

**EFFECT OF SYNTHESIS PARAMETERS ON STRUCTURAL AND
MORPHOLOGICAL PROPERTIES OF NANOCRYSTALLINE
BISMUTH PHOSPHORUS OXIDE MATERIALS**

HARTINI BINTI KHAIRI OSMAN

UNIVERSITI TEKNOLOGI MALAYSIA

EFFECT OF SYNTHESIS PARAMETERS ON STRUCTURAL AND
MORPHOLOGICAL PROPERTIES OF NANOCRYSTALLINE
BISMUTH PHOSPHORUS OXIDE MATERIALS

HARTINI BINTI KHAIRI OSMAN

A thesis submitted in partial fulfillment of the
requirements for the award of the degree of
Master of Science (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

AUGUST 2013

ACKNOWLEDGEMENT

First and foremost, all praise to be Allah S.W.T., the Almighty, the Benevolent for Allah S.W.T. blessing and guidance for giving me the inspiration to embark this work and instilling me the strength to complete my master research as well as this thesis. Many people have contributed and tough me during the period of this research as well as to the creation and completion of this thesis. I would like to express my gratitude to all who have helped me in one way to another in the research and writing of this thesis.

I especially indebted and grateful to my research supervisor and co-supervisor, Dr. Lee Siew Ling and Dr. Hendrik Oktendy Lintang for their guidance, support, patience, comments, and suggestions, it helped me a lot in my research and thesis writing. I would also like to extend my appreciation to Catalytic Science and Technology (CST) group lecturer, Prof. Dr. Hadi Nur, Dr. Dwi Gustiono, Dr. Leny Yuliati, Dr. Jon Effendi, and Dr. Zainab Ramli for also their comments and suggestions during this research. Not forgotten, the staff of Ibnu Sina Institute (IIS), especially to En. Mohamed Mohd. Salleh, En. Wan Faizal Wan Ahmad, En. Nazri Nawi, and Mrs. Nur Azleena Kasiran for their contribution and facilitate too.

I would also like to express my thanks to the staffs of Faculty of Science, En. Hanan, En. Azidy, Mrs. Suhani, and En. Yasin for their helped. Thanks also to all the lectures from Faculty of Science especially to PM. Dr. Zaiton Abd. Majid that has giving me useful and valuable ideas. On top of that, special thanks to PM. Dr. Mansor Ahmad, Chemistry Program Chairman of Faculty of Science, UPM for allowing me to run ICP analysis and surface area and pore distribution analyses at Faculty of Science, UPM, and also to Ms. Nurhidayu and Mrs. Rusnani, Assistant Science Officer of Faculty of Science, UPM for spending time to run both the ICP

and surface area and pore size distribution analyses. Special thanks also to Mr. Giorgio Schileo, post graduate student of Dr. Antonio Feteira from School of Chemistry, University of Birmingham, UK for times and ideas regarding this research.

Besides, not to be forgotten, my beloved labmates, Jamilah Ekhsan, Yong Shih Ween, Koh Pei Wen, Syafreena Attan, Surya Lubis, Umar Nizar, Syamsi Aini, and Hidayah Ran, for the fully support and helped to during these two years research. Last but not least, a very special thanks to my parents, Hajjah Habsah bt. Jaafar and Haji Khairi Osman b. Omar for their unending support and love. Not forgotten, to my family and friends as well. All of your contribution and support in completing this research so as this thesis are truly appreciated. Thank you so much.

ABSTRACT

Bismuth phosphorus oxide (BPO) has attracted much attention due to its various applications such as catalysts, photocatalysts, ionic conductors, and metal ion sensors. This material is usually produced via solid state reaction, hydrothermal synthesis, and ball milling which are associated with long reaction time, high synthesis temperature, and micro-sized products. Thus, an attempt was carried out in this research to synthesize nanocrystalline BPO using a relatively simple hot injection method at low reaction temperature. Bismuth acetate and calcium phosphide were used as precursors of bismuth and phosphorus, respectively. Phosphorus precursor reacted with 4 M hydrochloric acid (HCl) to generate phosphine (PH₃) gas which later reacted with bismuth precursor in a mixture of 1-octadecene (ODE) and myristic acid (MA). Several parameters in synthesis condition including reaction temperature, type of reaction solvent, ratio of stabilizer (MA) to reaction solvent (ODE), amount of reaction solvent, reaction time, and ageing time were investigated. X-ray diffraction (XRD) results suggested that single phase BPO material with high crystallinity was obtained at reaction temperature 180°C with reaction time of 30 minutes and ratio of MA:ODE of 1:90. The XRD pattern of this material was best fitted with that of reported Bi_{3.69}P_{0.31}O_{6.31} (PDF 2010:43-0455), implying formation of face centered cubic (FCC) phase with lattice parameter $a = 0.5416$ nm. This FCC phase was in good agreement with transmission electron microscopy (TEM) analysis with average lattice fringes spacing of 0.337 nm. As evidenced, TEM and XRD results showed that particle size of the materials were in range of 10 to 20 nm. These materials are interesting as they have an ordered lamellar structure with both large meso and macro pores, indicating the formation of porous structure between the layers of BPO materials. In conclusion, nanocrystalline BPO was successfully synthesized via hot injection method for the first time.

ABSTRAK

Bismut fosforus oksida (BPO) telah menarik banyak perhatian kerana ia boleh digunakan sebagai pemangkin, foto pemangkin, konduktor ionik, dan pengesan ion logam. Bahan ini biasanya dihasilkan melalui tindak balas keadaan pepejal, sintesis hidroterma, dan kaedah pengisaran bebola yang sering dikaitkan dengan masa tindak balas yang panjang, suhu tindak balas yang tinggi, dan penghasilan produk bersaiz mikro. Oleh itu, suatu usaha telah dijalankan dalam kajian ini untuk mensintesis BPO berhablur nano dengan menggunakan kaedah suntikan panas yang mudah pada suhu tindak balas yang rendah. Bismut asetat dan kalsium fosfida masing-masing telah digunakan sebagai bahan pelopor bismut dan fosforus. Bahan pelopor fosforus telah bertindak balas dengan 4 M asid hidroklorik (HCl) untuk menghasilkan gas fosfin (PH_3) yang kemudiannya bertindak balas dengan bahan pelopor bismut di dalam campuran 1-oktadekena (ODE) dan asid miristik (MA). Beberapa parameter sintesis termasuk suhu tindak balas, jenis pelarut, nisbah penstabil (MA) kepada pelarut (ODE), isipadu pelarut, masa tindak balas, dan masa penuaan telah disiasat. Keputusan pembelauan sinar-X (XRD) mencadangkan BPO berfasa tunggal dengan darjah penghabluran tinggi telah diperolehi pada suhu 180°C dengan masa tindak balas 30 minit dan nisbah MA:ODE bernilai 1:90. Bahan ini sepadan dengan $\text{Bi}_{3.69}\text{P}_{0.31}\text{O}_{6.31}$ yang telah dilaporkan (PDF 2010:43-0455), mencadangkan pembentukan fasa kiub berpusat muka (FCC) dengan kekisi malar, $a = 0.5416$ nm. Fasa FCC ini disokong oleh analisis mikroskop penghantaran elektron (TEM) dengan jarak pinggir kekisi berpurata 0.337 nm. Seperti yang dibuktikan, keputusan TEM dan XRD menunjukkan saiz zarah bahan adalah di antara 10 hingga 20 nm. Bahan ini menarik kerana mengandungi struktur lamela yang tersusun dengan liang meso yang besar berserta makro, menunjukkan pembentukan BPO yang berliang. Kesimpulannya, bahan berhablur nano BPO telah berjaya disintesis melalui kaedah suntikan panas untuk kali pertama.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENTS	iv
	ABSTRACT	vi
	ABSTRAK	vii
	TABLE OF CONTENTS	viii
	LIST OF TABLES	xii
	LIST OF FIGURES	xiv
	LIST OF ABBREVIATIONS	xxi
	LIST OF APPENDICES	xxii
1	INTRODUCTION	1
	1.1 Background of the Study	1
	1.2 Problem Statement	3
	1.3 Objectives of the Study	4
	1.4 Scope of the Study	4
	1.5 Significance of the Study	5
2	LITERATURE REVIEW	6
	2.1 Nanomaterial	6
	2.1.1 Types of Nanomaterial and Their Properties	7
	2.1.2 Nanosized Material versus Bulk Sized Material	8
	2.2 Lamellar Structured Materials	10

