UNIVERSITI PUTRA MALAYSIA

STRUCTURE, OPTICAL AND ELECTRICAL PROPERTIES OF POLYANILINE ENCAPSULATED NICKEL, COBALT, AND CHROMIUM NANOPARTICLES SYNTHESIZED BY GAMMA RADIATION

ABDO MOHAMMED ALI MEFTAH

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By

ABDO MOHAMMED ALI MEFTAH

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

January 2012

In the Name of Allâh, the Most Gracious, the Most Merciful

ان الله يمسك السماوات والارض ان تزولا ولئن زالتا ان امسكهما من احد من بعده انه كان حليما غفورا

Surely Allah upholds the heavens and the earth lest they come to naught; and if they should come to naught, there is none who can uphold them after Him; surely He is the Forbearing, the Forgiving.

Al-Quran, 35:41

DEDICATION

To the Soule of my brother Emad Yahya rewards him with paradise. To my patientful wife Dr.Muneera , my son and daughter Muhib and Maria and those who are sincerely pray for my success.

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

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Chairman: Professor Elias Saion, PhD

Faculty: Science

Nanomaterials have attracted much attention recently because of their many applications including in catalysis, microelectronics, biomedicine and photovoltaics. The composites of conducting polymer – magnetic metal nanoparticles are promising candidates based on the fact that the small sized particles enhance their physical properties while the conducting polymer matrix present electrical host – guest interaction to have a new magneto-electric phenomenon to occur at the same time, allowing coupling between magnetic and electric properties for future devices. Among the conducting polymers, polyaniline (PANI) has been of particular interest because of its environmental stability and controllable electrical conductivity and dissipation of electrostatic charges. In this work PANI was used to encapsulate nickel (Ni), cobalt (Co), and chromium (Cr) magnetic nanoparticles in polyvinyl alcohol (PVA) aqueous and film matrix. The solution composites were synthesized from aniline monomer (0.067 g), nickel, cobalt, and chromium chlorides at different concentrations (0.017, 0.025, 0.033, 0.042, and 0.5 g), and PVA (0.1 g), 10 ml

deionized water and completed by irradiation at doses of 0, 1, 2, 3, 4, 5 and 6 kGy. The film composites were made from aniline monomer (4 g), nickel, cobalt, and chromium chlorides at different concentrations (1, 1.5, 2, 2.5, and 3 g), and PVA (6 g) and completed by gamma irradiation at doses of 0, 10, 20, 30, 40 and 50 kGy. No chemical reducing or oxidising agent was used to synthesis metal nanoparticles or PANI.

The structural and morphology of metal nanoparticles in PVA solutions were studied using x-ray diffraction, atomic force microscopy, photon cross correlation spectroscopy, and transmission electron microscopy. The average particle size distributions in solution were found in the range of 22 – 54 nm for Ni nanoparticles, 14 – 50 nm for Co nanoparticles and 3 – 13 nm for Cr nanoparticles. The particle sizes of metal nanoparticles were controlled by the concentration of metal ions and radiation doses. The average diameter of Ni, Co and Cr nanoparticles decreased exponentially with the increase of dose D and fitted the expression of $d = d_{max} - B(1-e^{-D/D_0})$, with D_0 equal 2.2, 1.53, and 1.4 kGy for Ni, Co and Cr nanoparticles respectively.

A UV-visible spectrophotometer was used to measure optical characteristics of composites of PANI/Ni, PANI/Co and PANI/Cr nanoparticles. The maximum absorbance peaks λ_{max} appear at about 395, 520, 420 nm for Ni, Co, Cr nanoparticles respectively for both solution and film composites. The absorption peaks λ_{max} blue-shift towards shorter wavelengths with the increase of dose attributing to a decrease in the average diameter of metal nanoparticles with increasing dose. As a result, the conduction band increases with increase of radiation dose or decrease of particle size. The confinement effects of conducting band can be explained fundamentally in terms of the quantum mechanical description in which by reducing the nanoparticle size,

the number of atoms to form a nanoparticle is also reduced and less protons attracting the conduction electrons, thus enlarging the conduction band energy of metal nanoparticles.

