

**SILICON NANOPARTICLES SYNTHESIZED VIA
MICROEMULSION WITH VARIOUS
PARAMETERS**

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**SILICON NANOPARTICLES SYNTHESIZED VIA
MICROEMULSION WITH VARIOUS PARAMETERS**

by

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**Thesis submitted in fulfillment of the requirements for
the Degree of Master of Science**

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I declare that the contents presented in this thesis are my own work which was done at Universiti Sains Malaysia unless stated otherwise. The thesis has not been previously submitted for any other degree.

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	ix
LIST OF FIGURES	xi
ABSTRAK	xvi
ABSTRACT	xvii
CHAPTER 1: INTRODUCTION	1
1.0 Overview of nanotechnology and its importance	1
1.1 Challenges in nanotechnology	2
1.2 Silicon nanoparticles	3
1.3 Research objectives	6
1.4 Scope of project	7
CHAPTER 2: LITERATURE REVIEW	8
2.0 Introduction to nanotechnology	8
2.1 Bottom-up and top-down approaches	10
2.2 Nanomaterials	12
2.2.1 Classification of nanostructure materials	13
2.3 Nanoparticle	15
2.3.1 Silicon nanoparticles	16
2.4 Properties of silicon nanoparticles	17
2.4.1 Structural properties	17
2.4.2 Mechanical properties	18

2.4.3	Optical properties	19
2.4.4	Electronic/electrical properties	20
2.4.5	Thermal properties	21
2.4.6	Thermodynamic properties	21
2.5	Synthesis of silicon nanoparticles	22
2.5.1	Mechanical alloying or high-energy ball milling	23
2.5.2	Aerosol synthesis	24
	(i) Laser vaporization	25
	(ii) Pulsed laser ablation	25
	(iii) Plasma reactors	26
2.5.3	Wet chemical synthesis	26
	(i) Electrochemical treatment	27
	(ii) Chemical etching	27
	(iii) Sol-gel synthesis	28
	(iv) Microemulsions	29
	(v) Solution-based precursor reduction	31
2.6	Synthesis of nanoshell particles/core shell structure	35
2.7	Dispersion of Silicon Nanoparticles	37
2.7.1	Principles of nanoparticles stabilization against aggregation	37
2.7.1	(a) Interaction forces between particles	38
	(i) Van der Waals force	38
	(ii) Electrical double-layer interactions	39
	(iii) Steric interactions	40
2.7.2	Dispersion methods of nanoparticles	41
2.7.2	(a) Dispersing silicon nanoparticles with a stirred	41

	media mill	
2.7.2	(b) Dispersing and stabilizing silicon nanoparticles in a low-epsilon medium	41
2.7.2	(c) Production and dispersion stability of nanoparticles in nanofluids	42
2.8	Factors influence synthesis of nanoparticles	43
2.8.1	Influences of reduction reagents	43
	(i) Hydrazine	44
	(ii) Sodium borohydride	45
2.8.2	Influences of polymer stabilizer	45
	(i) Polyethylene glycol (PEG)	46
	(ii) Tetraoctylammonium bromide (TOAB)	47
2.9	Applications of nanoparticles	48
2.9.1	Light-emitting diode (LED)	48
2.9.2	Optical memories	48
2.9.3	Single electron devices	48
2.9.4	Fluorescent Biological Labels	49
2.10	Problems of nanoparticles	49
2.10.1	Determine coverage, thickness, and uniformity of thin coating on nanoparticles	49
2.10.2	Determining the surface chemistry of nanoparticles on the nanoscale	50
2.10.3	Statistical evaluation of dispersion of nanoparticles from synthesis through manufacturing and into the final consumer product	50
	CHAPTER 3: MATERIALS AND METHODS	52
3.0	Introduction	52
3.1	Materials and equipments	53

3.1.1	Silicon tetrachloride	54
3.1.2	Hydrazine	55
3.1.3	Sodium borohydride	55
3.1.4	Polyethylene glycol (PEG)	56
3.1.5	Tetraoctylammonium bromide (TOAB)	57
3.1.6	Sodium hydroxide	57
3.1.7	Ethanol	58
3.1.8	Acetone	59
3.1.9	Toluene	59
3.1.10	Methanol	60
3.1.11	1-butanol	60
3.1.12	2-propanol	61
3.1.13	De-ionized water	61
3.2	Synthesis of silicon nanoparticles	61
3.2.1	Preparation of reactant solution	61
3.2.2	Hydrazine reduction	62
3.2.3	Precipitation of silicon nanoparticles in colloidal condition	64
3.3	Experimental design	64
3.3.1	Effect of silicon precursor concentration	64
3.3.2	Effect of reducing agents concentration (hydrazine and sodium borohydride)	65
3.3.3	Effect of surfactant agents [PEG (200 & 10000wt%) and TOAB]	65
3.3.4	Effect of suspension/dispersion solvents	66
3.4	Characterization of silicon nanoparticles	67
3.4.1	Transmission electron microscopy (TEM)	67
3.4.2	Scanning electron microscopy (SEM)	69

3.4.3	Energy-dispersive X-ray spectroscopy (EDX)	70
3.4.4	UV-visible spectroscopy	71
3.4.5	Fourier transform infrared spectroscopy (FTIR)	73
3.4.6	X-ray diffraction analysis (XRD)	74
3.4.7	Raman spectroscopy	76
3.4.8	Electron energy loss spectroscopy (EELS)	78
CHAPTER 4: RESULT AND DISCUSSION		80
4.0	Introduction	80
4.1	Synthesis of silicon nanoparticles	82
4.1.1	Effect of the silicon precursor concentration	82
4.1.2	Effect of reducing agent concentration	90
4.1.2	(a) Effect of hydrazine concentration	90
4.1.2	(b) Effect of the sodium borohydride	98
4.1.2	(c) Comparison between hydrazine and sodium borohydride	105
4.1.3	Effect of surfactant and capping agent	106
4.1.3	(a) Effect of polyethylene glycol (PEG) amount [200 wt%]	106
4.1.3	(b) Effect of polyethylene glycol (PEG) amount [10Kwt%]	117
4.1.3	(c) Effect of tetraoctylammonium bromide (TOAB) concentration	124
4.1.3	(d) Comparison among the surfactant/ capping agent (PEG 200wt%, PEG 10Kwt% and TOAB)	130
4.1.4	Effect of suspension/dispersion solvents	131

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS	137
5.1 Conclusions	137
5.2 Recommendations for future work	138
REFERENCES	140
APPENDIX A	153
APPENDIX B	155
APPENDIX C	156
APPENDIX D	157
LIST OF PUBLICATIONS	159

LIST OF TABLES

Table		Page
2.1	Classification of nanomaterials with regard to different dimensions	14
2.2	Some type of classification of nanostructures materials	15
2.3	Test conditions and materials for producing nanofluids	42
2.4	The methods of producing nanofluids	43
3.1	List of chemical used in preparation silicon nanoparticles	53
3.2	List of equipments	54
3.3	The concentration of silicon source in different samples	64
3.4	The different reducing agents sodium borohydride (NaBH_4) concentration	65
3.5	The different reducing agents hydrazine ($\text{N}_2\text{H}_5\text{OH}$) concentration	65
3.6	The samples of different amount of PEG (200wt%)	66
3.7	The samples of different amount of PEG (10000wt%)	66
3.8	The samples of different concentration of TOAB	66
3.9	The samples in different suspension/dispersion solvents	67
4.1	Samples prepared with different concentration of sodium borohydride	80
4.2	Various samples prepared with different parameters labeling system	81
4.3	Sample with different silicon precursor concentration	83
4.4	EDX analysis for SiNPs with various concentration of silicon precursor (Si^{4+} ions), which was from 0.05M to 0.25M	87
4.5	Detail of UV-visible spectrum for samples with different silicon precursor concentration	90
4.6	Samples with different concentration of hydrazine (reducing agent)	91

