

# **UNIVERSITI PUTRA MALAYSIA**

PREPARATION OF NICKEL COBALT OXIDE ON TITANIA NANOTUBES VIA WET IMPREGNATION FOR SUPERCAPACITOR

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By

**CHUA CHI WING** 

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

July 2018

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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#### **CHUA CHI WING**

**July 2018** 

#### Chair: Professor Zulkarnain bin Zainal, PhD Faculty: Science

Titania nanotubes array and nickel cobaltite are both widely studied metal oxide materials for applications in the field of energy storage and delivery. However, the electrochemical capacitive charge storage of titania nanotubes is generally poor because of their inferior electrical conductivity. A number of attempts at chemical modifications by doping and making composites have been performed but the effect of decorating the surface of titania nanotubes with ternary metal oxide has not been adequately addressed. This study aims to evaluate the electrochemical performance of combining titania nanotubes array with nickel cobaltite for the purpose of fabricating composite electrochemical capacitors. Further, this study also aims to evaluate the possibility of using wet impregnation method to introduce metal oxides onto titania nanotubes array.

The techniques that were used in the characterisation of the samples were X-ray diffraction (XRD), cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS), field-emission–scanning electron microscopy (FESEM), and energy dispersive X-ray microanalyses (EDX). Parameters that were studied included anodisation duration, anodisation potential, initial molar concentration of nickel(II) nitrate solution and cobalt(II) nitrate solution, thermal treatment temperature of the precursor solution, impregnation duration, and types of electrolytes.

The optimum synthesis conditions for the unmodified titania nanotubes were 60 minutes anodisation duration and 17 V anodisation potential, whereas the optimum synthesis conditions for the nickel cobaltite – titania nanotubes composite were 1.0 M initial molar concentration of nickel (II) nitrate solution and cobalt(II) nitrate solution, thermal treatment temperature of the precursor solution was 375 °C, and an impregnation duration of 60 minutes. The nickel cobaltite – titania nanotubes composite performed optimally in 1.0 M KOH.

By the use of optimised synthesis conditions, it was found that the composite possessed the best electrochemical behaviour in 1.0 M KOH. CV tests demonstrated that the composite exhibited a small degree of electrocatalytic behaviour due to a sharp increase in current density in the 0.6 V region. The areal capacitance was 214.76  $\mu$ F/cm<sup>2</sup> at 350  $\mu$ A/cm<sup>2</sup>, which decreased to 210.02  $\mu$ F/cm<sup>2</sup> when the current density increased to 400  $\mu$ A/cm<sup>2</sup>. Further, it was found that the composites relied largely of electric double layer charge storage mechanism. Cycle stability study shows the composite deteriorated to 62.38% in 250 cycles of charge-discharge. Micrographs of the composite has shown that the nickel cobaltite nanoclusters preferred to deposit on the surface of the nanotubes rather than on the inside of the nanotube pores. EDX microanalyses indicated that the deposition of nickel and cobalt was very small, which were ~0.06 mol.% and ~0.13 mol.%, respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan ijazah Master Sains

#### PENYEDIAAN NIKEL KOBALT OKSIDA PADA TIUB NANO TITANIA MELALUI KAEDAH IMPREGNASI BASAH UNTUK SUPERKAPASITOR

Oleh

#### **CHUA CHI WING**

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Tiub nano titania tersusun serta nikel kobalt oksida merupakan bahan logam oksida yang lazim dikaji untuk kegunaan dalam bidang penyimpanan dan pembekalan tenaga. Walaubagaimanapun, penyimpanan cas kapasitif elektrokimia tiub nano titania secara amnya adalah kurang memuaskan kerana kekondusian elektriknya yang rendah. Pelbagai percubaan pengubahsuaian kimia melalui pendopanan dan pembuatan komposit telah dilakukan tetapi kesan daripada penghiasan permukaan tiub nano titania dengan logam pertigaan tidak dijelaskan dengan secukupnya. Kajian ini bertujuan membuat penilaian pada ciri-ciri elektrokimia tiub nano titania–nikel kobalt oksida, dengan tujuan membentuk kapasitor elektrokimia komposit. Selain itu, kesesuaian kaedah impregnasi basah untuk memperkenalkan logam oksida kepada tiub nano titania tersusun juga dinilai.

Teknik-teknik pencirian bahan yang digunakan dalam kajian ini termasuklah pembelauan sinar-X (XRD), voltametri berkitar (CV), cas-nyahcas galvanostatik (GCD), spektroskopi impedans elektrokimia (EIS), mikroskopi elektron imbasan pancaran medan (FESEM), dan analisis mikro sinar-X tenaga tersebar (EDX). Parameter-parameter yang dikaji termasuklah tempoh penganodan, potensi penganodan, kepekatan asal larutan nikel(II) nitrat dan kobalt(II), suhu rawatan haba larutan impregnasi, tempoh impregnasi, dan jenis elektrolit.

Kaedah sintesis optimum bagi tiub nano titania adalah tempoh penganodan selama 60 minit dan potensi penganodan 17 V manakala kaedah sintesis optimum bagi komposit nikel kobalt oksida – tiub nano titania adalah kepekatan molar permulaan larutan nikel(II) nitrat dan larutan kobalt(II) nitrat sebanyak 1.0 M, suhu rawatan haba bagi larutan pelopor pada 375 °C, dan tempoh impregnasi selama 60 minit. Komposit nikel kobalt oksida – tiub nano titania berfungsi secara optimum dalam 1.0 M KOH.

Melalui penggunaan kaedah sintesis optimum, komposit tersebut mempunyai ciri-ciri yang terbaik dalam elektrolit 1.0 M KOH. Ujian CV menunjukkan bahawa komposit tersebut juga mempunyai serba sedikit sifat elektropemangkin kerana berlakunya peningkatan ketumpatan arus mendadak pada sekitar potensi 0.6 V. Kapasitans spesifik permukaan pula mencatat nilai sebanyak 214.76  $\mu$ F/cm<sup>2</sup> pada ketumpatan arus 350  $\mu$ A/cm<sup>2</sup>, manakala nilai tersebut menurun ke 210.02  $\mu$ F/cm<sup>2</sup> pada ketumpatan arus 400  $\mu$ A/cm<sup>2</sup>. Tambahan pula, mekanisme pengecasan dwilapis elektrik merupakan kaedah utama yang digunakan oleh komposit tersebut untuk menyimpan cas. Ujian kitaran casnyahcas menentukan bahawa komposit tersebut mengalami penurunan kapasitans spesifik permukaan kepada 62.38% selepas 250 kitaran cas-nyahcas, berbanding dengan nilai pada kitaran cah-nyahcas pertama. Gambar mikro-gambar mikro komposit tersebut menunjukkan kluster mikro nikel kobalt oksida lebih cenderung termendap pada permukaan tiub nano dan bukannya dalam liang-liang tiub nano. Menurut ujian EDX, nikel(II) dan kobalt(II) masing-masing termendap pada nilai ~0.06 *mol.*% dan ~0.13 *mol.*%, dan nilai ini adalah amat kecil.

