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**Development of Anodised Aluminium Oxide
Nanostructure from Al-Mn Alloy**

by

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TABLE OF CONTENTS

	PAGE
THESIS DECLARATION	i
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF FIGURES	viii
LIST OF TABLES	xiv
LIST OF ABBREVIATIONS, SYMBOLS OR NOMENCLATURES	xv
ABSTRAK	xviii
ABSTRACT	xx
CHAPTER 1: INTRODUCTION	
1.1 Introduction	1
1.2 Problem Statement	4
1.3 Objectives	8
1.4 Thesis Outline	9
CHAPTER 2: LITERATURE REVIEW	
2.1 Aluminium	11
2.2 Aluminium-Manganese (Al-Mn) Alloys	12
2.3 Introduction to Anodising Process	13
2.4 Basis of Anodising of Aluminium	16
2.5 Formation of Anodic Aluminium Oxide	18

2.6	Types of Anodic Aluminium Oxide	21
2.6.1	General Structure of Porous AAO	22
2.7	Anodising of Aluminium and Its Alloys	26
2.8	Formation Mechanism of Porous AAO	29
2.8.1	Field Assisted Dissolution Mechanism	30
2.8.1.1	Pore Nucleation	32
2.8.1.2	Steady State Growth of Porous AAO	35
2.9	Variables that Affecting the Formation of Porous AAO	36
2.9.1	Substrate Composition	36
2.9.2	Anodising Voltage	39
2.9.3	Temperature of Electrolyte	40
2.9.4	Electrolyte Concentration	41
2.10	Self Organization of Porous AAO	42
2.11	Synthesis of Well Ordered Porous AAO	44
2.11.1	Two Steps Anodising	44
2.11.2	Pre Patterning Method	46
2.11.3	High Field Anodising	48
2.12	Growth Kinetics of Porous AAO	49
2.12.1	Study of Growth Kinetics of Porous AAO by Change of Mass	49
2.12.2	Study of Growth Kinetics of Porous AAO by Change of Thickness	52
 CHAPTER 3: RESEARCH METHODOLOGY		
3.1	Introduction	53

3.2	Raw Materials and Chemicals	55
3.2.1	Aluminium Granules	55
3.2.2	Aluminium Manganese Master Alloy	56
3.2.3	Oxalic Acid	56
3.2.4	Phosphoric Acid	57
3.2.5	Chromium Trioxide	58
3.3	Experimental Setup and Equipment	59
3.4	Methodology and Design of Experiment	60
3.4.1	Fabrication of Well Ordered Porous AAO Film by Oxide Dissolution Treatment	61
3.4.2	Study of Effect of Anodising Parameters on the Formation of Porous AAO	61
3.5	Experimental Procedure	62
3.5.1	Phase I: Fabrication and Preparation of Substrate	62
3.5.2	Phase II: Synthesis of AAO Film by Anodising Process of Porous AAO	65
3.5.2.1	Oxide Dissolution Treatment	67
3.5.3	Phase III: AAO Film Characterizations and Testing	68
3.5.3.1	Scanning Electron Microscopy (SEM)	68
3.5.3.2	Fast Fourier Transform Image Analysis	72
3.5.3.3	Growth Kinetic Study	73
3.5.3.3.1	Anodising Efficiency Measurement	73
3.5.3.3.2	Oxide Mass Measurements	74
3.5.3.4	X-Ray Diffraction	74

CHAPTER 4: RESULTS AND DISCUSSION

4.1	Fabrication of Well Ordered Porous AAO by Oxide Dissolution Treatment	76
4.1.1	Current Density versus Time Transient	77
4.1.2	Morphology and Regularity of Porous AAO	78
4.1.3	Pore Size and Interpore Distance Distribution Diagram	83
4.2	Effect of Manganese Content on the Synthesis of Porous AAO	87
4.2.1	Microstructure of As Cast 99.99% Al and Al-Mn Alloys	87
4.2.2	Current Density versus Time Transient	90
4.2.3	Morphology and Regularity of Porous AAO	93
4.2.4	Pore Size and Interpore Distance of Porous AAO	96
4.2.5	Thickness of Porous AAO	98
4.2.6	Anodising Efficiency	102
4.2.7	Oxide Mass of Porous AAO	104
4.2.8	XRD Patterns of Porous AAO	106
4.3	Effect of Anodising Voltage on the Synthesis of Porous AAO	
4.3.1	Current Density versus Time Transient	108
4.3.2	Morphology and Regularity of Porous AAO	112
4.3.3	Pore Size and Interpore Distance of Porous AAO	116
4.3.4	Thickness of Porous AAO	118
4.3.5	Anodising Efficiency	119
4.3.6	Oxide Mass of Porous AAO	121
4.3.7	XRD Patterns of Porous AAO	123
4.4	Effect of Concentration of Oxalic Acid on the Synthesis of Porous	124