2.2.1	Role of Surfactant in Forming Ordered Lamellar Structure	13
2.3	Bismuth Phosphate Materials	16
2.3.1	Applications of Bismuth Phosphate Materials	17
2.3.2	Preparation Methods of Bismuth Phosphate Materials	19
2.4	Hot Injection Method	20
2.4.1	Materials Prepared via Hot Injection Method	21
2.4.2	Parameters in Hot Injection Method	22
3	RESEARCH METHODOLOGY	25
3.1	Research Outline	25
3.2	Chemicals	25
3.3	Synthesis of Bismuth Phosphorus Oxide	26
3.4	Investigation on Parameters in Synthesis Condition	27
3.4.1	Reaction Temperature	28
3.4.2	Types of Reaction Solvent	28
3.4.3	Ratio of Stabilizer (MA) to Reaction Solvent (ODE)	29
3.4.4	Amount of Reaction Solvent	29
3.4.5	Reaction Time	29
3.4.6	Ageing Time	30
3.5	Characterization of Bismuth Phosphorus Oxide	30
3.5.1	X-ray Diffraction (XRD)	31
3.5.2	Transmission Electron Microscopy (TEM)	32
3.5.3	Field Emission Scanning Electron Microscopy (FESEM)	33

3.5.4	Energy Dispersive X-ray (EDX) Analysis	34
3.5.5	Surface Area and Pore Size Distribution Analyses	34
3.5.6	Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES)	35
4	RESULTS AND DISCUSSION	36
4.1	Synthesis and Characterization of Nanocrystalline Bismuth Phosphorus Oxide Materials	36
4.2	Effect of Reaction Temperature	36
4.2.1	Physical Appearance	37
4.2.2	X-Ray Diffraction Analysis	37
4.2.3	TEM Analysis	45
4.2.4	FESEM Analysis	58
4.2.5	EDX Analysis	62
4.2.6	Surface Area and Pore Size Distribution Analyses	62
4.2.7	ICP-OES Analysis	66
4.3	Effect of Reaction Solvent	67
4.3.1	Physical Appearance	67
4.3.2	X-Ray Diffraction Analysis	67
4.3.3	TEM Analysis	73
4.3.4	FESEM Analysis	76
4.3.5	EDX Analysis	77
4.4	Effect of Stabilizer (MA) to Reaction Solvent (ODE) Ratio	77
4.4.1	Physical Appearance	78
4.4.2	X-Ray Diffraction Analysis	78
4.4.3	TEM Analysis	86
4.4.4	FESEM Analysis	90

4.4.5 EDX Analysis	92
4.5 Effect of Reaction Solvent Amount	92
4.5.1 Physical Appearance	92
4.5.2 X-Ray Diffraction Analysis	93
4.5.3 FESEM Analysis	98
4.5.4 EDX Analysis	99
4.6 Effect of Reaction Time	99
4.6.1 Physical Appearance	100
4.6.2 X-Ray Diffractions Analysis	100
4.6.3 FESEM Analysis	106
4.6.4 EDX Analysis	108
4.7 Effect of Ageing Time	109
4.7.1 Physical Appearance	109
4.7.2 X-Ray Diffraction Analysis	109
4.7.3 FESEM Analysis	114
4.7.4 EDX Analysis	115
5 CONCLUSION	116
5.1 Conclusion	116
5.2 Recommendations	117
REFERENCES	118
APPENDICES	134

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Types of nanomaterial	7
2.2	Different properties of materials in their bulk and nanosizes	9
2.3	The preparation method and application of some reported lamellar structured materials	11
2.4	Bismuth phosphate materials and their applications	17
2.5	Preparation methods in synthesizing bismuth phosphate materials	19
2.6	Studied parameters in synthesis condition of hot injection method	23
4.1	Crystallite size of BPO materials synthesized at different reaction temperatures	42
4.2	Ratios of peak intensities at $2\theta=2.4^\circ$ and 4.5° of synthesized BPO materials at different reaction temperatures	45
4.3	Elemental analysis of synthesized single and mixed phase of BPO samples	66
4.4	Crystallite size of synthesized BPO materials using different reaction solvents	71
4.5	Ratios of peak intensities at $2\theta=27.5^\circ$ and 41.2° as well as 32.8° and 41.2° of BPO-MA:ODE-5:90 and BPO-MA:ODE-7:90 for phase purity determination	82
4.6	Crystallite size of the BPO materials synthesized using different MA:ODE ratios	83

4.7	Crystallite size of BPO materials synthesized using different ODE amount	96
4.8	Ratios of peak intensities at $2\theta=32.8^\circ$ and 47.2° of all synthesized BPO materials at different reaction times	102
4.9	Crystallite size of the BPO materials synthesized at different reaction times	104
4.10	Crystallite size of BPO materials synthesized at different ageing times	111

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Illustrations of (a) micelle in aqueous solution and (b) reverse micelle in non-aqueous solution	14
2.2	Illustration of schematic diagrams of inorganic-surfactant lamellar: (a) homogenous solution of inorganic species and surfactant molecules, (b) reverse micelle of surfactant molecules with inorganic species that aggregate, (c) assemble of the reverse micelle into lamellar structure, and (d) removal of surfactant and attainment of ordered layered lamellar inorganic material	16
3.1	Experimental set-up of hot injection method	26
4.1	X-ray diffractograms of BPO materials synthesized at different reaction temperatures (a) BPO-RT-130, (b) BPO-RT-140, (c) BPO-RT-150, (d) BPO-RT-160, (e) BPO-RT-170, (f) BPO-RT-180, (g) BPO-RT-190, (h) BPO-RT-200, and (i) BPO-RT-210	38
4.2	Wide angle X-ray diffractograms of BPO materials synthesized at different reaction temperatures (a) BPO-RT-130, (b) BPO-RT-140, (c) BPO-RT-150, (d) BPO-RT-160, (e) BPO-RT-170, (f) BPO-RT-180, (g) BPO-RT-190, (h) BPO-RT-200, (i) BPO-RT-210, and (j) matching with the reported $\text{Bi}_{3.69}\text{P}_{0.31}\text{O}_{6.31}$ (PDF 2010:43-0455)	40
4.3	Small angle X-ray diffractograms of BPO materials synthesized at different reaction temperatures (a)	

	BPO-RT-130, (b) BPO-RT-140, (c) BPO-RT-150, (d) BPO-RT-160, (e) BPO-RT-170, (f) BPO-RT-180, (g) BPO-RT-190, (h) BPO-RT-200, and (i) BPO-RT-210	43
4.4	TEM images of synthesized BPO-RT-130 under magnification of (a) 100 k and (b) 1 million with measured crystallites size	46
4.5	TEM images of synthesized BPO-RT-130 of (a) selected particle and (b) its electron diffraction pattern	47
4.6	TEM images of synthesized BPO-RT-180 under magnification of (a) 100 k and (b) 800 k with measured crystallites size	47
4.7	TEM images of synthesized BPO-RT-180 with (a) selected particle (b) its electron diffraction pattern and (c) its inverse electron diffraction pattern with measured lattice fringes spacing	48
4.8	TEM images of synthesized BPO-RT-200 under magnification of (a) 100 k and (b) 1 million with measured crystallites size	49
4.9	TEM images of synthesized BPO-RT-200 with (a) selected particle, (b) its electron diffraction pattern, (c) magnification of electron diffraction pattern, and (d) measured lattice fringes spacing	50
4.10	Hexagonal particle shape of synthesized BPO materials (a) BPO-RT-130, (b) BPO-RT-180, and (c) BPO-RT-200 with their crystallographic planes	52
4.11	Schematic presentation of the whole mechanism for the formation of lamellar BPO materials; (a) addition of reaction solvent of ODE and MA, (b) aggregate (micelle) formation from homogeneous solution of ODE and MA, (c) addition of Bi precursor and self-assemble of Bi precursor into	

	lamellar, (d) P precursor added and covalent bonding of Bi and P precursor formed, and (e) removal of ODE+MA by washing using EtOH (Note: ■ = Bi precursor, ▲ = P precursor, ~~~~~○ = surfactant (MA), and ~~~~~■ = reaction solvent (ODE))	53
4.12	Schematic diagram of lamellar structure formation in BPO materials: (a) single particle of BP material with hexagonal particle shape and face centered cubic (FCC) crystalline phase and (b-d) formation of ordered lamellar structure	55
4.13	TEM images of synthesized BPO materials with uniform particle size	56
4.14	TEM images of synthesized BPO materials with non-uniform particle size	57
4.15	Schematic diagram of Ostwald ripening effect of the synthesized BPO materials; (a) single particle BPO materials, (b) dissolution of less stable small particles in the solution, (c) reposition into larger particle, (d) attainment of small and large particles, (e) formation of BPO material in various particle size, and (f) TEM images of synthesized BPO material	58
4.16	FESEM micrographs of BPO materials synthesized at different reaction temperatures (a) BPO-RT-130, (b) BPO-RT-140, (c) BPO-RT-150, (d) BPO-RT-160, (e) BPO-RT-170, (f) BPO-RT-180, (g) BPO-RT-190, (h) BPO-RT-200, and (i) BPO-RT-210	60
4.17	FESEM micrographs showing formation of lamellar structures in single phase BPO materials synthesized at reaction temperature of (a) 170 °C, (b) 180 °C, and (c) illustration of ordered lamellar structure	61