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I certify that a Thesis Examination Committee has met on 26 July 2018 to conduct the final examination of Chua Chi Wing on his thesis entitled "Preparation of Nickel Cobalt Oxide on Titania Nanotubes via Wet Impregnation for Supercapacitor" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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# TABLE OF CONTENTS

			Page
ABSTRACT			i
ABSTRAK			iii
ACKNOWL	EDGEN	MENTS	v
APPROVAL	ı		vi
DECLARAT	ION		viii
LIST OF TA	BLES		xiii
LIST OF FIG	GURES		xiv
LIST OF AB	BREVI	IATIONS	xxi
CHAPTER			
1	INT	RODUCTION	1
	1.1	Research Background	1
	1.2	Problem Statement	1
	1.3	Objectives	2
2	LITI	ERATURE REVIEW	3
	2.1	Nanomaterials	3
	2.2	Synthesis and Applications of Titania-based	4
	2.2	Nanomaterials	-
	2.3	Wet Impregnation Technique	5
	2.4	Electrochemical Capacitors	6
	2.5	Litania Nanotube Array Formation	8
	2.6	Factors Affecting the Properties of Litania	10
		2.6.1 Anodisation Potential	10
		2.6.2 Anodisation Duration	11
		2.6.3 Self-Doping	11
		2.6.4 Annealing Temperature and Atmosphere	12
		2.6.5 Fluoride Ion Concentration	14
		2.6.6 Water Content of Anodising Solution	15
		2.6.7 Temperature of the Anodisation Bath	17
	2.7	Nickel Cobaltite and Nickel Cobaltite Composites	18
		2.7.1 Sol-Gel Method	18
		2.7.2 Corecipitation Method	18
		2.7.3 Hydrothermal Method	22
		2.7.4 Electrodeposition Method	24
		2.7.5 Direct Combustion Method	25
		2.7.6 Magnetic Frequency Irradiation	25
		2.7.7 Summary on Nickel Cobaltite and Nickel	25
		Cobaltite Composites	
	2.8	Chemical Modifications of Titania Nanotubes	26

MET	THODO	LOGY	34
3.1	Sample	e Preparation	34
	3.1.1	Pretreatment of Titanium Foils	34
	3.1.2	Preparation of Anodising Solution	34
	3.1.3	Titania Nanotubes Synthesis	34
	3.1.4	Preparation of Impregnation Solutions and	35
		Electrolytes	
	3.1.5	Preparation of Nickel Cobaltite – Titania	35
		Nanotubes Composites Through Wet	
	_	Impregnation	
3.2	Parame	eter Studies	36
3.3	Charac	terisation	36
	3.3.1	Electrochemical Characterisation	36
		3.3.1.1 Cyclic Voltammetry	36
		3.3.1.2 Galvanostatic Charge-Discharge	37
		3.3.1.3 Electrochemical Impedance	37
		Spectroscopy	• •
	3.3.2	X-ray Diffraction Characterisation	38
	3.3.3	Field Emission – Scanning Electron	38
		Microscopy and Elemental Microanalyses	
DES	III TS A	ND DISCUSSION	20
<b>KES</b>	V roy	Diffraction Characterisation	39
4.1	A-1ay 1	Anadiation Duration	20
	4.1.1	Anodisation Duration	20
	4.1.2	Anodisation Potential	39
	4.1.5	Nitrate Solution and Cobalt(II) Nitrate	41
		Solution	
	4.1.4	Thermal Treatment Temperature of the	42
		Precursor Solution	
	4.1.5	Impregnation Duration	44
4.2	Field-H	Emission Scanning Electron Microscopy	46
	(FESE	M)	
	4.2.1	Unmodified Titania Nanotubes	46
	4.2.2	Modified Titania Nanotubes Composite	47
	4.2.3	Modified Titania Nanotubes Composite	49
		After Cycle Stability Analysis	
	4.2.4	Modified Titania Nanotubes Composite	50
		After Electrochemical Analysis in 1.0 M	
43	Energy	Dispersive X-Ray Analyses (EDX)	51
4.4	Cylic	Voltammetry Galvanostatic Charge –	52
7,7	Discha	rge Analyses, and Electrochemical	52
	Impeda	ance Spectroscopy	
	4.4.1	Anodisation Duration	52
	4.4.0		

3

4

4.4.2 Anodisation Potential 55

4.4.3	Initial Molar Concentration of Nickel(II)	59
	Nitrate Solution and Cobalt(II) Nitrate	
	Solution	
4.4.4	Thermal Treatment Temperature of the	63
	Precursor Solution	
4.4.5	Impregnation Duration	67
4.4.6	Types of Electrolytes	
4.4.7	Cycle Stability Analysis	76
4.4.8	Electrochemical Impedance Spectroscopy	77

# 5 CONCLUSION AND RECOMMENDATIONS FOR FUTURE RESEARCH

REFERENCES APPENDICES BIODATA OF STUDENT LIST OF PUBLICATIONS

5

81 90

79

# LIST OF TABLES

Table		Page
2.1	Classification, Properties and Examples of Nanomaterials. (Lokhande <i>et al.</i> , 2016)	3
2.2	Classification of Electrochemical Capacitors Based on the Type of Electrode and Electrolyte. (Conway, 1996; Sharma and Bhatti, 2010)	7
2.3	Specific Capacitance Values of Nickel Cobaltite Obtained Through Different Synthesis Methods	20
2.4	Literature Review on the Chemical Modifications of Titania Nanotubes	29
3.1	Parameters and Corresponding Variables Used in the Study.	36
4.1	Average Dimensions of the Nanotubes Pore Diameter, Wall Thickness and Length.	46
4.2	Elemental Composition in Mole Percentage (mol.%) of the Samples Analysed.	52
4.3	The Equivalent Series Resistance, $R_s$ , and Equivalent Parallel Resistance, $R_p$ , Obtained from the Electrochemical Circle Fitting Using the NOVA 1.11 Software.	77

# LIST OF FIGURES

Figure		Page
2.1	Components of a Simple Electrochemical Capacitor. (Zhang et al., 2009)	7
2.2	SEM Micrographs of Anodised Titania Nanotubes Grown in NaF/Na <sub>2</sub> SO <sub>4</sub> Electrolyte, Obtained at $\times$ 40 000 Magnification. The Micrographs (a) and (b) Show That the Titania Nanotubes Structures Are Intact at 400 °C and 500 °C, Respectively, Whereas (c) and (d) Show Loss of Titania Nanotubes Structure at 550 °C and 600 °C, Respectively. (Jaroenworaluck <i>et al.</i> , 2010)	13
2.3	SEM Micrographs of Anodised Titania Nanotubes Grown in 50:50 vol.% Water/Glycerol Electrolyte for 3 hours at 20 V Containing Different Concentrations of NH <sub>4</sub> F, As Labelled. (Macak <i>et al.</i> , 2008)	14
2.4	SEM Micrographs of Anodised Titania Nanotubes Grown in Glycerol/ 0.27 M NH <sub>4</sub> F with Varying Water Content in vol.% for 3 hours at 20 V Using 250 mV/s Sweep Rate, As Labelled. (Macak <i>et al.</i> , 2008)	15
2.5	SEM Micrographs of Anodised Titania Nanotubes Grown in Anhydrous Ethylene Glycol/ 0.2 wt.% NH <sub>4</sub> F with Varying Water Content in vol.% for 45 minutes at 20 V. (a) and (b) Indicated the Absence of Water in the Anodisation Electrolyte, in the First and Second Attempt at Anodisation, Respectively. (c) and (d) Indicated the Presence of 0.18 wt.% Water in the Anodisation Electrolyte, in the First and Second Attempt at Anodisation, Respectively. A × 10 000 Magnification was Used. (Raja <i>et al.</i> , 2007)	16
2.6	SEM Micrographs of Anodised Titania Nanotubes Grown in (a) 1 M $(NH_4)_2SO_4$ , (b) 50 vol.% Aqueous Glycerol solution, and (c) Glycerol, Each Containing 0.5 wt.% $NH_4F$ for 3 hours at 20 V. (Macak & Schmuki, 2006)	17
4.1	X-ray Diffractograms of Titanium Foils That Were Obtained Through Anodisation at a Constant Anodisation Potential of 20 V with Anodisation Duration of (a) 20 Minutes, (b) 30 Minutes, (c) 40 Minutes, (d) 50 Minutes, and (e) 60 Minutes, Followed by Thermal Annealing at 450 °C for 2 hours.	40