AAO	
4.4.1	Current Density versus Time Transient 124
4.4.2	Morphology and Regularity of Porous AAO 126
4.4.3	Pore Size and Interpore Distance of Porous AAO 128
4.4.4	Thickness of Porous AAO 130
4.4.5	Anodising Efficiency 132
4.4.6	Oxide Mass of Porous AAO 133
4.4.7	XRD Patterns of Porous AAO 134
4.5	Effect of Temperature of Oxalic Acid on the Synthesis of Porous AAO 136
4.5.1	Current Density versus Time Transient 136
4.5.2	Morphology and Regularity of Porous AAO 139
4.5.3	Pore Size and Interpore Distance of Porous AAO 142
4.5.4	Thickness of Porous AAO 144
4.5.5	Anodising Efficiency 146
4.5.6	Oxide Mass of Porous AAO 148
4.5.7	XRD Patterns of Porous AAO 149
CHAPTER 5: CONCLUSIONS AND SUGGESTION	
5.1	Conclusions 150
5.2	Recommendation 154
REFERENCES 155	
APPENDIX A 167	
APPENDIX B 168	
APPENDIX C 169	
APPENDIX D 170	

LIST OF FIGURES

FIGURE	PAGE
2.1 Al – Mn phase diagram	13
2.2 Schematic representation of the production of O ²⁻ or OH ⁻ ions at the structure of AAO in sulphuric acid	19
2.3 Barrier and porous type AAO	22
2.4 Idealized structure model of porous AAO film	23
2.5 The plan and sectional views of a pore and adjacent cell for films formed in different major acids: (a) sulphuric acid, (b) oxalic acid, (c) phosphoric acid and (d) chromic acid	26
2.6 Time variation of current density (j vs t) at constant anodising voltage during anodising	28
2.7 Polarization of bonds at high electric field that lead to stretching and breaking of bonds (a) before polarization, (b) after polarization, (c) removal of Al ³⁺ and O ²⁻ ions, and (d) the remaining oxide	32
2.8 Schematic illustration of pore nucleation mechanism proposed by O'Sullivan and Wood	33
2.9 Schematic illustration of pore nucleation mechanism proposed by G.E. Thompson	35
2.10 Two steps anodising process by Masuda & Satoh	46
3.1 Summarized research flow	54
3.2 Aluminium manganese (Al- 20 wt % Mn) master alloy ingot	56
3.3 Anodising cell	60

3.4	Dimension of the disc shape sample	64
3.5	Experimental setup used in the study	66
3.6	Possible cleavage planes obtained on the film section	70
3.7	Measurements of pore size and interpore distance.	70
3.8	Measurements of porous AAO thickness from the film section	71
4.1	Current density versus time transient for the anodising of 99.99% aluminium substrate	77
4.2	Micrographs of porous AAO after subjecting to oxide dissolution treatment of duration of (a) 0 minute (b) 1 minute (c) 2 minutes and (d) 3 minutes respectively	80
4.3	FFT images of porous AAO subjected to oxide dissolution treatment of duration (a) 0 minute (b) 1 minute (c) 2 minutes and (d) 3 minutes respectively	83
4.4	Pore size distribution diagram of porous AAO (a) before subjecting to oxide dissolution treatment and (b) after subjecting to three minutes of oxide dissolution treatment	84
4.5	Interpore distance distribution diagram of porous AAO (a) before subjecting to oxide dissolution treatment and (b) after subjecting to three minutes of oxide dissolution treatment	86
4.6	Microstructure of substrates prior subjecting to anodising (a) 99.99% aluminium, aluminium with (b) 0.5 wt % Mn (c) 1.0 wt % Mn (d) 1.5 wt % Mn and (e) 2.0 wt % Mn respectively	88
4.7	Figure 4.7: Energy dispersive x-ray spectroscopy spot analysis spectra for (a) dark secondary phases at location 001 (b) bright grain structure at location 002	89

