



## Titania Nanotubes Synthesised via the Electrochemical Anodisation Method: Synthesis and Supercapacitor Applications

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**Abstract** – Titania nanotube is gaining tremendous interest for its unique features including high surface area, ion-exchange ability, photocatalytic potential and prominent electrical properties. Many attempts were made to manipulate the unique properties of titania nanotubes for supercapacitor application. In this review a comprehensive list of literatures on fabrication of titania nanotubes via anodisation method in fluoride-based electrolytes and its application as supercapacitor are discussed. This review shows that the nanotube morphology can be optimized by varying the anodisation parameter such as electrolyte concentration, pH, voltage, and bath temperature. The review also includes studies on the application of titania nanotubes as supercapacitor on improving the specific capacitance value by doping with metal oxides and conducting polymers.

**Keywords:** electro-thermal\_anodisation, titania nanotube, supercapacitor

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### Introduction

Enormous demands on clean energy and energy storage are the two great challenges of the twenty first century. Considering the needs of a modern society, the discovery of new, low cost and environmentally friendly energy conversion and storage system has become undoubtedly essential. Supercapacitor is one of the extensively studied energy storage due to its numerous potential applications in different fields. In comparison to batteries, supercapacitors possess higher power density and longer life cycle. However, supercapacitors have lower energy density which position them in the centre between batteries and conventional capacitors as shown in Figure 1. The performance of this device depends on the properties of the materials used. Recently, nanostructured materials have attracted much attention from worldwide researchers due to their superior mechanical, chemical, electrical and optical properties. Ever since the pioneer work on fabrication of carbon nanotube by Iijima (Iijima, 1991), extensive research has continued to explore the nanostructure of other transition metals and their properties. Nanostructured materials have been considered the best potential electrode material for supercapacitors as they can improve ion absorption or faster surface

redox reactions. Extensive research efforts have fostered the enhancement of electrochemically active sites for charge transfer and controlled ionic and electronic transport at small diffusion length scales which offers high surface area (Yu, Tetard, Zhai, & Thomas, 2015).

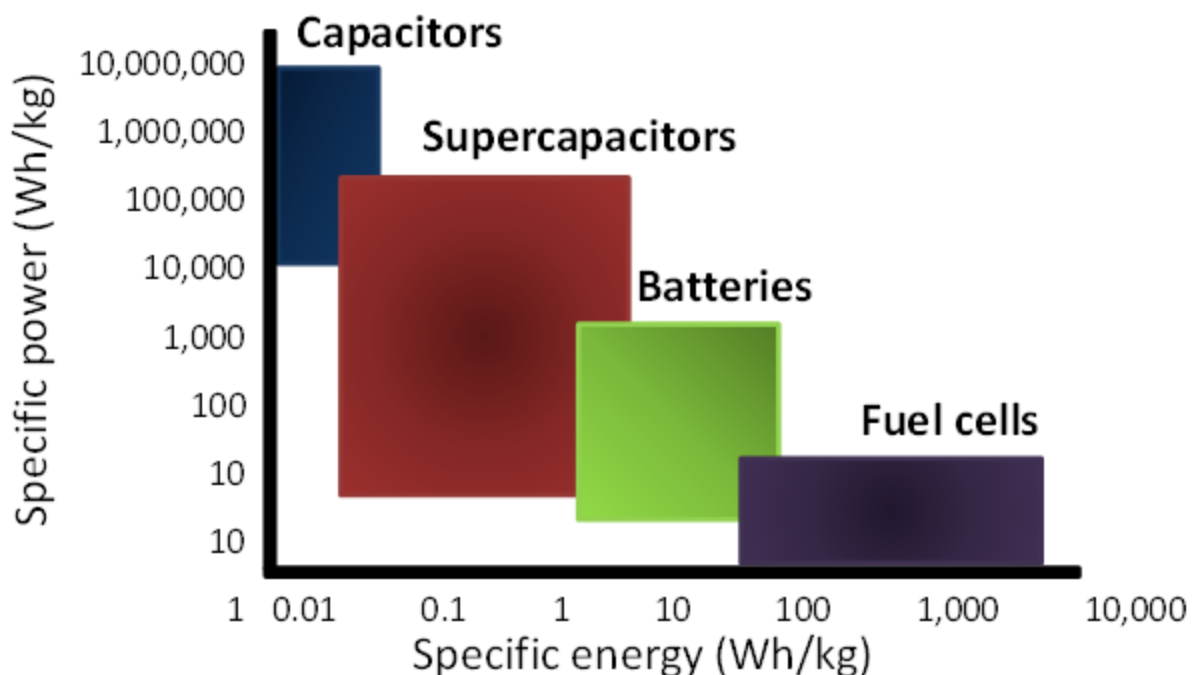


Figure 1: Comparison of various electrochemical energy conversion systems

Supercapacitors are generally classified into two types based on their storage mechanisms which are electrochemical double layer capacitor (EDLCs) and pseudocapacitors. EDLCs are based on charge separation at the electrolyte-electrode interface, while pseudocapacitors chemically store their charge via redox reaction at the vicinity of the surface electrode material. The crucial aspects in developing high performance supercapacitors are the surface area, electronic, the ionic conductivity and mechanical and chemical stability of the materials. The surface area of the materials plays a huge role on determining the capacitance since the charge is stored on the surface of the electrode materials. An electrode with higher surface area leads to an improved specific capacitance as it promotes more surface area for the reaction to take place. Nanostructuring of the electrode materials is a feasible method to considerably improve the specific capacitance. As specific capacitance and rate capability are dependent on both electronic and ionic conductivity of the electrode materials, the use of high electronic and ionic conductivity material will help to maintain the rectangular shape of cyclic voltammetry (CV) curve and symmetry of galvanostatic charge-discharge curve that leads to high capacitance. The high electronic and ionic conductivity of the materials also reduce the loss of specific capacitance as the scan rate or current density increases. The cycle stability of the materials has proven that the material is good enough to withstand a long cycle without affecting its capacitive performance. Generally, the cycle stability is influenced by the mechanical and chemical stability of the electrode materials during the cycling process. Phase change, dissolution and side reaction of the active materials are major reasons for causing cycle instability and sensible electrode surface protection may boost the cycle stability. Therefore, the study of new electrode materials designed with nanostructured properties offers promising results to fulfil high performance supercapacitors.

Transition metals have garnered great attention as a potential material for supercapacitor applications as its highly conductive materials can provide multiple oxidation states which lead to high capacitance. Among all transition metal oxide, titanium dioxide (TiO<sub>2</sub>) or titania is the most studied material, with more than 40,000 publications in different fields in the past 10 years. Titania is known as a highly functional compound with interesting chemical and physical properties. The synthesis of titania nanotubes (TNTs) has fascinated great interest for electrochemical supercapacitor application due to the high surface area and unique electron pathways. Various methods have been used in synthesizing TNTs, but the electrochemical anodisation of titanium foil has been extensively studied as it offers very convenient ways to achieve highly ordered and suitably back-connected nanotube layers on the substrate. In this review, the synthesising of TNT and its application as supercapacitors are discussed.

### **Electrochemical supercapacitor mechanisms**

In general, electrochemical supercapacitors (ES) charge storage mechanisms are based on two types of capacitive behaviour which are Electric Double Layer Capacitors (EDLC) and pseudocapacitors, depending on the nature of the electrode material.

#### *Electric double layer capacitor*

Electric double layer capacitors (EDLCs) which are also known as non-faradic electrical charge storage involve electrostatic charge energy storage by the separation of charge in a Helmholtz double layer at the interface between the conductive electrode and an electrolyte. There is no charge transfer across the electrode/electrolytes interface and no ion exchange occurs between the electrode and the electrolytes; hence, EDLCs can operate with stable charge-discharge performance, usually for as many as 10<sup>6</sup>. In this way, the energy is stored at the double layer interface.

