UNIVERSITI PUTRA MALAYSIA

GAMMA RADIATION SYNTHESIS AND CHARACTERIZATION OF COLLOIDAL Al-Ni AND Al-Cu BIMETALLIC NANOPARTICLES

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By

ALAM ABEDINI

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

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DEDICATIONS

This thesis is dedicated to:

My beloved husband and my precious mother and father

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

GAMMA RADIATION SYNTHESIS AND CHARACTERIZATION OF COLLOIDAL Al-Ni AND Al-Cu BIMETALLIC NANOPARTICLES

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Chairman : Professor Elias Saion, PhD

Faculty : Science

The last two decades have seen remarkable progress in nanoscience and nanotechnology particularly in the synthesis of metal nanomaterials, aiming at finding better materials that have desired physical and chemical properties from enhancement of the surface and quantum confinement effects. Intermetallic aluminides such as Al-Ni and Al-Cu bimetallic nanoparticles have attractive properties for examples low densities, high strength and stiffness at elevated temperatures, strong resistances to mechanical, corrosion, acids and alkalis, and outstanding catalytic activity. They are of significant for wide potential applications in pigments, catalysts, and absorbents for Al-Cu bimetallic nanoparticles and in turbine blades, automobile engines, aircraft, electricity generation, and anode electrode materials for Al-Ni bimetallic nanoparticles. Such impressive characteristics and applications of Al-Ni and Al-Cu bimetallic

nanoparticles have led us to research their functional systems with the objectives to synthesize Al-Ni and Al-Cu bimetallic nanoparticles and characterize their morphological and crystal structures, optical properties, and reduction mechanism by examining the influence of absorbed dose and initial precursors concentration on the yield, particle size, size distribution, and conduction band energy of the synthesized nanocrystals.

Colloidal Al-Ni and Al-Cu bimetallic nanoparticles may be synthesized using various methods, including the chemical, photochemical, electrochemical, sonochemical, and radiolytic reduction techniques. Of these techniques, the radiation-induced synthesis offers additional benefits over the other conventional methods because it produces fully reduced and highly pure bimetallic nanoparticles with free from by-products or reducing agents, and is capable of controlling the particle size. In this work, colloidal Al-Ni and Al-Cu bimetallic nanoparticles were synthesized by gamma irradiation technique in aqueous solutions containing metal chlorides as precursors, polyvinyl alcohol (PVA) as a capping agent, isopropyl alcohol as a radical scavenger of hydroxyl radicals, and distilled water as a solvent. The initial precursor concentrations were between 3.5×10^{-5} and 4.5×10^{-5}mol/mL for $AlCl_3$ and between 1.5×10^{-5} and 1.9×10^{-5}mol/mL for both $NiCl_2$ and $CuCl_2$ with Al/Ni and Al/Cu mole ratios of 20/80, 30/70, 50/50, 70/30, and 80/20. All the samples were irradiated with 1.25-MeV ^{60}Co gamma rays at absorbed doses from 50 to 100 kGy for colloidal Al-Ni nanoparticles and from 60 to 120 kGy for colloidal Al-Cu nanoparticles. Gamma rays interact with matter in aqueous solution to produce secondary electrons, which induced reactive species such as solvated electrons and radicals by hydrolysis of water. These electrons and radicals are strong reducing agents that reduce metal ions into zero-valent atoms, the mechanism controlled by the redox potentials of the ions before the atoms agglomerated to form metal nanoparticles. The formation Al-Ni and Al-Cu bimetallic nanoparticles were characterized by energy dispersive X-ray spectroscopy (EDX), powder X-ray diffractometer (XRD), transmission electron microscopy (TEM), and UV-visible absorption spectrometry.

The XRD, TEM, and absorption analyses confirmed the formation of Al–Ni bimetallic alloy nanoparticles at all mole ratio, Al-Cu bimetallic alloy nanoparticles at lower Al/Cu molar ratio, and a mixture of Al-Cu bimetallic and bimetallic core-shell nanoparticles at higher Al/Cu mole ratio. The TEM analysis for particle size and size distribution revealed that the average particle size of Al-Ni and Al-Cu bimetallic nanoparticles decreased with the increase of absorbed dose and increased with the increase of precursor concentrations. The average diameter d decreases exponentially with dose D and increases exponentially with precursor concentration C can be represented by an empirical equation $d = d_{\max} - A(1 - e^{-D/D_0})$ and $d = d_{\min} + B(1 - e^{-C/C_0})$ respectively.The smallest particle sizes of 4.4 and 3.7 nm have been achieved for Al-Ni and Al-Cu nanoparticles respectively, which were obtained at the lowest precursor concentration and the highest absorbed dose. At higher doses, the amount of nucleation is more than unreduced ions and smaller particle sizes are produced. On the other hand, at lower doses nucleation events are less than the total initial metal ions and large particle sizes are produced owing to the fact that metal nanoparticles can be ionized again into larger ions before the metal ions reduce into larger metal nanoparticles by solvated electrons. At higher precursor concentrations the amount of unreduced ions is more than the amount of nucleation induced by radiation and larger particle sizes are produced.