xiv

- 4.2 X-ray Diffractograms of Titanium Foils That Were Obtained Through Anodisation at a Constant Anodisation Duration of 60 Minutes with Anodisation Potentials of (a) 11 V, (b) 14 V, (c) 17 V, (d) 20 V, and (e) 23 V, Followed by Thermal Annealing at 450 °C for 2 hours.
- 4.3 X-ray Diffractograms of TNT/Ti That Were Wet Impregnated with Ni<sup>2+</sup> and Co<sup>2+</sup> in Volume Ratio of Ni<sup>2+</sup>:Co<sup>2+</sup> = 1:2, with Different Initial Precursor Concentrations of (a) 0.6 M, (b) 0.7 M, (c) 0.8 M, (d) 0.9 M, (e) 1.0 M. The TNT Was Prepared by Anodising It for 60 minutes at 17 V Anodisation Potential, Followed by Thermal Annealing at 450 °C for 2 Hours.
  - X-ray Diffractograms of TNT/Ti That Were Wet Impregnated with Ni<sup>2+</sup> and Co<sup>2+</sup> in Volume Ratio of Ni<sup>2+</sup>:Co<sup>2+</sup> = 1:2 Between 36.0° to 37.5°, with Different Initial Precursor Concentrations of (a) 0.6 M, (b) 0.7 M, (c) 0.8 M, (d) 0.9 M, (e) 1.0 M. The ( $\cdot$ ) Indicates the Apparent Peaks Within This Range. The TNT Was Prepared by Anodising it for 60 Minutes at 17 V Anodisation Potential, Followed by Thermal Annealing at 450 °C for 2 Hours.
  - X-ray Diffractograms of NCO/TNT/Ti Obtained from the Thermal Treatment of the Precursor Salts at Different Temperatures of (a) 300 °C, (b) 325 °C, (c) 350 °C, (d) 375 °C, (e) 400 °C. The TNT Was Prepared by Anodising It for 60 Minutes at 17 V Anodisation Potential, Followed by Thermal Annealing at 450 °C for 2 Hours. The Composite Was Prepared by Immersing TNT into Volume Ratio of Ni<sup>2+</sup>:Co<sup>2+</sup> = 1:2 with Initial Precursor Concentration of 1.0 M.
- 4.6

4.5

X-Ray Diffractograms of NCO/TNT/Ti Obtained from the Thermal Treatment of the Precursor Salts at Different Temperatures Between  $36.0^{\circ}$  to  $37.5^{\circ}$ , of (a)  $300 \,^{\circ}$ C, (b)  $325 \,^{\circ}$ C, (c)  $350 \,^{\circ}$ C, (d)  $375 \,^{\circ}$ C, (e)  $400 \,^{\circ}$ C. The TNT Was Prepared by Anodising It for 60 Minutes at 17 V Anodisation Potential, Followed by Thermal Annealing at  $450 \,^{\circ}$ C for 2 Hours. The Composite Was Prepared by Immersing TNT into Volume Ratio of Ni<sup>2+</sup>:Co<sup>2+</sup> = 1:2 with Initial Precursor Concentration of 1.0 M.

41

42

40

43

- 4.7 X-ray diffractograms of NCO/TNT/Ti obtained from impregnation at different impregnation durations of (a) 40 minutes, (b) 60 minutes, (c) 80 minutes, (d) 100 minutes, (e) 120 minutes. The TNT was prepared by anodising it for 60 minutes at 17 V anodisation potential, followed by thermal annealing at 450 °C for 2 hours. The composite was prepared by immersing TNT into volume ratio of Ni<sup>2+</sup>:Co<sup>2+</sup> = 1:2 with initial precursor concentration of 1.0 M, thermally-treated at 375 °C.
- 4.8 X-ray diffractograms of NCO/TNT/Ti obtained from impregnation at different impregnation durations in the scan range between  $36.0^{\circ}$  to  $37.5^{\circ}$ , of (a) 40 minutes, (b) 60 minutes, (c) 80 minutes, (d) 100 minutes, (e) 120 minutes. The TNT was prepared by anodising it for 60 minutes at 17 V anodisation potential, followed by thermal annealing at 450 °C for 2 hours. The composite was prepared by immersing TNT into volume ratio of Ni<sup>2+</sup>:Co<sup>2+</sup> = 1:2 with initial precursor concentration of 1.0 M, thermally-treated at 375 °C.
- 4.9 FESEM micrograph of unmodified titania nanotubes at 50  $000 \times$  magnification. The nanotubes were synthesised under the anodisation potential of 17 V for 60 minutes, followed by thermal annealing at 450 °C for 2 hours.
- 4.10 FESEM Micrograph of Modified Titania Nanotubes at 100 000 × Magnification. The Nanotubes Were Synthesised Under the Same Conditions as in Figure 4.9. The Nickel Cobaltite Was Deposited Using Wet Impregnation of a Nickel-Cobalt Nitrate Solution in Which Both Their Original Concentration Before Mixing Was 1.0 M. The Ni:Co Molar Ratio Was 1:2. Impregnation Was Performed over 60 Minutes and Thermal Treatment Temperature Was 375 °C.
- 4.11 Cross-Section FESEM Micrograph of the Modified Titania Nanotubes at 50 000  $\times$  Magnification. This Is the Cross Section View of the Same Sample in Figure 4.10.
- 4.12 FESEM Micrograph of Modified Titania Nanotubes After Cycle Stability Analysis in 1.0 M KOH, at 100 000 × Magnification. Identical Synthesis Conditions Used to Acquire the Composite Obtained in Figure 4.10 Were Used for the Synthesis of This Composite.

FESEM Micrograph of Modified Titania Nanotubes After Electrochemical Analysis in 1.0 M HCl, at 100 000 × Magnification. Identical Synthesis Conditions Used to Acquire the Composite Obtained in Figure 4.10 Were Used for the Synthesis of this Composite. 45

45

47

48

49

50

- 4.14 Cyclic Voltammograms of TNT/Ti Produced Using Different Anodisation Durations Ranging from 20 Minutes to 60 Minutes Under 20 V Anodisation Potential Followed by Thermal Annealing at 450 °C for 2 Hours, Whereby the Anodisation Durations Were (a) 20 Minutes, (b) 30 Minutes, (c) 40 Minutes, (d) 50 Minutes, and (e) 60 Minutes. (f) is a Compilation of the Cyclic Voltammograms Obtained at a Scan Rate of 200 mV/s for the Different Anodisation Durations Used.
- 4.15 Charge Discharge Profiles of TNT/Ti Produced Using Different Anodisation Durations Ranging from 20 Minutes to 60 Minutes Under 20 V Anodisation Potential Followed by Thermal Annealing at 450 °C for 2 Hours, Whereby the Anodisation Durations Were (a) 20 Minutes, (b) 30 Minutes, (c) 40 Minutes, (d) 50 Minutes, and (e) 60 Minutes. (f) is a Compilation of the Charge Discharge Profiles Obtained at a Current Density of 4  $\mu$ A/cm<sup>2</sup> for the Different Anodisation Durations Used.
- 4.16 The Areal Capacitance Values of Samples Produced Using Different Anodisation Durations.
- 4.17 Cyclic Voltammograms of TNT/Ti Produced Using Different Anodisation Potentials Ranging from 11 V to 23 V Under 60 Minutes Anodisation Duration Followed by Thermal Annealing at 450 °C for 2 Hours, Whereby the Anodisation Potentials Were (a) 11 V, (b) 14 V, (c) 17 V, (d) 20 V, and (e) 23 V. (f) is a Compilation of the Cyclic Voltammograms Obtained at a Scan Rate of 20 mV/s for the Different Anodisation Potentials Used.
- 4.18

V Under 60 Minutes Anodisation Duration Followed by Thermal Annealing at 450 °C for 2 Hours, Whereby the Anodisation Potentials Were (a) 11 V, (b) 14 V, (c) 17 V, (d) 20 V, and (e) 23 V. (f) is a Compilation of the Charge – Discharge Profiles Obtained at a Current Density of 4 μA/cm<sup>2</sup> for the Different Anodisation Potentials Used.
(a) Areal Capacitance Values of Samples Produced Using Different Anodisation Potentials and (b) Areal Capacitance

Charge – Discharge Profiles of TNT/Ti Produced Using Different Anodisation Potentials Ranging from 11 V to 23

(a) Areal Capacitance Values of Samples Produced Using Different Anodisation Potentials, and (b) Areal Capacitance Values of Samples Produced Using Different Anodisation Potentials for the Repeated Analysis.

