



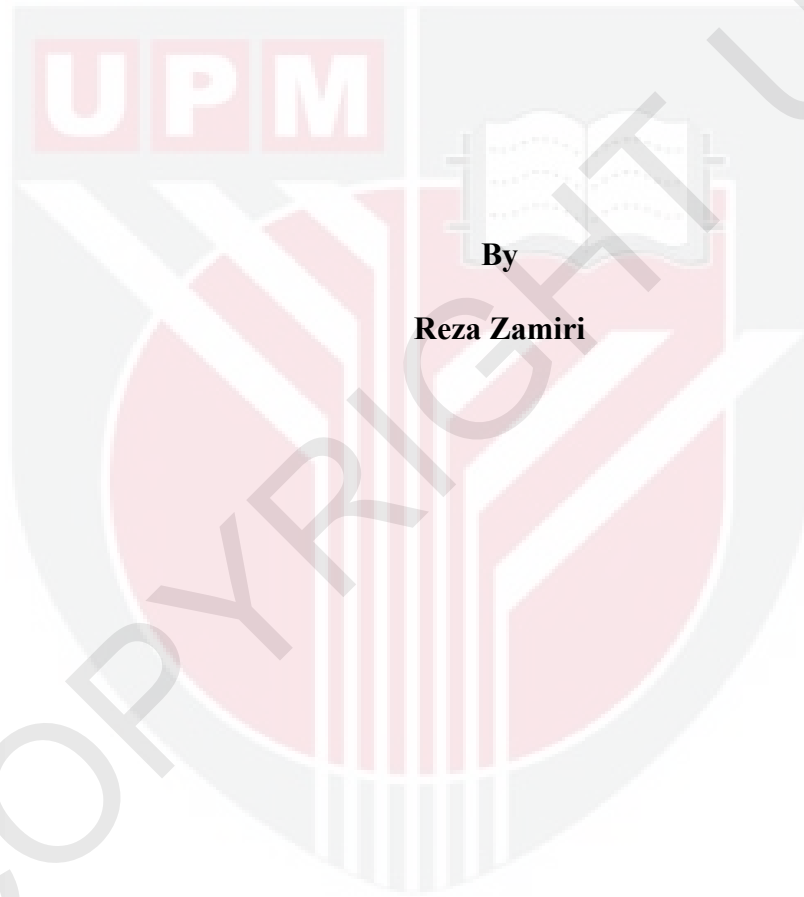
UNIVERSITI PUTRA MALAYSIA

**FABRICATION AND OPTICAL CHARACTERIZATION OF
NANOPARTICLES IN LIQUID MEDIA**

REZA ZAMIRI

FS 2011 87

**FABRICATION AND OPTICAL CHARACTERIZATION OF
NANOPARTICLES IN LIQUID MEDIA**



By

Reza Zamiri

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



UPM

This thesis dedicates to

My father (Ali Zamiri), my mother (Kobra Fazeli), my brother (Roosbeh Zamiri),

My dear sisters (Golriz and Golnoosh Zamiri)

And

*My dearest Forough beacuase of her beautiful conterbiution on my life from end of this
study to the future*

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

**FABRICATION AND OPTICAL CHARACTERIZATION OF
NANOPARTICLES IN LIQUID MEDIA**

By

REZA ZAMIRI

March 2011

Chairman : Professor Azmi Zakaria, PhD

Faculty : Science

In the present study we have investigated the fabrication of metal nanoparticles (NPs) using Laser Ablation (LA) technique and measured the thermal and non-linear optical properties of nanofluids. A big challenge in the synthesis of NPs is particle agglomeration. This tendency can be inhibited by stabilization of NPs with chemical species and therefore, much effort has been undertaken to use different materials as colloidal stabilizers. We performed LA to metal plate in chitosan solution, starch aqueous solutions and various vegetable oils to prepare metal NPs. It was revealed that the generation as well as the stability of NPs was increased in comparison with LA in water. The results suggested that the increased NPs generation is attributable to increased secondary etching efficiency by the solvent confined plasma toward the

plate. On the other hand, the size decrease of the NPs was remarkable. The effects of ablation time and frequency in some cases were also studied.