4.7	EDX analysis for SiNPs with various concentration of hydrazine (reducing agent), which were 0.10M, 0.30M, 0.40M and 0.50M	96
4.8	Detail of UV-visible spectrum for samples with different hydrazine (reducing agent)	98
4.9	Samples with different sodium borohydride (reducing agent) concentration	98
4.10	EDX analysis for SiNPs with various concentration of sodium borohydride (reducing agent), which were sample S10, S11, S12, and S13	103
4.11	Summary of UV-visible spectrum for samples with various sodium borohydride (reducing agent) concentration	105
4.12	EDX analysis for SiNPs with various amount of PEG 10000 wt% (surfactant agent & capping agent), which were sample PE1, PE2, PE3 and PE4	122
4.13	Samples with different concentration of TOAB (surfactant agent)	124
4.14	EDX analysis for SiNPs with various concentration of TOAB (surfactant agent), which were sample T1, T2, T3 and T4	128
4.15	Detail of UV-visible spectrum for samples with different TOAB concentration	129

LIST OF FIGURES

Figure		Page
2.1	Top-down and bottom-up approaches	10
2.2	TEM images of SiNPs	17
2.3	Fabrication techniques of silicon nanocrystals	22
2.4	Schematic diagram of the mechanical alloying process	23
2.5	Ball mill for fabrication of nanoparticles	24
2.6	Mechanism of the preparation for core-shell nanoparticles by C/W/O microemulsion	31
2.7	Variety of core shell particles. (a) Surface-modified core particles anchored with shell particles; (b) More shell particles reduced onto core to form a complete shell; (c) Smooth coating of dielectric core with shell; (d) Encapsulation of very small particles with dielectric material; (e) Embedding number of small particles inside a single dielectric particle; (f) Quantum bubble and (g) Multishell particle	36
2.8	TEM images: (a) PPy -coated Si particles and (b) a magnified part in the circle along with the inset for the selected area diffraction (SAD) pattern	37
2.9	Grafting of PEG on SiNPs	47
2.10	Reaction of TOAB on SiNPs	47
3.1	Structural formula of SiCl_4	54
3.2	Structural formula of $\text{N}_2\text{H}_5\text{OH}$	55
3.3	Structural formula of NaBH_4	56
3.4	Structural formula of PEG	57
3.5	Structural formula of TOAB	57
3.6	Chemical Structure of ethanol	58
3.7	Chemical Structure of acetone	59
3.8	Chemical Structure of toluene	59
3.9	Chemical Structure of methanol	60

3.10	Chemical Structure of 1-butanol	60
3.11	Chemical Structure of 2-propanol	61
3.12	Schematic of water bath setup for the preparation of silicon nanoparticles	62
3.13	Flow chart for preparation of silicon nanoparticles in PEG	63
3.14	Principle of transmission electron microscopy (TEM)	68
3.15	Principle of scanning electron microscopy (SEM)	70
3.16	Principle of energy-dispersive X-ray spectrometer (EDX)	71
3.17	Principle of UV-visible spectroscopy	73
3.18	Typical apparatus of FTIR spectrometer	74
3.19	Calculation based on Bragg law	75
3.20	Custom built of Raman Spectrometer	78
3.21	Principle of electron energy loss spectroscopy (EELS)	78
4.1	FESEM images showed the effect of silicon precursor (Si^{4+} ions) concentration on the size and the distribution of particle: (a) 0.05M (sample S4); (b) 0.10m (sample S5); (c) 0.15M (sample S6); (d) 0.20M (sample S7) and (e) 0.25M (sample S8)	84
4.2	TEM observation of samples with different concentration of silicon precursor (Si^{4+} ions): (a) sample S7 and (b) sample S8	85
4.3	Histogram of particle size from sample S7 of 200 particles from different regions	86
4.4	A representative schema of elemental analysis (EDX analysis) for SiNPs: (a) sample S4; (b) sample S5; (c) sample S6; (d) sample S7 and (e) sample S8	87
4.5	XRD pattern of SiNPs (sample S7)	88
4.6	Typical UV-visible spectra of samples with different silicon precursor concentration	89
4.7	FESEM images showed the effect of concentration hydrazine (reducing agent) on the size and the distribution of particles: (a) sample H1; (b) sample H2; (c) sample H3 and (d) sample H4	93

4.8	The mechanism of nanodisperse colloid growth of La Mer plot	93
4.9	TEM observation of sample H4	94
4.10	Histogram of particle sizes from sample H4 of 200 particles from different regions	95
4.11	EDX analysis for SiNPs: (a) sample H1; (b) sample H2; (c) sample H3 and (d) sample H4	96
4.12	Typical UV-visible spectra of samples with different hydrazine (reducing agent) concentration	97
4.13	FESEM images showed the sample of SiNPs with various concentration of sodium borohydride (reduction agent): (a) sample S10; (b) sample S11; (c) sample S12 and (d) sample S13	100
4.14	Particle size distribution of SiNPs (sample S10) determined by SEM analysis	101
4.15	TEM image of the SiNPs (sample S10)	101
4.16	EDX analysis obtained elemental composition of the samples with various concentration of sodium borohydride: (a) sample S10, (b) sample S11, (c) sample S12 and (d) sample S13	102
4.17	Raman spectrum of sample S10, which with 0.05M sodium borohydride	103
4.18	Typical UV-visible spectra of SiNPs with various concentrations of sodium borohydride: (a) sample S10, (b) sample S11, (c) sample S12 and (d) sample S13	105
4.19	Model of sample, which grafting with PEG	107
4.20	PEG chain absorbed on SiNPs surface	107
4.21	FESEM images of the SiNPs with PEG addition (a) sample S22 - 25ml, (b) sample S23 - 50ml (optimum), (c) sample S24 - 75ml and (d) sample S25 – without PEG	109
4.22	Raman spectrum of sample S23 with 50ml PEG addition	110
4.23	Particle size distribution determined by FESEM analysis of sample S23, which with 50ml PEG addition	111
4.24	FTIR spectrum of SiNPs with 50ml PEG addition (sample S23)	112

4.25	EDX analysis on SiNPs with 50ml PEG addition [sample S23] (elemental composition 32.77 At% silicon, 10.07At% oxide and 57.16 At % carbon)	113
4.26	Parallel EELS spectra of SiNPs (sample S23) with 50ml PEG addition: (a) Parallel EELS Si – K (silicon), (b) Parallel EELS C – K (carbon) and (c) Parallel EELS O– K (oxygen)	114
4.27	TEM images: (a) SiNPs with 50ml PEG addition [sample S23] (b) a magnified part of SiNPs [sample S23] (PEG-coated Si)	115
4.28	Typical UV-Visible spectra of SiNPs (a) with PEG [sample S22, sample S23 and sample S24] (b) without PEG [sample S25]	116
4.29	FESEM images of the SiNPs with PEG addition (a) sample PE1 – 25g, (b) sample PE2 – 50g, (c) sample PE3 – 75g and (d) sample PE4 – 100g	118
4.30	Proposed stabilization mechanism on SiNPs with (a) Stable uncoated particles (due to electrostatic repulsion), (b) Surface saturation PEG-coated particle and (c) Agglomeration of particle due to high amount of PEG	119
4.31	Model representations of SiNPs with different molecular weight of PEG: (a) high molecular weight of PEG [long chain], (b) low molecular weight of PEG [short chain]	119
4.32	Particle size distribution determined by FESEM analysis of sample PE1, which with 25g PEG addition	120
4.33	EDX analysis on SiNPs with PEG 10000 wt% addition, which is (a) sample PE1, (b) sample PE2, (c) sample PE3 and (d) sample PE4	121
4.34	Mechanism of the longer chains of higher molecular weight PEG which have trapped the contamination	122
4.35	UV-Visible spectra for SiNPs with PEG 10000 wt%: (a) sample PE1, (b) sample PE2, (c) sample PE3 and (d) sample PE4	123
4.36	FESEM images of the SiNPs with different TOAB concentration (a) sample T1 – 0.05M, (b) sample T2 – 0.10M, (c) sample T3 – 0.15M and (d) sample T4 – 0.20M	125
4.37	Particle size distribution of SiNPs (sample T3 - 0.15M TOAB and sample T4 - 0.20M TOAB), which determined by FESEM analysis	126

