UNIVERSITI PUTRA MALAYSIA

ELECTROCHEMICAL PROPERTIES OF MODIFIED TITANIA NANOTUBES INCORPORATED WITH Mn2O3 AND Co3O4 FOR SUPERCAPACITOR APPLICATION

NURUL ASMA BINTI SAMSUDIN

FS 2017 68

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By

NURUL ASMA BINTI SAMSUDIN

Thesis Submitted to the School of Graduate Studies,
Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of
Doctor of Philosophy

June 2017

Dedicated with much respect and gratefulness to

the love of my life after Allah and Prophet Muhammad, my beloved parents.

Abstract of this thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

ELECTROCHEMICAL PROPERTIES OF MODIFIED TITANIA NANOTUBES INCORPORATED WITH Mn_2O_3 AND Co_3O_4 FOR SUPERCAPACITOR APPLICATION

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Chairman: **Professor Zulkarnain Zainal, PhD**
Faculty : **Science**

Highly ordered titania nanotubes (TNTs) was used in this study as it known to have a remarkable chemical stability and its open ended nanotubes structure offers large surface area and good interfacial connectivity with the electrolyte which will enhance the capacitive performance. The TNTs were synthesised by electrochemical anodisation method in two-electrode cell containing NH_4F solution. Parameters affecting the morphological and geometrical aspects as well as electrochemical performance of TNTs were investigated by varying the electrolyte composition, applied anodisation voltage and anodisation time. The formation of TNTs were confirmed by x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) analyses. Meanwhile the electrochemical performance of the TNTs were evaluated in 1.0 M KCl electrolyte using cyclic voltammetry (CV) and galvanostatic charge-discharge test in a three electrode electrochemical cell system consisted of Pt as counter electrode, Ag/AgCl (3 M KCl) electrode as reference electrode and TNTs as the working electrode.

Single phase anatase TNTs were obtained upon calcination at 500 ^oC for samples prepared at all electrolyte compositions. FESEM revealed the nanotubes formed were uniform with well defined circular tubes. However, the tubes becomes disordered and clustered with irregular shape as the water content increased. All prepared TNTs displayed reversible unsymmetrical CV shapes with distorted anodic region and this was associated to the non-faradic charge-discharge of the oxide surface. TNTs 5 % exhibits highest current which leads to higher capacitance compared to other synthesised samples.

TNTs 5% was further modified by electrochemical reduction to enhance the capacitive properties. The applied voltage and reduction time were varied to obtain the optimum

condition. Excellent electrochemical performance of modified TNTs 5 % denoted as R-TNTs was observed with CV curve indicated 18 times higher in specific capacitance value than unmodified TNTs. Ideal capacitor behaviour and good electrochemical stability were observed for sample synthesised at applied voltage of 5 V for 30 s. A high average specific capacitance of 11.12 mF cm^{-2} was also observed from galvanostatic charge-discharge analysis. The enhancement of the capacitive performance can be attributed to the enhancement in conductivity and electrical performance of the sample due to the introduction of oxygen vacancy by conversion of Ti^{4+} to Ti^{3+} as revealed by X-ray photoelectron spectroscopy (XPS).

Pulse reverse electrodeposition was applied to deposit Mn_2O_3 and Co_3O_4 nanoparticles into the R-TNTs to further improve the capacitive performance of the samples. Electrodeposition parameter such as deposition potential, duty cycle, deposition time, concentration of metal precursor, pH of the metal precursor solution and heating temperature were varied to obtain the optimum samples XRD analysis confirmed that Mn_2O_3 and Co_3O_4 nanoparticles were successfully loaded into the R-TNTs while FESEM and TEM images revealed the presence of the nanoparticles along the R-TNTs tubes wall. Specific capacitance, as high as 37.00 mF cm^{-2} obtained for Mn_2O_3/R-TNTs and 16.89 mF cm^{-2} for Co_3O_4/R-TNTs due to the contribution of double-layered capacitance by the R-TNTs and pseudocapacitance of the metal oxides. The synthesised samples displayed a good electrochemical stability as they exhibits more than 85% capacitive retention after 1000 charge-discharge cycles.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SIFAT ELEKTROKIMIA TITANIA NANOTIUB TERUBAH SUAI YANG DIMUATKAN DENGAN Mn_2O_3 DAN Co_3O_4 UNTUK APLIKASI SUPERKAPASITOR