The optical absorbance peaks of PANI in solution composites appear at 620, 670, and 580 nm for PANI/Ni, PANI/Co, and PANI/Cr nanoparticles respectively. However, the absorbance peaks shifted to 720, 670, and 580 nm for film composites of PANI/Ni, PANI/Co and PANI/Cr nanoparticles respectively. The band gap of PANI decreased with increase of dose and increased with increase of chloride ion concentration. When the dose increased from 10 to 50 kGy, the band gap of PANI films decreases from 1.56 to 1.4 eV and from 1.54 to 1.33 eV for 10, and 22.5 wt% $NiCl_2$ respectively; from 1.8 to 1.71 eV and from 1.72 to 1.67 eV for 10 and 22.5 wt% $CoCl_2$ respectively; and from 1.92 to 1.87 eV and from 1.89 to 1.83 eV for 10 and 22.5 wt% $CrCl_3$ respectively.

The conductivity measurement reveals that the dc conductivity of PANI in film composites increased with increase of dose and ion concentration. When the dose increased from 10 to 50 kGy, the conductivity of PANI decreases from 2.38×10^{-4} to 5.98×10^{-3} (S/m) and from 7.10×10^{-4} to 3.48×10^{-2} (S/m) for 10 and 22.5 wt% of $NiCl_2$ respectively; from 1.13×10^{-4} to 2.01×10^{-3} (S/m) and from 7.16×10^{-4} to 8.03×10^{-2} (S/m) for 10 and 22.5 wt% of $CoCl_2$ respectively; from 3.68×10^{-5} to 1.60×10^{-3} (S/m) and from 2.69×10^{-4} to 1.68×10^{-3} (S/m) for 10 and 22.5 wt% of $CrCl_3$ respectively. The dc conductivity has an exponential expression of the form: $\sigma_{dc} = \sigma_0 \exp(D/D_0)$, where the σ_0 and D_0 vary with ion concentration.

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

CIRI-CIRI STRUKTUR, OPTIK DAN ELEKTRIK KOMPOSIT POLIANILIN BERKAPSUL NIKEL, KOBALT, AND KROMIUM ZARAHNANO DISINTISIS DENGAN KAEDAH SINAR GAMMA

Oleh

ABDO MOHAMMED ALI MEFTAH

Januari 2012

Pengerusi: Profesor Elias Saion, PhD

Faculti: Sains

Bahannano telah menjadi tarikan akhir-akhir ini kerana banyak kegunaannya termasuk dalam pemangkinan, mikroelektronik, bioperubatan dan fotovoltan. Komposit polimer konduksi – zarahnano logam magnet adalah calon harapan berdasarkan kepada saiz zarah kecil yang boleh menambahbaik ciri-ciri fizik manakala matrik polimer konduksi membolehkan tindakbalas ala rumah - tetamu dengan kehadiran suatu fenomenon baharu iaitu magneto-elektrik yang berlaku pada masa yang sama untuk membenarkan hubungan di antara ciri magnet dan ciri elektrik sebagai peranti masa hadapan. Diantara polimer konduksi, polianilin (PANI) adalah yang teristimewa kerana mempunyai kesatabilan persekitaran dan keboleh kawalan kekonduksian elektrik dan penyebaran cas elektrostatik. Di sini PANI digunakan untuk menyalut zarahnano magnet nikel (Ni), kobolt (Co), and kromium (Cr) dalam larutan dan film alkohol polivinal (PVA). Komposit larutan disintisis daripada monomer analin (0.067 g), nikel, kobalt, and kromium klorida pada kepekatan berbeza (0.017, 0.025, 0.033, 0.042 dan 0.5 g), PVA (0.1 g), dan 10 ml air ternyah ion lalu disempurnakan dengan penyinaran sinar gama pada dos 0, 1, 2, 3, 4,

5 dan 6 kGy. Komposit film pula disintisis daripada monomer analin (4 g), nikel, kobalt, and kromium klorida pada kepekatan berbeza (1, 1.5, 2, 2.5, and 3 g) dan PVA (6 g) lalu disempurnakan dengan penyinaran sinar gama pada dos 0, 10, 20, 30, 40 dan 50 kGy. Tiada bahan kimia penurunan atau pengoksidan digunakan untuk sintensis zarahnano logam atau PANI.