4.38	Mechanism of TOAB in producing smaller size of SiNPs	126
4.39	EDX analysis on SiNPs with TOAB addition, which is (a) sample T1, (b) sample T2, (c) sample T3 and (d) sample T4	127
4.40	Typical UV-visible spectra of SiNPs with various concentrations of TOAB	129
4.41	Orientation within the electric field of the light, which influence the response of the plasmon	129
4.42	FESEM images of the SiNPs, which suspended in different solvent/dispersion agent (a) sample E1– ethanol, (b) sample M1 – methanol, (c) sample B1– 1-butanol, (d) sample P1 – 2-propanol, (e) sample A1 – acetone and (f) sample TO1 – toluene	132
4.43	Particle size distribution of SiNPs (sample E1, sample M1 and sample B1), which determined by SEM analysis	133
4.44	TEM image of SiNPs dispersed in ethanol	134
4.45	(a) FESEM image showed the SiNPs which were dispersed in ethanol, (b) EDX analysis obtained elemental composition of the particles: 41.91 At% C, 35.31 At% Si and 22.78 At% O	135
4.46	Typical UV-visible spectra of SiNPs with suspended in various solvents (methanol, 1-butanol and ethanol)	136

SILIKON NANOPARTIKEL DISINTESIS MELALUI KAEDAH MIKROEMULSI DENGAN PELBAGAI PARAMETER

ABSTRAK

Silikon nanopartikel (SiNPs) telah menarik minat penyelidik terutamanya dalam bidang bioteknologi dan optoelektronik. Objektif kajian ini adalah untuk menghasilkan SiNPs (<100nm) tanpa gumpalan. Pelbagai parameter telah digunakan seperti kepekatan ion silikon dan agen penurunan, kuantiti agen permukaan dengan jisim molekul yang berbeza dan pelarut-pelarut organik. Dalam kajian ini, bahan permula, silikon tetraklorida (SiCl_4) dicampurkan dengan penstabil natrium hidroksida (NaOH), agen permukaan dan agen penurunan. Hanya 0.20M SiCl_4 , 0.50M hydrazine ($\text{N}_2\text{H}_5\text{OH}$), 0.05M natrium borohidrat (NaBH_4), 0.15M tetraoktilammonium bromida (TOAB), 50ml polietilena glicol (PEG) 200wt% dan 25g PEG 10Kwt% dapat menghasilkan penyerakan SiNPs yang baik. Semua SiNPs telah diuji melalui penyerakan tenaga sinar-X (EDX), mikroskopi elektron imbasan pancaran medan (FESEM), dan spektroskopi UV-nampak (UV-vis). Manakala, spektroskopi 'Fourier transform infrared' (FTIR), analisis pembelauan sinar-X (XRD), mikroskopi elektron tembusan (TEM), spektroskopi Raman dan spektroskopi kehilangan tenaga elektron (EELS) hanya untuk sampel yang tertentu sahaja. Bagi mengurangkan saiz, meningkatkan serakan dan megubahsuai nanovektor bagi aliran ubat, PEG telah digunakan. PEG 200 wt% telah menunjukkan kesan yang paling ketara terhadap saiz dan taburan SiNPs dimana struktur kelompang teras telah dihasilkan. Salutan PEG ini adalah berketebalan 5nm. Etanol merupakan pelarut yang terbaik dalam penyerakan dimana min saiznya adalah 55.68nm. SiNPs dengan serakan yang baik telah berjaya dihasilkan dalam kajian ini.

SILICON NANOPARTICLES SYNTHESIZED VIA MICROEMULSION WITH VARIOUS PARAMETERS

ABSTRACT

Silicon nanoparticles (SiNPs) have attracted considerable interests from researchers as it is an interesting material in pharmaceutical and optoelectronic field. Research objective is to obtain SiNPs (< 100nm) without agglomeration. Various parameters had been used such as variations of silicon precursor concentrations, reduction agent concentrations, surfactant agent amounts with different molecular weight, and different organic solvents. In this study, silicon tetrachloride (SiCl_4) was used as a starting material and mixed with stabilizer sodium hydroxide (NaOH), surfactant/capping agent and reduction agent. Only suitable concentration and amount that could be used to produce well disperse SiNPs were 0.20M of SiCl_4 , 0.50M of hydrazine ($\text{N}_2\text{H}_5\text{OH}$), 0.05M of sodium borohydride (NaBH_4), 0.15M of tetraoctylammonium bromide (TOAB), 50ml of polyethylene glycol (PEG) 200wt% and 25g of PEG 10Kwt%, respectively. All SiNPs had been confirmed by using FESEM, EDX, and UV-visible spectroscopy. Meanwhile, TEM, FTIR, Raman and EELS only emphasized on certain SiNPs samples. In order to reduce the size as well as to improve the dispersion and to modify nanovectors for drug delivery, the PEG was used. PEG 200wt% had obviously shown the impact and effect on the SiNPs, which core shell structure had been obtained. The thickness of the PEG coating was about 5nm. From this study, it also found that ethanol was the best solvent in disperse of SiNPs which with 55.68nm mean size. Well disperse SiNPs were successfully synthesized in this study.

CHAPTER 1

INTRODUCTION

1.0 Overview of nanotechnology and its importance

Generally, nanotechnology deals with small sized materials or small structures. The typical dimensions spans from sub nanometer to several hundred nanometers. The length of a nanometer (nm) is approximately equivalent to one billionth of a meter, or 1×10^{-9} m (Itoh 2003).

Nanotechnology is a study of the control of matter in an atomic and molecular scale. Small features permit more functionality in a given space. Besides, nanotechnology is not only a simply continuation of miniaturization from micron scale down to nanometer. Materials in micron size exhibit almost the same physical properties with the bulk materials. However, due to the high percentage of surface atoms, nanomaterials exhibit different properties from the bulk materials especially the properties of electronic, optical, and chemical. Materials in nanosize range exhibit some specific properties because of a transition from atoms or molecules to bulk form takes place in the size range. From this transition, it is known that atoms or molecules have different behaviors from those bulk materials. Besides, the properties of the former are described by quantum mechanics while the properties of the latter are governed by classic mechanics. Between these two distinct domains, the nanometer range is a murky threshold for the transition of a material's behaviour. For example, ceramics can easily be deformable when their grain size is reduced to a low nanometer range which ceramics are normally in a brittle condition. For metal example, a gold particle of 1 nm across shows red colour. Moreover, a small amount of nanosize species can bring up the performance of resultant system to an

unprecedented level when it interferes with matrix polymer that is usually in the similar size range. Due to these reasons, nanotechnology has attracted large amounts of federal funding, research activities and media attention (Cao 2004; Zhao & Ning 2000).

1.1 Challenges in nanotechnology

In 21st century, dynamics and prospects of nanotechnology pose abundance of challenges not only to scientists and engineers but also to society at large. This is because nanotechnology has become a rapid emerging and potential growing field. Besides that, the state-of-the-art philosophical, ethical, and sociological reflection on nanotechnology which are written by leading scholars from the humanities and social sciences in North America and Europe. It unravels the philosophical underpinnings of nanotechnology, metaphysical and epistemological foundations, and conceptual complexity. In addition, it explores the ethical issues of nanotechnology, its impacts on human, environmental, and social conditions, and options for reasonable risk management. It also examines the public discourse on nanotechnology and its related visions and provides both lessons from the past and outlooks for the future (Cao 2004).

Local growths of nanostructures in both solid state and molecular properties as well as consideration in controlling of local reactions are the requirement of a nanomaterial. These have become a great challenge of nanotechnology. Besides that, dealing with nano interfaces as connections and active components are the second set of challenges. Furthermore, the concern of novel components of electronic, mechanical, chemical functionality, energy and information transfer to autonomous nano systems, theory, in particular computational sciences, for complex nano

systems, and others like the nanometer sized liquid-solid interface is also one of the greatest challenges (Cao 2004).