4.18	Adsorption-desorption isotherm plot of single phase BPO-RT-180	63
4.19	BJH desorption $dV/d\log(W)$ pore volume of BPO-RT-180	64
4.20	Illustration of the lamellar structured BPO materials with large meso and macropores (in red oval shape) formation resulted from non-uniform slit shape	65
4.21	X-ray diffractograms of BPO materials synthesized using different reaction solvents (a) BPO-RS-DDE(12), (b) BPO-RS-TDE(14), (c) BPO-RS-HDE(16), and (d) BPO-RS-ODE(18)	68
4.22	Wide angle X-ray diffractograms of BPO materials synthesized using different reaction solvents (a) BPO-RS-DDE(12), (b) BPO-RS-TDE(14), (c) BPO-RS-HDE(16), (d) BPO-RSO-ODE(18), and (e) matching with the reported $\text{Bi}_{3.69}\text{P}_{0.31}\text{O}_{6.31}$ (PDF 2010:43-0455)	70
4.23	Small angle X-ray diffractograms of BPO materials synthesized using different reaction solvents (a) BPO-RS-DDE(12), (b) BPO-RS-TDE(14), (c) BPO-RS-HDE(16), and (d) BPO-RS-ODE(18)	72
4.24	TEM images of BPO-RS-DDE(12) under magnification of (a) 100 k and (b) 800 k with measured crystallites size	74
4.25	TEM images of BPO-RS-DDE(12) with (a) selected particle (b) its electron diffraction pattern, and (c) its inverse electron diffraction pattern with measured lattice fringes spacing	75
4.26	FESEM micrographs of BPO materials synthesized using different reaction solvents (a) BPO-RS-DDE(12), (b) BPO-RS-TDE(14), (c) BPO-RS-HDE(16), and (d) BPO-RS-ODE(18)	77

4.27	X-ray diffractograms of synthesized BPO materials using different MA:ODE molar ratios (a) BPO-MA:ODE-0:90, (b) BPO-MA:ODE-0.5:90, (c) BPO-MA:ODE-1:90, (d) BPO-MA:ODE-3:90, (e) BPO-MA:ODE-5:90, and (f) BPO-MA:ODE-7:90	79
4.28	Wide angle X-ray diffractograms of BPO materials synthesized using different MA:ODE molar ratios (a) BPO-MA:ODE-0:90, (b) BPO-MA:ODE-0.5:90, (c) BPO-MA:ODE-1:90, (d) BPO-MA:ODE-3:90, (e) BPO-MA:ODE-5:90, (f) BPO-MA:ODE-7:90, and (g) matching with the reported $\text{Bi}_{3.69}\text{P}_{0.31}\text{O}_{6.31}$ (PDF 2010:43-0455)	81
4.29	X-ray diffractogram of BPO-MA:ODE-0:90	84
4.30	Small angle X-ray diffractograms of synthesized BPO materials using different MA:ODE molar ratios (a) BPO-MA:ODE-0:90, (b) BPO-MA:ODE-0.5:90, (c) BPO-MA:ODE-1:90, (d) BPO-MA:ODE-3:90, (e) BPO-MA:ODE-5:90, and (f) BPO-MA:ODE-7:90	85
4.31	TEM images of synthesized BPO-MA:ODE-3:90 under magnification of (a) 100 k and (b) 800 k with measured crystallites size	87
4.32	TEM images of synthesized BPO-MA:ODE-3:90 with the selected area electron diffraction (SAED)	88
4.33	TEM images of synthesized BPO-MA:ODE-5:90 under magnification of (a) 100 k and (b) 800 k with measured crystallites size	89
4.34	The selected area electron diffraction (SAED) of mixed phase BPO-MA:ODE-5:90	90
4.35	FESEM micrographs of BPO materials synthesized using different MA:ODE molar ratios (a) BPO-MA:ODE-0:90, (b) BPO-MA:ODE-0.5:90, (c) BPO-MA:ODE-1:90, (d) BPO-MA:ODE-3:90, (e)	

	BPO-MA:ODE-5:90, and (f) BPO-MA:ODE-7:90	91
4.36	X-ray diffractograms of BPO materials synthesized using different ODE volumes (a) BPO-ODE-3, (b) BPO-ODE-13, (c) BPO-ODE-52, (d) BPO-ODE-78, (e) BPO-ODE-104, and (f) BPO-ODE-130	94
4.37	Wide angle X-ray diffractograms of synthesized BPO materials using different ODE volumes (a) BPO-ODE-3, (b) BPO-ODE-13, (c) BPO-ODE-52, (d) BPO-ODE-78, (e) BPO-ODE-104, (f) BPO-ODE-130, and (g) matching with the reported $\text{Bi}_{3.69}\text{P}_{0.31}\text{O}_{6.31}$ (PDF 2010:43-0455)	95
4.38	Small angle X-ray diffractograms of BPO materials synthesized using different ODE volumes (a) BPO-ODE-3, (b) BPO-ODE-13, (c) BPO-ODE-52, (d) BPO-ODE-78, (e) BPO-ODE-104, and (f) BPO-ODE-130	97
4.39	FESEM micrographs of BPO materials synthesized using different ODE volumes (a) BPO-ODE-3, (b) BPO-ODE-13, (c) BPO-ODE-52, (d) BPO-ODE-78, (e) BPO-ODE-104, and (f) BPO-ODE-130	99
4.40	X-ray diffractograms of BPO materials synthesized at different reaction times (a) BPO-RTime-5, (b) BPO-RTime-15, (c) BPO-RTime-25, (d) BPO-RTime-30, (e) BPO-RTime-40, (f) BPO-RTime-45, and (g) BPO-RT-60	101
4.41	Wide angle X-ray diffractograms of BPO materials synthesized at different reaction times (a) BPO-RTime-5, (b) BPO-RTime-15, (c) BPO-RTime-25, (d) BPO-RTime-30, (e) BPO-RTime-40, (f) BPO-RTime-45, (g) BPO-RT-60, and (h) matching with the reported $\text{Bi}_{3.69}\text{P}_{0.31}\text{O}_{6.31}$ (PDF 2010:43-0455)	103
4.42	Small angle X-ray diffractograms of BPO materials synthesized at different reaction times (a) BPO-	

	RTime-5, (b) BPO-RTime-15, (c) BPO-RTime-25, (d) BPO-RTime-30, (e) BPO-RTime-40, (f) BPO-RTime-45, and (g) BPO-RTime-60	105
4.43	FESEM micrographs of BPO materials synthesized at different reaction times (a) BPO-RTime-5 and (b) BPO-RTime-15 under low magnification	106
4.44	FESEM micrographs of BPO materials synthesized at different reaction times (a) BPO-RTime-5, (b) BPO-RTime-15, (c) BPO-RTime-25, (d) BPO-RTime-30, (e) BPO-RTime-40, (f) BPO-RTime-45, and (g) BPO-RTime-60	108
4.45	X-ray diffractograms of the BPO materials synthesized at different ageing times (a) BPO-AT-1, (b) BPO-AT-8, (c) BPO-AT-20, (d) BPO-AT-48, (e) BPO-AT-72, and (f) BPO-AT-168	110
4.46	Wide angle X-ray diffractograms of BPO materials synthesized at different ageing times (a) BPO-AT-1, (b) BPO-AT-8, (c) BPO-AT-20, (d) BPO-AT-48, (e) BPO-AT-72, (f) BPO-AT-168, and (g) matching with the reported $\text{Bi}_{3.69}\text{P}_{0.31}\text{O}_{6.31}$ (PDF 2010:43-0455)	112
4.47	Small angle X-ray diffractograms of BPO materials synthesized at different ageing times (a) BPO-AT-1, (b) BPO-AT-8, (c) BPO-AT-20, (d) BPO-AT-48, (e) BPO-AT-72, and (f) BPO-AT-168	113
4.48	FESEM micrographs of BPO materials synthesized at different ageing times (a) BPO-AT-1, (b) BPO-AT-8, (c) BPO-AT-20, (d) BPO-AT-48, (e) BPO-AT-72, and (f) BPO-AT-168	115