58

55

57

- 4.20 Cyclic Voltammograms of NCO/TNT/Ti Produced Using Different Initial Molar Concentration of Nickel(II) Nitrate Solution and Cobalt(II) Nitrate Solution, Whereby the Initial Molar Concentrations of the Respective Nitrate Solutions are (a) 0.6 M, (b) 0.7 M, (c) 0.8 M, (d) 0.9 M, and (e) 1.0 M. (f) is a Compilation of the Cyclic Voltammograms Obtained at a Scan Rate of 20 mV/s for the Different Initial Molar Concentrations Used. TNT/Ti Was Prepared Using 60 Minutes Anodisation Duration and 17 V Anodisation Potential, Thermally Annealed at 450 °C. The Impregnation Duration Was 40 Minutes and the Thermal Treatment Temperature Was 350 °C.
- 4.21 Charge Discharge Profiles of NCO/TNT/Ti Produced Using Different Initial Molar Concentration of Nickel(II) Nitrate Solution and Cobalt(II) Nitrate Solution, Whereby the Initial Molar Concentrations of the Respective Nitrate Solutions are (a) 0.6 M, (b) 0.7 M, (c) 0.8 M, (d) 0.9 M, and (e) 1.0 M. (f) Is a Compilation of the Charge – Discharge Profiles Obtained at a Current Density of 150  $\mu$ A/cm<sup>2</sup> for the Different Initial Molar Concentrations used. TNT/Ti Was Prepared Using 60 Minutes Anodisation Duration and 17 V Anodisation Potential, Thermally Annealed at 450 °C. The Impregnation Duration Was 40 Minutes and the Thermal Treatment Temperature Was 350 °C.
- 4.22 Areal Capacitance Values of NCO/TNT/Ti Produced Using Different Initial Molar Concentration of Nickel(II) Nitrate Solution and Cobalt(II) Nitrate Solution.
- 4.23 Cyclic Voltammograms of NCO/TNT/Ti Produced Using Different Thermal Treatment Temperature, Whereby the Temperatures Were (a) 300 °C, (b) 325 °C, (c) 350 °C, (d) 375 °C, and (e) 400 °C. (f) Is a Compilation of the Cyclic Voltammograms Obtained at a Scan Rate of 20 mV/s, for the Different Temperatures Used. TNT/Ti Was Prepared Using 60 Minutes Anodisation Duration and 17 V Anodisation Potential, Thermally Annealed at 450 °C. The Impregnation Duration Was 40 Minutes and the Initial Molar Concentration of Nickel(II) Nitrate Solution and Cobalt(II) Nitrate Solution was 1.0 M.

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- 4.24 Charge Discharge Profiles of NCO/TNT/Ti Produced Using Different Thermal Treatment Temperatures, Whereby the Temperatures Were (a) 300 °C, (b) 325 °C, (c) 350 °C, (d) 375 °C, and (e) 400 °C. (f) Is a Compilation of the Charge – Discharge Profiles Obtained at a Current Density of 350  $\mu$ A/cm<sup>2</sup> for the Different Temperatures Used. TNT/Ti Was Prepared Using 60 Minutes Anodisation Duration and 17 V Anodisation Potential, Thermally Annealed at 450 °C. The Impregnation Duration Was 40 Minutes and the Initial Molar Concentration of Nickel(II) Nitrate Solution and Cobalt(II) Nitrate Solution Was 1.0 M.
- 4.25 Areal Capacitance Values of NCO/TNT/Ti Produced Using Different Thermal Treatment Temperatures.
  - Cyclic Voltammograms of NCO/TNT/Ti Produced Using Different Impregnation Durations, Whereby the Durations are (a) 40 Minutes, (b) 60 Minutes, (c) 80 Minutes, (d) 100 Minutes, and (e) 120 Minutes. (f) Is a Compilation of the Cyclic Voltammograms Obtained at a Scan Rate of 20 mV/s for the Different Impregnation Durations Used. TNT/Ti Was Prepared Using 60 Minutes Anodisation Duration and 17 V Anodisation Potential, Thermally Annealed at 450 °C. The Thermal Treatment Temperature Was 375 °C and the Initial Molar Concentration of Nickel(II) Nitrate solution and cobalt(II) Nitrate Solution Was 1.0 M.
    - Charge Discharge Profiles of NCO/TNT/Ti Produced Using Different Impregnation Durations, Whereby the Durations are (a) 40 Minutes, (b) 60 Minutes, (c) 80 Minutes, (d) 100 Minutes, and (e) 120 Minutes. (f) Is a Compilation of the Charge – Discharge Profiles Obtained at a Current Density of 350  $\mu$ A/cm<sup>2</sup> for the Different Impregnation Durations Used. TNT/Ti Was Prepared Using 60 Minutes Anodisation Duration and 17 V Anodisation Potential, Thermally Annealed at 450 °C. The Thermal Treatment Temperature Was 375 °C and the Initial Molar Concentration of Nickel(II) Nitrate Solution and Cobalt(II) Nitrate Solution Was 1.0 M.
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Areal Capacitance Values of Samples Produced Using Different Impregnation Durations.

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- 4.29 Cyclic Voltammograms of NCO/TNT/Ti Analysed in Different Electrolytes, Whereby the Electrolytes Were (a) 1.0 M KCl, (b) 1.0 M HCl, (c) 1.0 M KOH, and (d) 0.27 M TBATFB. (e) Is a Compilation of the Cyclic Voltammograms Obtained at a Scan Rate of 20 mV/s for the Different Electrolytes Used. TNT/Ti Was Prepared Using 60 Minutes Anodisation Duration and 17 V Anodisation Potential, Thermally Annealed at 450 °C. The NCO/TNT/Ti Thermal Treatment Temperature Was 375 °C, Impregnated for 60 Minutes, and the Initial Molar Concentration of Nickel(II) Nitrate Solution and Cobalt(II) Nitrate Solution Was 1.0 M.
- 4.30 Cyclic Voltammograms Obtained for the Analyses of NCO/TNT/Ti in 1.0 M HCl, 5 mV/s Scan Rate.
- 4.31 Charge Discharge Profiles of NCO/TNT/Ti Analysed in Different Electrolytes, Whereby the Electrolytes Were (a) 1.0 M KCl, (b) 1.0 M HCl, (c) 1.0 M KOH, and (d) 0.27 M TBATFB. (e) Is a Compilation of the Charge Discharge Profiles Obtained at a Current Density of 350 μA/cm<sup>2</sup> for the Different Electrolytes Used. TNT/Ti Was Prepared Using 60 Minutes Anodisation Duration and 17 V Anodisation Potential, Thermally Annealed at 450 °C. The NCO/TNT/Ti Thermal Treatment Temperature was 375 °C, Impregnated for 60 Minutes, and the Initial Molar Concentration of Nickel(II) Nitrate Solution and Cobalt(II) Nitrate Solution Was 1.0 M.
- 4.32 Areal Capacitance Values of the Samples in Different Electrolytes.
- 4.33 Capacitance Retention of NCO/TNT/Ti in 1.0 M KOH over
   250 Cycles of Charge Discharge, Current Density Used
   Was 350 μA/cm<sup>2</sup>.
- 4.34 Electrochemical Impedance Spectra of (a) Unmodified Titania Nanotubes, TNT/Ti, Obtained from Section 4.1.2, and (b) Titania Nanotubes Impregnated with Nickel Cobaltite, NCO/TNT/Ti, Obtained from Section 4.1.5. In (a), the Inset Shows a Randles Circuit that Was Used to Fit the Data Obtained from the Nyquist Plot in (a) and (b).