Thus, it is undeniable that nanotechnology is expanding extensively in our scientific world. Nano-mechanics and nano-chemistry are expected to forge new pathways between the 'virtual' world of data processing of all kinds, including mechanical, chemical and thermal processing, and the 'real' world of sensing and actuation, bringing about a pervasive wave of new, integrated processing, sensing, and actuation technologies (Cao 2004).

1.2 Silicon nanoparticles

Currently, the preparation, characterization, and applications of the nanosized materials have attracted much considerable interests and attention from researchers in various fields such as physics, biology, chemistry, materials science, and also the corresponding engineering. Due to the small sizes and large specific surface areas, nanoparticles usually exhibit in different optical, electronic, and chemical properties compare with those bulk materials. Nanoparticles have various applications such as catalysis, electronic, optical, and mechanic devices, high performance engineering materials, dyes, pigments, adhesives, photographic suspensions, drug delivery and others (Chen & Wu 2000). These applications bring a lot of advantages to social as well as industrial uses. Meanwhile, preparation such as controlling of particle's size, shape, distribution, crystallinity, and colloidal are taken into consideration at a great extend by using synthesis methods. It emphasizes that the use of uniform particles can avoid negative effects from a wide range of particle size distribution.

In this study, silicon nanoparticle (SiNPs) is chosen to be characterized and investigated because SiNPs are produced by researchers by using various methods such as gas evaporation, high temperature aerosol reaction, co-sputtering and Si

implantation (Leparoux et al. 2007). However, those methods that have been used involve complex and expensive equipments, high cost materials, long time consumption and more complicated steps to produce the SiNPs. So, in this study, a simple, efficient, inexpensive and one pot method (chemical route) has been used to reduce the material cost, time and equipment complexity which has relatively low temperature (60°C), reaction time is as short as about 2.5 hours, only few chemicals are needed such as silicon tetrachloride (SiCl₄), sodium hydroxide (NaOH), polyethylene glycol (PEG), hydrazine (N₂H₅OH) and ethanol (C₂H₅OH), and simple equipments. This concurs with Wu and Chen (2003) in his previous work that, “Synthesis and characterization of nickel nanoparticles by hydrazine reduction in ethylene glycol”. Herein, by modification from the original system, we use this simple, direct and reproducible synthetic method to synthesize SiNPs. Moreover, SiNPs is chosen because silicon would be a suitable candidate for replacing fluorescent dyes which labelling *in vivo* cells and as an alternative to CdSe because abundant cheap and non-toxic of silicon (Fabbri et al. 2006). Besides, the fluorescent properties of SiNPs are also of interest for sensing and tagging application especially for drug delivery (Sudeep, Page & Emrick 2008).

In this project, the size distribution of SiNPs is compared by varying concentration/amount of precursor, reduction agents and surfactant/capping agents. Besides, different type of reducing agents and surfactant agents had also been used to make comparisons. These included N₂H₅OH, NaBH₄, PEG and TOAB.

If nanoparticles surface is not protected with surfactant/capping agent, SiNPs will possess a considerable surface energy due to the high surface area per unit mass. Therefore, the most important attribute of this high surface energy is interaction between particles and results in agglomeration (Yon & Jamie 2008). So, in this study,

by using a simple water bath at 60°C, surfactant/capping agent, PEG can be used for steric stabilization mechanisms, which prevent further aggregation and oxidation of the particles surface. This is because untreated SiNPs are nearly insulated due to the oxidation on the surface of particles, which obtain of native passivation shell. The surface oxidation of SiNPs results in enable interfacial charge transfer and unwanted perturbation of optical properties (Ogino et al 1999; Gupta & Wiggers 2009). In addition for stabilization, PEG can be carriers of specific functionalities for further applications (Poole & Owens 2003; Rotello 2004). Besides, PEG can also cap on the surface of SiNPs to produce core shell structure nanoparticles, especially for organic and inorganic hybrid nanoparticles. Thus, it is undeniable that PEG which is a kind of non-toxic, odourless, neutral and non-irritating agent such as PEG shell on silicon nanoparticles plays an important role in providing a biocompatible and protective layer around the particle surface. PEG shell also reduces protein and cell adsorption (Thangaraja, Savitha & Jegatheesan 2010). This also relates to Feng et al. (2009) that, “The PEG’s protective layer may prevent aggregation of nanoparticles and stabilizing nanoparticles”. To prepare the well disperse of PEG coating SiNPs, a novel PEG system is applied for the preparation of SiNPs (PEG at the lowest molecular weight, 200 wt% is so far has not been reported as far as to the author’s knowledge) due to molecular coverage increase with decreasing in PEG molecular weight (Butterworth, Illum & Davis 2001).

There are various types of organic solvent for suspension/dispersion SiNPs such as 1-butanol, toluene, 2-propanol and others (Reindl & Peukert 2008; Reindl et al. 2007; Zhu, Wang & Ong 2001). However, the polarity of the organic solvent plays a major role in controlling the dispersion level of SiNPs. For example, the SiNPs tend to agglomerate very easily if suspended in non-polarity organic medium

like toluene (Reindl et al. 2008). Suspension in alcoholic solvent is to prevent oxidation and produce a stable dispersion of SiNPs (Zhu, Wang & Ong 2001). To clarify the better suspension/dispersion solvents for SiNPs in this study, varying systems of ethanol, methanol, 1-butanol, 2-propanol, acetone and toluene, separately, have been studied.

Silicon nanoparticles are characterized by using transmission electron microscopy (TEM), X-ray diffraction (XRD), UV-Visible spectroscopy, electron energy loss spectroscopy (EELS), Raman spectroscopy, fourier transform infrared (FTIR), scanning electron microscopy (SEM) and energy disperse X-ray (EDX).

1.3 Research objectives

The main goal of this study was to synthesis the well dispersed (no aggregation) SiNPs by using chemical route which was known as bottom up approach. The synthesis process consisted of (i) generation of supersaturation, (ii) nucleation and (iii) subsequent growth. PEG was used as capping/surfactant agent while N_2H_5OH was a reducing agent in this system. NaOH was used as catalyst and stabilizer to accelerate the reduction rate to produce more nuclei in low concentration of precursor.

The main objectives in this study were as following:

- To synthesize silicon nanoparticles (< 100nm) via a chemical route
- To produce silicon nanoparticles with narrow size distribution (well dispersed)
- To produce core shell structure (organic and inorganic hybrid nanoparticles)

1.4 Scope of project

Bottom up approach was used to produce SiNPs via chemical route. In this route, there were four parameters of synthesis of SiNPs which were studied as below:

- Effects of silicon ions concentration
- Effects of reducing agent concentration ($\text{N}_2\text{H}_5\text{OH}$ and NaBH_4 , separately)
- Effects of capping/surfactant agent concentration (PEG 200wt%, PEG 10Kwt% and TOAB, separately)
- Effects of suspension/dispersion solvent (ethanol, methanol, 1-butanol, 2-propanol, acetone and toluene, separately)

These parameters had determined the formation of well disperse, un-agglomerated particles with controlled size, shape and narrow size distribution of SiNPs.

For the fabrication and processing of nanomaterials and nanostructures, the following challenges must be met:

- Overcome the huge surface energy, a result of enormous surface area or large surface to volume ratio.
- Ensure all nanomaterials with desired size, uniform size distribution, morphology, crystallinity, chemical composition, and microstructure that altogether result in desired physical properties.
- Prevent nanomaterials and nanostructures from coarsening through agglomeration as time evolves (Cao 2004).