Carbon materials are commonly exhibiting EDLCs. Different forms of carbon material such as activated carbon (Chang et al., 2012; Gamby, Taberna, Simon, Fauvarque, & Chesneau, 2001; Ruiz, Santamaría, Granda, & Blanco, 2009; Xu, Hou, Cao, Wu, & Yang, 2012), graphene (Bai, Rakhi, Chen, & Alshareef, 2013; Ramadoss & Kim, 2013), carbon nanotubes (Kiamahalleh, Zein, Najafpour, Sata, & Buniran, 2012) and carbon aerogels (Miller, Dunn, Tran, & Pekala, 1997) have been excessively studied as electrodes for supercapacitors due to their unique properties of high surface area, light weight, excellent electrical conductivity, compatibility with other materials, and controllable pore size distribution.

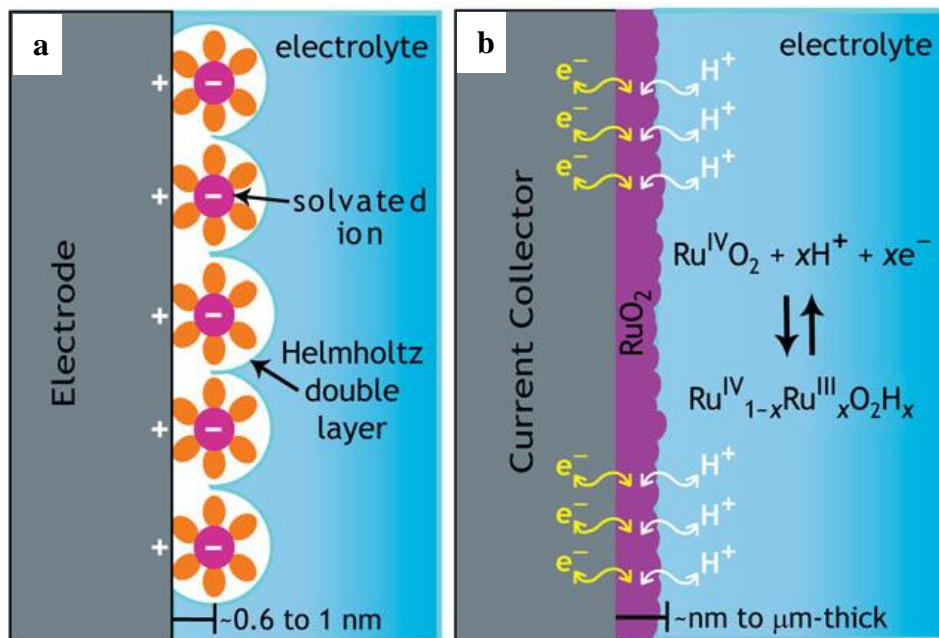


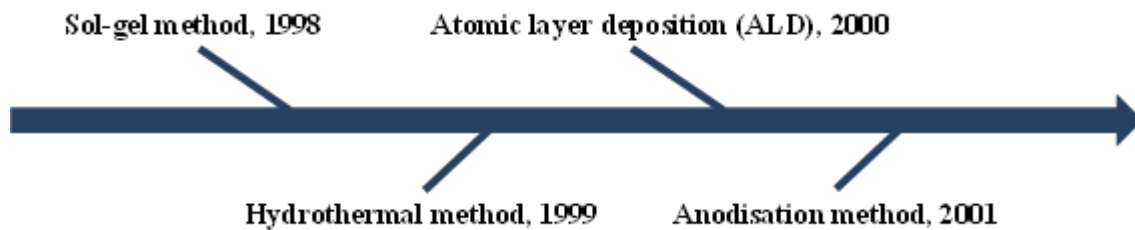
Figure 2: Schematic of charge storage via (a) EDLC and (b) pseudocapacitance (Jeffrey W. Long, 2011)

### Pseudocapacitors

In contrast, pseudocapacitors or faradic electrical charge storage associated with electron transfer which involve the transfer of charge across the double layer, are achieved by surface redox reaction on the material electrode. Materials undergoing such redox reactions are mainly metal oxides/nitrates/sulphides and conducting polymers (Conway, 1999). Since the reaction of pseudocapacitors occurred on the surface and in the bulk near the surface of the electrode, pseudocapacitors possess higher energy density than EDLCs. As reported by Conway et al. (1999), the specific capacitance of a pseudocapacitroelectrode can be 10-100 times higher than EDLC electrode, but it is generally limited to the cycling stability due to changes in the chemical composition. Furthermore, pseudocapacitor electrode also suffers from lower power density compared to EDLC electrode because of the faradic process which is normally much slower than non-faradic process (Chuang, Huang, Teng, & Ting, 2010). RuO<sub>2</sub> is a promising material that exhibits pseudocapacitance due to its excellent electricronic behaviour. Its pseudocapacitive behaviour is generally ascribed to a series of fast and reversible electron-transfer reaction that is coupled with adsorption of photon at or near the electrode surface (Figure 2) (P. Yang & Mai, 2014). However, the rarity and high cost of RuO<sub>2</sub> have led to its limitation in commercialization as a supercapacitor. Therefore, studies on other metal oxides and nitrides such as Co<sub>3</sub>O<sub>4</sub> (Jang, Yu, Park, Kim, & Ahn, 2015; Kandalkar, Lee, Chae, & Kim, 2011), NiO (Inamdar et al., 2011; Liu, Chang, Sun, & Gao, 2013; Z. Yang et al., 2014), MnO<sub>2</sub> (Ataherian, Lee, & Wu, 2010; K.-T. Lee & Wu, 2008; Wei, Cui, Chen, & Ivey, 2011) or their composites, or other combination of alternative metal oxides with different types of carbons (Chang et al., 2012; Chee, Lim, & Huang, 2015; Ng, Lim, Lim, Chee, & Huang, 2015) and conducting polymers (Mi, Zhang, Yang, Ye, & Luo, 2008; Mi, Zhang, Ye, & Yang, 2008), have been explored to develop more practical pseudocapacitive materials.

### Synthesis of titania nanotubes

The morphology of titania nanotubes (TNTs) has attracted worldwide researchers to study this material in both scientific and technological aspects. Nanotubes may provide a basis for many applications (such as photocatalyst, solar cell, batteries and supercapacitor) due to their unique combination of geometry and chemical/physical functionality. Compared to random TiO<sub>2</sub> nanoparticles, the open mesoporous structure can offer a high surface area to volume ratio (Cochran, Shyue, & Padture, 2007; J. Lee & Jho, 2011). The first study on synthesizing TNTs was by Hover (1996) who used an electrochemical deposition method into an ordered alumina template. Later the evolution of other techniques (Figure 3) such as sol-gel technique (Kasuga, Hiramatsu, Hoson, Sekino, & Niihara, 1999), hydrothermal method (Kasuga et al., 1999; Nian & Teng, 2006; Tsai, Nian, & Teng, 2006; Zhang et al., 2003), atomic layer deposition (ALD) (Knez, Nielsch, & Niinistö, 2007; Leskela & Ritala, 2003; Shin, Jeong, Lee, Sung, & Kim, 2004) and anodisation method (Zulkarnain Endut, Mohd Hamdi, & Wan Jeffrey Basirun, 2013; J. M. Macak et al., 2007; Maryam Salari, Aboutalebi, Konstantinov, & Liu, 2011) were introduced.



*Figure 3: The fabrication method for TNTs*

Over the past decades, TNTs have been extensively studied for many applications such as in solar cell, batteries and photocatalyst owing to their unique properties discussed earlier. As the development of synthesizing TNTs progresses, the application of electrochemical anodisation and hydrothermal treatment have been the most favourable as they give the most promising nanotube structure. However, each synthesising method has its own unique advantages and functional features. Titania dioxide is often synthesised by sol-gel or precipitation method in solutions and then the templates are removed. Therefore, the size and morphologies of the obtained materials can be easily controlled by the size of the template used (Marichy, Bechelany, & Pinna, 2012). The sol-gel method is an acid-catalysed hydrolysis reaction of titanium alkoxide precursor followed by a condensation reaction. The gel-type polymeric Ti-O-Ti chain will be formed, which will then be hydrolysed and thus resulting in the titania to precipitate. Then, the titania sol is sucked into the pores of the templates before a heat treatment is applied. The alumina template containing titania will then be selectively dissolved to obtain the prepared titania.