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Pengerusi: **Profesor Zulkarnain Zainal, PhD**
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Titania nanotiub yang tersusun rapi (TNTs) telah digunakan dalam kajian ini kerana diketahui memiliki ciri yang luar biasa termasuk kestabilan kimia dan struktur nanotiubnya yang berhujung terbuka menawarkan permukaan yang luas dan boleh menyediakan kesalinghubungan yang lebih baik antara bahan aktif dan elektrolit yang akan meningkatkan prestasi kapasitans. TNTs telah disediakan melalui elektrokimia penganodan dalam sel dua elektrod yang mengandungi larutan NH_4F. Parameter yang mempengaruhi morfologi, aspek geometri dan prestasi elektrokimia TNTs telah dikaji dengan mengubah komposisi elektrolit, voltan penganodan yang digunakan dan tempoh masa penganodan. Pembentukan TNTs telah disahkan dengan analisis pembelauan sinar-X (XRD) dan mikroskopi medan pancaran pengimbasan elektron (FESEM). Prestasi elektrokimia bagi TNTs telah dinilai menggunakan voltametri berkitar, galvanostat cas nyahcas dan spektroskopi elektrokimia impedans dalam sistem sel tiga elektrod yang terdiri daripada Pt sebagai elektrod kawalan, Ag/AgCl (3 M KCl) sebagai elektrod rujukan dan TNTs sebagai elektrod kerja. Ketiga-tiga analisis dilakukan dalam larutan KCl (1.0 M).

Fasa tungal titania telah diindekskan kepada anatase bagi kesemua sampel yang telah dikalsin pada suhu 500 ^oC. FESEM analisis juga menunjukkan bahawa TNTs 5 % menghasilkan tiub yang lebih seragam dan bulat. Namun, bentuk tiub menjadi tidak seragam dan berkelompok apabila kandungan air meningkat didalam elektrolit. Semua sampel TNTs menunjukkan bentuk CV yang tidak simetri dimana bahagian anod terherot yang dikaitkan dengan cas nyahcas tidak faraday oleh permukaan oksida. TNTs 5 % menghasilkan arus yang paling tinggi yang menghasilkan kapasitans yang lebih tinggi berbanding sampel lain.

Pengubahsuaian TNTs 5 % bagi meningkatkan prestasi kapasitans sampel tersebut telah dilakukan melalui kaedah penurunan elektrokimia. Voltan dan masa penurunan yang digunakan telah diubah untuk mendapatkan sampel yang optimum. Prestasi elektrokimia yang baik bagi sampel TNTs 5 % yang telah diubah suai (dinamakan sebagai R-TNTs) dapat diperhatikan melalui lengkung CV yang menunjukkan 18 kali ganda lebih tinggi dari segi kapasitans tentu berbanding dengan TNTs yang tidak diubah suai. Ciri kapasitor ideal dan kestabilan elektrokimia yang baik diperlihatkan bagi sampel yang disintesis pada voltan 5 V selama 30 saat. Kapasitans tentu yang tinggi iaitu 11.12 mF cm^{-2} juga diperlihatkan melalui galvanostat cas nyahcas analisis bagi sampel ini iaitu kira-kira 57 kali ganda lebih tinggi daripada TNTs yang tidak diubah suai.Peningkatan prestasi kapasitans ini dikaitkan dengan peningkatan kekonduksian dan prestasi elektrik sampel disebabkan oleh adanya kekosongan oksigen hasil daripada penurunan Ti^{4+} kepada Ti^{3+} seperti yang dibuktikan oleh sinar fotoelektron-X spekstroskopi (XPS).

Pengelektroenapan denyut berbalik telah digunakan untuk pengenapan Mn_2O_3 dan Co_3O_4 nanopartikel ke atas R-TNTs untuk meningkatkan prestasi kapasitans sampel. Pparameter pengelektroenapan seperti keupayaan enapan, kitaran kerja, masa enapan, kepekatan elektrolit logam, pH elektrolit logam dan suhu pemanasan telah dipelbagaikan untuk mendapat sampel yang optimum. Analisis melalui XRD mengesahkan Mn_2O_3 dan Co_3O_4 nanopartikel telah berjaya dienap ke atas R-TNTs manakala imej daripada FESEM dan TEM membuktikan kehadiran Mn_2O_3 dan Co_3O_4 nanopartikel disepanjang dinding tiub R-TNTs. Kapasitans tentu setinggi 37.00 mF cm^{-2} diperolehi oleh Mn_2O_3/R-TNTs dan 16.89 mF cm^{-2} oleh Co_3O_4/R-TNTs disebabkan oleh kapasitans dua lapisan yang dimiliki oleh R-TNTs dan pseudokapasitans dimiliki oleh logam oksida. Kesemua sampel yang disintesis memaparkan kestabilan elektrokimia yang baik kerana mengekalkan lebih daripada 85 % kapasitans selepas melalui cas nyahcas sehingga 1000 kali.