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction to nanotechnology

Since the past decades, nanotechnology is an attractive area of scientific development which covers a wide range of technologies such as research, development and industrial activity that concerns with structures and processes of a nanometer scale. A nanometer is one-billionth of a meter (10^{-9} m) which equals to the width of three or four atoms, roughly or about one hundred thousand of the width of a human hair. Besides that, nanotechnology is a multidisciplinary grouping of physical, chemical, biological, engineering, electronic, processes, materials, applications and concepts which has a defining characteristic that is one of size (Dutta et al. 1997). The first concept of 'nanotechnology' was used by a physicist, Richard Feynman on December 29, 1959 which described that nanotechnology as a process to manipulate individual atoms and molecules using one set of precise tools to build and operate another proportionally smaller set down to the needed scale. Meanwhile, according to Taniguchi (1974), the term of 'nanotechnology' was defined as mainly consisted of a process of separation, consolidation, and deformation of materials by one atom or by one molecule.

However, there is no generally recognized definition of nanotechnology to date. In a pragmatic approach, the present report uses the following definition:

1. Nanotechnology deals with structures which are smaller than 100 nm (at least one dimension).
2. Nanotechnology exploits characteristic effects and phenomena which occur in the transitional zone between the atomic and mesoscopic level.

3. Nanotechnology describes deliberate manufacture and manipulation of individual nanostructures. (El-Shall & Edelstein 1996)

Nanoparticles are the end product of a variety of physical, chemical and biological processes. Some of the nanoparticles are novel and radically different from others. Nanoparticle products include:

- i. nanotubes
- ii. nanowires
- iii. quantum dots
- iv. 'Others' nanoparticles

There are four main groups of nanoparticle production processes:

- i. Gas-phase
- ii. Vapor deposition
- iii. Colloidal
- iv. Attrition

All of these production processes may potentially expose by inhalation, dermal or ingestion routes (Aitken, Creely & Tran 2004).

In nanotechnology, there are two main approaches such as 'bottom-up' approach and 'top-down' approach. For the 'bottom-up' approach, materials and devices are built from molecular components which assemble themselves chemically using principles of molecular recognition. This approach is primarily featured in chemistry and biology in dealing with objects of the nanometer scale. Meanwhile, 'top-down' approach is a predominant particular in physics and physical technology which nano-objects are constructed from larger entities without atomic-level control (Yon & Jamie 2008).

2.1 Bottom-up and top-down approaches

Bottom-up approach and top-down approach play a very important role in manufacture of nanoparticles (Figure 2.1). Although both approaches are important, they consist of advantages and disadvantages.

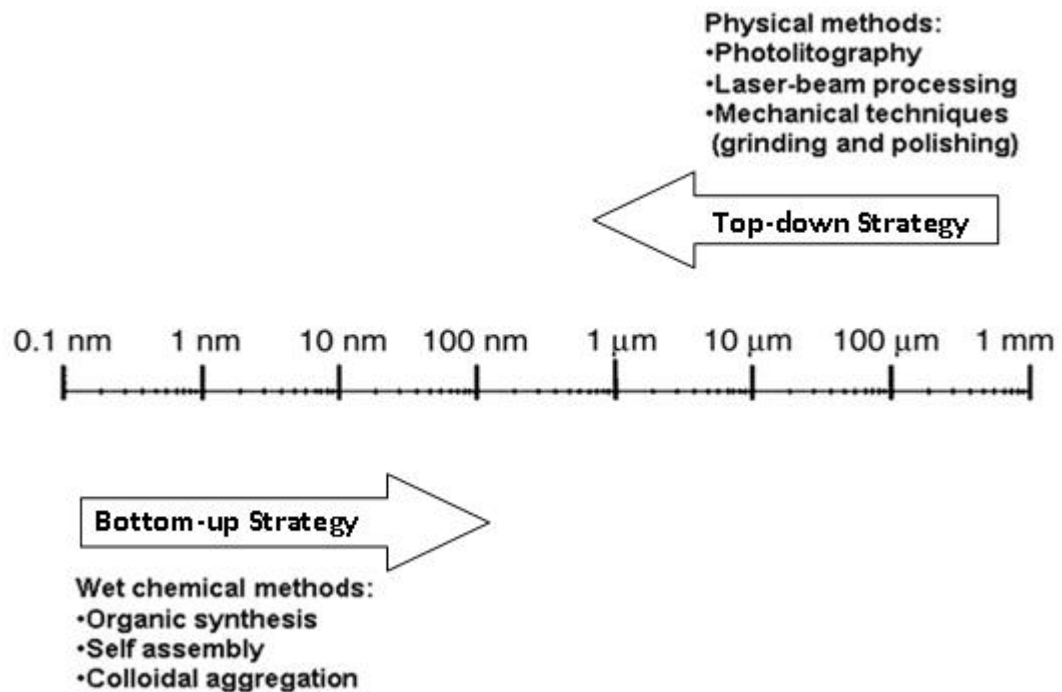


Figure 2.1: Top-down and bottom-up approaches (Yon & Jamie 2008).

The most common advantage of ‘top-down’ approach is the parts or components can be patterned and built in place without assembly step. Meanwhile, the disadvantage of the ‘top-down’ approach is the imperfection of the surface structure. Lithography is one of the well-known conventional of ‘top-down’ techniques in used. The surface imperfection of structure which means impurities and structure defects on surface would obviously give the influences and effects to the physical properties and surface chemistry of nanostructures. Besides, due to inelastic surface scattering, the imperfection of the surface would reduce the conductivity and impose extra challenges to the device design and manufacture of

the nanostructures and nanomaterials. ‘Top-down’ approach most likely introduces internal stress, in addition to surface defects and contaminations. Although there are many disadvantages, ‘top-down’ approach still plays an important role in the synthesis and fabrication of nanostructures and nanomaterials (Vieu et al. 2000).

Another approach which is used in the synthesis and fabrication of nanostructure and nanomaterials is ‘bottom-up’ approach. There are many ‘bottom-up’ approaches that have been developed to produce nanoparticles which are ranging from condensation of atomic vapours on surfaces to coalescence of atoms in liquids. For an example, inverse micelles is one of the ‘bottom-up’ approaches (liquid-phase techniques) which has been developed to size-selected nanoparticles of semiconductor. Nanostructures and nanomaterials with fewer defects, more homogeneous chemical composition and better short and long range ordering can always produce by ‘bottom-up’ approach due to driven mainly by the reduction of Gibbs free energy (Cao 2004).

However, differences in chemical composition, crystallinity, and microstructure of a material can be clearly portrayed by using different synthesis and processing approaches. Consequently, the properties of the material also exhibit differences such as physical properties, optical properties, chemical properties and mechanical properties.

There are many equipment and tools that have been developed to produce and characterize the nanostructures and nanomaterials such as scanning electron microscope (SEM) and transmission electron microscope (TEM). The two early versions of scanning probes that are launched for nanotechnology are atomic force microscope (AFM) and scanning tunneling microscope (STM). Scanning confocal microscope and scanning acoustic microscope (SAM) are other types of scanning

probe microscopy that play a crucial role in nanostructures characterization (Cao 2004).

2.2 Nanomaterials

Nanomaterials or nanostructured materials are materials with grain sizes of a billionth of a meter (1×10^{-9} m). Nanomaterials have attracted considerable attention due to their unique and useful properties. Examples of these properties are lower melting temperature of semiconductor (Goldstein et al. 1992), increased solid-solid phase transition pressure in semiconductor nanocrystals (Tolbert & Alivisatos 1995), lower effective Debye temperature in films of fine particles (Fujita, Oshima & Kuroishi 1976), decreased ferroelectric phase transition temperature for PbTiO_3 (Ishikawa, Yoshikawa & Okada 1988), higher self-diffusion coefficient in nanocrystalline materials (Horvath, Birringer & Gleiter 1987), changed thermophysical properties of Ag (Qin et al. 1996) and catalytic activity of metal oxide nanophase materials (Sarkas et al. 1993). These unique properties of nanomaterials are determined by their sizes, surface structures and interparticle interactions. Due to these properties, nanomaterials can be exploited for a variety of potential applications in fields such as electronic, optoelectronic, chemical, biology, mechanical and others.

