time in a glycerol-based electrolyte. TNTs were firstly synthesized using the anodization method before undergoing the cathodic reduction process to produce R-TNTs. Those factors were found to affect the physical properties during the synthesis process as well as the electrochemical capacitive performance of TNTs and R-TNTs as potential binder free electrodes for supercapacitor application.
2. Materials and Methods

2.1. Synthesis of TNTs

Pure commercially available titanium foil (0.25 mm thickness, 99.7% purity, Sigma-Aldrich, St. Louis, MO, USA) was cut into 1 × 2 cm dimensions and cleaned by subsequent sonication in acetone, isopropanol and deionized (DI) water, each for 15 min. This was followed by 10 min of chemical etching in 3 M HNO₃ (65%, MERCK, Fort kennelworth, NJ, USA) and a final rinsing with excess DI water thoroughly, before drying in air prior to use. The TNTs were synthesized by anodization using graphite as the cathode and the titanium foil as the anode. The electrolyte is a mixture of glycerol (99.8% purity, initial water content 0.03 wt %, Fisher Scientific, Waltham, MA, USA), 0.5 wt % NH₄F (FLUKA) and 25 v/v% water under constant magnetic stirring (400 rpm). The anodization was carried out at room temperature and at different anodization voltages and time in the range of 10–50 V and 30–120 min, respectively, using a DC power supply (Consort Mini, Cleaver Scientific Ltd., Rugby, UK). The distance between the two electrodes was maintained at 2 cm in all experiments. After the anodization, the samples were rinsed with DI water, dried in air and calcined at 500 °C under air atmosphere for 2 h at a heating rate of 2 °C min⁻¹.

2.2. Electrochemical Reduction of TNTs

The electrochemical reduction of TNTs was conducted at room temperature through cathodic reduction process in the same two-electrode cell as in anodization experiment but with TNTs as cathode while high density graphite served as anode in 0.5 M Na₂SO₄ as supporting electrolyte. The reduction process was performed under the voltage range of 4–8 V and reduction time range of 20–60 s. The samples were then rinsed with DI water and allowed to dry in air.

2.3. Material Characterizations and Electrochemical Measurements

The morphological and crystalline structures of the samples were characterized by field emission scanning electron microscopy (FESEM, JSM-7600F, JOEL, Tokyo, Japan) and X-ray diffractometer (XRD, Shimadzu, D60000, Japan) with Cu Kα (λ = 1.5406 Å) radiation. The oxidation states of the samples were determined by X-ray photoelectron spectroscopy (XPS, PHI Quantera II).

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) was employed to evaluate the electrochemical performance of the samples in a three-electrode cell containing 1 M aqueous KCl as electrolyte, Pt wire as counter electrode and Ag/AgCl as reference electrode using a potentiostat/galvanostat (Auto lab, PGSTAT204/FRA32M module).

The specific capacitance (SC) of the samples anodized at different voltages and time was calculated based on the charge—discharge curves or CV voltammogram using Equations (1) and (2), respectively [9,27]:

\[
SC = \frac{i\Delta t}{\Delta E A}
\]

\[
SC = \frac{\Delta Q}{A\Delta V} = \frac{i\Delta t}{A\Delta V}
\]

where \(i\) is the discharge current in amperes, \(\Delta t\) is the discharge time in seconds, \(\Delta E\) is the difference in discharge voltage in volts and \(A\) is the area of the active electrode in cm², \(\Delta Q\) is the total amount of charge accumulated over potential window \(\Delta V\), \(I\) is the respondent current and \(\Delta t/\Delta V\) is the CV scan rate.

3. Results and Discussion

3.1. Material Characterizations

Figure 1 shows the XRD patterns of TNTs before (1a) and after (1b) calcination and for the reduced TNTs (1c). Before calcination, peaks at around 35.1°, 38.4°, 40.2°, 53.2°, 63.0°, 71.0°, 76.2° and 77.4°
corresponding to hexagonal Ti substrate were found (JCPDS: 00-044-1294) that shows the TNTs were amorphous before calcination. Upon calcination at 500 °C, peaks at 25.7° and 48.5° were observed for which were indexed to 101 and 200 planes of pure anatase phase (JCPDS: 01-075-1537). This indicates that the anatase phase is the preferred growth orientation for TNTs as transformation to the rutile phase usually occurs at a higher temperature. After cathodic reduction, the XRD pattern of the R-TNTs remained the same as the calcined TNTs with slight increments in the intensity of anatase peak in the R-TNTs sample as compared to the TNTs. The crystallite size of the samples was calculated using Scherrer’s equation [27]:

