UNIVERSITI PUTRA MALAYSIA

THEORY, SYNTHESIS, AND CHARACTERIZATION OF COLLOIDAL PLATINUM NANOPARTICLES

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By

ELHAM GHARIBSHAHI

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

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DEDICATION

I lovingly dedicate this thesis to my sweet heart and my dearest in my life, my loving husband "Ahmadreza" and my sweetie son "Sina" for their endless love, support and encouragement. I give my deepest expression of love and appreciation for the encouragement that they gave me and the sacrifices they made during this graduate program, love both with all my heart and soul.

Elham Gharibshahi

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

THEORY, SYNTHESIS, AND CHARACTERIZATION OF COLLOIDAL PLATINUM NANOPARTICLES

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Chairman: **Professor Elias Saion, PhD**

Faculty: **Science**

The immense interest in nanoscience nowadays confined within the metal nanoparticles, semiconductor quantum dots, colloids, and clusters of nanoscale dimensions of 1 – 100 nm from the fact that they possess fundamentally discrete electronic states that cause quantum confinement effects of optical, electronic, electrical, and magnetic properties which are substantially different from those of their bulk and useful in technological applications. Metal nanoparticles in particular, exhibit unique optical absorption phenomenon caused by conduction electrons excitation simulated by electromagnetic field of light, which may be described by quantum or classical physics. However, the classical physics models based on Maxwell's equations deal only with a continuous system and free electrons, thus neglecting the discrete nature of electronic structures of metal nanoparticles.

The first objective of the thesis is to establish a new theory of metal nanoparticles based on the intra-band quantum excitation of conduction electrons from the lowest energy states to higher energy states induced by the electromagnetic photon. Metal

nanoparticles possess both geometrical and electronic structures, which are thermodynamically stable. The geometrical structure has a minimum isotropic surface energy resulting symmetrically perfect sphere made of Bravais lattice structure. The electronic structure follows the spherical Jellium model and the Thomas-Fermi-Dirac-Weizsacker Model for the density energy functional of conduction electrons at the ground state density satisfying the density functional theory fundamental, where the electron density $\rho(r)$ is the basic quantity. However, using a continuous relationship between the density and absorption, the absorption energy functional is derived and solved numerically using Newton iterative integration method. We simulated the single-band absorption spectra of Al, Ag, Au, and Co nanoparticles of various particle sizes of 4-50 nm and found the conduction band energy decreases sharply with increasing particle size. The agreement between the measured absorption maxima found from literatures and our calculated values encouraged us to extend our simulation for the double-band absorption spectra of Ru, Ce, and Pt nanoparticles at 4 nm size. Two absorption maxima in UV and visible wavelength regions are witnessed but no experimental data in literature worth comparing with our calculation. This led us to the second objective of the thesis, which is to synthesize Pt nanoparticles and exploited the optical absorption results and verify that the theory is applicable also to metal nanoparticles with the double-band absorption spectra.

Attempts to produce colloidal Pt nanoparticles with steady absorption spectra previously by various chemical reduction methods often ended up in fast disappearance of the absorption maxima, which open to a speculative interpretation on their optical properties. Stable colloidal Pt nanoparticles were successfully synthesized using the gamma radiolytic method in aqueous solution containing platinum tetraammine chloride ($Pt(NH_3)_4Cl_2.H_2O$) as metal precursor, polyvinyl pyrrolidone (PVP) as capping agent,

isopropyl alcohol as radical scavengers of hydrogen and hydroxyl radicals, and tetra hydrofuran and deionized water as solvents for $Pt(NH_3)_4Cl_2$ and PVP respectively. Nitrogen was bubbled through the homogeneous solutions before they were irradiated with ^{60}Co gamma-rays of different doses without a reducing agent. The synthesized Pt nanoparticles were characterized using XRD, TEM, and UV-visible spectroscopy.

The XRD peaks showed the FCC crystalline structure with a lattice parameter of 0.3924 nm. The TEM images confirmed Pt nanoparticles were a spherical shape with the mean particle size decreased from 5.8 to 2.7 nm with increasing dose from 80 to 120 kGy and increased with increasing Pt ions concentration (5.0 - 20.0) $\times 10^{-4}$ M. The synthesized Pt nanoparticles were fully reduced and highly pure demonstrated by steady double-band absorption maxima in the regions of 215 and 265 nm, which blue shifted to lower wavelengths with increasing dose due to decrease of particle size. The absorption maxima originated from the intra-band quantized transitions of conduction electrons of energy state with quantum numbers of $\{ n = 5;\ l = 2$ or 5d $\}$ to higher energy states with quantum numbers of $\{ n \geq 6\ ; \Delta l = 0,\ \pm 1; \Delta s = 0,\ \pm 1 \}$ for the absorption maxima of 215 nm and from energy state with quantum numbers $\{ n = 6;\ l = 0$ or 6s $\}$ to higher energy states with quantum numbers of $\{ n \geq 7\ ; \Delta l = 0;\ \Delta s = 0 \}$ for the absorption maxima of 265 nm. To study this possibility, we calculated the absorption spectra of Pt nanoparticles of spherical diameters similar to those obtained from the experiment in the regions from 2.7 to 5.8 nm. We found good agreement between the experimental data of conduction bands and the theoretical conduction bands within less than 1% variance. This suggests that intra-band quantized excitation of conduction electrons can occur in metal nanoparticles and the new theory is fundamentally valid to describe the quantum mechanical absorption phenomenon in metal nanoparticles.