Struktur dan marfologi zarahnano logam dalam larutan PVA dikaji dengan menggunakan The structural and morphology of metal nanoparticles in solutions were studied using belauan sinar-x, mikroskopi daya atom, spektroskopi korelasi silang foton dan mikroskopi electron transmisi. Taburan saiz zarah purata dalam larutan ialah dalam julat 22 – 54 nm untuk zarahnano Ni, 14 – 50 nm untuk zarahnano Co dan 3 – 13 nm untuk zarahnano Cr. Saiz zarahnano logam dikawal oleh kepekatan ion logam dan dos sinaran. Diameter purata zarahnano Ni, Co dan Cr berkurangan secara eksponen dengan pertambahan dos D dan memuaskan ungkapan $d = d_{\max} - B(1- e^{-D/D_0})$, dengan D_0 bersamaan dengan 2.2, 1.53, dan 1.4 kGy untuk masing-masing zarahnano Ni, Co and Cr.

Spektroskopi UV-cahaya tampak telah digunakan untuk mengukur ciri-ciri optik komposit PANI/Ni, PANI/Co and PANI/Cr zarahnano. Puncak penyerapan maksimum λ_{max} berlaku pada dearah 395, 520, 420 nm untuk masing-masing zarahnano Ni, Co, Cr. Puncak penyerapan maksimum λ_{max} melakukan anjakan-biru ke panjang gelombang yang lebih pendek dengan pertambahan dos kerana penggecilan saiz zarah dengan pertambahan dos. Kesan kepungan bagi jalur konduksi ini pada asasnya telah terangkan menurut mekanik kuantum dimana dengan pengurang saiz zarah bilangan atom untuk membentuk zarahnano adalah kecil bilangannya dan dengan ini kurang tarikan proton kepada electron konduksi, maka tenaga jalur konduksi zarahnano logam menjadi besar.

Puncak penyerapan optik PANI dalam komposit larutan berlaku pada 620, 670, dan 580 nm untuk masing-masing PANI/Ni, PANI/Co, dan PANI/Cr zarahnano. Bagaimanapun puncak penyerapan beranjak kepada 720, 670 dan 580 nm untuk komposit film masing-masing PANI/Ni, PANI/Co dan PANI/Cr zarahnano. Tenaga celah PANI berkurangan dengan dos dan bertambah dengan kepekatan ion klorida. Apabila dos ditambah daripada 10 ke 50 kGy, tenaga celah PANI berkurangan daripada 1.56 ke 1.4 eV dan daripada 1.54 ke 1.33 eV untuk masing-masing10, dan 22.5 wt% $NiCl_2$; daripada 1.8 ke 1.71 eV dan daripada 1.72 to 1.67 eV untuk masing-masing 10 dan 22.5 wt% $CoCl_2$; dan daripada 1.92 ke 1.87 eV dan daripada 1.89 to 1.83 eV untuk masing-masing 10 dan 22.5 wt% $CrCl_3$.

Pengukuran konduksi elektrik menunjukkan bahawa kekonduksian dc komposit film PANI bertambah dengan dos dan kepekatan ion. Apabila dos ditambah daripada 10 ke 50 kGy, kekonduksian PANI bertambah daripada 2.38×10^{-4} ke 5.98×10^{-3} (S/m) dan daripada 7.10×10^{-4} ke 3.48×10^{-2} (S/m) untuk masing-masing 10 and 22.5 wt% $NiCl_2$; daripada 1.13×10^{-4} ke 2.01×10^{-3} (S/m) dan daripada 7.16×10^{-4} ke 8.03×10^{-2} (S/m) untuk masing-masing 10 and 22.5 wt% $CoCl_2$; daripada 3.68×10^{-5} ke 1.60×10^{-3} (S/m) dan daripada 2.69×10^{-4} ke 1.68×10^{-3} (S/m) untuk masing-masing 10 dan 22.5 wt% $CrCl_3$. Kekonduksian dc mempunyai ungkapan eksponen dalam bentuk: $\sigma_{dc} = \sigma_0 \exp(D/D_0)$, dimana σ_0 dan D_0 berubah mengikut kepekatan ion.

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I certify that a Thesis Examination Committee has met on 17 January 2012 to conduct the final examination of Abdo Mohammed Ali Meftah on his thesis entitled "Structure, optical and electrical Properties of Polyaniline Encapsulated - (Ni, Co, Cr) nanoparticles synthesized by gamma radiation" 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 degree of Doctor of Philosophy.

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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:

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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.

ABDO MOHAMMED ALI MEFTAH

Date: 17 January 2012

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