LIST OF ABBREVIATIONS

BPO	-	Bismuth phosphorus oxide
RT	-	Reaction temperature
RS	-	Reaction solvent
RTime	-	Reaction time
AT	-	Ageing time
ODE	-	1-octadecene
HDE	-	1-hexadecene
TDE	-	1-tetradecene
DDE	-	1-dodecene
MA	-	Myristic acid
XRD	-	X-ray diffraction
FESEM	-	Field emission scanning electron microscopy
EDX	-	Energy dispersive X-ray
TEM	-	Transmission electron microscopy
ICP-OES	-	Inductively couple plasma-optical emission spectroscopy
PDF	-	Powder diffractogram file
SAED	-	Selected area electron diffraction
FCC	-	Face centered cubic
BCC	-	Body centered cubic
etc.	-	Et cetera/and other things/and so on
e.g.	-	For example/such as
i.e.	-	Id est./that is/that is to say
h	-	hour
k	-	10^3
2θ	-	Bragg angle
nm	-	nanometer

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Research flow chart	134
B	PDF 2010 file number 43-0455	135
C	XRD pattern of BiP material reported by Allen <i>et al.</i> (1997)	136
D	EDX analysis of BPO materials synthesized at different reaction temperature	137
E	EDX analysis of BPO materials synthesized using different reaction solvent	142
F	EDX analysis of BPO materials synthesized using different MA:ODE ratios	144
G	EDX analysis of BPO materials synthesized using different ODE amount	147
H	EDX analysis of BPO materials synthesized at different reaction time	150
I	EDX analysis of BPO materials synthesized a different ageing time	154
J	List of publications	157

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Nanotechnology could be defined as an area of engineering of functional systems at a molecular scale. It covers both current works and concepts that are more advanced. Generally, nanotechnology deals with structures of size ranging 1-100 nanometers in at least one dimension. It also involves developing materials or devices within that particular size [1]. Besides, nanotechnology offers diverse research and applications ranging from extensions of conventional device physics to completely new approaches based on molecular self-assembly. In this era, nanotechnology is a rapidly progressing field in pharmaceuticals, sensors, semiconductors, etc. [2]. Recently, the applications of nanotechnology for advanced material, electronic, and medicine fields have been intensively studied to give enormous impact to mankind [2].

Research in nanotechnology for materials science has been focused on morphological features and unique properties at their nanoscale dimensions. One of the interesting topics is functional modifications of materials having not only different structures such as grains, particles, fibres, pores, crystals or other constituent components but also dimensional such as one-, two-, or three-dimension [3-4]. Usually, materials such as carbon nanotubes, zeolites, and metal oxides are having different physical and chemical properties from their bulk counterparts. Most of the nanostructured materials have high potential applications as drug carriers, catalysts, semiconductors, and electronic materials [5]. Moreover, the nanostructured

materials have shown different functions when their structures or dimensions are different from the bulk. For example, the lamellar structure of zinc oxide could extend its surface and interphases in order to retain semiconductor properties of the material [3].

Recently, lamellar nanostructured materials have been widely studied for the development of catalysts, photocatalysts, sensors, solar cells, photoelectrodes, optoelectronics, interconnectors, and nanoscale electronics [3, 6-8]. In general, the lamellar structured materials could be defined as a material with an ordered layered structure e.g. clay, graphite, tungsten disulfide, boron nitride, nickel oxide, and molybdenum sulfides [6, 9-10]. The structure is usually formed by self-assembly of organic surfactant with inorganic species to produce tubes, wires, and sheets structures [3, 6, 11-14]. These different kinds of lamellar structures can also be applied in other potential applications such as separation membranes, drug and gene delivery, etc. [11, 15].

Bismuth-based materials have been intensively investigated for their versatile applications as catalysts, photocatalysts, ionic conductors, metal ion sensors, and separating radioactive elements [16-19]. Up to the past decades, different crystal structures were reported such as monoclinic with monazite-type at low temperature and trigonal at high temperature using hydrothermal synthesis, ball milling synthesis, and chemical vapour deposition (CVD) process [16-20]. These various crystal structures would offer different properties making them useful for different applications. For instance, trigonal bismuth phosphate was used as a catalyst in several reactions [16, 21]. Meanwhile, the monoclinic crystal structure of bismuth phosphate is a potential candidate in ionic conductor field [22-23]. The formation and application of cubic type i.e. face centered cubic (FCC) and body centered cubic (BCC) of bismuth phosphate material, however, were rarely reported.

Nowadays, bismuth-based nanostructured materials have attracted particular attention for their potential applications as catalysts, semiconductors, sensors, optical, and electronic devices [16, 24-25]. The examples of these bismuth based nanostructured materials are bismuth vanadate, bismuth sulphide, bismuth titanate,

bismuth selenide, bismuth ferrite, and bismuth phosphate. In order to further enhance their performances, various types of nanostructured materials have been synthesized such as rods, tubes, plates, spheres, cocoons, flower-likes, and flakes [17-18, 26-27]. They were usually synthesized via solid state reaction, combustion technique, microwave irradiation, co-precipitation, etc. Similarly, nanostructured bismuth phosphorus oxide (BPO) materials have attracted attention due to low band gap that are useful in applications mentioned above [17]. Unfortunately, nanocrystalline BPO could not be obtained through the synthesis methods mentioned above. Moreover, there is no report on formation of nanocrystalline BPO with lamellar structure.

Recently, relatively new and economical method of hot injection has been successfully developed for the synthesis of monodisperse nanocrystals materials such as cadmium selenide (CdSe), cadmium sulphide (CdS), cadmium telluride and indium phosphide (InP) [28-31]. The method was based on injection of cold precursor into a hot solvent, resulting in nucleation burst of nanocrystals in the reaction solvent. It was found that this method has the advantage to separate nucleation and growth stage of synthesized materials, thus particle size of the materials could be easily controlled [30]. In this research, an attempt was carried out to synthesize nanocrystalline BPO materials with lamellar structure via hot injection method. Several parameters in synthesis condition were investigated in order to get the optimum condition for producing high quality nanocrystalline BPO materials.

1.2 Problem Statement

Nanocrystalline BPO material is a potential candidate for catalyst, photocatalyst, ionic conductor, ion sensor, humidity sensor, separating radioactive element, and modifier for electric properties improvement in phosphate glasses. It was reported that the lamellar layered geometry could enhance the effectiveness or efficiencies of the respective applications due to several unique properties e.g. larger surface area and interphases, hence it is challenging to synthesize nanocrystalline BPO with lamellar structure. However, there were limitations of using previous

methods such as inhomogeneous products, long reaction time, and high reaction temperature which subsequently lead to high cost in production. Obviously, the conventional synthesis methods such as hydrothermal synthesis, ball milling, and CVD process are not able to produce materials in lamellar structure.

Therefore, the hot injection method would be used for solving the above problems in order to produce nanocrystalline BPO with lamellar structure since it appears as a promising method in producing nanostructured materials. For this purpose, several parameters in synthesis condition such as reaction temperature, types of reaction solvent, ratio of stabilizer to reaction solvent, amount of reaction solvent, reaction time, and ageing time were investigated to study their effects on the synthesized nanocrystalline BPO materials.

1.3 Objectives of the Study

The objectives of the study were:

- a. To synthesize and characterize nanocrystalline BPO materials via hot injection method.
- b. To investigate effect of synthesis parameters on structural and morphological properties in producing high quality nanocrystalline BPO materials.

1.4 Scope of the Study

In this research, study was focused on synthesizing BPO nanocrystalline via hot injection method. The possibility to synthesize single phase material with high crystallinity and purity as well as the formation of lamellar structure via this method was explored. In addition, the effectiveness of this hot injection method for preparing good quality nanocrystalline BPO materials was also studied.