The hydrothermal method which is known as a well-established method in fabricating titania nanotubes was first reported by Kasuga et al. (Kasuga et al., 1999). In this method, bulk TiO<sub>2</sub> powder was treated with alkaline solution in a Teflon-lined autoclave at 100-150° C for several hours, followed by an acid treatment in HCl (Du, Chen, Che, Yuan, & Peng, 2001; Kasuga, Hiramatsu, Hoson, Sekino, & Niihara, 1998; Kasuga et al., 1999). The formation of the tube geometry was based on the exfoliation of TiO<sub>2</sub> crystal planes in the alkali environment and stabilization as Ti-O-Na<sup>+</sup> (Roy,

2011). The nanolayer sheets were then rolled into the tubes during the cooling process or in the HCl treatment. Some argument exists in the literature on several experimental factors that are crucial to obtaining a tubular material. The amount of synthesised nanotubes and their geometrical distribution are actually dependent on the specific reaction conditions (Du et al., 2001). The template technique is also a popular method for fabricating nanotubular structure. Apart from TiO<sub>2</sub>, other transition metals such as WO<sub>3</sub>, ZnO, ZrO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, MnO and CuO are widely fabricated using this technique. This technique produces single tubes or loose agglomerates of tubes that are dispersed in solution, and a wide distribution of tube lengths is obtained. The tube is usually compacted into layers on an electrode surface for its usage in electrical devices. However, this technique leads to the arbitrary orientation of the nanotube on the electrode which unfortunately exceeded many advantages of the nanotube structure.

An atomic layer deposition (ALD) is a thin film deposition technique which is based on a sequential use of the gas phase in the chemical process. The ALD appears to be a promising method in depositing target samples due to its simplicity, reproducibility and high conformity of the as-deposited films. This method is basically based on the reaction between precursor materials which are separated into successive surface relation. The reactant will be kept separated and will react with surface species in a self-laminating process. Each surface reaction will be separated with a purge step to remove unreacted precursor and by-products. The synthesis of TNTs by an ALD is done by altering the cycle of exposure to a titania precursor (such as TiCl<sub>4</sub> or Ti(OiPR)) on the surface of templates (such as porous alumina)—one layer after another and then followed by purging and hydrolysis (Roy, 2011). This approach allows nanotubular or rod structure to be vertically aligned to the substrate.

In contrast, the electrochemical anodisation is widely known for producing self-organized structures with an array of oxide nanotubes aligned perpendicular to the substrate surface. The tubes are attached to the metal surface and are electrically connected and need no additional treatment in electrode preparation. This method is discussed in the next topic.

### **Electrochemical anodisation method**

Anodisation is a facile, useful and low cost method to synthesize different self-organized porous structures on different materials. When a metal sheet (M) is exposed to a sufficiently anodic voltage in an electrochemical configuration with the presence of fluoride ions (Figure 4), an oxidation reaction occurs as in Equation 1 (Roy, 2011) forming a compact oxide layer on the surface of the metal sheet.



There are four different oxide morphologies as shown in Figure 5 (b) and they can be obtained by an anodisation method.

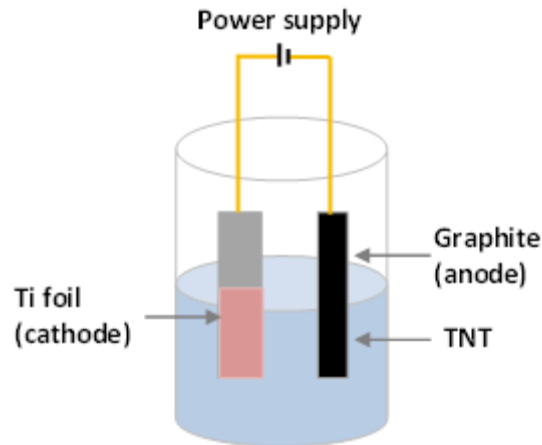


Figure 4: The electrochemical anodisation set-up

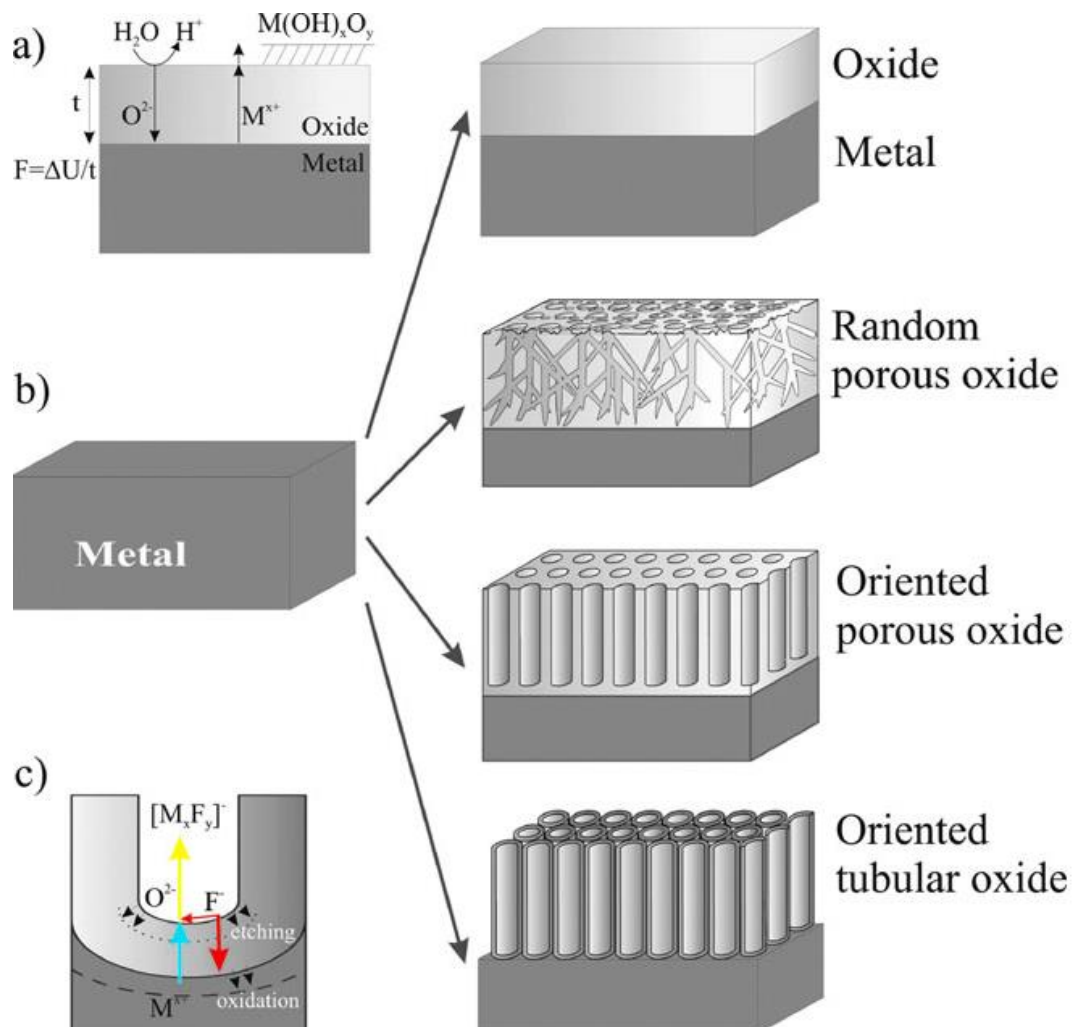


Figure 5: (a) Mechanisms of oxide formation on the metal sheet, (b) Metallic titanium morphologies obtained by electrochemical anodisation-compact oxide film, disordered nanoporous layer, a self-ordered nanoporous or self-ordered nanotubes layer, (c) Mechanism of nanotubes formation (Ghicov & Schmuki, 2009).