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# LIST OF ABBREVIATIONS

CPE	Constant phase element
CV	Cyclic voltammetry analysis
EDX	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
FESEM	Field emission scanning electron microscopy
GCD	Galvanostatic charge – discharge analysis
NCO/TNT/Ti	NiCo <sub>2</sub> O <sub>4</sub> /Titania nanotubes/Titanium foil
R <sub>p</sub>	Equivalent parallel resistance
R <sub>s</sub>	Equivalent series resistance
SEM	Scanning electron microscopy
TNT/Ti	Titania nanotubes/Titanium foil
vol.%	Volume percentage
wt.%	Weight percentage
$Z_w$	Warburg impedance



#### CHAPTER 1

#### **INTRODUCTION**

#### 1.1 Research Background

Different classes of materials have been researched for creating supercapacitors. An extremely broad class of these materials consist of carbon-based materials and its derivatives such as activated carbon, carbon nanotubes, and graphene (Lokhande et al., 2016). Carbon-based materials store charge predominantly via electric double layer charging mechanism. On the other hand some metal oxides and conducting polymers store charge through redox reactions apart from electric double layer charging mechanism, in which the active materials can gain or release electrons to and from ionic species in the electrolyte to enable charge storing and delivery. This kind of charge-storing mechanism is called pseudocapacitance (Lokhande et al., 2016). The formation of composites or mixing of materials for the fabrication of supercapacitors is common due to a few reasons. Firstly, pure materials such as carbon, that store charge solely through electric double layer charging mechanism generally possess very low capacitance, that is, it is not able to store a lot of charge, measured in Farads. Secondly, materials as metal oxide powders usually possess low porosity and may impede electrolyte diffusion. Thus, composites are usually fabricated and their electrochemical charge storage performance usually outperforms their original constituents, or novel synthesis methods to generate unique microscale or nanoscale architecture are often performed to improve the charge storage properties of the materials. To date, various composites have been reported in literature such as metal oxides on carbon nanotubes (Wu et al., 2015), metal oxides on carbon microfibre (Chiam et al., 2017), metal oxides on graphene (Bai et al., 2016; Naveen & Selladurai, 2015; Xu et al., 2015), metal oxides on metal oxides (Bo et al., 2006), conducting polymer on graphene (Alvi et al., 2011; Gómez et al., 2011), and conducting polymer on metal oxide (Xie et al., 2011; Xie et al., 2014), to list a few. Titania nanotubes store charge using electric double layer mechanism and does not possess very apparent pseudocapacitance properties. It is highly resistive and possesses low capacitance values, but the ease of tailoring its nanostructure is one of the main attractive features that can be exploited for the fabrication of nanotubes. To date, many titania nanotubes composite supercapacitors have been reported, such as conducting polymer-graphene-titania nanotubes composite (Huang et al., 2015), metal oxide-titania nanotubes composite (Zhou & Zhang, 2014b), and conducting polymer-titania nanotubes composite (Shao et al., 2015), to name a few. The number of literature continues to grow with more new methods of composite preparation being discovered frequently.

#### **1.2 Problem Statement**

Supercapacitors are useful charge-storing electronic components that deliver huge bursts of energy in a short time and are used in video recorders, car electronic devices such as radios and taxi meters, cameras, mobile phones, toys, and much larger applications such as electric buses running on supercapacitors, to providing electric

pulse burst to start diesel locomotive engines (Kötz & Carlen, 2000). Ideally, supercapacitors should possess high power and energy density, long life expectancy, long storage life, robust operating conditions, use environmentally-friendly materials, economically feasible to be produced, and safe for consumer consumption. However, current supercapacitors are plagued with problems such as relatively low from desired energy density, high materials and fabrication costs, rapid self-discharging rates, and also the lack of industrial standards pertaining to the commercialisation of supercapacitors. (Wang et al., 2012). Regarding titania nanotubes, the largest obstacle that prevents it from being commercialised as it is is due to its very large resistivity and small capacitance values, owing to its semiconducting nature. To improve its capacitance values, self-doping and/or adding dopants such as metal oxides or conducting polymers can be performed. However, the methods to introduce self-doping and/or adding dopants often involves the use of equipments such as potentiostat and special vessels for hydrothermal growth, as well as complex automation, which could lead to increased cost, increased chemical usage, and may sometimes be an obstacle for research facilities that can only afford low-cost approach to introduce these chemical modifications to titania nanotubes.

Through our study, we aim to improve the the low capacitance values of titania nanotubes through doping of the nanotubes using wet impregnation method. This method has been widely used to prepare titania nanotubes for photocatalysis applications but is not sufficiently understood for the application in the preparation of titania nanotubes for supercapacitors application. The rationale of using this technique is two-fold; it requires no complex equipments and automation as it can be done by simply immersing the unmodified titania nanotubes into metal ion precursors followed by thermal treatment and the usage of chemicals for doping is largely minimised to only the use of precursor solutions. This study is also aimed at exploring the feasibility of this technique to form mixed metal oxides on titania nanotubes, which was found to be possible using hydrothermal growth (Yang et al., 2013) and electrodeposition (Yuan et al., 2012) on various substrates, but not documented for this technique, particularly on titania nanotubes. Nickel and cobalt were selected as the metal species due to their high theoretical capacitance values, as high as 3750 F/g for nickel(II) oxide (Wang et al., 2012) and 3560 F/g for cobalt(II,III) oxide (Lokhande et al., 2016), and relatively cheaper cost compared many other metal oxides with charge-storage properties.

### 1.3 Objectives

To synthesise and optimise synthesis parameters for  $TiO_2$  nanotubes/Ti (TNT/Ti).

- To synthesise and optimise synthesis parameters for NiCo<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> nanotubes/Ti composites (NCO/TNT/Ti).
- To characterise the prepared TNT/Ti and NCO/TNT/Ti composites using cyclic voltammetry analysis (CV), galvanostatic charge discharge analysis (GCD), electrochemical impedance spectroscopy (EIS), X-ray diffractometry analysis (XRD), field emission scanning electron microscopy energy dispersive X-ray spectroscopy (FESEM-EDX), and cycle stability analysis using GCD for the sample obtained from optimised synthesis parameters.

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#### REFERENCES

- Alvi, F., Ram, M. K., Basnayaka, P. A., Stefanakos, E., Goswami, Y., & Kumar, A. (2011). Graphene–polyethylenedioxythiophene conducting polymer nanocomposite based supercapacitor. *Electrochimica Acta*, 56(25), 9406-9412.
- Bai, Y., Liu, M., Sun, J., & Gao, L. (2016). Fabrication of Ni-Co binary oxide/reduced graphene oxide composite with high capacitance and cyclicity as efficient electrode for supercapacitors. *Ionics*, 22(4), 535-544.
- Bo, G., Xiaogang, Z., Changzhou, Y., Juan, L., & Long, Y. (2006). Amorphous  $Ru_{1-y}Cr_yO_2$  loaded on TiO<sub>2</sub> nanotubes for electrochemical capacitors. *Electrochimica Acta*, 52(3), 1028-1032.
- Brockner, W., Ehrhardt, C., & Gjikaj, M. (2007). Thermal decomposition of nickel nitrate hexahydrate, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, in comparison to Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O. *Thermochimica Acta*, 456(1), 64-68.
- Chang, Thind, S. S., Tian, M., Hossain, M. M., & Chen, A. (2015). Significant Enhancement of the Photoelectrochemical Activity of Nanoporous TiO<sub>2</sub> for Environmental Applications. *Electrochimica Acta*, 173, 728-735.
- Chang, S. K., Zainal, Z., Tan, K. B., Yusof, N. A., Yusoff, W., Daud, W. M., & Prabaharan, S. (2015). Synthesis and electrochemical properties of nanostructured nickel–cobalt oxides as supercapacitor electrodes in aqueous media. *International Journal of Energy Research*, 39(10), 1366-1377.
- Chi, B., Li, J., Han, Y., & Chen, Y. (2004). Effect of temperature on the preparation and electrocatalytic properties of a spinel NiCo<sub>2</sub>O<sub>4</sub>/Ni electrode. *International Journal of Hydrogen Energy*, 29(6), 605-610.
- Chiam, S. L., Lim, H. N., Foo, C. Y., Pandikumar, A., & Huang, N. M. (2017). How Did Nickel Cobaltite Reinforced Carbon Microfibre Symmetrical Supercapacitor Fare Against A Commercial Supercapacitor? *Electrochimica Acta*, 246, 1141-1146.
- Conway, B. (1996). Supercapacitor behavior resulting from pseudocapacitance associated with redox processes. Paper presented at the Proceedings of the Symposium on Electrochemical Capacitors.
- Cortes-Jácome, M., Morales, M., Angeles Chavez, C., Ramírez-Verduzco, L., López-Salinas, E., & Toledo-Antonio, J. (2007). WO<sub>x</sub>/TiO<sub>2</sub> Catalysts via Titania Nanotubes for the Oxidation of Dibenzothiophene. *Chemistry of Materials*, 19(26), 6605-6614.
- Ding, R., Qi, L., & Wang, H. (2012). A facile and cost-effective synthesis of mesoporous NiCo<sub>2</sub>O<sub>4</sub> nanoparticles and their capacitive behavior in

electrochemical capacitors. Journal of Solid State Electrochemistry, 16(11), 3621-3633.

