UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF SILVER NANOPARTICLES IN MONTMORILLONITE AND GELATIN USING PHYSICAL AND CHEMICAL METHODS

MAJID DARROUDI

ITMA 2011 1

PREPARATION AND CHARACTERIZATION OF SILVER NANOPARTICLES IN MONTMORILLONITE AND GELATIN USING PHYSICAL AND CHEMICAL METHODS

By

MAJID DARROUDI

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

This thesis dedicates to:

My dear wife

(SAMANEH SADAT)

&

My son

(AMIR ALI)

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

PREPARATION AND CHARACTERIZATION OF SILVER NANOPARTICLES IN MONTMORILLONITE AND GELATIN USING PHYSICAL AND CHEMICAL METHODS

By

MAJID DARROUDI

April 2011

Chairman : Assoc. Professor Mansor Bin Ahmad, PhD

Faculty : Institute of Advanced Technology

Metal nanoparticles in inorganic and organic materials have generated novel materials that display unique optical, catalysis, or biological properties making them attractive for using in various application areas. A big challenge in the synthesis of nanoparticles is particle aggregation or precipitation. This phenomenon can be inhibited with stabilization of nanoparticles by suitable polymers or chemical species as colloidal stabilizers. This thesis describes the different preparation methods and characterization of silver nanoparticles (Ag-NPs) in organic and inorganic materials as well as their potential applications. The methods used consist of green chemical method and physical methods, e.g., UV irradiation, pulsed laser ablation (PLA), and γ-irradiation. Silver nitrate, montmorillonite (MMT), gelatin, glucose, NaOH, and silver plate were used as starting materials in this work. In UV irradiation method, Ag-NPs were prepared at different irradiation times (i.e., 1, 3, 18, 48, and 96 hr) in MMT and gelatin (i.e., 1, 3, 6,

18, 24, and 48 hr) as inorganic and organic matrix, respectively. UV-vis spectra and transmission electron microscopy (TEM) images demonstrate the particles size of Ag-NPs decrease with the increase of UV irradiation time. In γ-irradiation method, when the irradiation dose was increased (from 5 to 50 kGy); the mean size of particles reduced continuously (from 20.4 to 16.4 nm) due to the γ-induced Ag-NPs fragmentation. In PLA technique it was found smaller particle size distributions of Ag-NPs were obtained with smaller repetition rates and longer laser ablation times. Also, the UV-vis and TEM images demonstrated that the mean diameter of Ag-NPs increased (from 8.9 to 14.7 nm) as the laser repetition rate was increased (from 10 to 40 Hz). The use of inexpensive chemicals and non-toxic solvents – environmentally friendly and renewable/biodegradable – are central to materials synthesis. The green chemistry rules were applied for preparation of Ag-NPs in gelatin using glucose as a reducing agent, where the particle diameters of Ag-NPs at different temperatures and reaction times were investigated. It was found that with increasing of reaction times (from 6 to 48 hr) the size of Ag-NPs decreased (from 9.6 to 5.3 nm). The particle size of Ag-NPs obtained in gelatin solutions (3.7 nm) is smaller than in gelatin-glucose solutions (5.3 nm) which can be related to rate of reduction reaction. The stability of prepared Ag-NPs, as shown by UV-vis spectral analysis, was significant. The obtained Ag-NPs were characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM). In addition, the Ag-NPs prepared in this work may have value for the creation of antibacterial and antimicrobial paints and coatings for household materials, surgical and food storage equipments.