Formation of self-ordered TNTs by an anodisation method in chromic acid electrolytes containing hydrofluoric acid was first reported by (Zwilling, Aucouturier, & Darque-Ceretti, 1999). This pioneering work reported that the material formed was amorphous but might contain crystallites, due to the current fluctuations. Furthermore, limited thickness of the tube layers formed in the sample was ascribed to oxide growth/chemical-dissolution equilibrium (steady-state) (Beranek, Hildebrand, & Schmuki, 2003). Grimes et al. further discussed the formation of anodized TNTs from titanium foil in a fluoride-based solution (Gong et al., 2001). They reported that the tubes morphology obtained by anodized titanium films were more complicated compared to anodized aluminium. In contrast with that reported by Zwilling et al., well-aligned nanotube structures composed by titanium oxide were found to grow from the discontinuous nanoporous titanium oxide film (Gong et al., 2001). Improvements to the tube geometry were then established by Macak et al. (Albu et al., 2008; J. M Macak, Gong, Hueppe, & Schmuki, 2007; J. M. Macak et al., 2007; Jan M. Macak, Tsuchiya, Taveira, Aldabergerova, & Schmuki, 2005; Jan M Macak, Zlamal, Krysa, & Schmuki, 2007). They demonstrated that pH played a crucial role in improving the tube thickness. Macak et al. reported that at natural pH much longer tube could be grown (Jan M. Macak, Tsuchiya, et al., 2005; Jan M Macak et al., 2007). They also reported that smooth tubes without sidewall inhomogeneity (ripples) could be grown with higher aspect ratios and showed highly improved ordering in non-aqueous electrolytes.

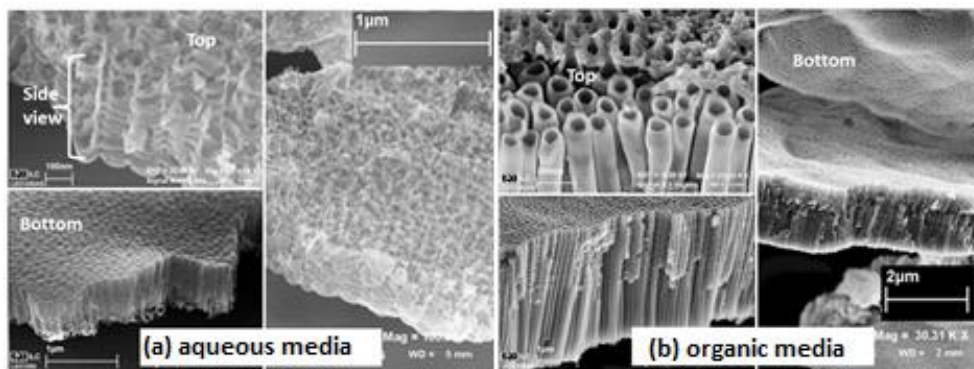


Figure 6: TNTs obtained in fluoride containing (a) aqueous and (b) organic electrolytes (Regonini, Bowen, Jaroenworuluck, & Stevens, 2013)

Extensive research on organic electrolytes such as ethylene glycol demonstrates that almost ideal hexagonally arranged tubes can grow to a thickness of several hundreds of micrometres (Albu et al., 2008). Figure 6 shows the morphologies of TNTs prepared in fluoride containing aqueous and organic electrolytes. A closed scalloped bottom, an open tube (mouth) and the presence of ripples at the side walls of the tubes displayed by TNTs were prepared in aqueous electrolyte. In comparison, TNTs prepared in organic electrolytes showed smooth and partially rippled tube walls, depending on the water content. Lim et al. (2012) studied the effect of water content in organic electrolytes on the TNT morphology. The study reported that TNTs synthesized without the addition of water had a circular shape and they became disordered with irregular shapes upon the addition of water to 50 vol%. The surface morphology of the TNTs became rougher, less dense and less well-packed with increasing water content as displayed in Figure 7 (Ying-Chin Lim, Zulkarnain, Mohd Zobir, & Tan, 2012). This study established that water content also plays a role in forming the tubes in organic based electrolyte.



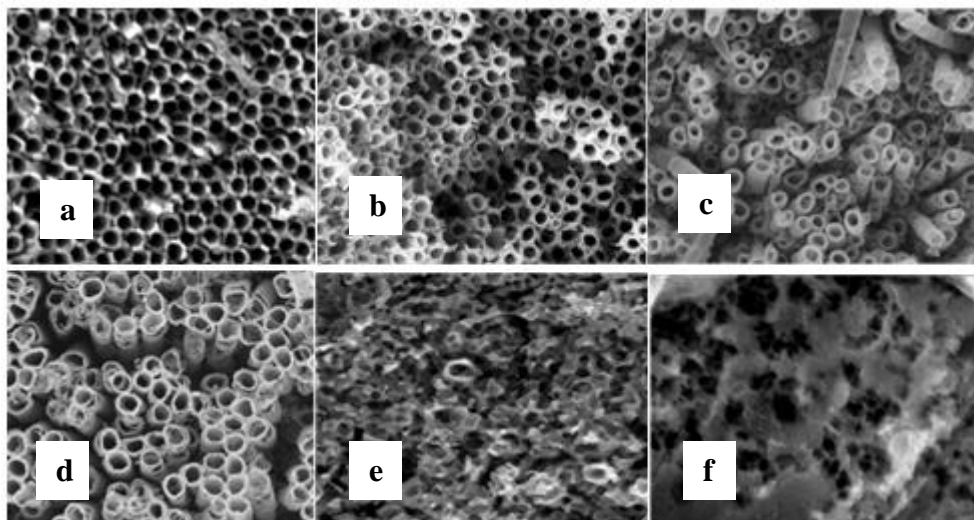
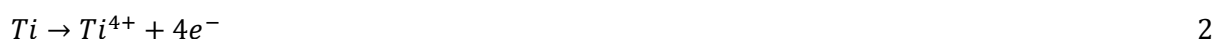


Figure 7: Top view FESEM image of TNTs synthesized in (a) <1 vol%, (b) 5 vol%, (c) 25 vol%, (d) 50 vol%, (e) 75 vol% and 100 vol% H<sub>2</sub>O (Ying-Chin Lim et al., 2012)

#### *Mechanisms of titania nanotubes formation*

In the initial phase of the anodisation process, the titanium surface is electrochemically oxidized to form a compact oxide layer on the titanium surface as displayed in Equation 2-4. These reactions are known as a field-assisted oxidation process, since the applied potential controls the ion migration within the metal/metal oxide interface.



Simultaneously, hydrogen evolution will take place at cathode (Equation 5)



The presence of fluoride ions in the electrolytes will form fluoride water soluble  $[TiF_6]^{2-}$  species. The fluoride ions that are present in the electrolytes can react with  $Ti^{4+}$  (Equation 6) or can chemically attack the formed  $TiO_2$  (Equation 7).



These fluoride ions will lead the pitting of the oxide layers, which will provide locations for the field-assisted chemical dissolution of  $TiO_2$  (Equation 7). As the pits are chemically dissolved further into the oxide layer, the nanotubes will form. The pits function as routes for the electric current, for the development of nanotubes, therefore, the high dissolution rate forms inside the tubes from the pits.

*Factors affecting the growth of titania nanotubes* The desired nanotube morphology can be formed by controlling the experimental condition of the anodisation process. The pH of electrolytes, fluoride concentration in the electrolyte, aging of the electrolytes, temperature, duration and voltage of the anodisation process are identified as the primary control of the nanotube length and diameter.

The ability of the electrolytes to dissolve the foaming oxides is affected by the pH of electrolytes. Sreekantan et al. (2009) reported that the nanotube lengths from ~0.7 to 2.5  $\mu\text{m}$  could be formed by adjusting the pH of electrolytes. Figure 8 displays the top view and cross-section of TNTs prepared in different pHs of electrolytes (from pH 3 to pH 7). Results showed that pH 3 gave highly defined tubes with longest tube length (700 nm) compared to pH 5 and pH 7 which gave slightly rough and less-dense nanotubes with shorter tube length (600 nm and 500 nm respectively). They concluded that the thickness of the tubes was strongly affected by the pH of the electrolytes which ultimately controls the rate of the TNT formation. The rate formation of TNTs at pH 3 reported more or less  $23 \text{ nm min}^{-1}$ ;  $15 \text{ nm min}^{-1}$  and  $8 \text{ nm min}^{-1}$  for pH 5 and pH 7 respectively which supported the conclusion. The reduced rate of tube formations due to increased pH of electrolytes were probably associated with the decreased chemical dissolubility of the electrolyte as explained in Equation 7. The presence of fluoride ions also played a critical factor in governing the formation of TNTs where fluoride ions act as a pore initiating agent. The effect of fluoride ion concentration demonstrated by Lim et. al. (2011) showed that the fluoride ion concentration had to be kept low to minimize dissolution (Ying-Chin Lim, Zulkarnain, Mohd Zobir, & Tan, 2011). However, it also had to be at sufficient concentration to ensure the TNT growth. They reported that increasing fluoride ions from 0.07 M to 0.20 M led to good coverage, uniformed and well aligned TNTs. In contrast, 0.25 M forming completely loose structures with thorny-like structure observed. In terms of tube length, increasing fluoride ions from 0.07 M to 0.10 M gave 397 nm and 541 nm respectively. Further increase of the ion concentration led to shorter tube length which ascribed to faster chemical dissolution of oxide by a higher amount of fluoride ions (Ying-Chin Lim et al., 2011).