All materials are constituted of grains where, within one grain consists of many atoms. The average size of an atom is 1 to 2 angstroms (\AA) in radius. But for the ranging grain size of conventional materials are from microns (μm) to several millimeters (mm). Meanwhile, nanomaterial has grain size from 1 to 100 nanometer (nm) which 1nm equal to 10 \AA . Grain size strongly influences the chemical and physical properties of the nanomaterial. This is shown when the grain size decreases, it will increase the volume fraction of grain boundaries or interfaces (Rotello 2004).

There are many methods to produce nanoparticles such as:

- Sol-gel synthesis
- Inert gas condensation
- Mechanical alloying or high-energy ball milling
- Electrodeposition
- Aerosol synthesis
- Microemulsion
- Co-sputtering
- Ion implantation

(Leparoux et al. 2008; Araujo-Andrade et al. 2003; Lam et al. 2000)

2.2.1 Classification of nanostructure materials

The number of dimensions which within nanometer range is the main factor to classify nanostructure materials and system. There are three systems to confine particles which are in three dimensions, two dimensions and one dimension. Disc or platelets, ultra thin films on the surface and multilayered materials which can be included in system are confined in one dimension. The thin films themselves could be amorphous, single crystalline or nanocrystalline (Rotello 2004). Besides, nanowires, nanorods, nanofilaments and nanotubes are the examples of two dimensions that can be confined in a system. Table 2.1 shows the classification of nanomaterials with regard to different parameters, which are dimension (3 dimensions, 2 dimensions and 1 dimension), phase composition (single phase solids, multi phase solids and multi phase systems) and manufacturing process (gas phase reaction, liquid phase condition and mechanical reaction).

Table 2.1: Classification of nanomaterials with regard to different dimensions (Coffin 2006).

Classification	Examples
<p>Dimension</p> <ul style="list-style-type: none"> ▪ 3 dimensions < 100 nm ▪ 2 dimensions < 100 nm ▪ 1 dimension < 100 nm 	<p>Particles, quantum dots, hollow spheres, etc.</p> <p>Tubes, fibers, wires, platelets, etc.</p> <p>Films, coatings, multilayers, etc.</p>
<p>Phase composition</p> <ul style="list-style-type: none"> ▪ Single phase solids ▪ Multi phase solids ▪ Multi phase systems 	<p>Crystalline, amorphous, particles and layers, etc.</p> <p>Matrix composites, coated particles, etc.</p> <p>Colloids, aerogels, ferrofluids, etc.</p>
<p>Manufacturing process</p> <ul style="list-style-type: none"> ▪ Gas phase reaction ▪ Liquid phase condition ▪ Mechanical reaction 	<p>Flame synthesis, condensatin, CVD, etc.</p> <p>Sol-gel, precipitation, hydrothermal processing, etc.</p> <p>Ball milling, plastic deformation, etc.</p>

In principle, a nano-scale dimension can be obtained in all conventional materials such as metals, semiconductors, glasses, ceramics or polymers. However, the spectrum of nanomaterials ranges from inorganic, crystalline or amorphous particles can be found as single particles, aggregates, powders, colloids, suspensions, emulsions, nanolayers, films and supramolecular structures (dendrimers, micelles or liposomes). Besides, it also can be found up to the class of fullerenes and their derivatives. Table 2.2 shows some type of classification of nanostructures materials, which are cluster, nanocrystals, quantum dots, others nanoparticles, nanowires and nanotubes.

Table 2.2: Some types of classification of nanostructures materials (Brydson & Hammond 2005).

Nanostructure	Size	Example Materials
Cluster, nanocrystals, quantum dots.	Radius: 1-10 nm	Insulators, semiconductors, metals, magnetic materials.
Others nanopartilces	Radius: 1-100 nm	Ceramic oxides, buckyballs
Nanowires	Radius: 1-100 nm	Metals, semiconductors, oxides, sulfides, nitrides
Nanotubes	Radius: 1-100 nm	Carbon, including fullerenes, layered chalcogenides

2.3 Nanoparticle

In the early 1990s, the term of ‘nanoparticle’ was widely used with the related concepts, ‘nanoscaled’ or ‘nanosized’ particle. A nanoparticle is a microscopic particle that defines a particle with diameter smaller than 100 nm in at least one dimension (El-Shall & Edelstein 1996).

Nanoparticles function as a bridge between bulk materials and atomic or molecular structures, effectively. Nano-scale materials should not have constant physical properties if compare with bulk material which is regardless of its size. Size-dependent properties which are observed are quantum confinement in semiconductor particles, surface plasmon resonance in metal particles and superparamagnetism in magnetic particles (are the size-dependent properties which can be observed). Semi-solid and soft nanoparticles are formed. Liposome is a prototype nanoparticle of semi-solid nature.

Due to the surface of the material which dominates the properties of the bulk materials, the properties of materials change when the particle size of materials is reduced to nanoscale. When the size of material approaches the nanoscale, the atoms percentage at the surface of a material will become significant. This is because the

atoms percentage at the surface of bulk materials ($>1\mu\text{m}$) is miniscule relative to the total number of atoms of the material. There are possibilities for the suspensions of nanoparticles due to their surface interaction with the solvent which come across with different density. Unexpected visible properties always occur in nanoparticles due to visible light scattering (Dutta et al. 1997).

Cluster is referred to the nanoparticles at the small end of the size range. Metal, dielectric and semiconductor nanoparticles have been manufactured, as well as hybrid structures like core-shell nanoparticles. Nanospheres, nanorods, nanocups, quantum dots are the types of nanoparticles. For biomedical applications, nanoparticles are used as drug carriers and imaging agents. There are various types of liposome nanoparticles which are used as delivery systems for anticancer drugs and vaccines (Schmid 2004).

2.3.1 Silicon nanoparticles

The fabrication of semiconductor nanoparticles has attracted much considerable attention due to their potential properties such as physical, chemical, mechanical, electronic, and optical properties. For example, the optical and electronic properties of the SiNPs have become a base of the optoelectronic devices such as applications in light emitting diodes and chemical sensor. SiNPs can be produced by using gas-phase evaporation, high temperature aerosol reactions, co-sputtering, Si implantation, ball milling, laser ablation, chemical etching, and gas-phase pyrolysis (Scriba et al. 2008).

One of the common issues of SiNPs is tendency to agglomerate easily (especially when dispersed in an organic medium). However, to reduce or prevent the agglomeration, some techniques such as polymerization and intrinsically stable suspension have been used which without the application of an additive (Sudeep,

Page & Emrick 2008; Reindl & Peukert 2008). Figure 2.2 shows a transmission electron microscope (TEM) image of SiNPs.

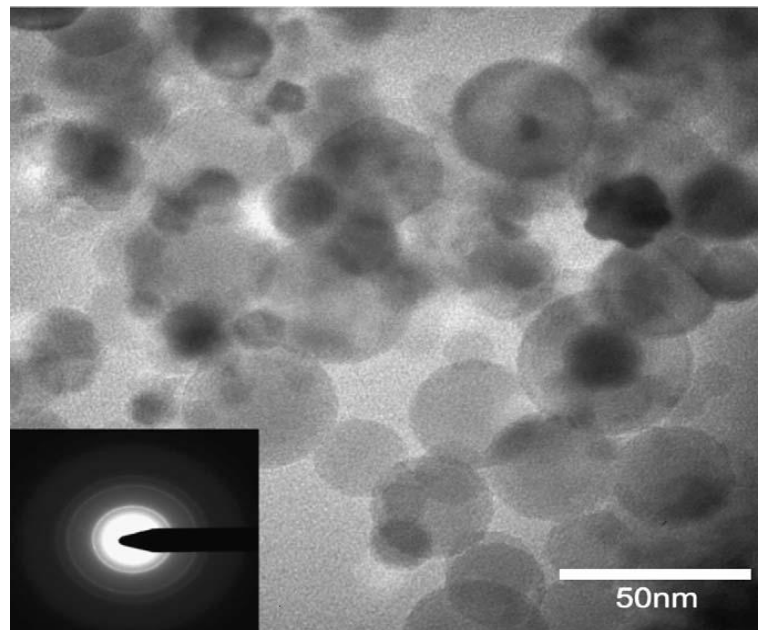


Figure 2.2: TEM image of SiNPs (Meier et al. 2006).