\[
d = \frac{0.89 \lambda}{\beta \cos \theta}
\]

where \(d\), \(\lambda\), \(\theta\), and \(\beta\) are the crystallite size, X-ray wavelength (1.542 Å), Bragg diffraction angle and full width at the half maximum (FWHM) of the diffraction peak, respectively. The crystallite size for TNTs before and after calcination and that of R-TNTs calculated from the average of all the peaks in non-calcined TNTs and from the anatase peak based on 101 plane of calcined TNTs and R-TNTs were found to be 36, 28 and 31 nm, respectively. The crystallite size decreased after calcination and increased slightly from 28 to 31 nm after cathodic reduction, which might be caused by the oxygen vacancies due to partial oxygen loss in R-TNTs structure [17].

![Figure 1. XRD pattern of (a) as-anodized TNTs, (b) TNTs calcined at 500 °C for 2 h and (c) R-TNTs.](image)

The samples are further characterized by XPS analysis to investigate the oxidation states of the samples. Figure 2a–d depict the Ti 2p and O 1s XPS spectra for TNTs and R-TNTs. There are two broad peaks centered at 458.8 and 464.5 eV corresponding to Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) of Ti\(^{4+}\) peak of TNTs, respectively [24,26]. Similar peaks were also observed for R-TNTs but with a slight negative shift at 458.6 and 464.3 eV corresponding to Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) of Ti\(^{3+}\) peak, respectively [14,24,26,28]. For O 1s peaks, both TNTs and R-TNTs exhibited a broad peak at 529.9 and 529.8 eV, respectively, which is a characteristic of Ti-O-Ti [26]. However, broader peaks centered at 531.5 and 531.3 eV with slightly higher intensity were observed for R-TNTs, which was attributed to the Ti-OH species [13,28]. These XPS results indicate that oxygen vacancies were successfully created in the R-TNTs lattice through the cathodic reduction of TNTs.
The voltage was increased from 10 to 30 V. This is in correlation with the average tube diameter, which was seen in Figure 4a,b, respectively. The CV analysis of all the prepared samples was performed to facilitate fluoride ion mobility for the formation of desired morphology of TNTs [29]. Based on these findings, there is a need for sufficient applied voltage for adequate driving forces to facilitate fluoride ion mobility for the formation of desired morphology of TNTs [29,32].

3.2. Effect of Anodization Voltage and Time

The strength of the electric field depends on the applied potential difference across the oxide layer and can affect the pore/tube diameter, whereas anodization time affects the tube morphology [29,30]. The effect of anodization voltage on the synthesized samples was investigated in range of 10–50 V and the time was fixed at 60 min. Figure 3a–e depict the FESEM images of the TNTs synthesized at different anodization voltages. At 10 V, non-circular and disordered nanopores that have not been transformed to the tubes were formed due to the mild anodization voltage coupled with the high viscosity of glycerol electrolyte. For anodization at low applied voltage, the tube growth occurred at a slow rate due to low driving field across the bottom oxide to maintain the growth process [31]. Between anodization voltages of 20 to 40 V, the nanotubes transformed into highly ordered nanotubular structures with circular nanopores and dense walls with an increase in average tube diameter from 20 to 129 nm and wall thickness from 19 to 37 nm, as displayed in Table 1. This is in consonance with the findings of [10] and [17]. On the other hand, at applied voltage of 50 V, the nanotubes layers collapsed, and sponge-like structures were formed. At this particular voltage, there is a strong fluoride ions attack on the surface of the nanotubes, which resulted in the thinner and more flexible tube walls that lead to the collapse of the nanotubes, these findings are in agreement with the reported literature [29,32]. Based on these findings, there is a need for sufficient applied voltage for adequate driving forces to facilitate fluoride ion mobility for the formation of desired morphology of TNTs [29].

The relationship between tubes morphology and capacitive performance was further observed from the analysis of capacitive performance using the CV and GCD curves obtained at different applied voltage as seen in Figure 4a,b, respectively. The CV analysis of all the prepared samples was performed at a scan rate of 20 mV/s with the potential window of 0.6V, whereas SC was evaluated from the GCD analysis at a current density of 0.02 mA cm$^{-2}$. All the CV curves are symmetrical with distorted anodic regions, showing the TNTs were less electroactive at high anodic potentials.