Some parameters in synthesis condition were investigated in order to study their effects on the properties of the resulted nanocrystalline BPO materials. These parameters included the reaction temperature, types of reaction solvent, ratio of stabilizer to reaction solvent, amount of reaction solvent, reaction time, and ageing time.

The characterization of synthesized materials was carried out to examine the structural and morphological properties of nanocrystalline BPO materials. In this research, several techniques of characterization were used, including X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) analysis, surface area and pore size analyses, and inductively coupled plasma-optometry emission spectrometry (ICP-OES).

1.5 Significance of the Study

In this research, the feasibility of synthesizing lamellar structured nanocrystalline BPO materials via hot injection method was investigated. This hot injection method could also be a potential route to prepare good quality nanocrystalline BPO materials in industry scale since this method requires shorter reaction duration and lower reaction temperature.

These BPO materials are potentially applied as semiconductor, ionic conductor, capacitor, catalyst, photocatalyst, separating radioactive elements, ion sensor, thermoelectric devices, etc. It is widely accepted that the performance of these materials could be further increased if they are in their nanoscale having ordered structure which provides them higher surface area and more active sites.

REFERENCES

1. Alan, L. P., Jan, Y., Philip, S. and David, J. S. Refining Search Terms for Nanotechnology. *Journal of Nanoparticle Research*. 2007. 10(5): 715-728.
2. Anisa, M., Abdallah, S. D. and Peter, A. S. 'Mind the Gap': Science and Ethics in Nanotechnology. *Nanotechnology*. 2003. 14(3).
3. Segovia, M., Lemus, K., Moreno, M., Ana, M. A. S., González, G., Ballesteros, B., Sotomayor, C. and Benavente, E. Zinc Oxide/Carboxylic Acid Lamellar Structures. *Materials Research Bulletin*. 2011. 46(11): 2191-2195.
4. Zhang, L. and Webster, T. J. Nanotechnology and Nanomaterials: Promises for Improved Tissue Regeneration. *Nano Today*. 2009. 4: 66-80.
5. Schoonman, J. Nanostructured Materials in Solid State Ionics. *Solid State Ionics*. 2000. 135: 5-19.
6. Wang, J. and Li, Y. Rational Synthesis of Metal Nanotubes and Nanowires from Lamellar Structures. *Advanced Materials*. 2003. 15(5): 445-447.
7. Bai, N., Li, S., Chen, H. and Pang, W. Preparation, Characterization and Photoluminescence Properties of Mesolamellar Titanium Dioxide Films. *Journal of Materials Chemistry*. 2001. 11(12): 3099-3102.
8. Dasgupta, S., Agarwal, M. and Datta, A. Mesolamellar Vanadium Phosphate Phases Obtained by Intercalation of a Long Chain Alkylamine into Different Catalytically Important VPO Host Lattices. *Journal of Molecular Catalysis A: Chemical*. 2004. 223(1-2): 167-176.

9. Wang, Y., Ma, C., Sun, X. and Li, H. Preparation and Photoluminescence Properties of Organic-Inorganic Nanocomposite with a Mesolamellar Nickel Oxide. *Microporous and Mesoporous Materials*. 2004. 71(1-3): 99-102.
10. Wang, Y., Chen, J. S., Xin, M. H. and Xu, R. R. Mesolamellar Molybdenum Sulfides with Intercalated Cetyltrimethylammonium Cations. *Inorganic Chemistry Communications*. 2000. 3(3): 129-131.
11. Li, Y., Li, X., Deng, Z. X., Zhou, B., Fan, S., Wang, J. and Sun, X. From Surfactant-Inorganic Mesostructures to Tungsten Nanowires. *Angewandte Chemie*. 2002. 114(2): 343-345.
12. Qi, L., Ma, J., Cheng, H. and Zhao, Z. Reverse Micelle Based Formation of BaCO₃ Nanowires. *The Journal of Physical Chemistry B*. 1997. 101(18): 3460-3463.
13. Li, Y. D., Li, X. L., He, R. R., Zhu, J. and Deng, Z. X. Artificial Lamellar Mesostructures to WS₂ Nanotubes. *Journal of the American Chemical Society*. 2002. 124(7): 1411-1416.
14. Liu, X. Y., Zeng, J. H., Zhang, S. Y., Zheng, R. B., Liu, X. M. and Qian, Y. T. Novel Bismuth Nanotube Arrays Synthesized by Solvothermal Method. *Chemical Physics Letters*. 2003. 374(3-4): 348-352.
15. Rosa, M., Rosa Infante, M., Miguel, M. G. and Lindman, B. Spontaneous Formation of Vesicles and Dispersed Cubic and Hexagonal Particles in Amino Acid-Based Catanionic Surfactant Systems. *Langmuir*. 2006. 22(13): 5588-5596.
16. Romero, B., Bruque, S., Aranda, M. A. G. and Iglesias, J. E. Syntheses, Crystal Structures, and Characterization of Bismuth Phosphates. *Inorganic Chemistry*. 1994. 33(9): 1869-1874.
17. Xue, F., Li, H., Zhu, Y., Xiong, S., Zhang, X., Wang, T., Liang, X. and Qian, Y. Solvothermal Synthesis and Photoluminescence Properties of BiPO₄

- Nanococoons and Nanorods with Different Phases. *Journal of Solid State Chemistry*. 2009. 182(6): 1396-1400.
18. Lin, Y. F., Change, H. W., Lu, S. Y. and Liu, C. W. Preparation, Characterization, and Electrophysical Properties of Nanostructured BiPO₄ and Bi₂Se₃ Derived from a Structurally Characterized, Single-source Precursor Bi[Se₂P(OiPr)₂]₃. *Journal of Physical Chemistry C*. 2007. 111: 18538-18544.
 19. Pan, C. and Zhu, Y. New Type of BiPO₄ Oxy-Acid Salt Photocatalyst with High Photocatalytic Activity on Degradation of Dye. *Environmental Science Technology*. 2010. 44: 5570-5574.
 20. Lee, S. L., Lee, C. K. and Sinclair, D. C. Synthesis and Characterization of Bismuth Phosphate-Based Sillenites. *Solid State Ionics*. 2005. 176: 393-400.
 21. Chang, T. S., Gujia, L., Shin, C. H., Lee, Y. K. and Yun, S. S. Catalytic Behavior of BiPO₄ in the Multicomponent Bismuth Phosphate System on the Propylene Ammoxidation. *Catalysis Letters*. 2000. 68(3): 229-234.
 22. Mauvy, F., Launay, J. C. and Darriet, J. Synthesis, Crystal Structures and Ionic Conductivities of Bi₁₄P₄O₃₁ and Bi₅₀V₄O₈₅. Two Members of the Series Bi_{18-4m}M_{4m}O_{27+4m} (M=P, V) Related to the Fluorite-Type Structure. *Journal of Solid State Chemistry*. 2005. 178(6): 2015-2023.
 23. Darriet, J., Launay, J. C. and Zúniga, F. J. Crystal Structures of the Ionic Conductors Bi₄₆M₈O₈₉ (M=P, V) Related to the Fluorite-Type Structure. *Journal of Solid State Chemistry*. 2005. 178(6): 1753-1764.
 24. Masoud, S. N., Mehdi, B. and Fatemeh, D. Hydrothermal Synthesis and Characterization of Bismuth Selenide Nanorods via a Co-Reduction Route. *Inorganica Chimica Acta*. 2011. 365(1): 61-64.
 25. Foos, E. E., Stroud, R. M. and Berry, A. D. Synthesis and Characterization of Nanocrystalline Bismuth Telluride. *Nano Letters*. 2001. 1(12): 693-695.