2.4 Properties of silicon nanoparticles

2.4.1 Structural properties

If compare to “bulk” structure, the structure of SiNPs is more flexible due to its small size and large surface-to-volume ratio. This results in significant difference to the bulk material, which is the distribution of atoms over different lattice sites (Fang, Weng & Ju 2009).

For example, when the magnitude of the applied strain increases from 0.067 to 0.086, the amorphous phase cone of the SiNPs disappear and the surface regions begin to transform into an amorphous state. This transformation phenomenon is quite different in silicon bulk material as the particle microstructure reconstructs to a more stable form (Fang, Weng & Ju 2009).

Besides, due to the flexibility of the nanoparticles crystal structure, nanoparticles chemical composition can allow large compositional deviations from the bulk stoichiometry without losing the single-phase structure. The different crystallinity state of nanoparticles is depending on the synthesis methods in used (Makovec 2007).

2.4.2 Mechanical properties

Mechanical properties of the materials such as hardness, elastic modulus, fracture toughness, scratch resistance, fatigue strength, and hardness are modified due to the nanosized of materials. At the nanoscale, structuring components have been influenced by the energy dissipation, mechanical coupling within arrays of components, and mechanical nonlinearities. Besides, the mechanical properties of materials at the nanoscale always differ with the materials at macroscopic scale. Although the continuum mechanics are applied, the surface effects can be controlled by the deformation of properties when the sizes of materials are above the 10nm range. Meanwhile, for micrometer sizes structures, the elastic strain energy is used to by the deformation of properties when the size of material is above 10nm range. Meanwhile, for micrometer sizes structures, the elastic strain energy is used to control the mechanical properties. At nanoscale, surface effects become predominant and significantly modify the macroscopic properties due to the increment of surface-to-volume ratio (Cuenot et al. 2004).

For example, stress value of SiNPs which approximately 24GPa is higher than bulk silicon (12GPa). This is because of the suppression of the dislocations in the current small volume particles. Besides, SiNPs have a higher maximum strength and hardness than the bulk silicon (Gerberich et al. 2003). In addition, Young's moduli of SiNPs are significantly higher than bulk silicon due to the different

structure of the nanoscale particles from the bulk silicon (Fang, Weng & Ju 2009). However, when the volume of the particle is reduced, smaller particles will reduce the maximum strength significantly.

2.4.3 Optical properties

There is much significance for the optical properties of nanoparticles in both traditional and emerging technologies. For the traditional technologies, nanoparticles are used as coloring agents in glass and paints. In the 1970s, nanoparticle optics researches were developed frequently due to the increased of solar-energy applications interest. Today, nanoparticles are used to absorb at particular solar wavelengths (commercial coatings). Due to the increment and enhancement of local fields close to particle surfaces, nanoparticles are used to detect single molecules by using surface-enhanced spectroscopy.

The origin colour of nanomaterials is known as surface plasmons, which is a natural oscillation of the electron gas inside a given nanosphere. The surface plasmons will absorb energy if the sphere is smaller compare to a wavelength of light which has a frequency close to the surface plasmons. Besides that, the dielectrics function and the shape of the nanoparticles may influence the frequency of the surface plasmons (Pinchuk 2005).

Optical emission and absorption depend on the transitions between these states; in particular, there are large changes in optical properties that are shown by semiconductors and metals, which the colour as a function of particle size. For example, SiNPs colloidal solutions have a colorless but become dark grey color when particles size is increased (Sudeep, Page & Emrick 2008).

Normally, due to the intensity of absorption or transmittance, the optical properties of SiNPs are characterized by UV-vis spectroscopy. For example, the

large blue shift in the absorption spectra of the SiNPs are corresponding to quantum confinement effects on the SiNPs (Sudeep, Page & Emrick 2008; Aihara et al. 2001). However, due to the quantum confinement effects, the red shift in the absorption spectra of SiNPs occurred with increasing of particles size. The size-dependent optical absorption observation is the quantum confinement signature (Brus 1994). In addition, the surface defects of the nanoparticles also play an important role in the absorption spectra for SiNPs (Zou et al. 2006). Besides, the shifting of SiNPs absorption spectra could be formed from the oxidation of silicon surface due to the incomplete or complete surface coverage (Scriba et al. 2008; Gupta & Wiggers 2009). For the SiNPs with polymer coating, the effect depends on the thickness of polymer coating (Blummel et al. 2007).

2.4.4 Electronic/electrical properties

In macroscopic systems, scattering at rough interfaces or scattering with phonons, impurities or other carriers can be determined by the electronic transport. Each electron path resembles a random walk and transport is diffusive. Electrons can travel through the system without the phase randomization when dimensions of the system are smaller than the electron means free path (inelastic scattering). This gives rise to additional localization phenomena which are specifically related to phase interference. All scattering centers can be eliminated completely if the system is sufficiently small. Meanwhile, if the sample boundaries are smooth, boundary reflections will be purely specular and the electron transport becomes purely ballistic, which the sample acts as a wavelength for the electron wavefunction (Cao 2004).

However, surface modification has been changed in electrical conductivity of the particles. The electrical conductivity of pure and modified particles is totally different. Due to the deprotonation of hydroxyl groups, the surface of pure and

modified particles is negatively charged. By the way, the electric conductivity is lower for the modified particles than pure particles which polymer (such as PEG and PPG) grafted on the modified particles surface is non-conductive (Shin et al, 2008).

2.4.5 Thermal properties

The properties of the silicon nanomaterials such as optical, electronic and mechanical properties have been well developed. However, the thermal properties of nanomaterials have only shown slower progression because of the difficulties in experimental measuring and controlling the thermal transport in nanoscale dimensions. Moreover, the theoretical simulations and analysis of thermal transport in nanostructures are still in infancy due to the limitation of the available approaches (numerical solutions of Fourier's law, computational calculation based on Boltzmann transport equation and Molecular-dynamics (MD) simulation). On the other hand, Atomic force microscope (AFM) with nanometer-scale high spatial resolution is an effective way to measure the thermal properties such as measuring the nanostructures of thermal transport (Cao 2004).

2.4.6 Thermodynamic properties

Thermodynamic properties of SiNPs are corresponded to the cohesive energy and the surface energy. It reveals that negative cohesive energy of the particles increasing when the particle size increases. That means that the stability of the particles can be improved as particles become larger. When the small particles have more suspension bond and activation energy, the atoms on the particle's surface will be reconstructed to be a more stable structure. Subsequently, when the particles size increases, it can attribute to the surface/volume ratio. Besides, surface energy of

silicon nanoparticles increases significantly when the particles decreases, which smaller particles have a higher chemical activity (Fang, Weng & Ju 2009).

2.5 Synthesis of silicon nanoparticles

There are many widely known methods to produce SiNPs such as aerosol synthesis, wet chemical synthesis, sol-gel synthesis, microemulsion, mechanical alloying or high-energy ball milling, electrodeposition and others. Figure 2.3 shows the fabrication techniques of silicon nanocrystals.