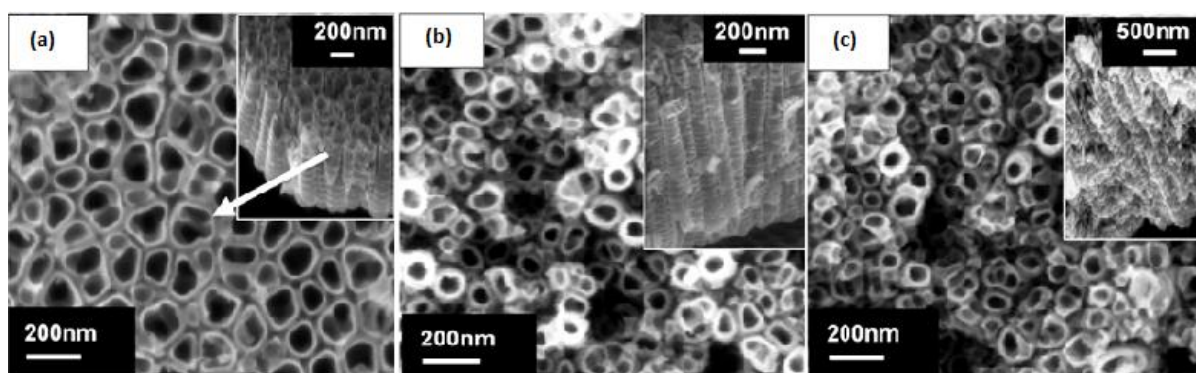


Figure 8: SEM image of TNTs prepared in electrolyte at (a) pH 3, (b) pH 5 and (c) pH 7 (The insert images show the length of nanotubes) (Sreekantan et al., 2009).

For organic electrolytes, the aging time of the electrolytes is another factor that should be taken into account in synthesizing well defined TNTs. The aging of the electrolytes involved in the reusing of the electrolytes reportedly enhanced the electrical conductivity (K. Lee, Lee, J., Kim, H., Lee, Y., Kim, D., Schmuki, P., Tak, Y., 2009). These were due to the increase of the  $[\text{TiF}_6]^{2-}$  content in the

electrolyte, and a higher water content which eventually reached saturation due to moisture adsorption (Regonini et al., 2013). Moreover, a higher electrical conductivity also enhances the growth rate of the TNTs, as it will facilitate the passage of current required to form the oxide.

The synthesis of TNTs are majorly performed by potentiostatic conditions, whereas a constant potential was applied and current generated by anodisation was monitored. The applied potential that usually used ranges from 5 to 30 V in aqueous electrolytes while 10 to 60 V in organic electrolytes (Roy, 2011). The applied potential determines the electric field strength across the oxide, thus affecting the migration of ions and the tube diameter. Other factors that contributed to the tube diameter is the temperature of the electrolytes. Regonini et al. (2012) reported that the temperature of the electrolytes affected the dissociation rate of the TNTs. Larger tube diameters formed at higher anodising temperatures were reported by Wang et al. (2009) to have caused a high viscosity of the electrolyte solution at a low temperature and this reduced the ion migration and dissolution of TiO<sub>2</sub> and Ti by fluoride ions. Figure 9 shows the study of anodisation potential and temperature by Sulka et al. (2013) which suggested that with increasing electrolyte temperature at different applied potentials, the rate of oxide growth increased and the TNT layer became thicker (Sulka, Kapusta-Kołodziej, Brzózka, & Jaskuła, 2013). As shown in Figure 9, the tube thickness increases when the temperature increases for both applied potentials. It can be attributed to the effect of decreasing electrolyte viscosity on the rate of tube growth applied for organic electrolytes. However, the tube diameter is not strongly affected by the temperature of the electrolytes but exponentially decreases with increasing applied potential (Figure 9).

Studies on an optimal anodisation time are required to extend the maximum length of TNTs. Anodisation in aqueous electrolytes was reported as aggressive since it allowed the tubes to grow longer by a few mm (Jan M. Macak, Sirotna, & Schmuki, 2005; Jan M Macak et al., 2007; Tsuchiya et al., 2005). Such thickness can be reached within minutes from the onset of the anodisation process; however, the anodisation time should be prolonged from 30 minutes to 2 hours to allow the structure to rearrange itself thus increase the degree of self-order. An opposite condition has been applied to organic electrolytes, as the reaction that takes place is much slower and the dissolution process is not as significant as in aqueous. However by using organic electrolytes, it is common to observe a porous layer on the top of the tubes, which is a remnant of the initial barrier layer formed during the early stage of anodisation process (Mor, Varghese, Paulose, Shankar, & Grimes, 2006). The nanotubes grow underneath the porous layer and it is assumed that there are preferential paths for the organic electrolytes which leads to inhomogeneous over-dissolution for the entire tube structure (Regonini et al., 2012).

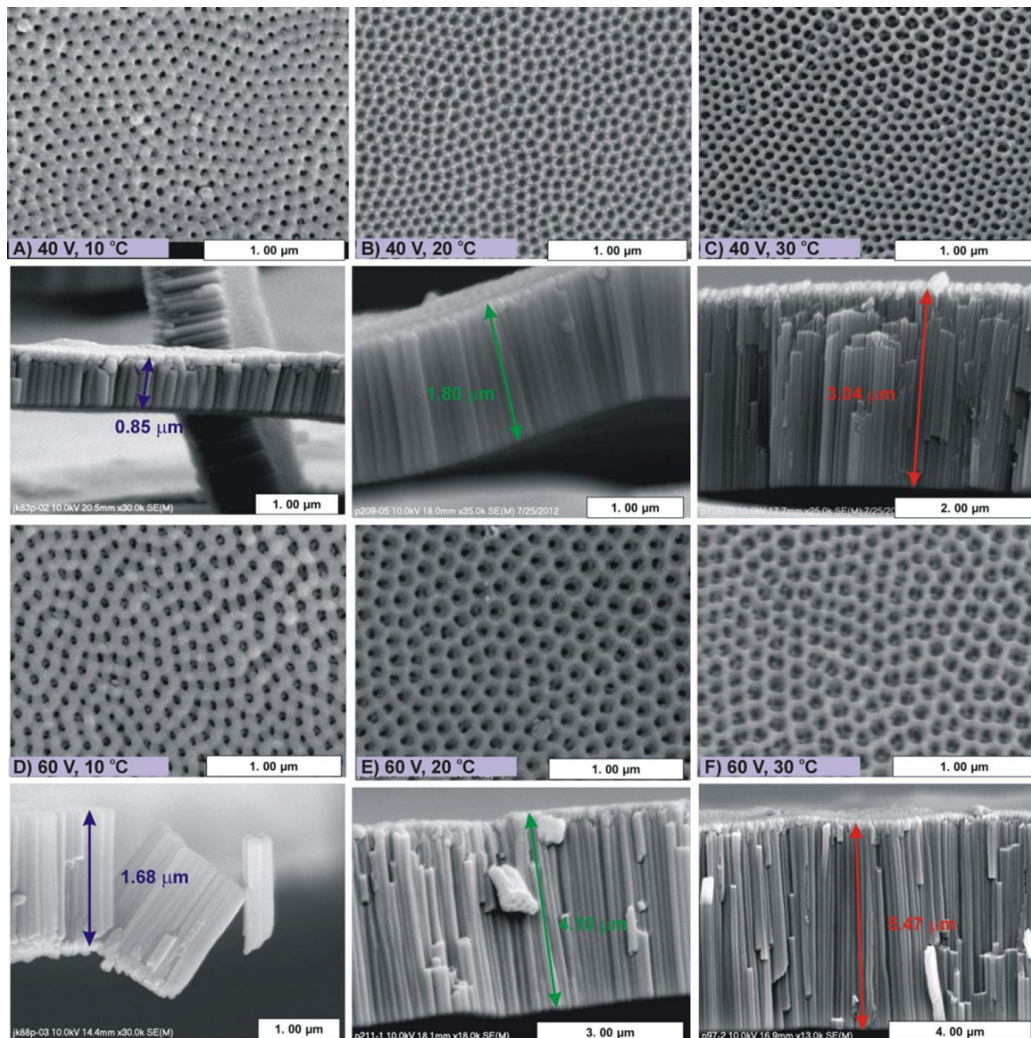


Figure 9: FESEM image of top view and cross-sectional view of TNTs prepared at 40 V (A, B and C) and 60 V (D, E and F) and at the temperature of 10 °C (A and D), 20 °C (B and E) and 30 °C (C and F) (Sulka et al., 2013)