26. Thongtem, T., Phuruangrat, A., Wannapop, S. and Thongtem, S. Characterization of Bi_2S_3 with Different Morphologies Synthesized using Microwave Radiation. *Materials Letters*. 2010. 64(2): 122-124.
27. Farhadi, S. and Zaidi, M. Bismuth Ferrite (BiFeO_3) Nanopowder Prepared by Sucrose-Assisted Combustion Method: A Novel and Reusable Heterogeneous Catalyst for Acetylation of Amines, Alcohols and Phenols Under Solvent-Free Conditions. *Journal of Molecular Catalysis A: Chemical*. 2009. 299(1-2): 18-25.
28. Murray, C. B., Norris, D. J. and Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse CdE (E=Sulfur, Selenium, Tellurium) Semiconductor Nanocrystallites. *Journal of the American Chemical Society*. 1993. 115(19): 8706-8715.
29. Williams, J. V., Kotov, N. A. and Savage, P. E. A Rapid Hot-Injection Method for the Improved Hydrothermal Synthesis of CdSe Nanoparticles. *Industrial & Engineering Chemistry Research*. 2009. 48(9): 4316-4321.
30. Zhang, L. J., Shen, X. C., Liang, H. G., Shiyi, L. and Zhen, H. Hot-Injection Synthesis of Highly Luminescent and Monodisperse CdS Nanocrystals Using Thioacetamide and Cadmium Source with Proper Reactivity. *Journal of Colloid and Interface Science*. 2010. 342(2): 236-242.
31. Li, L., Protière, M. and Reiss, P. Economic Synthesis of High Quality InP Nanocrystals Using Calcium Phosphide as the Phosphorus Precursor. *Chemistry of Materials*. 2008. 20(8): 2621-2623.
32. Rai, M., Yadav, A. and Gade, A. Silver Nanoparticles as a New Generation of Antimicrobials. *Biotechnology Advances*. 2009. 27(1): 76-83.
33. Monika, K. and Priska, G. Informing, Involving or Engaging? Science Communication, in the Ages of Atom-, Bio- and Nanotechnology. *Public Understanding of Science*. 2009. 18: 559-573.

34. Whatmore, R. W. *Ferroelectrics, Microsystems and Nanotechnology. Ferroelectrics*. 1999. 225(1): 179-192.
35. Hughes, M. P. *AC Electrokinetics: Applications for Nanotechnology. Nanotechnology*. 2000. 11: 124-132.
36. Bogunia, K. K. and Sugisaka, M. From Molecular Biology to Nanotechnology and Nanomedicine. *Biosystems*. 2002. 65(2-3): 123-138.
37. Drexler, K. E. Nanotechnology: From Feynman to Funding. *Bulletin of Science, Technology & Society*. 2004. 24: 21-27.
38. Phoenix, C. and Drexler, E. Safe Exponential Manufacturing. *Nanotechnology*. 2004. 15: 869-872.
39. Dresselhaus, M. S., Dresselhaus, G. and Eklund, P. C., *Science of Fullerenes and Carbon Nanotubes*. ed London, UK: Elsevier Science. 1995.
40. Ajayan, P. and Zhou, O., *Applications of Carbon Nanotubes*. ed USA: Springer Berlin Heidelberg. 2001.
41. Iijima, S. and Ichihashi, T. Single-Shell Carbon Nanotubes of 1 nm Diameter. *Nature*. 1993. 363(6430): 603-605.
42. Kikuchi, K., Nakahara, N., Wakabayashi, T., Suzuki, S., Shiromaru, H., Miyake, Y., Saito, K., Ikemoto, I., Kainosho, M. and Achiba, Y. NMR Characterization of Isomers of C₇₈, C₈₂ and C₈₄ Fullerenes. *Nature*. 1992. 357(6374): 142-145.
43. Sahoo, P., Misra, D. K., Salvador, J., Makongo, J. P. A., Chaubey, G. S., Takas, N. J., Wiley, J. B. and Poudeu, P. F. P. Microstructure and Thermal Conductivity of Surfactant-Free NiO Nanostructures. *Journal of Solid State Chemistry*. 2012. 190: 29-35.

44. Miyoshi, H., Sakamoto, K., Kurashina, M. and Kanezaki, E. Photoinduced Electron Accumulation of Titanium Dioxide Nanoparticles Modified Electrodes. *International Journal of Modern Physics: Conference Series*. 2012. 6(1): 61-66.
45. Mahurin, S. M., Meyer, K. A. and Shaw, R. W. Nanoscale Chemical Imaging of Zinc Oxide Nanowire Corrosion. *Journal of Physical Chemistry C*. 2012. 116: 10405-10414.
46. Liang, A., Liu, Q., Wen, G. and Jiang, Z. The Surface-Plasmon-Resonance Effect of Nanogold/Silver and its Analytical Applications. *Trends in Analytical Chemistry*. 2012. 37: 32-47.
47. Jun, L., Bin, K., Shuquan, C. and Yaodong, D. Gamma Radiation Synthesis of Plasmonic Nanoparticles for Dark Field Cell Imaging. *Micro & Nano Letters*. 2012. 7(4): 360-362.
48. Sampathkumar, S. G. and Yarema, K. J. Targeting Cancer Cells with Dendrimers. *Chemistry & Biology*. 2005. 12(1): 5-6.
49. Hovestad, N. J., Ford, A., Jastrzebski, J. and Koten, G. Functionalized Carbosilane Dendritic Species as Soluble Supports in Organic Synthesis. *The Journal of Organic Chemistry*. 2000. 65(20): 6338-6344.
50. Gilman, J. W. Flammability and Thermal Stability Studies of Polymer Layered-Silicate (Clay) Nanocomposites. *Applied Clay Science*. 1999. 15(1-2): 31-49.
51. Gavriiliuk, A. G., Trojan, I. A. and Struzhkin, V. V. Insulator-Metal Transition in Highly Compressed NiO. *Physical Review Letters*. 2012. 109(8): 86402-86407.
52. Alivisatos, A. P. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science*. 1996. 271(5251): 933-937.

53. Poizot, P., Laruelle, S., Grugeon, S., Dupont, L. and Tarascon, J. M. Nano-Sized Transition-Metal Oxides as Negative-Electrode Materials for Lithium-Ion Batteries. *Nature*. 2000. 407(6803): 496-499.
54. Astruc, D. and Chardac, F. Dendritic Catalysts and Dendrimers in Catalysis. *Chemical Reviews*. 2001. 101: 2991-3023.
55. Sato, A. and Mehrabian, R. Aluminum Matrix Composites: Fabrication and Properties. *Metallurgical and Materials Transactions B*. 1976. 7(3): 443-451.
56. Choudhary, T. V. and Goodman, D. W. Oxidation Catalysis by Supported Gold Nano-Clusters. *Topics in Catalysis*. 2002. 21(1): 25-34.
57. Choudhary, V. R., Jha, R. and Jana, P. Solvent-Free Selective Oxidation of Benzyl Alcohol by Molecular Oxygen over Uranium Oxide Supported Nano-Gold Catalyst for the Production of Chlorine-Free Benzaldehyde. *Green Chemistry*. 2007. 9(3): 267-272.
58. Sinha, A. K., Suzuki, K., Takahara, M., Azuma, H., Nonaka, T. and Fukumoto, K. Mesoporous Manganese Oxide/Gold Nanoparticle Composites for Extensive Air Purification. *Angewandte Chemie*. 2007. 119(16): 2949-2952.
59. Shi, F., Zhang, Q., Ma, Y., He, Y. and Deng, Y. From CO Oxidation to CO₂ Activation: An Unexpected Catalytic Activity of Polymer-Supported Nanogold. *Journal of the American Chemical Society*. 2005. 127(12): 4182-4183.
60. Daimatsu, K., Sugimoto, H., Kato, Y., Nakanishi, E., Inomata, K., Amekawa, Y. and Takemura, K. Preparation and Physical Properties of Flame Retardant Acrylic Resin Containing Nano-Sized Aluminum Hydroxide. *Polymer Degradation and Stability*. 2007. 92(8): 1433-1438.