4.8	Current density versus time transient for the anodising of substrates of different compositions up to (a) sixty seconds and (b) sixty minutes	92
4.9	Top view SEM images of anodised substrate of (a) and (b) 99.99% aluminium, (c) and (d) Al-0.5 wt % Mn, (e) and (f) Al-1.0 wt % Mn, (g) and (h) Al-1.5 wt % Mn, (i) and (j) Al-2.0 wt % Mn	95
4.10	Variation of pore size and interpore distance of anodised substrate as a function of Mn content of substrates	98
4.11	Cross sectional SEM images of anodised substrates of (a) 99.99% aluminium, (b) Al-0.5 wt % Mn, (c) Al-1.0 wt % Mn, (d) Al-1.5 wt % Mn and (e) Al-2.0 wt % Mn	100
4.12	(a) SEM images of cross section of porous AAO formed on Al – 1.0 wt % Mn near the oxide/metal interface, (b) Elemental distribution map of Mn, (c) SEM-EDS result of line analysis in the direction A	101
4.13	Thickness of porous AAO as a function of Mn content	102
4.14	Anodising efficiency of anodising process as a function of Mn content	104
4.15	Oxide mass of porous AAO formed on various substrates as a function of time	106
4.16	XRD patterns of porous AAO formed on substrates of (a) 99.99% Al, (b) Al-0.5wt % Mn, (c) Al-1.0wt % Mn, (d) Al-1.5wt % Mn and (e) Al-2.0wt % Mn	107
4.17	Current density versus time transient for the anodising of Al-0.5 wt % Mn alloy substrates under the influence of increasing anodising	

	voltage from 30 V to 70 V up to (a) sixty seconds and (b) sixty minutes	111
4.18	Top view SEM images of porous AAO anodised at voltage of (a) and (b) 300 V, (c) and (d) 40 V, (e) and (f) 50 V, (g) and (h) 60 V, (i) and (j) 70 V	109 114
4.19	SEM images of porous AAO of (a) burnt area with cracks and protrusion (b) burnt area at higher magnification	116
4.20	Variation of pore size and interpore distance of anodised substrate as a function of anodising voltage	117
4.21	Thickness of porous AAO as a function of anodising voltage	118
4.22	Cross sectional SEM images of porous AAO anodised at (a) 30 V, (b) 40 V, (c) 50 V, (d) 60 V and (e) 70 V	119
4.23	Anodising efficiency of anodising process as a function of anodising voltage	120
4.24	Oxide mass of porous AAO formed under influence of different voltages as a function of time	122
4.25	XRD patterns of porous AAO anodised at (a) 30 V, (b) 40 V, (c) 50 V, (d) 60 V and (e) 70 V	123
4.26	Current density versus time transient for the anodising of Al-0.5wt % substrates in oxalic acid of different concentration up to (a) sixty seconds and (b) sixty minutes	125
4.27	Top view SEM images of porous AAO anodised in oxalic acid of (a) and (b) 0.1 M, (c) and (d) 0.3 M, (e) and (f) 0.5 M and (g) and (h) 0.7 M	127
4.28	Variation of pore size and interpore distance of anodised substrate	

	as a function of concentration of oxalic acid	130
4.29	Thickness of porous AAO as a function of concentration of oxalic acid	131
4.30	Cross sectional SEM images of porous AAO anodised in oxalic acid of (a) 0.1 M, (b) 0.3 M, (c) 0.5 M and (d) 0.7 M	131
4.31	Anodising efficiency of anodising process as a function of concentration of oxalic acid	133
4.32	Oxide mass of porous AAO formed in oxalic acid of different concentration as a function of time	134
4.33	XRD patterns of porous AAO anodised in oxalic acid of concentration (a) 0.1 M, (b) 0.3 M, (c) 0.5 M and (d) 0.7 M	135
4.34	Current density versus time transient for the anodising of Al-0.5wt % substrates in 0.5 M oxalic acid of different temperatures up to (a) sixty seconds and (b) sixty minutes	137
4.35	Top view SEM images of porous AAO anodised in 0.5 M oxalic acid of (a) and (b) 5 °C, (c) and (d) 10 °C, (e) and (f) 15 °C, (g) and (h) 20 °C, (i) and (j) 25 °C	140
4.36	Variation of pore size and interpore distance of anodised substrate as a function of temperature of oxalic acid	144
4.37	Thickness of porous AAO as a function of temperature of oxalic acid	145
4.38	Cross sectional SEM images of porous AAO anodised in oxalic acid of (a) 5 °C, (b) 10 °C, (c) 15 °C, (d) 20 °C and (e) 25 °C	146
4.39	Anodising efficiency of anodising process as a function of temperature of oxalic acid	147