- Endut, Z., Hamdi, M., & Basirun, W. J. (2013). Supercapacitance of bamboo-type anodic titania nanotube arrays. *Surface and Coatings Technology*, *215*, 75-78.
- Faraji, M., Amini, M., & Anbari, A. P. (2016). Preparation and characterization of TiO<sub>2</sub>-nanotube/Ti plates loaded Cu<sub>2</sub>O nanoparticles as a novel heterogeneous catalyst for the azide–alkyne cycloaddition. *Catalysis Communications*, 76, 72-75.
- Fujishima, A., & Honda, K. (1972). Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, 238(5358), 37-38.
- Ge, H., & Hua, T. (2016). Synthesis and characterization of poly(maleic acid)-grafted crosslinked chitosan nanomaterial with high uptake and selectivity for Hg(II) sorption. *Carbohydrate Polymers*, *153*, 246-252.
- Gobal, F., & Faraji, M. (2013). Fabrication of nanoporous nickel oxide by dezincification of Zn-Ni/(TiO<sub>2</sub>-nanotubes) for use in electrochemical supercapacitors. *Electrochimica Acta*, 100, 133-139.
- Gómez, H., Ram, M. K., Alvi, F., Villalba, P., Stefanakos, E., & Kumar, A. (2011). Graphene-conducting polymer nanocomposite as novel electrode for supercapacitors. *Journal of Power Sources*, 196(8), 4102-4108.
- Guan, D., Gao, X., Li, J., & Yuan, C. (2014). Enhanced capacitive performance of TiO<sub>2</sub> nanotubes with molybdenum oxide coating. *Applied Surface Science*, 300, 165-170.
- Hu, G., Tang, C., Li, C., Li, H., Wang, Y., & Gong, H. (2011). The sol-gel-derived nickel-cobalt oxides with high supercapacitor performances. *Journal of The Electrochemical Society*, 158(6), A695-A699.
- Huang, H., Gan, M., Ma, L., Yu, L., Hu, H., Yang, F., Li, Y., & Ge, C. (2015). Fabrication of polyaniline/graphene/titania nanotube arrays nanocomposite and their application in supercapacitors. *Journal of Alloys and Compounds*, 630, 214-221.
- Iglesias-Rubianes, L., Skeldon, P., Thompson, G., Habazaki, H., & Shimizu, K. (2002). Ionic transport in anodically oxidized Al/W layers. *Journal of The Electrochemical Society*, 149(2), B23-B26.
- ISO. (2010). International Organization for Standardization. Nanotechnologies -Vocabulary - Part 1: Core Terms. ISO/TS 80004-1 : 2010
- Jaroenworaluck, A., Regonini, D., Bowen, C. R., & Stevens, R. (2010). A microscopy study of the effect of heat treatment on the structure and properties of anodised TiO<sub>2</sub> nanotubes. *Applied Surface Science*, *256*(9), 2672-2679.

- Kanta, A. F., Poelman, M., & Decroly, A. (2015). Electrochemical characterisation of TiO<sub>2</sub> nanotube array photoanodes for dye-sensitized solar cell application. *Solar Energy Materials and Solar Cells*, 133, 76-81.
- Kim, B. C., Rajesh, M., Jang, H. S., Yu, K. H., Kim, S.-J., Park, S. Y., & Raj, C. J. (2016). Facile synthesis and capacitive properties of nickel-cobalt binary metal oxide nanoaggregates via oxalate route. *Journal of Alloys and Compounds*, 674, 376-383.
- Kötz, R., & Carlen, M. (2000). Principles and applications of electrochemical capacitors. *Electrochimica Acta*, 45(15–16), 2483-2498.
- Kungurova, O. A., Khassin, A. A., Cherepanova, S. V., Saraev, A. A., Kaichev, V. V., Shtertser, N. V., Chermashentseva, G. K., Gerasimov, E. Y., Paukshtis, E. A., Vodyankina, O. V., Minyukova, T. P., & Abou-Jaoudé, G. (2017). δ-Alumina supported cobalt catalysts promoted by ruthenium for Fischer-Tropsch synthesis. *Applied Catalysis A: General*, 539, 48-58.
- Lai, C. W., & Sreekantan, S. (2013). Incorporation of WO<sub>3</sub> species into TiO<sub>2</sub> nanotubes via wet impregnation and their water-splitting performance. *Electrochimica Acta*, 87, 294-302.
- Lapham, D. P., & Tseung, A. C. C. (2004). The effect of firing temperature, preparation technique and composition on the electrical properties of the nickel cobalt oxide series  $Ni_xCo_{1-x}O_y$ . Journal of materials science, 39(1), 251-264.
- Li, D., Cheng, X., Yu, X., & Xing, Z. (2015). Preparation and characterization of TiO<sub>2</sub>based nanosheets for photocatalytic degradation of acetylsalicylic acid: Influence of calcination temperature. *Chemical Engineering Journal*, 279, 994-1003.
- Li, W., Zhao, Z., Jiao, Y., & Wang, G. (2016). Morphology effect of zirconia support on the catalytic performance of supported Ni catalysts for dry reforming of methane. *Chinese Journal of Catalysis*, 37(12), 2122-2133.
- Lin, S., Shi, X., Yang, H., Fan, D., Wang, Y., & Bi, K. (2017). Reduced graphene oxide-NiCo<sub>2</sub>O<sub>4</sub> nanoflowers as efficient electrocatalysts for the oxygen reduction reaction. *Journal of Alloys and Compounds, 720*(Supplement C), 147-155.
- Liu, C., Bi, Q., & Matthews, A. (2001). EIS comparison on corrosion performance of PVD TiN and CrN coated mild steel in 0.5 N NaCl aqueous solution. *Corrosion Science*, 43(10), 1953-1961.
- Lockman, Z., Sreekantan, S., Ismail, S., Schmidt-Mende, L., & MacManus-Driscoll, J. L. (2010). Influence of anodisation voltage on the dimension of titania nanotubes. *Journal of Alloys and Compounds*, 503(2), 359-364.

- Lokhande, V. C., Lokhande, A. C., Lokhande, C. D., Kim, J. H., & Ji, T. (2016). Supercapacitive composite metal oxide electrodes formed with carbon, metal oxides and conducting polymers. *Journal of Alloys and Compounds, 682*, 381-403.
- Macak, J. M., Hildebrand, H., Marten-Jahns, U., & Schmuki, P. (2008). Mechanistic aspects and growth of large diameter self-organized TiO<sub>2</sub> nanotubes. *Journal of Electroanalytical Chemistry*, *621*(2), 254-266.
- Macak, J. M., & Schmuki, P. (2006). Anodic growth of self-organized anodic TiO<sub>2</sub> nanotubes in viscous electrolytes. *Electrochimica Acta*, *52*(3), 1258-1264.
- Macak, J. M., Tsuchiya, H., Ghicov, A., Yasuda, K., Hahn, R., Bauer, S., & Schmuki, P. (2007). TiO<sub>2</sub> nanotubes: Self-organized electrochemical formation, properties and applications. *Current Opinion in Solid State and Materials Science*, 11(1-2), 3-18.
- Marcus, Y. (2012). Volumes of aqueous hydrogen and hydroxide ions at 0 to 200 °C. *The Journal of Chemical Physics, 137*(15), 154501.
- Moazeni, M., Hajipour, H., Askari, M., & Nusheh, M. (2015). Hydrothermal synthesis and characterization of titanium dioxide nanotubes as novel lithium adsorbents. *Materials Research Bulletin, 61*, 70-75.
- Moretti, E., Molina, A. I., Sponchia, G., Talon, A., Frattini, R., Rodriguez-Castellon, E., & Storaro, L. (2017). Low-temperature carbon monoxide oxidation over zirconia-supported CuO-CeO<sub>2</sub> catalysts: Effect of zirconia support properties. *Applied Surface Science*, 403, 612-622.
- Naveen, A. N., & Selladurai, S. (2015). Novel low temperature synthesis and electrochemical characterization of mesoporous nickel cobaltite-reduced graphene oxide (RGO) composite for supercapacitor application. *Electrochimica Acta, 173,* 290-301.
- Nguyen, V. H., & Shim, J.-J. (2016). Microwave-assisted synthesis of porous nickel cobaltite with different morphologies in ionic liquid and their application in supercapacitors. *Materials Chemistry and Physics*, 176, 6-11.
- Pastrana-Martínez, L. M., Pereira, N., Lima, R., Faria, J. L., Gomes, H. T., & Silva, A. M. T. (2015). Degradation of diphenhydramine by photo-Fenton using magnetically recoverable iron oxide nanoparticles as catalyst. *Chemical Engineering Journal*, 261, 45-52.
- Perillo, P. M., & Rodríguez, D. F. (2012). The gas sensing properties at room temperature of TiO<sub>2</sub> nanotubes by anodization. Sensors and Actuators B: Chemical, 171–172, 639-643.