ACKNOWLEDGEMENTS

First of all, thank you to Allah the almighty for His bless and strength throughout this journey. My deep gratitude and sincere thanks goes to my supervisor Professor Dr. Zulkarnain Zainal for his brilliant insight, invaluable guidance, support, patience, and continuous supervision throughout my study. I wish to express my sincere appreciation to my co-supervisors, Associate Professor Dr. Janet Lim Hong Ngee and Dr. Yusran Sulaiman for their supportive advices, guidance and insightful comments in ensured my continuous enthusiasm for this study. The constructive ideas, guidance and immense knowledge from Dr. Lim Ying Chin are indeed appreciable.

Special thanks are credited to staffs of Microscopy Unit, Institute of Bioscience, Universiti Putra Malaysia, Faculty of Science, Universiti Teknologi Mara and Failure Analysis Laboratory, MIMOS Berhad for their helps in conducting FESEM, EDX, TEM and XPS analysis on my samples. I would like to thank Dr. Chang Sook Keng for her helps, guidance and meaningful discussion about electrochemistry and supercapacitor. Many thanks to Chia Chew Ping and Saudah for their guidance in XRD analysis and data interpretation. My appreciation to my labmates, who supported me from the initial to the final level of this project. Their helpfulness, kindness and friendship have boosted me morally throughout this study. To warda and elmi, thank you very much for the support, foods, memories, vitamin k and j and 2 days 1 night road trips. Many thanks to my PhD financial support from Ministry of Higher Education, Malaysia for this golden opportunity for me to further my study in this prestigious university.

Lastly, special thanks to my brothers, sister and sister in laws for lending their ears and shoulder every time I accounted hardship, their encouragement and love always give me strength to make another step forward. To my nieces and nephews, you are my vitamins, thank you for never fail to make me energised, especially throughout my study. Infinite thanks to my parents Hj. Samsudin Mat Ali and Hjh Wan Zabedah Yusof for their endless love, prayers and support throughout these 4 years journey. Thank you for your understanding for allowing me to peruse my third degree. I never would made it here without your prayers and blessings.

Thank you so much. May Allah gather us in Jannahtul Firdaus.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS AND SYMBOLS

ALD	Atomic Layer Deposition
CV	Cyclic voltammetry
DC	Direct Current
DI	Deionised Water
E	Energy Density
EDLC	Electric Double-Layer Capacitance
EDX	Energy Dispersive X-Ray Spectorscopy
EG	Ethylene Glycol
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
IHP	Inner Helmholtz Plane
OHP	Outer Helmholtz Plane
P	Power Density
R_{ct}	Charge-transfer Resistance
R_s	Cell-electrolyte Resistance
R-TNTs	Reduced Titania Nanotubes
R-TNTs/ Co_3O_4	Reduced Titania Nanotubes/Cobalt Oxide
R-TNTs/ Mn_2O_3	Reduced Titania Nanotubes/ Manganese Oxide
SC	Specific Capacitance
T_{on}	On-time
T_{off}	Off-time
TEM	Transmission Electron Microscopy
TNTs	Titania Nanotubes

XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 General Introduction

In response to the rapid development of the global economy, a fast growing market for portable electronic devices, the growing human population and the development of hybrid electric vehicles, the global energy consumption is accelerating at an alarming rate (Arico *et al*,. 2005; Chu *et al*., 2012; Wang, *et al*., 2012). The increasing of energy demand becomes unavoidable based on the current energy consumption rate. Therefore, the urge to develop energy storage system with high energy, high power, low-cost, and environmentally friendly have increased to satisfy the needs of modern society. Among various energy conversion and storage devices, supercapacitor, which is also known as electrochemical capacitor or ultracapacitor have attracted a great deal of attention from both industry and academia due to their unique characteristics that fill the gap between batteries and capacitors, by delivering higher power burst than batteries and storing more energy than capacitors. The device possesses remarkable characteristics as it is robust in withstanding hundred thousand of charging/discharging cycles without degrading. Supercapacitor has been undergoing rapid developments since the conception was proposed by Conway in the 1970s. The uprising of the researches on supercapacitor have given new hope in improvement of power of batteries (Simon *et al.*, 2008) which is desperately needed for many application such as cameras, cell phones, hybrid and electric vehicles.