NPs appear to be ideally suited for applications in targeted thermal effects in medical therapies and photothermally activated drug delivery; all depend critically on the thermal transport between the NPs and the surrounding liquid. In this second part of work, thermal lens spectroscopy was used to determine the thermal diffusivity of Copper and Silver NPs in polyvinyl pyrrolidone prepared by gamma radiation method and thermal diffusivity of clay containing Silver NPs prepared by UV-irradiation and chemical reduction methods. The effect of size and concentration of NPs on thermal diffusivity of nanofluid was also studied. The obtained results showed that the thermal diffusivity of nanofluids increases with the increase of metal NPs concentration.

We studied the effect of nanoparticle size on thermal diffusivity of silver nanofluid containing silver nanoparticles in polyvinylpyrrolidone. The obtained result showed a decrease of the thermal diffusivity of nanofluid with the decrease of particle size. We attributed this decrement in thermal diffusivity to phonon scattering at interface of particles-liquid and poor contact between the nanoparticles and surrounded liquid. The thermal diffusivity of fluids containing Cu-NPs was measured by pulsed laser thermal lens technique. The obtained results showed that the rapid electron-phonon scattering of NPs causes the thermal diffusivity of the solutions increases with the increase of Cu-NPs density.

Materials with high non-linear refractive index are always of huge interests for their potential applications on many non-linear optical devices. Composite systems containing metal NPs such as Silver, Gold, and Copper also have high non-linear refractive index because of metal NPs unique ability to support surface plasmon resonance at visible wavelengths. In this study the investigation of non-linear optical properties of media such as clay, palm oil, monoolein, starch, and polyvinyl pyrrolidone containing metal NPs is presented. The obvious spatial self-phase modulation and the influence of thermal-induced negative lens are observed when a beam propagates through these solutions, indicating promising applications such as optical limiting and beam flattening. The obtained results showed that the addition of NPs inside the fluids can induce strong non-linear optical properties due to the presence of surface plasmon peak in visible region. The nonlinear optical properties of prepared Ag-NPs in Monoolein and Palam oil have been studied using Z-scan, and spatial self phase modulation techniques. The samples displayed nonlinear optical properties which strongly depend on volume fraction of particles into the Monoolein solutions.

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

PEMBUATAN DAN KARAKTERISASI OPTIK NANOPARTIKEL DALAM MEDIA CAIR

Oleh

REZA ZAMIRI

March 2011

Pengerusi : Profesor. Azmi Zakaria, Ph.D

Fakulti : Sains

Dalam kajian ini, kami menyelidiki fabrikasi zarah-nano (NPs) logam menggunakan teknik Ablasi Laser (LA) dan mengukur ciri-ciri terma dan ketak-linearan optik nano-bendalir. Cabaran besar dalam mensintesis NPs adalah agglomerasi zarah. Kecenderongan ini boleh dihalang melalui penstabilan NPs oleh spesis kimia dan oleh itu, banyak usaha telah dilakukan untuk mengguna bahan-bahan berbeza sebagai penstabil koloid. Kami telah melakukan LA keatas plat logam didalam larutan chitosan, larutan gelembair kanji dan pelbagai minyak sayuran untuk menyediakan NPs logam. Ujikaji membuktikan bahawa penghasilan begitu juga kestabilan NPs meningkat berbanding dengan LA di dalam air. Keputusan ujikaji mencadangkan bahawa peningkatan penjanaan NPs adalah disumbang oleh peningkatan kecekapan

punaran sekunder oleh pelarut mengandung plasma kearah plat. Selain itu, pengurangan saiz NPS adalah mengujakan. Kesan daripada masa dan frekuensi ablasi dalam beberapa kes juga telah dikaji.