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

PENYEDIAAN DAN PENCIRIAN NANOPARTIKEL PERAK DALAM MONTMORILONIT DAN GELATIN MENGGUNAKAN KAEDAH FIZIK DAN KIMIA

Oleh

MAJID DARROUDI

April 2011

Pengerusi : Profesor Madya Mansor Bin Ahmad, PhD

Fakulti : Institut Teknologi Maju

Nanozarah logam dalam bahan organik dan bukan organik telah menghasilkan bahan baharu yang mempamerkan ciri optikal, mangkin dan biologi unik yang menjadikan bahan tersebut menarik untuk kegunaan dalam pelbagai bidang. Cabaran yang sukar dalam penghasilan nanozarah ialah pergumpalan zarah atau mendakan. Fenomena ini dapat dielakkan dengan menstabilkan nanozarah menggunakan polimer yang sesuai atau bahan kimia sebagai penstabil koloid. Tesis ini menerangkan kaedah penyediaan yang berbeza dan pencirian nanozarah perak (Ag-NPs) dalam bahan organik dan bukan organik serta kegunaan lain yang berpotensi. Kaedah yang telah digunakan merangkumi kaedah kimia hijau dan kaedah fizikal seperti sinaran UV, penghakisan laser (PLA), dan sinaran-γ. Argentum nitrat, montmorillonit (MMT), gelatin, glukos, NaOH, dan kepingan perak digunakan sebagai bahan pemula dalam kajian ini. Untuk kaedah sinaran UV, Ag-NPs telah dihasilkan pada tempoh sinaran yang berbeza (1, 3,

18, 48, dan 96 jam) dalam MMT dan gelatin (1, 3, 6, 18, 24, dan 48 jam), masing-masing sebagai matriks bukan organik dan organik. Hasil spektra sinaran UV dan imej mikroskop elektron transmisi (TEM) bagi Ag-NPs menunjukkan saiz zarah menurun apabila tempoh sinaran UV ditingkatkan. Bagi sinaran-γ, apabila dos sinaran ditingkatkan (daripada 5 ke 50 kGy) saiz purata zarah menurun secara berterusan (daripada 20.4 ke 16.4 nm) disebabkan oleh kesan γ dalam fragmentasi Ag-NPs. Untuk teknik PLA, sebaran saiz zarah Ag-NPs lebih kecil diperoleh pada kadar pengulangan kecil dan jangka masa penghakisan yang lebih lama. Keputusan spektra sinaran UV dan imej TEM juga menunjukkan purata diameter Ag-NPs meningkat (daripada 8.9 ke 14.7 nm) dengan peningkatan kadar pengulangan laser (daripada 10 ke 40 Hz). Penggunaan bahan kimia kos rendah dan pelarut tidak toksik – mesra alam dan boleh diperbaharui/terurai – adalah penting bagi sintesis bahan. Peraturan kimia hijau telah diaplikasikan bagi penyediaan Ag-NPs dalam gelatin menggunakan glukosa sebagai agen penurunan, di mana diameter zarah Ag-NPs yang terhasil pada suhu dan tempoh tindak balas yang berbeza telah dikaji. Didapati peningkatan tempoh tindak balas (daripada 6 ke 48 jam) menyebabkan saiz Ag-Nps berkurangan (daripada 9.6 ke 5.3 nm). Saiz zarah Ag-NPs dalam gelatin didapati lebih kecil (3.7 nm) daripada zarah dalam larutan gelatin-glukos (5.3 nm) yang dapat dikaitkan dengan kadar tindak balas penurunan. Kestabilan Ag-NPs, seperti ditunjukkan melalui analisis spektra UV, adalah sangat signifikan. Ag-NPs yang terhasil telah diciri menggunakan pembelauan sinar-X (XRD) dan microskop daya atom (AFM). Sebagai tambahan, penyediaan Ag-NPs dalam kajian ini kemungkinan berguna untuk penciptaan cat dan litupan anti-bakteria dan anti-mikrobia bagi kegunaan alatan rumah, pembedahan dan peralatan penyimpanan makanan.

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, Assoc. Prof. Dr. Mansor Bin Ahmad 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; Assoc. Prof. Dr. Abdul Halim Abdullah, and Dr. Nor Azowa Ibrahim, for their invaluable suggestions, beneficial advices and their endless helps.

I wish to acknowledge my gratitude to all lecturers and staffs in Chemistry Department, 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 labmates; Kamyar Shameli, Reza Zamiri, and my dear friend Mr. Ali Khorsand Zak.