On the other hand, all the GCD curves are triangular and symmetrical in shape with no IR drop observed. The SC of the samples increased about 4 times from 90 to 330 µF cm$^{-2}$ as the applied voltage was increased from 10 to 30 V. This is in correlation with the average tube diameter, which also increased about four times from 20 to 86 nm. Although sample synthesized at 40 V exhibited the highest average tube diameter of 129 nm, SC decreased by about 15% as the applied voltage was...
increased from 30 to 40 V. This may be attributed to the existence of more spacing between the tubes at 30 V as compared to 40 V, as can be seen clearly from the FESEM image in Figure 3c. This favors rapid diffusion rate of electrolyte ions from the bulk into the tubes that would essentially increase the capacitive performance. It has been suggested that a well-defined and separated nanotubes is more desirable in supercapacitor applications in contrary to the photocatalytic applications as the spacing between the nanotubes can be utilized in charge storage which can offer higher specific capacitance [16]. On the other hand, when the applied voltage was increased to 50 V, SC decreased drastically by about 48% to 170 µF cm⁻² as shown in Figure 4c. This may be associated with the collapse of the nanotubes at this high voltage, as they suffered from the high etching rates by the excessive attack of fluoride ions as mentioned before. Thus, the diffusion of electrolyte ions throughout the nanotubes became limited as the pathways were blocked leading to short discharging time that eventually decreased the SC value.

Figure 3. Top view FESEM images of TNTs at the same magnification (×100,000) synthesized at applied voltages of (a) 10 V, (b) 20 V, (c) 30 V, (d) 40 V and (e) 50 V.
Table 1. Morphological parameters of the TNTs at different anodization voltage.

| Voltage (V) | 10  | 20  | 30  | 40  |
|------------|-----|-----|-----|-----|
| Tube diameter (nm) | 20  | 60  | 86  | 129 |
| Wall thickness (nm) | -   | 19  | 21  | 37  |

For the influence of anodization time on morphology and capacitive performance of TNTs, anodization time was varied in the range of 30–120 min at 30 V applied voltage. Figure 5a–d show the cross-sectional view of FESEM images synthesized at different anodization times. From these FESEM images, we can see that the tube length increases with an increase in anodizing time with an average length of 0.6 to 1.7 µm, as shown in Table 2. The tube length increased about three times from 0.6 to 1.6 µm as anodization time was increased from 30 to 90 min. On the other hand, there is a negligible increase in tube length when the anodization time was varied from 90 to 120 min. Increase in anodization time increases oxide layer thickness, which led to increase in tube length until a balance occurred between a competing reactions of formation and dissolution of titanium oxide layer [31,33].

![Figure 4](image-url)

Figure 4. (a) CV curves at scan rate of 20 mV s\(^{-1}\), (b) GCD curves of TNTs at different applied voltage at current density of 0.02 mA cm\(^{-2}\) and (c) variation of SC with applied voltage.

For the influence of anodization time on morphology and capacitive performance of TNTs, anodization time was varied in the range of 30–120 min at 30 V applied voltage. Figure 5a–d show the cross-sectional view of FESEM images synthesized at different anodization times. From these FESEM images, we can see that the tube length increases with an increase in anodizing time with an average length of 0.6 to 1.7 µm, as shown in Table 2. The tube length increased about three times from 0.6 to 1.6 µm as anodization time was increased from 30 to 90 min. On the other hand, there is a negligible increase in tube length when the anodization time was varied from 90 to 120 min. Increase in anodization time increases oxide layer thickness, which led to increase in tube length until a balance occurred between a competing reactions of formation and dissolution of titanium oxide layer [31,33].
Figure 4. (a) CV curves at scan rate of 20 mV s\(^{-1}\), (b) GCD curves of TNTs at different applied voltage at current density of 0.02 mA cm\(^{-2}\) and (c) variation of SC with applied voltage.

Figure 5. Side view FESEM images of TNTs at the same magnification (×50,000) synthesized at anodization time of (a) 30 min (b) 60 min (c) 90 min and (d) 120 min.

Table 2. Tube length as a function of anodization time.

| Anodization time (min) | 30  | 60  | 90  | 120 |
|------------------------|-----|-----|-----|-----|
| Tube length (µm)       | 0.6 | 1.1 | 1.6 | 1.7 |
Based on this, we can say that the tube length is highly dependent on the anodization time and achieved its maximum elongation at 90 min. More uniform nanotubes are formed during a shorter anodization time, whereas a long anodizing duration led to the formation of non-uniform nanotubes, because of continued dissolution occurring across the whole tube length [30]. Figure 6a–c show the CV and GCD curves at different anodization times, and the variation of SC of TNTs with respect to anodization time. The SC increased more than two times from 140 to 310 µF cm$^{-2}$ as the anodizing time was increased from 30 to 90 min. Contrarily, only 6% of SC increment from 310 to 330 µF cm$^{-2}$ was observed at 120 min anodizing time. These results are related to the capacitive performance of TNTs and the tube length as an anodization time beyond 90 min did not give a significant increase in SC. The length of electron diffusion exceeded at longer anodizing time which affects the electron transport within the nanotubes as suggested by Regonini and Clemens [18].