The optical absorption spectra reveal that the absorption peaks blue shifted from 391 to 377 nm with the increase of dose from 50 to 100 kGy for Al-Ni nanoparticles and from 580 to 576 nm with the increase of dose from 60 to 120 kGy for Al-Cu nanoparticles, owing to a decrease of particle size with increasing dose. It was confirmed by the TEM measurements. This quantum confinement effect permits the conduction band energy increases from 3.17 to 3.29 eV for Al-Ni nanoparticles and from 2.139 to 2.154 eV for Al-Cu nanoparticles with decreasing particle sizes.

In conclusion, it was found that the absorbed dose and the precursors' molar ratio and concentration are key parameters to influence the composition, crystalline structure, particle size, size distribution, and optical properties the final products of colloidal Al-Ni and Al-Cu bimetallic nanoparticles stabilized in PVA. This is because the competition between nucleation, growth, and agglomeration processes in the formation of nanoclusters during and after irradiation by 1.25 MeV gamma rays.

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

SINTESIS SINARAN GAMA DAN PENCIRIAN KOLOID NANOPARTIKEL DWILOGAM Al-Ni DAN Al-Cu

Oleh

ALAM ABEDINI

Jun 2012

Pengerusi : Profesor Elias Saion, PhD

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Dua dekad yang lalu menyaksikan anjakan pembangunan yang menakjubkan di dalam bidang nanosains dan nanoteknologi terutamanya di dalam bidang sintesis nanobahan logam. Anjakan yang disasarkan adalah untuk mengenalpasti bahan-bahan yang mempunyai pencirian fizikal dan kimia daripada peningkatan saiz permukaan dan kesan pembatasan quantum. Nanopartikel intermetalik alumida seperti Al-Ni dan dwilogam Al-Cu mempunyai pencirian yang menarik seperti kepadatan yang rendah, kekuatan anjalan pada suhu tinggi, rintangan yang tinggi untuk mekanikal, kakisan, asid dan alkali serta sebagai bahan pemangkin yang efektif. Pencirian ini adalah penting untuk pelbagai aplikasi yang berpotensi di dalam pigmen, pemangkin dan penyerap untuk

nanopartikel dwilogam Al-Cu dan di dalam bilah turbin, enjin kereta, pesawat udara, penjanaan elektrik dan bahan-bahan anod elektrod untuk nanopartikel dwilogam Al-Ni. Ciri-ciri yang memberansangkan yang dapat diaplikasi di dalam teknologi yang disebutkan tadi telah membawa kepada penyelidikan terhadap fungsi dengan memfokus kepada proses sintesis nanopartikel Al-Ni dan nanopartikel dwilogam Al-Cu dengan mengkaji struktur morfologi, struktur kristal, ciri-ciri optik mekanisme pengurangan dengan memeriksa dos terserap dan kepekatan prekursor awal terhadap hasil, saiz zarah, taburan saiz dan jalur tenaga kekonduksi nanokristal yang disintesis.

Koloid nanopartikel dwilogam boleh disintesis dengan menggunakan pelbagai kaedah, termasuk teknik kimia, fotokimia, elektrokimia, sonokimia, dan sinaran. Berbanding dengan teknik-teknik yang dinyatakan, sintesis sinaran gama menawarkan manfaat tambahan iaitu dari segi kesederhanaan, penurunan nanopartikel sepenuhnya, tiada keperluan mengurangkan bahan penurunan atau pemangkin, dan mampu mengawal saiz zarah. Dalam kajian ini, koloid Al-Ni dan Al-Cu nanopartikel dwilogam telah disintesis oleh teknik sinaran gama di dalam larutan akueus yang mengandungi klorida logam sebagai prekursor, polivinil alkohol (PVA) sebagai ejen penetapan, isopropanol sebagai fungsi penyingkiran radikal-radikal hidroksil dan air suling sebagai pelarut. Kepekatan awal adalah di antara 3.5×10^{-5} dan 4.5×10^{-5}mol/mL untuk $AlCl_3$ dan antara 1.5×10^{-5} dan 1.9×10^{-5}mol/mL bagi kedua-dua $NiCl_2$ dan $CuCl_2$ dengan nisbah molar Al / Ni dan Al/Cu adalah 20/80, 30/70, 50/50, 70/30, dan 80/20. Terdahulu, semua sampel disinarkan dengan 1.25 MeV sinar gama ^{60}Co pada dos terserap dari 50 hingga 100 kGy untuk nanopartikel Al-Ni koloid dan 60-120 kGy untuk nanopartikel koloid Al-Cu.