Supercapacitor is characterised as electric double layer capacitors (EDLC) and pseudocapacitors. In EDLC, the capacitance of the material comes from the adsorption of both anions and cations at the electrode/electrolyte interface. Thus, it is strongly dependent on the surface area of the electrode materials that is accessible to the electrolyte ions (Huang *et al*., 2015). In contrast to EDLC, pseudocapacitor stores energy through a faradaic process that involves fast and reversible redox reaction occurring at or near the electrode surface (Conway *et al.*, 2003).

The field of research and development of supercapacitor is currently focusing finding new materials which possess high capacitive performance and at the same time required minimal cost for the study. Countless effort have been done towards these criteria including mixing the oxides to become binary or ternary oxides, incorporating metal oxide with conducting polymer and compositing metal oxide with carbonaceous materials such as activated carbon, carbon nanotubes and graphene. Many attempts also have been done in adopting nanostructured materials for the use as supercapacitor. It is well noted that nanostructured material attributes high surface area which may contribute to higher capacitive performance due to the larger contact area between the

electrode/electrolyte. As reported in many literature, nanostructured materials indeed possess high electrical conductivity that makes them as a promising energy storage. Therefore, many efforts have been put to develop effective yet practical method synthesising the nanostructured oxide and hydroxide in various forms such as nanoparticles, nanotubes, nanorod, nanowire, nanosheets and others. Different methods have been applied by researchers such as precipitation (Chang *et al.*, 2015; Khalil, 2015), hydrothermal (Holi *et al.*, 2016; Myahkostupov *et al.*, 2011; Zaman *et al.*, 2012), sol-gel (Portet *et al.*, 2004), chemical bath deposition (Li *et al.*, 2011), anodisation (Macak *et al*., 2006; Salari *et al*., 2011a), electrospinning (Kim *et al*., 2011), electrochemical deposition (Adelkhani *et al.*, 2010; Ali *et al.*, 2015; Kung *et al.*, 2012) and others.

Ever since Iijima discovered carbon nanotubes, (Iijima, 1991) one-dimensional (1D) nanostructured material has been widely explored. Although carbon is still the most explored nanotube material with fascinating properties, inorganic nanotubes (especially metal oxides or sulphides) are also widely studied to exploit their other material-specific properties and potential for biomedical, photochemical, electrical and environmental applications. Among all transition-metal oxides, titania is the most extensively studied material with more than 40 000 publications over the past 10 years, which makes titania as the most investigated compounds in materials science. Researchers have developed different preparative methods in synthesising 1D titania nanostructured including sol-gel method (Lakshmi *et al.*, 1997), template-assisted methods (Motonari *et al.*, 2000; Sander *et al.*, 2004), hydro/solvothermal method (Kasuga *et al.*, 1999), atomic layer deposition (ALD) (Shin *et al.*, 2004) and electrochemical anodisation method. Among various method introduced to synthesise titania nanotubes (TNTs), electrochemical anodisation method has been the most promising method as it offers suitably back-connected nanotubes on the Ti foil substrate which can be used directly as a binder-free supercapacitor electrode (Salari *et al*., 2014).

However, it has been proclaimed that TNTs electrode suffered a very low specific capacitance (less than 1 mF cm^{-2}) which resemble conventional electric double-layer capacitor (Salari *et al*., 2011b) due to poor electrical conductivity (Wu *et al*., 2014). Therefore, many attempts have been done to improve the capacitive performance of this material by thermal treatment (Lu *et al*., 2012; Salari *et al*., 2012), electrochemical doping approach (Wu *et al*., 2014; Zhou *et al*., 2013) and incorporation with metal oxides (Lu *et al.*, 2012; Xie *et al.*, 2009a; Xie *et al.*, 2009b) and conductive polymers (Mujawar *et al.*, 2011; Xie *et al.*, 2012; Xie *et al.*, 2014).