![Figure 6. (a) CV curves at scan rate of 20 mV s$^{-1}$, (b) GCD curves of TNTs at different anodization time at current density of 0.02 mA cm$^{-2}$ and (c) variation of SC with anodization time.](image-url)
3.3. Effect of Reduction Voltage and Time

The electrochemical reduction process is accompanied by color transformation from grey to dark blue at all the applied reduction voltages as shown in Figure 7a,b. This change in optical properties may be due to the increase in defect density [25]. The FESEM image of R-TNTs as displayed in Figure 7c shows that there is no change in the morphology of optimized TNTs in terms of tube diameter and wall thickness after the reduction process. This indicates that the nanotubes suffered no damage during the cathodic reduction process as highly ordered, well-aligned and separated nanotubes can be observed.

Figure 7. (a) Color of TNTs and (b) R-TNTs (c) FESEM image of R-TNTs.

Reduction voltages in the range of 4–8 V were applied, and the time of cathodic reduction process were varied from 20–60 s. The current-voltage graph was attached in supplementary material (Figures S1 and S2). Figure 8a–d show the CV voltammograms and GCD curves at all the applied reduction voltage and time. All the CV voltammograms are nearly rectangular in shape, which is a typical characteristic of an EDLC that resulted from the highly reversible adsorption and desorption of ions at interface between electrode and electrolyte [34]. In addition, the GCD curves are nearly symmetrical and linear indicating good reversibility and coulombic efficiency of the samples. SC evaluated from both CV and GCD show similar trend whereby it increased as the voltage was increased from 4 to 5 V and then decreased continuously as the voltage increased from 5 to 8 V. When the reduction time was increased from 20 to 60 s, a short circuit error was detected at 8 V, which possibly caused the decline in specific capacitance performance at higher voltages [9]. The decrease in SC as the
reduction time was increased might be due to the increase surface defect density and combination rate [25]. It was found that 30 s was considerably enough to induce the cathodic reduction of TNTs. The highest SC of 3.82 mF cm$^{-2}$ at 200 mV s$^{-1}$ and 2.28 mF cm$^{-2}$ at 0.5 mA cm$^{-2}$ was obtained from the CV and GCD curves as shown in Figure 8e,f, respectively at optimized reduction voltage of 5 V for 30 s reduction time.

![CV voltammograms of R-TNTs at scan rate of 200 mV s$^{-1}$ recorded at different times.](#)

![GCD curves of R-TNTs at current density of 0.02 mA cm$^{-2}$ recorded at different times.](#)

![Variation of specific capacitance as a function of reduction voltages and times.](#)

**Figure 8.** CV voltammograms of R-TNTs at scan rate of 200 mV s$^{-1}$ recorded at different (a) reduction voltages and (c) times. GCD curves of R-TNTs at current density of 0.02 mA cm$^{-2}$ recorded at different (b) reduction voltages and (d) times. Variation of specific capacitance as a function of (e) reduction voltages and (f) times.

To evaluate the rate capability of the R-TNTs, the GCD test was conducted at different current densities from 0.1 to 0.5 mA cm$^{-2}$ in which about 99% of capacitance retention with no observable IR drop were obtained as shown in Figure 9a. This indicates good electrical conductivity and excellent rate capability of the sample in these current densities range with an operated potential of 1.2 V. Figure 9b,c compare the CV and GCD profiles of the pristine TNTs and R-TNTs, respectively. From those figures, we can clearly see that R-TNTs has recorded higher current response and larger integrated area.
with longer charging–discharging times than pristine TNTs with seven times capacitive performance enhancement (0.33 to 2.28 mF cm$^{-2}$). To further evaluate the electrochemical performance of the samples, a stability test was conducted for 1000 continuous charging–discharging cycles at 0.02 and 0.2 mA cm$^{-2}$ current density for pristine TNTs (Figure 9d) and R-TNTs (Figure 9e), respectively. R-TNTs maintained 86% of its initial capacitance despite the high current density applied which is 10 times higher than that of pristine TNTs, which could only maintain 61% at the lower current density of 0.02 mA cm$^{-2}$. The slight increase in capacitance of TNTs and R-TNTs at some stages during the charge–discharge cycles could be due to the self-activation of more non-stoichiometric states of titanium dioxide during the processes which contribute to the enhancement of the specific capacitance. On the other hand, the loss in capacitance of TNTs and R-TNTs during the long cycling may be ascribed to the structural defects and gradual diffusion of incorporated hydrogen in R-TNTs. R-TNTs also maintained around 98% of coulombic efficiency throughout the 1000-cycling test as compared with 90% for pristine TNTs. These results implied longer capacitive stability and good reversibility of the R-TNTs as compared to pristine TNTs.