4.40	Oxide mass of porous AAO formed in oxalic acid of different temperature	148
4.41	XRD patterns of porous AAO anodised in oxalic acid of temperature (a) 5 °C, (b) 10 °C, (c) 15 °C, (d) 20 °C and (e) 25 °C	149

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LIST OF TABLES

TABLE		PAGE
3.1	The chemical and physical data of aluminium granules	55
3.2	The properties of oxalic acid	57
3.3	The properties of phosphoric acid	58
3.4	The properties of chromium trioxide	58
3.5	Experimental conditions that were used to study the morphology, composition and growth kinetics of porous AAO in oxalic acid	63
3.6	Calculated mass of Al granules and Al- 20 wt % Mn master alloys used for the fabrication of Al-Mn alloys of different compositions	64

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LIST OF ABBREVIATIONS, SYMBOLS OR NOMENCLATURES

AAO	Anodic aluminium oxide
AFM	Atomic force microscope
Al-Mn	Aluminium manganese
Al ³⁺	Aluminium ions
Al ₂ O ₃	Aluminium oxide
Au	Gold
BMP	Bitmap
CdS	Cadmium sulfide
CNT	Carbon nanotube
Cu	Copper
DC	Direct Current
DUV	Deep ultraviolet
EDX	Element dispersive X ray spectroscopy
FFT	Fast Fourier transform
Fe	Iron
GPa	Giga pascal
H ⁺	Hydrogen ions
Mg	Magnesium
Mn	Manganese
O ²⁻	Oxygen ions
OH ⁻	Hydroxide ions
PBR	Pilling Bedworth ratio
Pd	Palladium

Pt	Platinum
PTFE	Polytetrafluoroethylene
SEM	Scanning electron microscope
Si	Silicon
SPM	Scanning probe microscope
TSA	Templated self assembly
XRD	X-ray diffraction
ZnO	Zinc oxide
A_t	Area of sample
at%	Atomic percent
F	Faraday constant
g/cm^3	Gram per cubic centimetre
g/mol	Gram per mole
j	Current density
mA/cm^2	Milliampere per square centimetre
$M_{Al_2O_3}$	Molecular weight of aluminium oxide
m_{Al}	Mass of aluminium metal converted to oxide
M_{Al}	Molecular weight of aluminium metal
$(m_{Al})_{\eta=100}$	Mass of aluminium metal calculated using equation with $\eta=100\%$
m_{di}	Mass of specimen before dissolution
m_{df}	Mass of specimen after the dissolution
m_i	Mass of sample before anodising
m_f	Mass of sample after anodising
m_p	Total mass of porous oxide

t	Time
wt %	Weight percent
z	Number of electrons changed in reaction
%	Percent
$^{\circ}\text{C}$	Degree Celsius
$\Delta G^{\circ}/n$	Gibbs free energy per equivalent
η	Anodising efficiency
$\gamma\text{-MnO}_2$	Gamma manganese dioxide

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Perkembangan Aluminium Oksida Teranod Daripada Aloj Al-Mn