### Modification of titania nanotubes

Despite its excellent morphological structure and surface area, the synthesised TNTs have very low specific capacitance. It has been widely reported that the specific capacitance of TNTs (less than 1 mF cm<sup>-2</sup>) only resembles conventional electric double-layer capacitor (Maryam Salari, Konstantinov, & Liu, 2011). This is attributed to low conductivity of TNTs (Wu et al., 2014). Therefore, modification of the TNT surface by electrochemical and thermal approaches by adding active materials such as metal oxides, nitride, sulphides or conducting polymers have been attempted to improve the conductivity and capacitance.

#### *Electrochemical/thermal approach*

The modification of TNTs by an electrochemical approach is widely used as it is simple, facile and cost effective compared to other methods. The pioneering work on modification using an electrochemical approach was done by Macak et al. (2007). Their study reported on a reductive doping process to form higher conductivity layer at the bottom of the TNT layers and this was done at an ambient temperature and required simple preparation steps. In the doping process, the Ti<sup>4+</sup> was

reduced to  $Ti^{3+}$  which acted as a donor centre and formed a highly conducting barrier layer. They claimed that only 1% of the  $Ti^{4+}$  in the TNT layers could be reduced to  $Ti^{3+}$  and the effect of the reductive doping process could be seen by colour changes of the films from light grey to black. Further study by Zhou et al. (2013) where a facile cathodic reduction process was carried out to introduce oxygen vacancies into the TNTs (Zhou & Zhang, 2013). Apart from oxygen vacancies, a hydroxyl group was also formed on the surface of the TNTs, leading to the improvement in the electrochemical performance of the modified electrode. They reported that the specific capacitance of the modified TNTs increased by 13 times larger than unmodified counterparts. Wu et al. (2014) developed an electrochemical doping method to enhance the capacitive performance of their TNT electrode. Their so-called electrochemical hydrogenation doping adopted the same approach as the studies by Macak et al. (2007) and Zhou and Zhang (2013) reported that the oxygen vacancy  $e$  was introduced to the TNTs by the reduction of  $Ti^{4+}$  and the interstitial of the hydrogen ions. Wu et al. (2014) also reported that the modified TNTs showed slight increase in the tube diameter; however, it did not significantly change the tube morphology which proved that modification by the electrochemical approach did not damage the tube structure. The evolution on the TNT colour was also reported as the colour of the TNT electrode changed from white (TNTs) to dark grey (modified TNTs) as shown in Figure 10. The capacitive performance of the modified TNT electrode showed an excellent result as it gave specific capacitance of  $20.08 \text{ mF cm}^{-2}$  and  $9.07 \text{ mF cm}^{-2}$  at  $4.00 \text{ mA cm}^{-2}$  and  $0.05 \text{ mA cm}^{-2}$  in  $2 \text{ M LiSO}_4$ . Wu et al. (2014) also reported on a self-assembled supercapacitor device based on modified TNT electrodes which gave specific capacitance of  $5.42 \text{ mF cm}^{-2}$  and with a power density of  $27.66 \text{ mW cm}^{-2}$  at the current density of  $0.05 \text{ mA cm}^{-2}$ . This self-assembled device displayed outstanding capacitive rate capability with 60% specific capacitance retained when current density increased from  $0.05$  to  $4.00 \text{ mA cm}^{-2}$ .

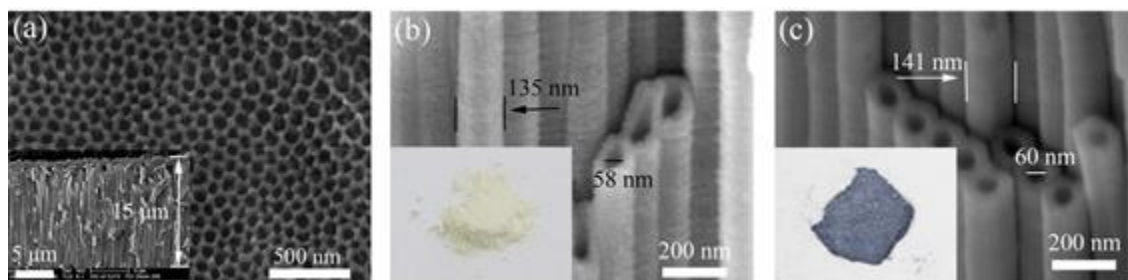


Figure 10: FESEM image for (a) top view of TNTs, (b) Cross-sectional of TNTs and (c) cross-sectional of modified TNTs. The insert shows (a) the length, (b) the colour of TNT powder and (c) the colour of modified TNT powder (Wu et al., 2014).

Other than electrochemical method, thermal approach has also been studied as a method to modify the TNTs in order to enhance the electrochemical behaviour. This method introduces different heat-treatments in the synthesizing step of TNTs. Salari et al. (2011) reported that upon the reduction of  $Ti^{4+}$  to  $Ti^{3+}$ , and with oxygen depletion of the structure, the anatase to rutile transformation was promoted, hence enhancing the electrochemical behaviour of the electrode (Maryam Salari, Konstantinov, et al., 2011). The oxygen vacancies created inside the TNT structure enhance the capacitance of the TNT electrode due to the increase in the TNT conductivity (Maryam Salari, Konstantinov, et al., 2011). However, Salari et al. (2012) reported that the enhancement in specific

capacitance through the thermal approach could be attributed to the partially reduced valence state created at the surface of the TNTs, and the presence of other defects during the thermal treatment (M. Salari et al., 2012). The cyclic voltammetry profile for modified TNTs (IV) in Figure 11 (b) displayed almost rectangular-shaped curve with a large integrated area compared to unmodified TNTs (I). The specific capacitance of modified TNTs was reported to be  $911 \mu\text{F cm}^{-2}$  while that of the unmodified TNTs was  $30 \mu\text{F cm}^{-2}$  at the scan rate  $1 \text{ mV s}^{-1}$  in  $1 \text{ M KCl}$ . There was an almost linear relationship observed between voltage and charging-discharging time at high current density as shown in Figure 11 (c), which was expected from a non-faradic electron double-layer capacitor. However, a slightly non-linear curve was observed at high current density, indicating the reaction in the charging process. Salari et al. (2012) reported that this might be due to the introduction of oxygen vacancies during the thermal treatment. The modified TNT electrode also displayed an excellent cycle stability as it still possessed fairly stable capacitance with 98% capacitive retention even after 500 cycle (Figure 11 (d)).