![Figure 9](image_url)

**Figure 9.** (a) GCD curves of R-TNTs at different current densities. Comparison of CV voltammograms (b) and GCD curves (c) of pristine TNTs and R-TNTs at a scan rate of 200 mV s$^{-1}$ and at current density of 0.02 mA cm$^{-2}$. Specific capacitance and coulombic efficiency versus number of cycles for (d) pristine TNTs at 0.02 mA cm$^{-2}$ and (e) R-TNTs at 0.2 mA cm$^{-2}$ current density.
Electrochemical impedance spectroscopy (EIS) was then used to evaluate the electrical resistance of the pristine TNTs and R-TNTs in the frequency range from 0.01 Hz to 1 MHz. Figure 10a,b represent the Nyquist plots of the pristine TNTs and R-TNTs, respectively. It can be seen that the impedance line of R-TNTs at the low frequency region is almost perpendicular to the imaginary axis as compared to the impedance line for pristine TNTs. From the diameter of semicircle, the charge transfer resistance ($R_{ct}$) at the electrode–electrolyte interface was acquired while the cell-electrolyte resistance ($R_s$) was the first intercept of the semicircle corresponding to the high frequency region. Using electrochemical circle fit, the values of $R_s$ and $R_{ct}$ were determined and are presented in Table 3. We can see that both $R_s$ and $R_{ct}$ values for R-TNTs are significantly lower as compared to the corresponding values for pristine TNTs. This indicates an improvement in the electrons and ions transfer after the cathodic reduction as demonstrated by the CV and GCD profiles, which led to higher capacitive performance of R-TNTs than pristine TNTs.

![Figure 10. Nyquist plots of (a) pristine TNTs and (b) R-TNTs with inset showing a magnified high frequency region.](image)

**Table 3.** $R_s$ and $R_{ct}$ values for pristine and R-TNTs deduced from Nyquist plots.

| Samples      | $R_s$ (Ω) | $R_{ct}$ (Ω) |
|--------------|-----------|--------------|
| Pristine TNTs| 15.2      | 6.2          |
| R-TNTs       | 1.49      | 0.55         |

4. Conclusions

In this study, the influence of anodization voltage and time on morphology and capacitive performance of pristine TNTs and R-TNTs were investigated. For pristine TNTs, anodization voltage greatly affects the tube diameter, wall thickness and spacing between the tubes, whereas anodization time particularly affects the tube length. Highly ordered TNTs were formed at the voltage range of 20 to 40 V. It was found that apart from the tube diameter, spacing between the tubes also influenced the electrode–electrolyte interaction that affected the overall capacitive performance. The sample synthesized at 30 V for 1 h and reduced at 5 V for 30 s gave the highest SC of 3.82 mF cm$^{-2}$ at 200 mV s$^{-1}$ of scan rate. The R-TNTs showed improved electrochemical performance such as higher capacitance, excellent rate capability, better coulombic efficiency, cycling stability and lower charge transfer resistance as compared with pristine TNTs. Considering these properties, the R-TNTs can be a potential binder free electrode in supercapacitor application.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/1996-1073/13/11/2767/s1, Figure S1: Current-voltage graph for cathodic reduction process; Figure S2: Current-time graph for cathodic reduction process.
Author Contributions: Conceptualization, Z.Z. and M.M.M.; methodology, Z.Z. and M.M.M.; validation, Z.Z., H.N.L. and A.H.A.; formal analysis, M.M.M. and M.S.A.; investigation, M.M.M.; data curation, Z.Z. and M.M.M.; writing—original draft preparation, M.M.M.; writing—review and editing, Z.Z. and N.N.B.; visualization, Z.Z., M.M.M. and N.N.B.; supervision, Z.Z., H.N.L. and A.H.A. All authors have read and agreed to the published version of the manuscript.

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