Majid Darroudi

April 2011

I certify that an Examination Committee has met on 08/04/2011 to conduct the final examination of Majid Darroudi on his Doctor of Philosophy thesis entitled " Preparation and characterization of silver nanoparticles in montmorillonite and gelatin using physical and chemical methods" 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 Phylosophy.

Members of the Examination Committee were as follows:

Prof. Dr. Anuar kassim
Department of Chemistry
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Assoc. Prof. Dr. Sidik Silong
Department of Chemistry
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Assoc. Prof. Dr. Mohamad Zaki Abd Rahman
Department of Chemistry
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Prof. Dr. M. M. Bettahar
Department of Chemistry
Faculty of Science
Universite Henri Poincare-Nancy
France
(External Examiner)

HASSANAH MOHD. GHAZALI, 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 fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Mansor B. Ahmad, PhD
Assoc. Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim Abdullah, PhD
Assoc. Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Nor Azowa Ibrahim, PhD
Senior Lecturer
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.

_____

Majid Darroudi

Date: 08 April 2011

ABSTRACT ii
ABSTRAK iv
ACKNOWLEDGMENTS vi
APPROVAL vii
DECLARATION ix
TABLE OF CONTENTS x
LIST OF TABLES xii
LIST OF FIGURES xiii
LIST OF ABBREVIATIONS xvi

CHAPTER

1 INTRODUCTION
1.1 Background of the study 1
1.2 Synthesis of M-NPs 2
1.3 Problem statements 4
1.4 Objectives of research 5

2 LITERATURE REVIEW
2.1 Nanomaterial properties 6
2.1.1 Surface area effect 6
2.1.2 Quantum size effect 8
2.1.3 Surface plasmon resonance (SPR) 9
2.2 Green synthesis of nanoparticles 11
2.2.1 Ag-NPs in clay matrix by physical irradiation methods 13
2.2.2 Ag-NPs in polymeric media by irradiation methods 16
2.2.3 Green reduced Ag-NPs in polymeric media 19
2.2.4 Ag-NPs in polymeric media using reducing agents 23
2.2.5 Effect of accelerator reagents in synthesis of Ag-NPs 28
2.3 Laser ablated Ag-NPs 29
2.4 γ-irradiated Ag-NPs 34
2.5 Characterization of nanomaterials 38

3 METHODOLOGY
3.1 Green synthesis methods of Ag-NPs 41
3.1.1 Synthesis of Ag-NPs in MMT by UV irradiation 41
3.1.2 Synthesis of Ag-NPs in gelatin by UV irradiation 42
3.1.3 Synthesis of Ag-NPs in gelatin and gelatin/glucose media 42

3.1.4 Time-dependent synthesis of Ag-NPs in gelatin/glucose media 43
3.1.5 Synthesis of Ag-NPs in gelatin/glucose using NaOH 44
3.2 Fabrication of Ag-NPs in gelatin media by pulsed laser ablation (PLA) 44
3.2.1 Fabrication of Ag-NPs in gelatin by PLA at different repetition rates 44
3.2.2 Fabrication of Ag-NPs in gelatin by PLA at different irradiation times 46
3.3 Preparation of Ag-NPs in gelatin by γ-irradiation 47

4 RESULTS AND DISCUSSIONS
4.1 Ag-NPs prepared in MMT by UV irradiation 49
4.2 Ag-NPs synthesized in gelatin by UV irradiation 56
4.3 Ag-NPs in gelatin and gelatin/glucose media 64
4.4 Ag-NPs synthesized in gelatin/glucose at different reaction times 70
4.5 Effect of NaOH in synthesis of Ag-NPs in gelatin 75
4.6 Ag-NPs fabricated in gelatin by PLA at different repetition rates 81
4.7 Ag-NPs fabricated in gelatin by PLA at different irradiation times 87
4.8 Ag-NPs prepared in gelatin by γ-irradiation 94

5 CONCLUSION AND RECOMMENDATIONS FOR FUTURE STUDY 103
REFERENCES 108
BIODATA OF STUDENT 122
LIST OF PUBLICATION 123