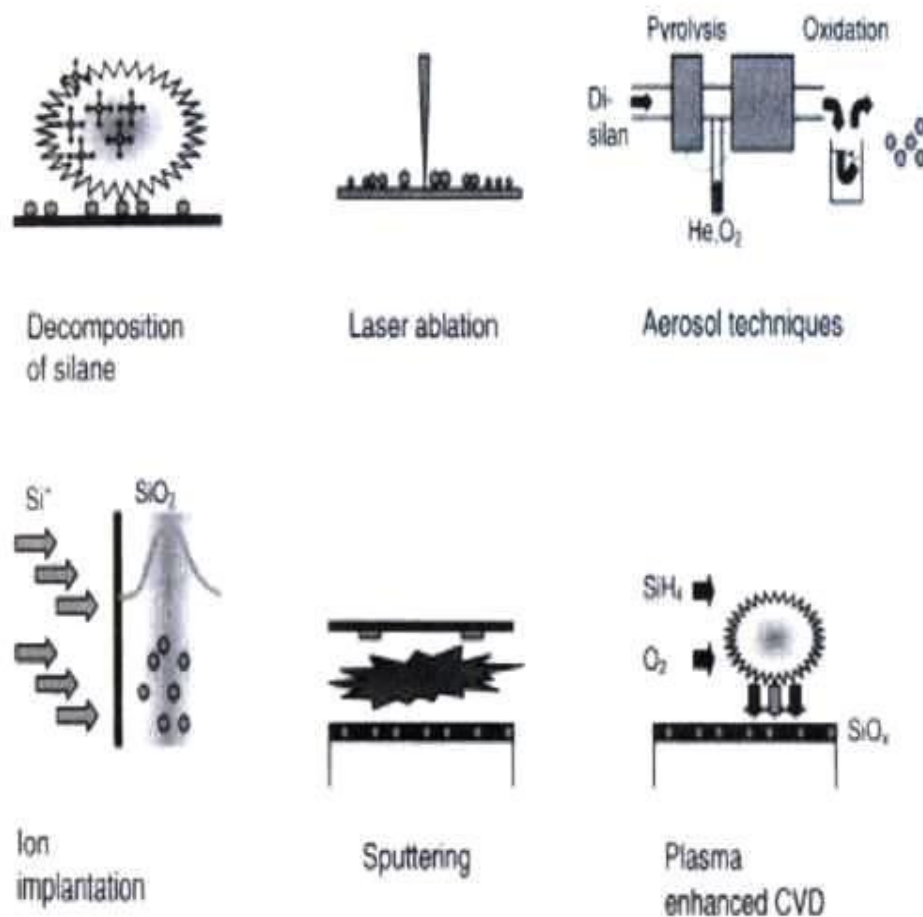


Figure 2.3: Fabrication techniques of silicon nanocrystals (Gaburro et al 2005).

2.5.1 Mechanical alloying or high energy ball milling

The mechanical alloying process can be used for the preparation of nanoparticles (Figure 2.4). For the mechanism of mechanical alloying process, coarse-grained materials such as metals, ceramics, and polymers in the form of powder are crushed mechanically in rotating drums by tungsten carbide balls or hard steel. Normally, this process is under controlled by atmospheric conditions to prevent unwanted reactions such as oxidation. Large reductions of grain size may be caused by the repeated deformation. Nanostructured alloys can be produced by different components, where alloys produce together by cold welding, mechanically. Besides, one phase nanometer dispersion in another can also be achieved. Microstructures and phase produces with this mechanical alloying process can always be thermodynamically interest (Brydson & Hammond 2005).

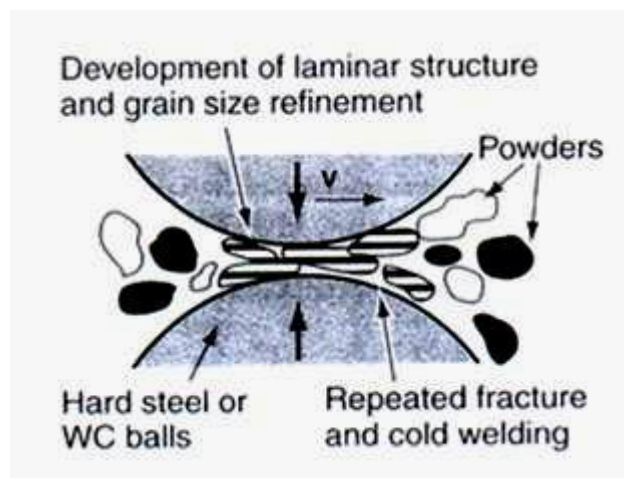


Figure 2.4: Schematic diagram of the mechanical alloying process (Brydson & Hammond 2005).

In general, the formation of nanostructures can be produced by any form of mechanical deformation under shear conditions and high strain rates. The lattice defects can be obtained when the energy is being continuously pumped into crystalline structures (Brydson & Hammond 2005). This process is simple but the

grinding balls contribute to impurities. Figure 2.5 shows ball mill for fabrication of nanoparticles (Fahrner 2005).

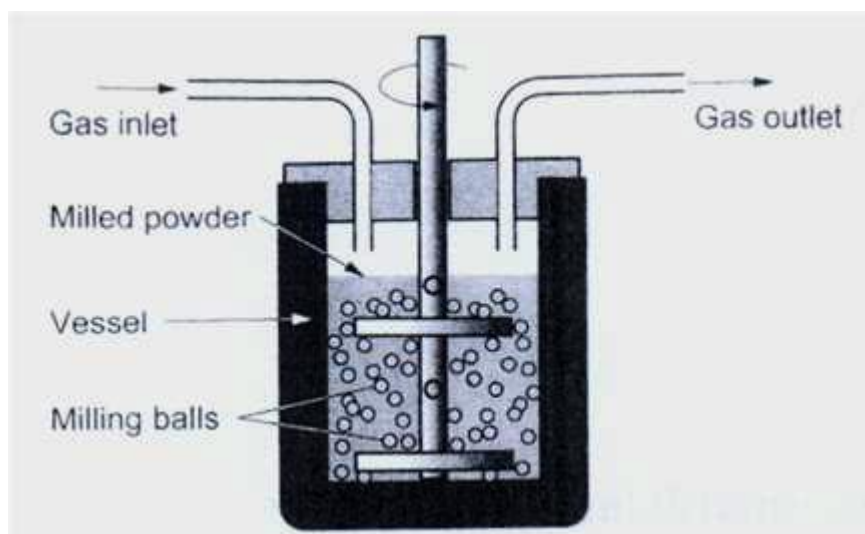


Figure 2.5: Ball mill for fabrication of nanoparticles (Fahrner 2005).

Micron sized particles can usually be produced by the conventional ball-milling easily. Furthermore, the used of high-energy millers allows the preparation of silicon nanoparticles, which the requirement of milling times is about few hours. Silicon nanoparticles are obtained from a solid phase reaction during the ball milling of mixture SiO_2 and high purity metallic aluminum (Al). The thermodynamically solid phase reaction as Equation 2.1: (Araujo-Andrade et al. 2003).



2.5.2 Aerosol synthesis

Aerosol synthesis which involves gas phase precursor (undergoes chemical reaction or thermal decomposition) is the most common method to fabricate SiNPs. Vaporization and deposition are the important steps for aerosol synthesis to form nanoparticles. Silane is the most popular gas phase precursor which will undergo

pyrolysis to produce SiNPs. Due to the configuration set up, there are various types of aerosol synthesis to produce nanoparticles.

Advantages of the gas-phase processing systems are shown as follows:-

- The purity of nanoparticles which produce by gas-phase processes is generally higher than liquid-based processes.
- Aerosol synthesis provides a good process and product control because of particle size, degree of agglomeration, chemical homogeneity, and crystallinity can be controlled easily.
- Aerosol synthesis being a non-vacuum technique which provides a cheap alternative rather than expensive vacuum synthesis technique for synthesis of thin or thick film (Wang, Zhong & Snyder 1990).

i) Laser vaporization

A laser is used to evaporate a sample target in an inert gas flow reactor. Vaporization is caused by laser which has heated the source material to a high temperature, locally. Supersaturation occurs when the vapor is cooled by collisions with the inert gas molecules. Nanoparticles formation is induced by the supersaturation. For example, CO₂ laser is used to induce pyrolysis of silane. Meanwhile, it produces gram-scale quantities of SiNPs. High purity loosely agglomerated particles with controlled primary particle size and size distribution can also be produced by CO₂ laser (Li et al 2003).

ii) Pulsed laser ablation

Pulsed laser ablation is one of the most common used deposition methods in preparing nanocrystalline silicon films due to the rapid thermogenic speed and small surface contamination (Wang et al. 2006). Energetic plasma above a thin layer of