ABSTRAK

Kajian ini dibahagi kepada dua bahagian. Bahagian pertama kajian ini memberi tumpuan kepada sintesis aluminium oksida teranod (AAO) berliang tersusun dengan menggunakan rawatan pelarutan oksida. AAO berliang telah dihasil dengan penganodan aluminium 99.99% di dalam asid oxalik 0.3 M pada suhu 15°C selama 15 minit. Substrat teranod terdedah kepada rawatan pelarutan oksida dengan direndam di dalam campuran asid kromik dan asid fosforik yang dikacau. Kesan rawatan pelarutan oksida terhadap morfologi dan keteraturan AAO berliang telah dikaji dengan menggunakan mikroskop imbasan elektron. Keputusan menunjukkan pendedahan AAO berliang kepada rawatan pelarutan oksida selama tiga minit mendedahkan susunan liang yang tersusun atur yang terhasil pada peringkat pertumbuhan mantap. Keteraturan AAO berliang telah ditambahbaikkan. Dalam bahagian kedua kajian, AAO berliang telah dihasil daripada substrat aloj aluminium mangan dan kesan kandungan mangan, voltan penganodan, kepekatan asid oxalik dan suhu asid oxalik terhadap sifat penganodan, morfologi, sifat-sifat dimensi dan kinetik pertumbuhan telah dikaji. Keputusan menunjukkan penambahan mangan dari 0.5 wt % hingga 2.0 wt % ke dalam substrat Al mengurangkan ketumpatan arus, keteraturan dan kinetik pertumbuhan AAO berliang. Saiz liang dan jarak antara liang juga didapati berkurang dengan penambahan mangan. Kecekapan arus proses penganodan berkurang apabila kandungan Mn bertambah kepada 1.0 wt %, tetapi meningkat apabila kandungan Mn bertambah kepada 2.0 wt %. Analisa corak XRD menunjukkan alumina amorfus telah terhasil di dalam substrat untuk semua komposisi dan MnO₂ telah didapati di dalam substrat teranod Al-1.5 wt % Mn dan Al -2.0 wt % Mn. Untuk kajian mengenai kesan voltan penganodan, penganodan substrat Al-0.5 wt % di bawah pengaruh voltan penganodan yang meningkat dari 30 – 70V telah membawa kepada ketumpatan arus yang lebih tinggi, Saiz liang, jarak antara liang yang lebih besar dan kadar pertumbuhan yang lebih tinggi. Keteraturan susunan liang AAO berliang telah dipertingkatkan apabila voltan penganodan dinaikkan dari 30 V kepada 50 V, tetapi merosot apabila dipertingkatkan kepada 70 V. Pecahan dielektrik berlaku apabila penganodan dijalankan pada 70 V. Didapati amaun alumina amorfus bertambah apabila voltan penganodan dinaikkan dari 30 V kepada 70 V. Penganodan Al-0.5 wt % Mn pada 50 V dalam asid oxalik yang kekekatannya meningkat dari 0.1 M kepada 0.7 M meningkatkan ketumpatan arus dan kinetik pertumbuhan. AAO berliang tersusun diperolehi apabila asid oksalik yang kekekatannya kecuali 0.1 M digunakan. Pertambahan kepekatan asid oxalik mengurangkan saiz liang manakala tiada perbezaan ketara antara jarak antara liang diperhati. Kecekapan arus berkurang dengan fungsi kepekatan asid oxalik. Keamatan relatif puncak luas dalam corak XRD menunjukkan amaun alumina amorfus meningkat dengan fungsi kepekatan asid oxalik. Untuk kajian kesan suhu asid oxalik, penganodan Al-0.5 wt % Mn pada 50 V dibuat dalam asid oxalik 0.5 M antara suhu 5 °C hingga 25 °C. Ketumpatan arus dan kinetik pertumbuhan bertambah manakala keteraturan susunan liang dan kecekapan arus berkurang dengan suhu asid oxalik yang meningkat. Suhu asid oxalik tidak mempunyai kesan ketara terhadap kedua-dua saiz liang dan jarak antara

liang. Keamatan relatif puncak luas meningkat menunjukkan amaun alumina amorfus bertambah dengan peningkatan suhu asid oxalik.