61. Hong, C. W., Hsin, J. O., Hsiao, C. H. and Tung, S. S. Explosion Characteristics of Aluminum Nanopowders. *Aerosol and Air Quality Research*. 2010. 10: 38-42.
62. Chan, C. K., Peng, H., Liu, G., McIlwrath, K., Zhang, X. F., Huggins, R. A. and Cui, Y. High-Performance Lithium Battery Anodes using Silicon Nanowires. *Nature Nanotechnology*. 2008. 3(1): 31-35.
63. Wu, M., Han, Z. and Van, V. Conductor-Gap-Silicon Plasmonic Waveguides and Passive Components at Subwavelength Scale. *Optics Express*. 2010. 18(11): 11728-11736.
64. Wen, S. S., Hong, Y. P., Yu, F. Z., Ning, W., Nai, G. S., Zhen, W. P., Chun, S. L. and Shuit, T. L. Synthesis of Large Areas of Highly Oriented, Very Long Silicon Nanowires. *Advanced Materials*. 2000. 12: 1343-1345.
65. Du, H., Lee, S. W., Gong, J., Sun, C. and Wen, L. S. Size Effect of Nano-Copper Films on Complex Optical Constant and Permittivity in Infrared Region. *Materials Letters*. 2004. 58(6): 1117-1120.
66. Arletti, R., Dalconi, M. C., Quartieri, S., Triscari, M. and Vezzalini, G. Roman Coloured and Opaque Glass: A Chemical and Spectroscopic Study. *Applied Physics A*. 2006. 83: 239-245.
67. Kierzek, K., Frackowiak, E., Lota, G., Gryglewicz, G. and Machnikowski, J. Electrochemical Capacitors Based on Highly Porous Carbons Prepared by KOH Activation. *Electrochimica Acta*. 2004. 49(4): 515-523.
68. Huo, Q., Margolese, D. I. and Stucky, G. D. Surfactant Control of Phases in the Synthesis of Mesoporous Silica-Based Materials. *Chemistry of Materials*. 1996. 8(5): 1147-1160.
69. Adelhelm, P., Hu, Y. S., Chuenchom, L., Antonietti, M., Smarsly, B. M. and Maier, J. Generation of Hierarchical Meso- and Macroporous Carbon from

- Mesophase Pitch by Spinodal Decomposition using Polymer Templates. *Advanced Materials*. 2007. 19(22): 4012-4017.
70. Baeck, S. H., Choi, K. S., Jaramillo, T. F., Stucky, G. D. and McFarland, E. W. Enhancement of Photocatalytic and Electrochromic Properties of Electrochemically Fabricated Mesoporous WO₃ Thin Films. *Advanced Materials*. 2003. 15(15): 1269-1273.
71. Braun, P. V. and Stupp, S. I. CdS Mineralization of Hexagonal, Lamellar, and Cubic Lyotropic Liquid Crystals. *Materials Research Bulletin*. 1999. 34(3): 463-469.
72. Bing, S. Y., Jyotsana, L., Philippe, R., Carlos, M. M., William, B. R. and Robert, K. P. Interaction of Hydrophobically Modified Polymers and Surfactant Lamellar Phase. *Langmuir*. 2001. 17: 5834-5841.
73. Venables, D. S., Huang, K. and Schmittenmaer, C. A. Effect of Reverse Micelle Size on the Librational Band of Confined Water and Methanol. *The Journal of Physical Chemistry B*. 2001. 105(38): 9132-9138.
74. Zhang, J., Sun, L., Liao, C. and Yan, C. Size Control and Photoluminescence Enhancement of CdS Nanoparticles Prepared via Reverse Micelle Method. *Solid State Communications*. 2002. 124(1-2): 45-48.
75. Wikander, K., Petit, C., Holmberg, K. and Pileni, M. P. Size Control and Growth Process of Alkylamine-Stabilized Platinum Nanocrystals: A Comparison between the Phase Transfer and Reverse Micelles Methods. *Langmuir*. 2006. 22(10): 4863-4868.
76. Zhang, L. and Eisenberg, A. Multiple Morphologies and Characteristics of "Crew-Cut" Micelle-Like Aggregates of Polystyrene-*b*-poly(Acrylic acid) Diblock Copolymers in Aqueous Solutions. *Journal of the American Chemical Society*. 1996. 118(13): 3168-3181.

77. Zhang, L. and Eisenberg, A. Multiple Morphologies of "Crew-Cut" Aggregates of Polystyrene-b-poly(Acrylic acid) Block Copolymers. *Science*. 1995. 268(5218): 1728-1731.
78. Trnovcová, V., Furár, I. and Schultze, D. Electrical Properties of Bismuth Phosphate and Bismuth Germanate Single Crystals. *Solid State Ionics*. 2008. 179(1-6): 131-134.
79. Hölgye, Z. Separation of Plutonium from Feces and Urine by Coprecipitation with Bismuth Phosphate. *Journal of Analytical Chemistry*. 1985. 320(2): 181-182.
80. El-Adawy, A. A. Effect of Annealing Temperature on the Elastic Properties of Bismuth Phosphate Glasses. *Journal of Materials Science Letters*. 1996. 15(23): 2061-2064.
81. Iitaka, K., Tani, Y. and Umezawa, Y. Orthophosphate Ion-Sensors Based on a Quartz-Crystal Microbalance Coated with Insoluble Orthophosphate Salts. *Analytica Chimica Acta*. 1997. 338(1-2): 77-87.
82. Abadzhieva, N., Tzokov, P., Uzunov, I., Minkov, V., Klissurski, D. and Rives, V. Methanol Oxidation to Formaldehyde on Bismuth Phosphate-Based Catalyst. *Reaction Kinetics and Catalysis Letters*. 1994. 53: 413-418.
83. Shapaan, M., El-Badry, S. A., Mostafa, A. G., Hassaan, M. Y. and Hazzaa, M. H. Structural and Electric-Dielectric Properties of some Bismuth Phosphate Glasses. *Journal of Physics and Chemistry of Solids*. 2012. 73(3): 407-417.
84. Kimura, T. Simultaneous Determination of Neptunium, Plutonium, Americium and Curium using Coprecipitation with Bismuth Phosphate. *Journal of Radioanalytical and Nuclear Chemistry*. 1990. 139(2): 297-305.
85. Chen, Y., Johnson, E. and Peng, X. Formation of Monodisperse and Shape-Controlled MnO Nanocrystals in Non-Injection Synthesis: Self-Focusing via

- Ripening. *Journal of the American Chemical Society*. 2007. 129(35): 10937-10947.
86. Battaglia, D. and Peng, X. Formation of High Quality InP and InAs Nanocrystals in a Noncoordinating Solvent. *Nano Letters*. 2002. 2: 1027-1030.
87. Yordanov, G. G., Yoshimura, H. and Dushkin, C. D. Fine Control of the Growth and Optical Properties of CdSe Quantum Dots by Varying the Amount of Stearic Acid in a Liquid Paraffin Matrix. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2008. 322(1-3): 177-182.
88. Yordanov, G. G., Gicheva, G. D., Bochev, B. H., Dushkin, C. D. and Adachi, E. The Effects of Temperature and Carboxylic Acid Ligand on the Growth of Nanocrystalline CdSe in a Hot Paraffin Matrix. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2006. 273(1-3): 10-15.
89. Yordanov, G. G., Dushkin, C. D. and Adachi, E. Early Time Ripening During the Growth of CdSe Nanocrystals in Liquid Paraffin. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2008. 316(1-3): 37-45.
90. Yordanov, G. G., Adachi, E. and Dushkin, C. D. Characterization of CdS Nanoparticles During Their Growth in Paraffin Hot-Matrix. *Materials Characterization*. 2007. 58(3): 267-274.
91. Yordanov, G. G., Adachi, E. and Dushkin, C. D. Growth Kinetics and Characterization of Fluorescent CdS Nanocrystals Synthesized with Different Sulfur Precursors in Paraffin Hot-Matrix. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2006. 289(1-3): 118-125.
92. Yordanov, G., Dushkin, C., Gicheva, G., Bochev, B. and Adachi, E. Synthesis of High-Quality Semiconductor Nanoparticles in a Composite Hot-Matrix. *Colloid & Polymer Science*. 2005. 284(2): 229-232.