1.2 Problem Statement

The rapid growth of population and global economy has significantly increase the demand for energy consumption. Therefore, the urgency to find an energy storage that possess high energy, high power, low cost and environmentally friendly have become the 21st century problem. The current energy storage such as batteries can hold a large amount of power, however it have low cycle life and charge-discharge characteristics, while capacitor can charge almost instantly but suffered with low storage. As for our electric power future, we need to store and release large amount of electricity quickly

and quite likely supercapacitor possess both good values from batteries and capacitor. Supercapacitor is a high-capacity capacitor that attempts to combine the high power density of the conventional capacitors with the high energy density of a battery. This energy storage device also possess long cycle life and fast charge-discharge capability. Supercapacitor have attract significant attention mainly due to their numerous potential application as energy storage system in different field. The development of supercapacitor focuses on enhancing the capacitive performance of the material as well as power density, energy density and its life cycle.

Nanostructured material such as titania nanotubes have gain much attention as they possess high surface area which may contribute to higher capacitive performance (Lu *et al.*, 2012). Many researcher attempt to synthesis titania nanotubes in a powder form as they can easily modified by make it to binary or ternary metal oxide during the initial synthesis. Nevertheless, powder based sample is not practical to the industry. They needed to be further prepared as an electrode by adding binder and coated to a substrate. Therefore, in this study titania nanotubes were synthesised using anodisation method whereby the nanotubes were grown directly on the Ti substrate surface which make it as a binder less electrode and ready to be use. However, titania nanotubes was reported to have very low capacitive value which resemble conventional capacitor (Zhou *et al.*, 2016). To address this obstacle, many strategies have been done to improve the capacitive performance of titania nanotubes such as incorporation of metal oxides (Cui *et al.*, 2016; Kontos *et al.*, 2009; Xie *et al.*, 2008; Xie *et al.*, 2009b). However, some of the strategies requires intensive controlled condition, toxic chemical and long preparation time which leads to high cost for a large scale production. Therefore, it is crucial to find an alternative method that environmentally friendly, energy efficient and low cost. Modification through electrochemical technique is known to have these criteria and capable of producing surface of desired characteristics.

Countless efforts have been done using various electrodeposition method to deposit metal oxides onto the titania nanotubes. However, due to the overlapping of diffusion zones of the active ions during the electrodeposition leading to formation of larger metal oxide particle size which end up covering the nanotubes opening. In this work, pulse reverse electrodeposition method has been adopted to overcome this problem. In this method a series of pulse potential referred to as on-time separated by intervals of zero current potential (off-time) are applied which leads to formation of nano or quantum dot size particles evenly distributed as a compact crystalline structure. The effect of operating parameters of pulse reverse deposition of Mn_2O_3 and Co_3O_4 into titania nanotubes based on the capacitive performance have been performed. Up to this date there is no report on pulse reverse electrodeposition of Mn_2O_3 and Co_3O_4 into the modified titania nanotubes. Modification on titania nanotubes done in this work may provide new pathways in order to enhance the capacitive performance of titania nanotubes.