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Development of Anodised Aluminium Oxide Nanostructure from Al-Mn Alloy

ABSTRACT

This study was divided into two parts. The first part of the study was focused on the synthesis of well ordered porous AAO by using oxide dissolution treatment. The porous AAO was formed by anodising of 99.99 % aluminium in 0.3 M oxalic acid at 15 °C for 15 minutes. Anodised substrates were subjected to oxide dissolution treatment by immersing in stirred mixture of chromic acid and phosphoric acid. The effect of oxide dissolution treatment on the morphology and regularity of porous AAO was studied by using scanning electron microscope. The results showed that exposure of porous AAO to oxide dissolution treatment up to three minutes revealed the well ordered pores arrangement that formed during the steady state growth stage. Regularity of the porous AAO was improved. In the second part of the study, porous AAO was formed from aluminium manganese (Al-Mn) alloy substrates and the effect of manganese content, anodising voltage, concentration of oxalic acid, and temperature of oxalic acid on the anodising behaviour, morphology, dimensional properties and growth kinetics were studied. Results showed that the addition of Mn from 0.5 wt % to 2.0 wt % into Al substrates reduced the current density, regularity and growth kinetics of porous AAO. The pore size and interpore distance were also found to decrease with the addition of Mn. Anodising efficiency of anodising process decreased as the Mn content increased up to 1.0 wt %, but increased when the Mn content was further increased to 2.0 wt %. Analysis of XRD patterns showed that amorphous alumina was formed in substrates of all compositions and MnO₂ was found to present in Al-1.5 wt % Mn and Al -2.0 wt % Mn substrates. For the study of effect of anodising voltage, anodising of Al-0.5 wt % Mn under the influence of increasing anodising voltage of 30-70V has led to higher current density, larger pore size and interpore distance and higher growth rates. The regularity of pore arrangement of porous AAO was improved when the anodising voltage was increased from 30 V to 50V, but deteriorated when further increased to 70V. Dielectric breakdown occurred when anodising was conducted at 70V. Amount of amorphous alumina was found to increase when the anodising voltage was increased from 30 V to 70 V. Anodising of Al-0.5 wt % Mn at 50 V in oxalic acid of increasing concentration from 0.1 M to 0.7 M increased the current density and growth kinetics. Well ordered porous AAOs were obtained when oxalic acid of all concentration was used, except 0.1 M. Increase of concentration of oxalic acid decreased the pore size while no significant difference in interpore distance was observed. Anodising efficiency decreased as a function of concentration of oxalic acid. The relative intensity of broad peaks in XRD patterns showed that amount of amorphous alumina increased as a function of concentration of oxalic acid. For the study of effect of temperature of oxalic acid, anodising of Al-0.5 wt % Mn was conducted at 50V in 0.5 M oxalic acid of temperature ranging from 5°C to 25°C. Current density and oxide thickness increased while regularity of pores arrangement and anodising efficiency decreased with the increasing temperature of oxalic acid. Temperature of oxalic acid did not have obvious effect on both pore size and interpore distance. Relative intensities of broad peaks increased indicating the amount of amorphous alumina increased with the increasing temperature of oxalic acid.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Nanotechnology primarily involves the study of control and manipulation of matter at nanometre scale. These matters, known as nanostructured material, are defined as materials whose basic units with at least one dimension falls within the range of one to one hundred nanometres (Gogotsi, 2006). The confined dimensionality of these nanostructured materials has led to the discovery of novel biological, chemical and physical properties of these materials. Novel and unique properties of nanostructured materials are attributed to the specific size effect and quantum confinement effect. Controlled manipulation of these properties has led to new devices and technologies. For example, due to the size and shape dependant properties, gold nanoparticle is red in colour instead of golden colour for bulk material (Bhattacharya & Srivastava, 2003). The change in colour of the gold nanoparticles indicates the change in the optical properties and they have bio applications in four area, which are labelling, delivery, heating and sensing (Sperling et al., 2008). Due to the good lubricative property and softness of graphite, it is used in the making of pencils. The structure of carbon nanotube (CNT) is considered similar to that of graphite in which the CNT is conceptualized as a single or multiple rolled layers of graphite. However, the mechanical strength of CNT which has similar structure to that of graphite is higher than the mechanical strength of stainless steel (Yu et al., 2000). This high strength leads

to extensive applications of CNT as reinforcement in various matrixes (Cha et al., 2005; Echeberria et al., 2011; Gojny et al., 2004). The confined dimensionality in the nanometre scale has led to the discovery of novel properties of nanostructured materials. Thus, there is an increasing research interest on the synthesis, characterisation, exploration and exploitation of nanostructured materials.