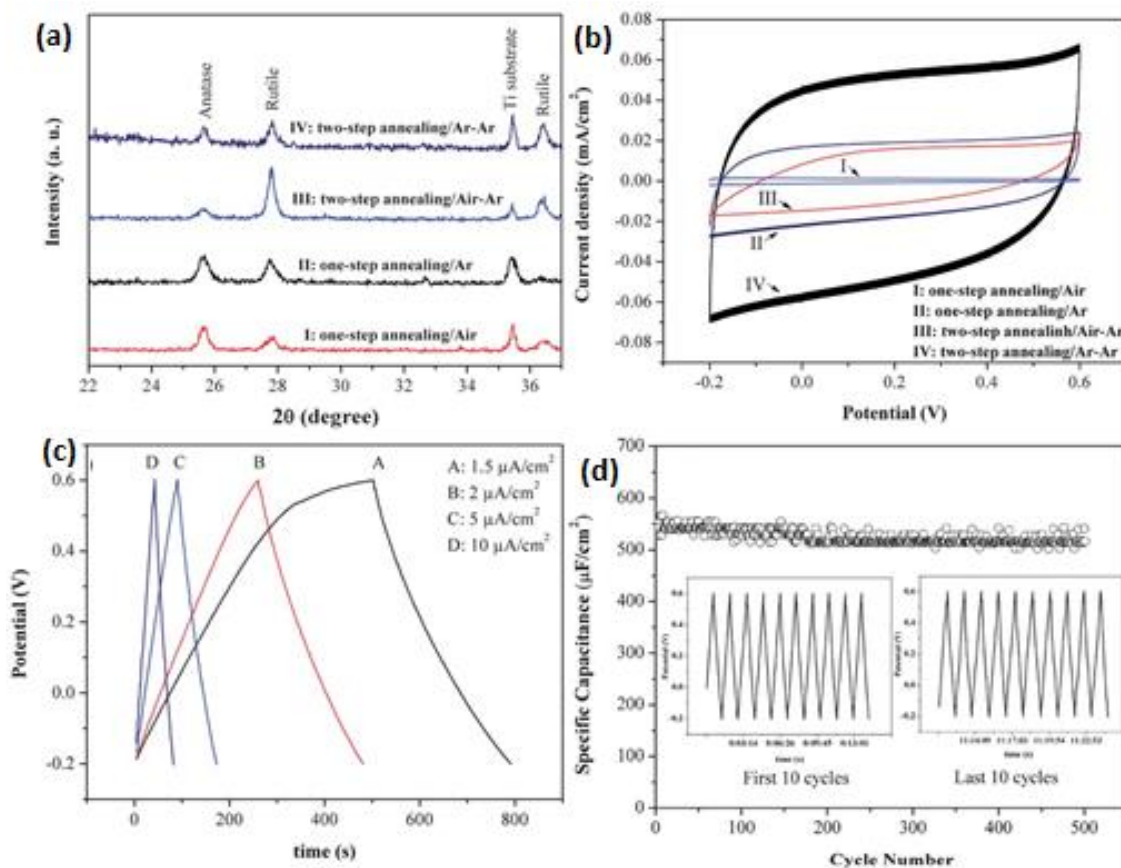


Figure 11: (a) XRD patterns of unmodified TNTs and modified TNTs (b) Cyclic voltammogram of all samples in  $1 \text{ M KCl}$  (c) Galvanostatic charge-discharge plots of modified TNTs at different current densities and (d) Cycle stability profile of modified TNTs (M. Salari et al., 2012).

#### Metal and conducting polymers doping approach

Generally, transition metal oxides such as  $\text{RuO}_4$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{NiO}$  and  $\text{MnO}_2$  have received immense attention for application as an electrode for supercapacitors. The presence of multiple valence states in the transition metals can lead to efficiency redox reaction with the electrolytes, hence increasing the capacitive behaviour of the electrode. Due to these properties, metal oxides are preferable to be

deposited into the TNTs in order to enhance their electrochemical properties either by covering the tubes or by coating throughout the tubes wall as shown in Figure 12.

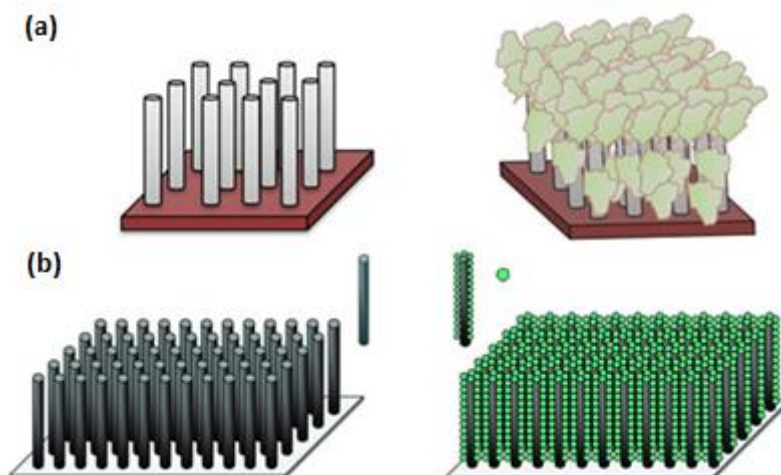


Figure 12: Decorating approach on the modification of TNTs

Researchers have immersed deeply on modifying TNTs with depositing metal oxides into them in order to enhance the capacitive behaviour of the TNT electrode as supercapacitors. Xie and Fu (2010) reported on depositing  $\text{RuO}_2$  by an electroreduction and electrooxidation process which enhanced the specific capacitance of the electrodes to  $241 \text{ F g}^{-1}$  and  $640 \text{ F g}^{-1}$  for  $\text{RuO}_2/\text{TiO}_2$  and  $\text{RuO}_2/\text{TiO}_2/\text{Ti}$  respectively. The specific energy obtained was  $48.2$  and  $128.0 \text{ Wh Kg}^{-1}$  and the specific power was  $0.8$  and  $2.4 \text{ kWh kg}^{-1}$  respectively (Xie & Fu, 2010).  $\text{NiO-TiO}_2$  nanotube electrode was reported by Kim et al. (2010) when Ni-Ti alloy foils were used in the anodisation process. This approach gave specific capacitance of  $40$  to  $100 \text{ F g}^{-1}$  for the optimum  $\text{NiO-TiO}_2$  nanotube morphology while specific capacitance of  $120$  to  $300 \text{ F g}^{-1}$  obtained with a Ni-Ti ratio of 1:2 (Kim, Zhu, Yan, Perkins, & Frank, 2010). Xie et al. (2009) extensively studied the deposition of NiO into TNTs. Different approaches were studied by Xie et al. (2009) such as electrochemical, hydrothermal and multi-cycle electrodeposition-oxidation methods. All approaches gave different morphologies of deposited NiO into the TNTs as shown in Figure 13. The specific capacitance obtained were  $42.3$  and  $72.7 \text{ mF cm}^{-2}$  at current density of  $0.5 \text{ mA cm}^{-2}$  in  $1.0 \text{ M NaOH}$  for NiO-TNTs via one-cycle and multi-cycle electrodeposition-oxidation synthesis respectively (Xie, Huang, Zhou, Liu, & Huang, 2009).

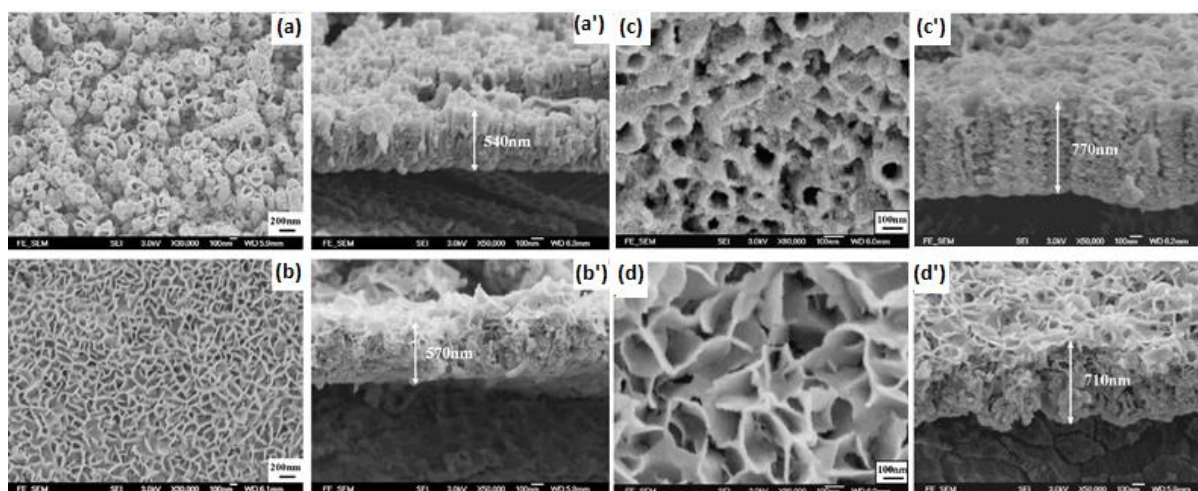


Figure 13: FESEM images of top view and cross-sections of (a, a') deposited of NiO into TNTs via one-cycle, (b, b') multi-cycle electrodeposition-oxidation synthesis, (c, c') hydrothermal synthesis and (d, d') electrochemical synthesis (Xie et al., 2009; Xie, Zhou, Huang, Huang, & Lu, 2008).