Sinar gama ini berinteraksi dengan bahan-bahan dalam larutan akueus untuk menghasilkan elektron sekunder, yang mendorong kepada pengeluaran spesies reaktif seperti elektron dan radikal terhidrat oleh hidrolisis air. Elektron dan radikal ini adalah agen penurunan yang kuat untuk menurunkan ion logam menjadi atom-valent sifar, suatu mekanisme yang dikawal oleh kepuayaan redoks ion sebelum atom-atom digabungkan untuk membentuk nanopartikel logam. Pembentukan Al-Ni dan Al-Cu nanopartikel dwilogam telah dicirikan oleh spektroskopi serakan tenaga sinar-X (EDX), meter belauan serbuk sinar-X (XRD), mikroskopi penghantaran elektron (TEM), dan spektrometri penyerapan UV (UV-Vis).

Analisis XRD, TEM, dan penyerapan mengesahkan pembentukan nanopartikel aloi dwilogam Al-Ni pada kesemua nisbah mol, Al-Cu nanopartikel aloi dwilogam pada nisbah mol Al/Cu rendah, dan Al-Cu campuran dwilogam adan dwilogam teras-shell nanopartikel pada nisbah mol Al/Cu lebih tinggi. Analisis TEM untuk saiz zarah dan taburan saiz menunjukkan bahawa saiz purata zarah Al-Ni dan Al-Cu nanopartikel dwilogam menurun dengan peningkatan dos terserap dan meningkat dengan peningkatan kepekatan prekursor. Diameter purata d menurun secara eksponen dengan dos D dan meningkat mendadak dengan kepekatan prekursor C dan masing-masing boleh diwakili oleh persamaan empirik $d = d_{\max} - A\left(1 - \mathrm{e}^{-D/D_0}\right)$ dan $d = d_{\min} + B(1 - \mathrm{e}^{-C/C_0})$. Saiz zarah nanopartikel yang paling kecil adalah 4.4 nm untuk Al-Ni dan 3.7nm untuk Al-Cu yang mana ia diperolehi pada kepekatan prekursor yang paling rendah dan dos terserap tertinggi. Pada dos yang lebih tinggi jumlah penukleusan adalah lebih daripada ion yang belum diturunkan kepada atom maka saiz zarahy ang lebih kecil telah terhasil. Sebaliknya, pada dos yang lebih rendah peristiwa penukleusan kurang daripada jumlah awal ion logam dan saiz zarah yang besar dihasilkan menurut kepada fakta bahawa nanopartikel logam boleh terion lagi ke ion yang lebih besar sebelum ion logam diturunkan ke pada nanopartikel logam yang lebih besar oleh elektron terhidrat. Pada kepekatan prekursor yang lebih tinggi jumlah ion awal adalah lebih daripada jumlah penukleusan yang didorong oleh penyinaran gama dan saiz zarah yang lebih besar telah dihasilkan.

Spektrum penyerapan optik mendedahkan bahawa penyerapan puncak biru beralih dari 391 hingga 377nm dengan peningkatan dos 50-100 kGy nanopartikel untuk Al-Ni dan 580-576 nm dengan peningkatan dos dari 60 hingga 120kGy untuk Al-Cu nanopartikel, yang mana ia bergantung kepada pengurangan saiz zarah dengan peningkatan dos. Ianya dibuktikan dengan pengukuran menggunakan TEM. Kesan pembatasan kuantum ini membenarkan meningkatkan jalur konduksi daripada 3.17 ke 3.29 eV untuk nanopartikel Al-Ni dan daripada 2.139 ke 2.154 eV untuk nanopartikel Al-Cu dengan saiz zarah berkurangan.

Kesimpulannya, dapat dinyatakan di sini bahawa dos terserap dan nisbah mol prekursor serta kepekatan parameter adalah parameter-parameter yang mempengaruhi komposisi, struktur kristal, saiz zarah,taburan saiz dan ciri-ciri optik produk akhir koloid Al-Ni dan Al-Cu nanopartikel dwilogam yang di stabil kan dalam PVA. Ini adalah disebabkan oleh persaingan antara proses-proses penukleusan, pertumbuhan, dan aglomerasi dalam pembentukan nanokluster semasa dan selepas penyinaran oleh 1.25 MeVsinar gama.

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I certify that an Examination Committee has met on (29 June 2012) to conduct the final examination of Alam Abedini on her Doctor of Philosophy thesis entitled " **Gamma radiation synthesis and characterization of colloidal Al-Ni and Al-Cu bimetallic nanoparticles"** 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.

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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.

ALAM ABEDINI

Date: 29/June/2012

TABLE OF CONTENTS