Generally, there are two approaches to control and manipulate the size of nanostructured materials, which are top-down approach and bottom-up approach. Top-down approach is the successive manipulation of bulk material to obtain nanostructured material. The most commonly used top-down approach is the lithographic method. Lithographic method involves the adding and patterning of layers of materials on the wafer surface. Nanostructures are then formed by selectively etching away materials of certain area. Today, lithography method has revolutionized human lives in the way we communicate, travel, and interact. Although top-down approach provides a promising way to produce nanostructured materials, the use of lithography methods in the fabricating of nanostructured materials faces limitation in the achievable smallest length scale and highest aspect ratio of the nanostructured materials.

Bottom-up approach also played an important role in the development of nanotechnology. The principle behind the bottom-up approach is the self assembly process. Self assembly process provides a route to spontaneous generation and hierarchical organisation of materials by biological or chemical process for the fabrication of nanostructured materials (Lin et al., 2001; Zhang et al., 2002). Bottom-up approach is increasingly being used as an alternative for the fabrication of nanostructured materials due to the fact that it allows smaller geometries than the lithography methods. Furthermore, it is more economic than lithography methods because it does not waste material to etch and does not employ high cost electron beam

lithography techniques. Examples of nanostructured materials fabricated by self assembly methods are arrays of magnetic nanowires which may be useful as data storage media (Nielsch et al., 2001) and type 1 collagen which may be useful in tissue engineering and synthesis of biosensor (Xu et al., 2009). However, the weakness of self assembly process in the synthesis of nanostructured materials is the low degree of control over the regularity and uniformity of the nanostructured materials. This is due to the fact that structure of self assembled nanostructured materials is formed based on their own guiding or driving force. This limits the structure and design of self assembled nanostructured materials.

With a template, more complicated designs can be achieved by self assembly method. Therefore, templated self assembly (TSA) was used for the fabrication of nanostructured materials. TSA combines both the top-down and bottom-up approaches to fabricate and control the morphology and size distribution of the nanostructured materials by limiting the self forming and self ordering processes to occur in the templates. Examples of TSA include chemically directed (Stoykovich et al., 2007), lithographically assisted (Cheng et al., 2002) and mechanically assisted (Angelescu et al., 2004). Thus, TSA provides the benefits of both lithography and self assembly and has profound potential in the synthesis of nanostructured materials. The major limitation of TSA is the availability of suitable template for the synthesis of nanostructured materials. The discovery of well ordered nanoporous anodic aluminium oxide (AAO) has enlightened their applications as template for TSA.

Initially, anodic alumina was used as corrosion resistance protective coating in 1923 (Durney, 1984). Since then, the range of applications has increased significantly and anodising process was extensively studied and investigated. Generally, there are two types of anodic alumina, namely barrier type and porous type anodic alumina.

Barrier type anodic alumina is formed when the aluminium is anodised in alkaline or neutral electrolyte while porous AAO is formed when aluminium is anodised in slightly acidic electrolytes. AAO is a self organising porous material. Although there is still no conclusive evidence that supports the forming mechanism, it is generally accepted that porous AAO is formed by field assisted dissolution mechanism. The dimensional parameters of AAO such as pore size, interpore distance and thickness are dependant on the anodising conditions. Another important feature of AAO is that when the anodising of aluminium is conducted under certain conditions, well ordered closely packed hexagonally arranged porous AAO with parallel pores is formed. AAO also has excellent mechanical and thermal stability. Thus, AAO has attracted enormous attentions of scientists and researchers such that it can be used as inexpensive template for the fabrication of various nanostructured materials by TSA without the need of costly and complex lithographic techniques

1.2 Problem Statement

The fabrication of nanostructured materials by TSA method employs well ordered porous AAO instead of disordered porous AAO. This is because well ordered porous AAO provides regular pore shape, narrow distribution of specific pore size and interpore distance for the synthesis of nanostructured materials of uniform dimensions (Jeong et al., 2004; Qu et al., 2009; Zhao et al., 2005). The properties of nanostructured materials are significantly influenced by the dimensions and shapes. This can be observed experimentally by the change of antibacterial effect of CNT as a function of their diameter (Kang et al., 2008). The conductivity of nanosilver colloids is also greatly influenced by the changes in the size of the colloids (Zhao et al., 2010). Therefore, it is