Lu et al. (2012) developed an electrochemical deposition of  $\text{MnO}_2$  into TNTs that displayed excellent specific capacitance as high as  $912 \text{ F g}^{-1}$  at a scan rate of  $10 \text{ mV s}^{-1}$ . Furthermore, it also showed good rate capability with capacitance retention of 69.9 % when the scan rate increased from 10 to  $100 \text{ mV s}^{-1}$  (Lu et al., 2012). Further exploration on depositing  $\text{MnO}_2$  into TNTs was done by Gao et al. (2015) when they studied  $\text{MnO}_2\text{-TiO}_2/\text{C}$  nanocomposite. The coaxial of TNTs with carbon was done by a hydrothermal method then followed by electrodeposition of  $\text{MnO}_2$ . The introduction of a carbon material into the TNTs was expected to enhance the capacitive behaviour of the TNTs as it performed in combination of EDLS and pseudocapacitors. The  $\text{MnO}_2\text{-TiO}_2/\text{C}$  electrode showed a specific capacitance of  $580 \text{ F g}^{-1}$  at a current density of  $2.6 \text{ A g}^{-1}$  in  $1.0 \text{ M H}_2\text{SO}_4$  with an excellent rate capability and a capacitance retention of 60 % (Gao et al., 2015).

Among the advanced materials, conducting polymers such as polyaniline, polythiophene and polypyrrole present fascinating properties of electrode materials for electrochemical capacitors. Excellent properties such as fast doping-dedoping during charge-discharge, easy chemical-electrochemical synthesis and low cost compared to other metal oxide conducting polymers became favourable to be doped into TNTs. The infiltrate conducting polymers also can act as an active site for the faradic reaction to store higher amount of electrical charge in an aqueous electrolyte. Mujawar et al. (2011) reported on the electropolymerization of polyaniline into TNT electrodes that exhibited a specific capacitance  $740 \text{ F g}^{-1}$  at a current density of  $3 \text{ A g}^{-1}$ . Xie and Du (2012) came out with the idea of polypyrrole-TNT hybrid by an electrochemical synthesis route. This hybrid electrode displayed a high specific capacitance of  $179 \text{ F g}^{-2}$  based on a mass of polypyrrole at a current density of  $1.85 \text{ mF cm}^{-2}$ . It also showed excellent cycle stability as it could retain a specific capacitance of 85 % of the initial capacitance after 200 cycles (Xie & Du, 2012). A further study by Xie et al. (2012) developed the polypyrrole/titania/polyaniline coaxial nanotube hybrid by a stepwise electrodeposition process. This hybrid electrode exhibited excellent capacitive performance as the specific capacitance reported was  $497 \text{ F g}^{-1}$  at a current density of  $0.5 \text{ A g}^{-1}$  in  $1 \text{ M H}_2\text{SO}_4$ . The cycle stability of this hybrid



electrode also showed a great performance as it possessed 72.3 % capacitive retention after 500 cycles at a high current density of 2.0 A g<sup>-1</sup>.

### **Application of titania nanotube as a supercapacitor**

TNTs are widely used in many applications such as solar cells, photocatalysts, electrochromic devices and also supercapacitors. Nowadays, supercapacitors have attracted great attention for the investigation of energy storage and conversion systems. The properties of TNTs which are known to be chemically stable, large surface area and the interconnectivity of the active material will enhance the capacitance performance. to be charged and discharged continuously without degrading, thus gave huge advantage to supercapacitors over batteries. Extensive studies have been done on the application of TNTs as a potential electrode material for supercapacitors (Zulkarnain Endut et al., 2013; Z. Endut, M. Hamdi, & W. J. Basirun, 2013; Hui et al., 2013; Maryam Salari, Aboutalebi, Chidembo, Konstantinov, & Liu, 2014; Maryam Salari, Aboutalebi, et al., 2011; Wu et al., 2014). In terms of charging mechanisms, it has been mostly suggested that TNTs contribute very low non-faradic capacitance (Conway & Pell, 2003). In general, titania capacitors would resemble conventional electric double-layer capacitors, which act as non-faradic mechanisms with a very low specific capacitance of 10-40  $\mu\text{F cm}^{-2}$  in the charge-discharge process (M. Salari et al., 2012). However, the high surface area that is possessed by TNTs may lead to a higher specific capacitance of the sample. The anodisation of the titanium foil has been extensively studied as it offers favourable ways to achieve highly ordered and suitably back-connected TNTs on substrate which can be used directly as a binder-free supercapacitor electrode. The good capacitive performance of TNTs has been reported by Salari et al. (2011) at a specific capacitance of 538 to 911  $\mu\text{F cm}^{-2}$  at the scan rate decrease from 100  $\text{mV s}^{-1}$  to 1  $\text{mV s}^{-1}$  in 1 M KOH. In comparison to titania powder, the specific capacitance obtained is much lower than TNTs which is 33 to 181  $\mu\text{F cm}^{-2}$  at the same scan rate (Maryam Salari, Aboutalebi, et al., 2011). Meanwhile, Endut et al. (2013) have studied the effect of calcination condition on capacitive performance of the TNT electrode as supercapacitors. They concluded that a longer calcination time gave a higher specific capacitance whereby at 5-hour calcination, TNTs possessed specific capacitance of 52  $\mu\text{F cm}^{-2}$  while at 1-hour calcination time, TNTs possessed a specific capacitance of 16  $\mu\text{F cm}^{-2}$  at the scan rate of 5  $\text{mV s}^{-2}$  (Endut et al., 2013). Endut et al. (2013) also reported on the effect of an anodisation parameter on the capacitive performance of a TNT electrode. In this study they used Box-Behnken design to investigate the best parameter that gave a higher specific capacitance. The study concluded that the anodisation of Ti foil for 97.78 min using a voltage of 39.11 V and 0.42 wt% of  $\text{NH}_4\text{F}$  concentration gave the highest specific capacitance of 145.6  $\mu\text{F cm}^{-2}$  (Zulkarnain Endut et al., 2013). Even though many studies have been done on tailoring the surface morphologies and geometrical of the TNTs (Zulkarnain Endut et al., 2013; Raj, Sundheep, & Prasanth, 2015; Xiao et al., 2008), the capacitive performance of the TNTs is still low compared to other transition metal-based supercapacitors. Therefore, many studies on the modification of TNTs were carried out as discussed in the previous sub-section. The modification of TNTs by electrochemical, thermal and metal/non-metal doping indeed have enhanced the capacitive performance of the TNTs as an electrode for the supercapacitor application.

## Conclusion

Undeniable demands by modern society, the discovery of new, low cost and environmentally friendly energy conversion and storage system have become undoubtedly essential. This has led to the development of an electrochemical supercapacitor that possesses high power density and longer life cycle. In this context, nanostructured materials have been considered the best potential electrode material for supercapacitors as they improve ion adsorption or faster surface redox reactions. The extensive research on the anodisation method in synthesizing TNTs has shown steady improvements of its morphological control. Since the first anodised TNT study, many other studies were carried out in controlling the nanotube length, but the studies also showed that systematically controlling the nanotube diameter and wall thickness to the narrow dimensions could enhance the capacitive behaviour of the electrode. In spite of many studies done in investigating the chemical structure and formation of TNTs, there is still an ambiguous space to explore and explain. Furthermore, the modifications of TNTs by an electrochemical, thermal approach and doping with metal oxides or conducting polymers have been widely investigated to improve the performance of the TNTs as supercapacitors. In fact, the versatility and feasibility of the TNTs as a supercapacitor application has been demonstrated and the results are yet to be confirmed.

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