93. Xu, S., Kumar, S. and Nann, T. Rapid Synthesis of High-Quality InP Nanocrystals. *Journal of the American Chemical Society*. 2006. 128(4): 1054-1055.
94. Peng, Z. A. and Peng, X. Nearly Monodisperse and Shape-Controlled CdSe Nanocrystals via Alternative Routes: Nucleation and Growth. *Journal of the American Chemical Society*. 2002. 124(13): 3343-3353.
95. Osman, H. K. *Synthesis and Characterization of Nanocrystalline Bismuth Phosphate Material via Hot Injection Method*. Undergraduate Project Report. Universiti Teknologi Malaysia; 2010.
96. Si, R., Zhang, Y. W., Zhou, H. P., Sun, L. D. and Yan, C. H. Controlled-Synthesis, Self-Assembly Behavior, and Surface-Dependent Optical Properties of High-Quality Rare-Earth Oxide Nanocrystals. *Chemistry of Materials*. 2006. 19(1): 18-27.
97. Bogomolov, V. N. and Petranovsky, V. P. Growth of Na-X Zeolite Monocrystals Up to 0.5 mm. *Zeolites*. 1986. 6(6): 418-419.
98. Qi, L., Gao, Y. and Ma, J. Synthesis of Ribbons of Silver Nanoparticles in Lamellar Liquid Crystals. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 1999. 157(1-3): 285-294.
99. Lee, U. H., Lee, H., Wen, S., Mho, S.-i. and Kwon, Y.-U. Mesoporous titania thin films with pseudo-cubic structure: Synthetic studies and applications to nanomembranes and nanotemplates. *Microporous and Mesoporous Materials*. 2006. 88(1-3): 48-55.
100. Allen, G. C., Carmalt, C. J., Cowley, A. H., Hector, A. L., Kamepalli, S., Lawson, Y. G., Norman, N. C., Parkin, I. P. and Pickard, L. K. Preparation and Characterization of a Material of Composition BiP (Bismuth Phosphide) and Other Intergroup 15 Element Phases. *Chemistry of Materials*. 1997. 9(6): 1385-1392.

101. Batista, J. N. M., De Faria, E. H., Calefi, P. S., Ciuffi, K. J., Nassar, E. J., Cunha, W. R., Caiut, J. M. A. and Rocha, L. A. Controlling Silicate Meso-Structures using Sucupira Oil as a New Swelling Agent. *Applied Surface Science*. 2012. 258(12): 5111-5116.
102. Bizeto, M. A. and Constantino, V. R. L. Structural Aspects and Thermal Behavior of the Proton-Exchanged Layered Niobate $K_4Nb_6O_{17}$. *Materials Research Bulletin*. 2004. 39(11): 1729-1736.
103. Toussaint, G., Brisbois, M., Grandjean, J., Cloots, R. and Henrist, C. Hybrid Lamellar Silica: Combined Template Extraction and Hydrophilic Silanation. *Journal of Colloid and Interface Science*. 2009. 329(1): 120-126.
104. Yu, X., Xu, Z., Han, S., Che, H., Yan, X. and Liu, A. Synthesis of Well-Ordered Lamellar Mesoporous Molybdenum Oxide. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2009. 333(1-3): 194-198.
105. Wang, L., Yan, Z., Qiao, S., Max Lu, G. Q. and Huang, Y. Structural and Morphological Transformations of Mesostructured Titanium Phosphate through Hydrothermal Treatment. *Journal of Colloid and Interface Science*. 2007. 316(2): 954-961.
106. Takai, A., Yamauchi, Y. and Kuroda, K. Tailored Electrochemical Synthesis of 2D-Hexagonal, Lamellar, and Cage-Type Mesostructured Pt Thin Films with Extralarge Periodicity. *Journal of the American Chemical Society*. 2009. 132(1): 208-214.
107. On, D. T. A Simple Route for the Synthesis of Mesostructured Lamellar and Hexagonal Phosphorus-Free Titania (TiO_2). *Langmuir*. 1999. 15(25): 8561-8564.
108. Mizuno, N., Hatayama, H., Uchida, S. and Taguchi, A. Tunable One-Pot Syntheses of Hexagonal-, Cubic-, and Lamellar-Mesostructured Vanadium-Phosphorus Oxides. *Chemistry of Materials*. 2000. 13(1): 179-184.

109. Ikawa, N., Oumi, Y., Kimura, T., Ikeda, T. and Sano, T. Synthesis of Lamellar Mesostuctured Calcium Phosphates using *n*-alkylamines as Structure-Directing Agents in Alcohol/Water Mixed Solvent Systems. *Journal of Materials Science*. 2008. 43(12): 4198-4207.
110. Deng, B., Wang, C. C., Li, Q. G. and Xu, A. W. Highly Ordered Lamellar Mesostucture of Nanocrystalline PbSO₄ Prepared by Hydrothermal Treatment. *The Journal of Physical Chemistry C*. 2009. 113(43): 18473-18479.
111. Cao, J., Ji, H., Liu, J., Zheng, M., Chang, X., Ma, X., Zhang, A. and Xu, Q. Controllable Syntheses of Hexagonal and Lamellar Mesostuctured Lanthanum Oxide. *Materials Letters*. 2005. 59(4): 408-411.
112. Zhang, L., Wang, W., Sun, S., Xu, J., Shang, M. and Ren, J. Hybrid Bi₂SiO₅ Mesoporous Microspheres with Light Response for Environment Decontamination. *Applied Catalysis B: Environmental*. 2010. 100(1-2): 97-101.
113. Alberius, P. C. A., Frindell, K. L., Hayward, R. C., Kramer, E. J., Stucky, G. D. and Chmelka, B. F. General Predictive Syntheses of Cubic, Hexagonal, and Lamellar Silica and Titania Mesostuctured Thin Films. *Chemistry of Materials*. 2002. 14(8): 3284-3294.
114. Qian, G., Ji, D., Lu, G., Zhao, R., Qi, Y. and Suo, J. Bismuth-Containing MCM-41: Synthesis, Characterization, and Catalytic Behavior in Liquid-Phase Oxidation of Cyclohexane. *Journal of Catalysis*. 2005. 232(2): 378-385.
115. Wooding, A., Kilner, M. and Lambrick, D. B. Studies of the Double Surfactant Layer Stabilization of Water-Based Magnetic Fluids. *Journal of Colloid and Interface Science*. 1991. 144(1): 236-242.

116. Valivety, R., Jauregi, P., Gill, I. and Vulfson, E. Chemo-Enzymatic Synthesis of Amino Acid-Based Surfactants. *Journal of the American Oil Chemists' Society*. 1997. 74(7): 879-886.
117. Svenson, S. Controlling Surfactant Self-Assembly. *Current Opinion in Colloid & Interface Science*. 2004. 9(3-4): 201-212.
118. Lootens, D., Vautrin, C., Van Damme, H. and Zemb, T. Facetted Hollow Silica Vesicles Made by Templating Catanionic Surfactant Vesicles. *Journal of Materials Chemistry*. 2003. 13(9): 2072-2074.
119. Wang, X., Jia, J., Zhao, L. and Sun, T. Mesoporous SBA-15 Supported Iron Oxide: A Potent Catalyst for Hydrogen Sulfide Removal. *Water, Air, and Soil Pollution*. 2008. 193(1-4): 247-257.
120. Lindfors, L., Forssén, S., Westergren, J. and Olsson, U. Nucleation and Crystal Growth in Supersaturated Solutions of a Model Drug. *Journal of Colloid and Interface Science*. 2008. 325(2): 404-413.
121. Ingo, H. L. Particle Nucleation and Growth Models. *Current Opinion in Colloid & Interface Science*. 2000. 5(1-2): 151-159.
122. Mikhlin, Y., Karacharov, A., Likhatski, M., Podlipskaya, T., Zubavichus, Y., Veligzhanin, A. and Zaikovski, V. Submicrometer Intermediates in the Citrate Synthesis of Gold Nanoparticles: New Insights into the Nucleation and Crystal Growth Mechanisms. *Journal of Colloid and Interface Science*. 2011. 362(2): 330-336.
123. Fletcher, N. H. Size Effect in Heterogeneous Nucleation. *Journal of Chemical Physics*. 1958. 29(3): 572-577.
124. Ciesla, U. and Schüth, F. Ordered Mesoporous Materials. *Microporous and Mesoporous Materials*. 1999. 27(2-3): 131-149.

125. AlOthman, Z. A. and Apblett, A. W. Synthesis and Characterization of a Hexagonal Mesoporous Silica with Enhanced Thermal and Hydrothermal Stabilities. *Applied Surface Science*. 2010. 256(11): 3573-3580.
126. Huang, S.-C., Stump, M. D., Weiss, R. and Caldwell, K. D. Binding of Biotinylated DNA to Streptavidin-Coated Polystyrene Latex: Effects of Chain Length and Particle Size. *Analytical Biochemistry*. 1996. 237(1): 115-122.
127. Sordelet, D. and Akinc, M. Preparation of Spherical, Monosized Y_2O_3 Precursor Particles. *Journal of Colloid and Interface Science*. 1988. 122(1): 47-59.
128. Sugimoto, T. and Matijević, E. Formation of Uniform Spherical Magnetite Particles by Crystallization from Ferrous Hydroxide Gels. *Journal of Colloid and Interface Science*. 1980. 74(1): 227-243.