- Pletcher, D., Li, X., Price, S. W. T., Russell, A. E., Sönmez, T., & Thompson, S. J. (2016). Comparison of the Spinels Co<sub>3</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> as Bifunctional Oxygen Catalysts in Alkaline Media. *Electrochimica Acta*, 188(Supplement C), 286-293.
- Possato, L. G., Chaves, T. F., Cassinelli, W. H., Pulcinelli, S. H., Santilli, C. V., & Martins, L. (2017). The multiple benefits of glycerol conversion to acrolein and acrylic acid catalyzed by vanadium oxides supported on micromesoporous MFI zeolites. *Catalysis Today*, 289, 20-28.
- Potočnik, J. (2011). Commission Recommendation of 18 October 2011 on the definition of nanomaterial Text with EEA relevance. *Official Journal of the European Union*, L275, 38.
- Qin, D.-D., Bi, Y.-P., Feng, X.-J., Wang, W., Barber, G. D., Wang, T., Song, Y.-M., Lu, X.-Q., & Mallouk, T. E. (2015). Hydrothermal Growth and Photoelectrochemistry of Highly Oriented, Crystalline Anatase TiO<sub>2</sub> Nanorods on Transparent Conducting Electrodes. *Chemistry of Materials*, 27(12), 4180-4183.
- Raj, C. C., Sundheep, R., & Prasanth, R. (2015). Enhancement of electrochemical capacitance by tailoring the geometry of TiO<sub>2</sub> nanotube electrodes. *Electrochimica Acta*, 176, 1214-1220.
- Raja, K. S., Gandhi, T., & Misra, M. (2007). Effect of water content of ethylene glycol as electrolyte for synthesis of ordered titania nanotubes. *Electrochemistry Communications*, 9(5), 1069-1076.
- Regonini, D., Jaroenworaluck, A., Stevens, R., & Bowen, C. R. (2010). Effect of heat treatment on the properties and structure of TiO2 nanotubes: phase composition and chemical composition. *Surface and Interface Analysis*, 42(3), 139-144.
- Reyes-Coronado, D., Rodríguez-Gattorno, G., Espinosa-Pesqueira, M., Cab, C., de Coss, R. d., & Oskam, G. (2008). Phase-pure TiO<sub>2</sub> nanoparticles: anatase, brookite and rutile. *Nanotechnology*, *19*(14), 145605.
- Salunkhe, R. R., Jang, K., Yu, H., Yu, S., Ganesh, T., Han, S.-H., & Ahn, H. (2011). Chemical synthesis and electrochemical analysis of nickel cobaltite nanostructures for supercapacitor applications. *Journal of Alloys and Compounds*, 509(23), 6677-6682.
- Sato, N. (1971). A theory for breakdown of anodic oxide films on metals. *Electrochimica Acta, 16*(10), 1683-1692.
- Şennik, E., Çolak, Z., Kılınç, N., & Öztürk, Z. Z. (2010). Synthesis of highly-ordered TiO<sub>2</sub> nanotubes for a hydrogen sensor. *International Journal of Hydrogen Energy*, 35(9), 4420-4427.

- Shao, Z., Li, H., Li, M., Li, C., Qu, C., & Yang, B. (2015). Fabrication of polyaniline nanowire/TiO<sub>2</sub> nanotube array electrode for supercapacitors. *Energy*, 87, 578-585.
- Sharma, P., & Bhatti, T. S. (2010). A review on electrochemical double-layer capacitors. *Energy Conversion and Management*, 51(12), 2901-2912.
- Skeldon, P., Thompson, G., Garcia-Vergara, S., Iglesias-Rubianes, L., & Blanco-Pinzon, C. (2006). A tracer study of porous anodic alumina. *Electrochemical* and Solid-State Letters, 9(11), B47-B51.
- Sreekantan, S., Zaki, S. M., Lai, C. W., & Tzu, T. W. (2014). Copper-incorporated titania nanotubes for effective lead ion removal. *Materials Science in Semiconductor Processing*, 26, 620-631.
- Su, Z., & Zhou, W. (2009). Formation, microstructures and crystallization of anodic titanium oxide tubular arrays. *Journal of Materials Chemistry*, 19(16), 2301-2309.
- Su, Z., & Zhou, W. (2011). Formation, morphology control and applications of anodic TiO<sub>2</sub> nanotube arrays. *Journal of Materials Chemistry*, 21(25), 8955-8970.
- Sun, Y., Xiao, X., Ni, P., Shi, Y., Dai, H., Hu, J., Wang, Y., Li, Z., & Li, Z. (2014). DNA-templated synthesis of nickel cobaltite oxide nanoflake for highperformance electrochemical capacitors. *Electrochimica Acta*, 121, 270-277.
- Szczeszak, A., Ekner-Grzyb, A., Runowski, M., Szutkowski, K., Mrówczyńska, L., Kaźmierczak, Z., Grzyb, T., Dąbrowska, K., Giersig, M., & Lis, S. (2016). Spectroscopic, structural and in vitro cytotoxicity evaluation of luminescent, lanthanide doped core@shell nanomaterials GdVO<sub>4</sub>:Eu<sup>3+</sup>5%@SiO<sub>2</sub>@NH<sub>2</sub>. *Journal of Colloid and Interface Science, 481*, 245-255.
- Tan, L., Huang, R., Li, X., Liu, S., Shen, Y.-M., & Shao, Z. (2017). Chitosan-based core-shell nanomaterials for pH-triggered release of anticancer drug and nearinfrared bioimaging. *Carbohydrate Polymers*, 157, 325-334.
- Toledo-Antonio, J. A., Ángeles-Chávez, C., Cortés-Jácome, M. A., Cuauhtémoc-López, I., López-Salinas, E., Pérez-Luna, M., & Ferrat-Torres, G. (2012).
  Highly dispersed Pt–Ir nanoparticles on titania nanotubes. *Applied Catalysis A: General*, 437–438, 155-165.
- Van Doorslaer, X., Dewulf, J., De Maerschalk, J., Van Langenhove, H., & Demeestere, K. (2015). Heterogeneous photocatalysis of moxifloxacin in hospital effluent: Effect of selected matrix constituents. *Chemical Engineering Journal*, 261, 9-16.
- Varghese, O. K., Gong, D., Paulose, M., Grimes, C. A., & Dickey, E. C. (2011). Crystallization and high-temperature structural stability of titanium oxide nanotube arrays. *Journal of Materials Research*, 18(1), 156-165.