1.3 Background of Study

TNTs anodised from pure Ti foil are studied extensively as a potential supercapacitor electrode material due to its high surface area, high ion accessibility, controllable tube structure and relatively low cost. Moreover, vertically oriented TNTs standing directly on the current collector (Ti foil) have the advantages of eliminating contact impedance and reducing additional weight arising from the addition of conductive agent and binder. However, it was widely reported that TNTs possess a low specific capacitance ~ 50 to 911 μF cm^{-2} that impede their application on a large scale due to the poorer electrochemical activity and lower electronic conductivity (Huang *et al*., 2016; Hui *et al*., 2013). Although it is a transition metal oxide, TNTs are mostly considered as an EDLC capacitor due to its semiconducting nature, which limits the conductivity and prevents fast electron transfer. In this study, two major methods were adopted to enhance the electrochemical capacitance of the TNTs electrode. The first method was by electrochemical reduction of TNTs which demonstrates remarkable capacitance improvement of 40 to 60 times higher than the sole TNTs. The second method was by constructing hybrid arrays by utilising the unique tubular channels of the TNTs, which provide a regular architecture for feasible loading of various electroactive materials (for this study are Mn_2O_3 and Co_3O_4) (Wu *et al*., 2014; Zhou *et al*., 2014). This structure promotes the utilisation of these electroactive materials because of available large species and effective ion diffusion path for the electrochemical reactions. Prior to the modification, a study on influence of anodisation parameters to the morphology and architecture of the anodised TNTs was done to find the optimum condition for the synthesis of TNTs. Anodisation parameters such as electrolyte composition, anodisation voltage and time are varied throughout the study. The overview of the study was presented in Figure 1.1. Manganese oxide (Mn_2O_3) and cobalt oxide (Co_3O_4) are one of the pseudocapacitive materials with a large theoretical specific capacitance ~1300 for Mn_2O_3 and ~3560 F g^{-1} for Co_3O_4 (Huang *et al*., 2015). Nevertheless, both metal oxides sustain the relatively low electrical conductivity which leads to the poor specific capacitance. One promising way is by incorporating the metal oxides into the electrically conductive skeleton to enhance its electrochemical performance. Therefore, in this study the TNTs was modified by electrochemical reduction method (sample denoted as R-TNTs) prior the incorporation with the metal oxides. Pulse reverse electrodeposition was used for the electrodeposition of Mn_2O_3 and Co_3O_4 onto the R-TNTs as it is considered a useful technique for the production of novel electroactive materials as it can tune in the electrodeposited material to the desired morphology.

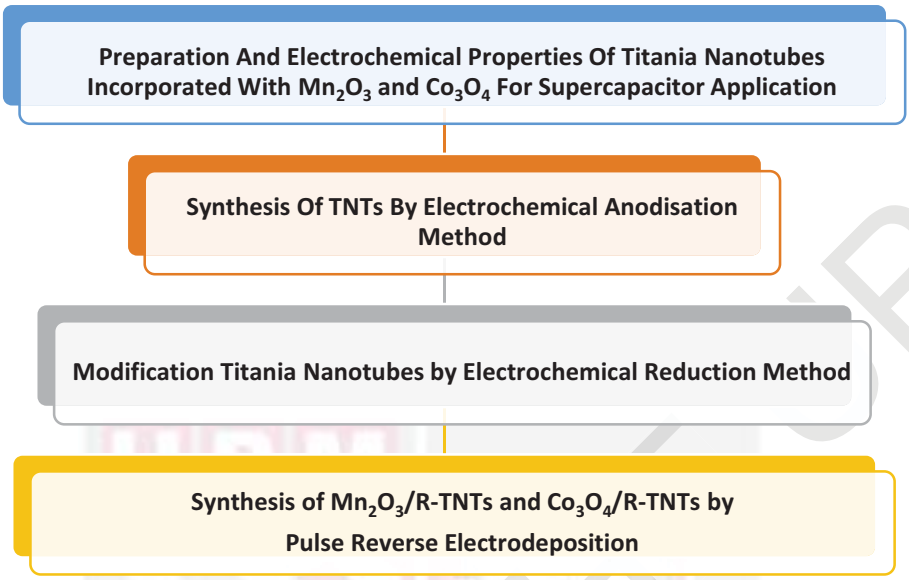

Figure 1.1: Overview of the study.

1.4 Objectives of the Study

The aim of this study is to prepare highly ordered titania nanotubes thin film and incorporate it with metal oxides in order to enhance the specific capacitance of the electrode. Several objectives were outlined towards the aim. Experimental works have been planned and done appropriately to ensure the smooth conduct towards the completion of the study. Therefore, the objectives of the study are as follow:

1. To synthesise highly ordered titania nanotubes thin film (TNTs) via electrochemical anodisation of titanium in mixture of ethylene glycol and water containing NH_4F solution.
2. To modify the TNTs thin films via electrochemical cathodic reduction.
3. To synthesise the manganese oxide doped modified titania nanotubes thin films (Mn_2O_3/R-TNTs) and cobalt oxide doped modified titania nanotubes thin film (Co_3O_4/R-TNTs) via pulse reverse electrodeposition method.
4. To evaluate the surface morphology and chemical states of TNTs, R-TNTs, Mn_2O_3/R-TNTs and Co_3O_4/.R-TNTs.
5. To analyse the specific capacitance, power density and energy density of the prepared samples from galvanostatic charge-discharge tests.
6. To evaluate the electrochemical stability and coulombic efficiency of the samples through cycle stability tests.

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