NPs kelihatan sangat sesuai untuk aplikasi dalam kesan-kesan terma tertarget dalam terapi medikal dan penghantaran ubatan teraktif secara fototerma; kesemuanya bergantung secara kritikal diatas pengangkutan terma diantara NPs dan cecair persekitaran. Dalam bahagian kedua kajian, spektroskopi kanta terma telah digunakan untuk menentukan keresapan terma NPs Kuprum dan Perak dalam polivinil pyrrolidon yang disediakan secara kaedah radiasi gamma dan keresapan terma tanah liat mengandungi NPs Perak yang disediakan secara kaedah-kaedah sinaran-UV dan reduksi kimia. Kesan terhadap saiz dan kepekatan NPs keatas keresapan terma ke atas bendalir-nano juga dikaji. Keputusan diperolehi menunjukkan bahawa keresapan terma bendalir-nano meningkat dengan pertambahan kepekatan NPs logam.

Kami menyelidiki kesan saiz zarah-nano keatas keresapan terma bendalir-nano perak mengandungi nano-zarah perak dalam polyvinylpyrrolidone. Hasil diperolehi menunjukkan penurunan keresapan terma nano-bendalir dengan penurunan saiz zarah. Kami sabitkan penurunan keresapan terma ini oleh penyerakan fonon pada antaramuka zarah-cecair dan sentuhan lemah diantara nano-zarah dan bendalir sekeliling. Keresapan terma bendalir mengandungi Cu-NPs telah diukur dengan teknik kanta terma laser denyut. Hasil menunjukkan bahawa serakan elektron-fonon cepat dari NPs

menyebabkan keresapan terma larutan bertambah dengan pertambahan ketumpatan Cu-NPs.

Bahan-bahan yang berindeks biasan tak-linear tinggi adalah sentiasa amat diminati disebabkan oleh keupayaan aplikasi mereka pada kebanyakan peranti optik tak-linear. Sistem-sistem komposit mengandungi NPs logam seperti Perak, Emas, dan Kupram juga selalunya mempunyai indeks biasan tak-linear yang tinggi kerana kebolehan unik NPs logam untuk menyokong resonan plasmon permukaan pada panjang gelombang boleh-nampak. Ini seterusnya boleh memberi pertambahan pada penambahbaikan raksaksa keatas respon optik tak-linear dalam medium. Dalam kajian ini, penyelidikan ciri-ciri optik tak-linear medium seperti tanah liat, minyak kelapa sawit, larutan kanji dan polivinil pyrrolidon mengandungi NPs logam dibentangkan. Modulasi fasa-sendiri ruang dan pengaruh kanta negatif teraruh-terma adalah diperhatikan apabila alur merambat melalui larutan-larutan ini, menandakan peluang-cerah kepada aplikasi seperti penghadan optik dan perataan alur. Keputusan diperolehi menunjukkan bahawa penambahan NPs didalam bendalir boleh mengaruh secara kuat ciri-ciri optik tak-linear disebabkan oleh kehadiran puncak plasmon permukaan dalam renj boleh-nampak. Ciri-ciri optik tak-linear dari Ag-NPs tersedia dalam Monoolein dan minyak kelapa sawit telah dikaji menggunakan teknik-teknik imbasan-z dan modulasi swafasa ruang. Sampel memaparkan ciri-ciri optik tak-linear yang mana bergantung secara kuat dengan pecahan isipadu zarah terhadap larutan Monoolein.

ACKNOWLEDGEMENTS

At the end of this step of my graduate period has allowed for a bit of reflection, and the many people who have contributed to both my work, and my life during of this period of time.