- Vosoughi, V., Badoga, S., Dalai, A. K., & Abatzoglou, N. (2017). Modification of mesoporous alumina as a support for cobalt-based catalyst in Fischer-Tropsch synthesis. *Fuel Processing Technology*, 162, 55-65.
- Wanag, A., Rokicka, P., Kusiak- Nejman, E., Markowska-Szczupak, A., & Morawski, A. W. (2016). TiO<sub>2</sub>/glucose nanomaterials with enhanced antibacterial properties. *Materials Letters*, 185, 264-267.
- Wang, G., Zhang, L., & Zhang, J. (2012). A review of electrode materials for electrochemical supercapacitors. *Chemical Society Reviews*, 41(2), 797-828.
- Wang, Q., Li, S., Qiao, J., Jin, R., Yu, Y., & Gao, S. (2015). CdS–CdSe (CdTe) coreshell quantum dots sensitized TiO2 nanotube array solar cells. *Solar Energy Materials and Solar Cells*, 132, 650-654.
- Wantala, K., Khemthong, P., Wittayakun, J., & Grisdanurak, N. (2011). Visible lightirradiated degradation of alachlor on Fe-TiO<sub>2</sub> with assistance of H<sub>2</sub>O<sub>2</sub>. *Korean Journal of Chemical Engineering*, *28*(11), 2178-2183.
- Wei, T. Y., Chen, C. H., Chien, H. C., Lu, S. Y., & Hu, C. C. (2010). A cost-effective supercapacitor material of ultrahigh specific capacitances: spinel nickel cobaltite aerogels from an epoxide-driven sol-gel process. Advanced Materials, 22(3), 347-351.
- Wu, L. K., Wu, W. Y., Xia, J., Cao, H. Z., Hou, G. Y., Tang, Y. P., & Zheng, G. Q. (2017). Nanostructured NiCo@NiCoOx core-shell layer as efficient and robust electrocatalyst for oxygen evolution reaction. *Electrochimica Acta*, 254(Supplement C), 337-347.
- Wu, M. S., Zheng, Z. B., Lai, Y. S., & Jow, J. J. (2015). Nickel cobaltite nanograss grown around porous carbon nanotube-wrapped stainless steel wire mesh as a flexible electrode for high-performance supercapacitor application. *Electrochimica Acta, 182*, 31-38.
- Xia, X. H., Liang, Y., Wang, Z., Fan, J., Luo, Y. S., & Jia, Z. J. (2008). Synthesis and photocatalytic properties of TiO<sub>2</sub> nanostructures. *Materials Research Bulletin*, 43(8), 2187-2195.
- Xie, K., Li, J., Lai, Y., Zhang, Z., Liu, Y., Zhang, G., & Huang, H. (2011). Polyaniline nanowire array encapsulated in titania nanotubes as a superior electrode for supercapacitors. *Nanoscale*, 3(5), 2202-2207.
- Xie, S., Gan, M., Ma, L., Li, Z., Yan, J., Yin, H., Shen, X., Xu, F., Zheng, J., Zhang, J., & Hu, J. (2014). Synthesis of polyaniline-titania nanotube arrays hybrid composite via self-assembling and graft polymerization for supercapacitor application. *Electrochimica Acta*, 120, 408-415.
- Xie, Y., & Fu, D. (2010). Supercapacitance of ruthenium oxide deposited on titania and titanium substrates. *Materials Chemistry and Physics*, 122(1), 23-29.

- Xie, Y., Huang, C., Zhou, L., Liu, Y., & Huang, H. (2009). Supercapacitor application of nickel oxide–titania nanocomposites. *Composites Science and Technology*, 69(13), 2108-2114.
- Xie, Z. B., & Blackwood, D. J. (2010). Effects of anodization parameters on the formation of titania nanotubes in ethylene glycol. *Electrochimica Acta*, 56(2), 905-912.
- Xu, J., Li, L., Gao, P., Yu, L., Chen, Y., Yang, P., Gai, S., & Yang, P. (2015). Facile preparation of NiCo<sub>2</sub>O<sub>4</sub> nanobelt/graphene composite for electrochemical capacitor application. *Electrochimica Acta*, *166*, 206-214.
- Xu, S., Du, A. J., Liu, J., Ng, J., & Sun, D. D. (2011). Highly efficient CuO incorporated TiO<sub>2</sub> nanotube photocatalyst for hydrogen production from water. *International Journal of Hydrogen Energy*, 36(11), 6560-6568.
- Yang, F., Yao, J., Liu, F., He, H., Zhou, M., Xiao, P., & Zhang, Y. (2013). Ni–Co oxides nanowire arrays grown on ordered TiO<sub>2</sub> nanotubes with high performance in supercapacitors. *Journal of Materials Chemistry A*, 1(3), 594-601.
- Yang, X., Chi, L., Chen, C., Cui, X., & Wang, Q. (2015). The nearly 100% filling of PEDOT in TiO<sub>2</sub> nanotube array by a simple electropolymerization method. *Physica E: Low-dimensional Systems and Nanostructures*, 66, 120-124.
- Yasuda, K., & Schmuki, P. (2007). Control of morphology and composition of selforganized zirconium titanate nanotubes formed in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/NH<sub>4</sub>F electrolytes. *Electrochimica Acta*, *52*(12), 4053-4061.
- Yu, Q., Zhang, L., Guo, R., Sun, J., Fu, W., Tang, T., & Tang, T. (2017). Catalytic performance of CoMo catalysts supported on mesoporous ZSM-5 zeolitealumina composites in the hydrodesulfurization of 4,6dimethyldibenzothiophene. *Fuel Processing Technology*, 159, 76-87.
- Yuan, C., Li, J., Hou, L., Zhang, X., Shen, L., & Lou, X. W. D. (2012). Ultrathin mesoporous NiCo<sub>2</sub>O<sub>4</sub> nanosheets supported on Ni foam as advanced electrodes for supercapacitors. *Advanced Functional Materials*, 22(21), 4592-4597.
- Zhang, D., Yan, H., Lu, Y., Qiu, K., Wang, C., Zhang, Y., Liu, X., Luo, J., & Luo, Y. (2014). NiCo<sub>2</sub>O<sub>4</sub> nanostructure materials: morphology control and electrochemical energy storage. *Dalton Transactions*, *43*(42), 15887-15897.
- Zhang, G., & Lou, X. W. D. (2013). General Solution Growth of Mesoporous NiCo<sub>2</sub>O<sub>4</sub> Nanosheets on Various Conductive Substrates as High-Performance Electrodes for Supercapacitors. *Advanced Materials*, 25(7), 976-979.

- Zhang, G. Q., Wu, H. B., Hoster, H. E., Chan-Park, M. B., & Lou, X. W. D. (2012). Single-crystalline NiCo<sub>2</sub>O<sub>4</sub> nanoneedle arrays grown on conductive substrates as binder-free electrodes for high-performance supercapacitors. *Energy & Environmental Science*, 5(11), 9453-9456.
- Zhang, J., Wang, Y., Qin, Y., Yu, C., Cui, L., Shu, X., Cui, J., Zheng, H., Zhang, Y., & Wu, Y. (2017). A facile one-step synthesis of Mn<sub>3</sub>O<sub>4</sub> nanoparticles-decorated TiO<sub>2</sub> nanotube arrays as high performance electrode for supercapacitors. *Journal of Solid State Chemistry*, 246, 269-277.
- Zhang, W., Wang, S., Li, J., & Yang, X. (2015). Photocatalytic hydrogen production from methanol aqueous solution under visible-light using Cu/S–TiO<sub>2</sub> prepared by electroless plating method. *Catalysis Communications, 59*, 189-194.
- Zhang, Y., Feng, H., Wu, X., Wang, L., Zhang, A., Xia, T., Dong, H., Li, X., & Zhang, L. (2009). Progress of electrochemical capacitor electrode materials: A review. *International Journal of Hydrogen Energy*, 34(11), 4889-4899.
- Zhao, C., Pelaez, M., Dionysiou, D. D., Pillai, S. C., Byrne, J. A., & O'Shea, K. E. (2014). UV and visible light activated TiO<sub>2</sub> photocatalysis of 6-hydroxymethyl uracil, a model compound for the potent cyanotoxin cylindrospermopsin. *Catalysis Today*, 224, 70-76.
- Zhou, H., & Zhang, Y. (2013). Enhancing the capacitance of TiO<sub>2</sub> nanotube arrays by a facile cathodic reduction process. *Journal of Power Sources*, 239, 128-131.
- Zhou, H., & Zhang, Y. (2014a). Electrochemically self-doped TiO2 nanotube arrays for supercapacitors. *The Journal of Physical Chemistry C*, 118(11), 5626-5636.
- Zhou, H., & Zhang, Y. (2014b). Enhanced electrochemical performance of manganese dioxide spheres deposited on a titanium dioxide nanotube arrays substrate. *Journal of Power Sources*, 272, 866-879.