First, I would like to express my full thanks and sincere gratitude to my great dear supervisor, Prof. Dr Azmi Zakaria for all of guidance, discussions, unlimited assistance consultations and support. He also taught me how to look at the life and science. I owe him in whole of my life. I also would like to thank my committee members; Prof. Dr. Mohd Adzir Mahdi, and Assoc. Prof. Dr. Zaidan Abd. Wahab, for their invaluable suggestions, beneficial advices and their endless helps.

I wish to acknowledge my gratitude to all lecturers and staffs in Physics Department of Faculty of Science and TEM Unit of Institute of Bioscience, UPM, for technical assistance. I would like to express my full thanks and sincere gratitude to my dear family for their encouragements, emotional supports and fortitude efforts in my life time. I am also grateful to my lab mates; Mohd. Shahril Husin, Mohd Sabri Mohd Ghazali, Dr. Zahid Rizwan, Monir Noroozi and my dear friends Amir Reza Sadrolhosseini and Majid Darroudi.

I certify that an Examination Committee has met on **11 February** 2010 to conduct the final examination of Reza Zamiri on his Doctor of Philosophy thesis entitled " Fabrication and optical characterization of nanoparticles in liquid media " in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U. (A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Examination Committee were as follows:



HASSANAH MOHD. GHZALI, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia
Date:

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

Azmi Zakaria, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd Adzir Mahdi, PhD

Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Zaidan Abd. Wahab, PhD

Assoc. Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

HASANAH MOHD. GHAZALI, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

REZA ZAMIRI

Date: 29 March 2011

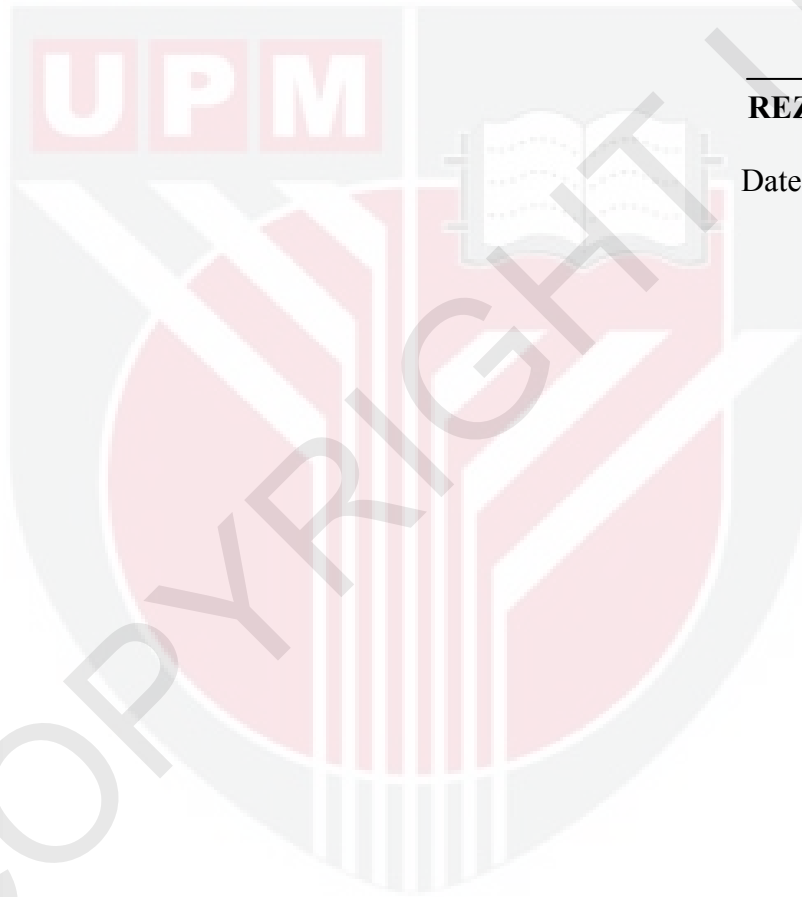


TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	vi
ACKNOWLEDGMENTS	ix
APPROVAL	x
DECLARATION	xii
LIST OF TABLES	xvi
LIST OF FIGURES	xvii
LIST OF ABBREVIATIONS	xxii
LIST OF SYMBOLS	xxiii
CHAPTER	
1 INTRODUCTION	
1.1 Metal nanoparticle	1
1.2 Laser ablation technique	4
1.3 Non-linear interaction of light with matter	6
1.3.1 Non-linear refractive index	7
1.3.2 Self-focusing and self-defocusing	10
1.4 Thermal lens spectroscopy	11
1.5 Spatial self-phase modulation	12
1.6 Z-scan technique	13
1.7 Statement of problem	14
1.8 Objective of research	15
1.9 Outline of the dissertation	16
2 LITERATURE REVIEW	
2.1 Fabrication of Ag-NPs using LA methods	17
2.2 Thermal properties of metal nanoparticle using thermal lens technique	20
2.3 Non-linear optical properties of nanofluids	23
3 THEORY	
3.1 Optics of metal nanoparticles	26
3.2 Theory of the mode-mismatched dual-beam thermal lens spectrometry	29

3.3	Z-scan theory	36
3.4	Theory spatial self-phase modulation	40
4	METOTHOLOGY	
4.1	Preparation of Ag-NPs by using LA methods	45
4.1.1	Ag-NPs in starch solution effect of laser repetition rate	45
4.1.2	Ag-NPs in starch solution and effect of LA time	47
4.1.3	Ag-NPs in chitosan	48
4.1.4	Ag-NPs in virgin coconut oil	49
4.1.5	Ag-NPs in palm oil	30
4.1.6	Ag-NPs in Caster oil	53
4.1.7	Ag-NPs in Monoolein	54
4.2	Preparation of Cu-NPs by γ -radiation	54
4.3	Preparation of Ag-NPs in PVP by γ -radiation	55
4.4	Preparation of Ag-NPs in MMT suspension by chemical reduction method	56
4.5	Preparation of Ag-NPs in MMT suspension by UV-radiation method	57
4.6	Characterize of the prepared nanoparticles	58
4.7	Thermal lens experimental setup	59
4.7.1	The mode-mismatched dual-beam thermal lens experimental set-up	59
4.7.2	Pulsed laser thermal lens technique experimental set-up	62
4.8	Z-scan experimental setup	65
4.9	Spatial self-phase modulation experimental set-up	66
5	RESULTS AND DISCUSSION	
5.1	Characterization of the Ag-NPs in starch solution prepared under different laser repetition rate	68
5.2	Characterization of the Ag-NPs in starch solution prepared under different LA times	76
5.3	Characterization of the Ag-NPs in chitosan solutions	82
5.4	Characterizations of Ag-NPs dispersed in palm oil	89
5.5	Characterizations of Ag-NPs in virgin coconut oil	94
5.6	Characterizations of Ag-NPs dispersed in castor oil	100
5.7	Characterizations of Ag-NPs dispersed in monoolein	105
5.8	Thermal diffusivity of the MMT containing Ag-NPs prepared by chemical reduction method	108
5.9	Thermal diffusivity measurement of Cu-NPs prepared by γ -radiation method	116
5.10	Thermal diffusivity of Ag-NPs in PVP solution prepared by γ - radiation method	122

5.11	Thermal diffusivity of MMT containing Ag-NPs prepared by UV-radiation method	127
5.12	Investigation of spatial self-phase modulation effect of Ag-NPs in MMT	132
5.13	Spatial self-phase modulation properties of starch stabilized Ag-NPs	135
5.14	Non-linear optical properties of palm oil containing Ag-NPs	136
5.15	Non-linear optical properties of monoolein containing Ag-NPs	141
5.16	Measurement of non-linear refractive index of MMT containing Ag-NPs	146
6	CONCLUSION AND FUTURE WORK	149
	REFERENCES	153
	BIODATA OF STUDENT	163
	LIST OF PUBLICATION	164