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

TEORI, SINTISIS DAN PENCIRIAN NANOPARTIKEL PLATINUM KOLODIAL

Oleh

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Kepentingan besar dalam nanosains kini terbatas kepada nanopartikel logam, bintik kuantum semikonduktor, koloid, dan kluster berdimensi nanoskala 1 - 100 nm yang menunjukkan fakta bahawa mereka mempunyai keadaan elektronik asas diskret yang menyebabkan kesan kuantum pergantungan saiz sifat-sifat optik, elektronik, elektrik, dan magnet amat berguna dalam aplikasi teknologi yang ketara perbezaannya daripada keadaan pukal mereka. Khasnya nanopartikel logam mempamerkan fenomena unik penyerapan optik yang disebabkan oleh penujaan elektron konduksi disimulasi oleh medan elektromagnet cahaya, yang boleh digambarkan dalam kedua-dua fizik kuantum dan klasik. Walau bagaimanapun, model fizik klasik berdasarkan persamaan Maxwell yang bekait dengan sistem berterusan dan elektron bebas, sekali gus mengabaikan sifat diskret struktur elektronik nanopartikel logam.

Bahagian pertama objektif tesis ini adalah dikhaskan untuk menerbitkan teori baru nanopartikel logam berdasarkan pergujaan kuantum intra-jalur bagi elektron konduksi dari keadaan tenaga terendah kepada keadaan tenaga yang lebih tinggi diinduksikan oleh foton elektromagnet. Nanopartikel logam mempunyai struktur kedua-dua geometri

dan elektronik, yang keadaan termodinamiknya stabil. Struktur geometri mempunyai tenaga permukaan isotropi minimum mengakibatkan ia berbentuk sfera simetri sempurna mengikut struktur kekisi Bravais. Struktur elektronik pula mengikut model sfera Jellum dan model tenaga ketumpatan berfungsi Thomas-Fermi-Dirac-Weizsäcker bagi elektron konduksi pada ketumpatan keadaan asas yang memuaskan teori ketumpatan berfungsi, di mana ketumpatan elektron $\rho(r)$ adalah kuantiti asasnya. Walau bagaimanapun, dengan menggunakan hubungan berterusan antara ketumpatan dan penyerapan, penyerapan tenaga berfungsi dibangunkan dan diselesaikan secara berangka menggunakan kaedah Newton integrasi lelaran. Kami simulasikan spektrum penyerapan jalur tunggal bagi nanopartikel Al, Ag, Au, dan nanopartikel Co pada pelbagai saiz 4-50 nm dan mendapati tenaga jalur konduksi berkurangan mendadak dengan peningkatan saiz naanopartikel. Persetujuan diantara penyerapan maksima diukur yang didapati daripada ulasan karya dan nilai yang kami kira menggalakkan kami untuk melanjutkan simulasi untuk spektrum penyerapan jalur-dedua bagi nanopartikel Ru, Ce, dan Pt pada saiz 4 nm. Kami mendapati dua puncak penyerapan maksima di rantau panjang gelombang UV dan tampak dihasilkan tetapi tiada data eksperimen daripada ulasan karya ternilai dapat dibandingkan dengan pengiraan kami. Ini menyampaikan kami kepada objektif kedua tesis ini, iaitu mensintesis nanopartikel Pt dan digunakan hasil penyerapan optik untuk menentusahkan teori baharu ini terpakai juga untuk nanopartikel logam yang mempunyai spectrum penyerapan jalur dedua.

Percubaan untuk menghasilkan nanopartikel Pt koloid mempunyai spektrum penyerapan yang mantap sebelum ini oleh pelbagai kaedah pengurangan kimia sering berakhir dengan kehilangan cepat penyerapan maksima, yang terbuka untuk tafsiran spekulatif pada sifat optiknya. Nanopartikel Pt koloid yang stabil telah berjaya disintesis menggunakan kaedah gamma radiolytic dalam larutan akueus yang mengandungi

tetraammine platinum klorida ($Pt(NH_3)_4Cl_2.H_2O$) sebagai pelopor logam, pyrrolidone polyvinyl (PVP) sebagai ejen menutup, isopropyl alkohol sebagai pembangkai radikal hidrogen dan radikal hidroksil, dan tetra hydrofuran dan air ternyahion sebagai pelarut untuk masing-masing $Pt(NH_3)_4Cl_2$ dan PVP. Gas nitrogen telah dipam melalui larutan homogen sebelum mereka telah sinarkan dengan ^{60}Co sinar-gama pada dos yang berbeza tanpa ejen mengurangan. Nanopartikel Pt yang telah disintesis dicirikan dengan menggunakan XRD, TEM, dan spektroskopi UV tampak.

Puncak XRD menunjukkan struktur kristal FCC dengan parameter kekisi 0.3924 nm. Imej-imej TEM mengesahkan nanopartikel Pt bentuk sfera dengan saiz zarah min menurun daripada 5.8 kepada 2.7 nm dengan dos meningkat 80-120 kGy dan meningkat dengan pertambahan ion Pt (5.0 - 20.0) $\times 10^{-4}$ M . Nanopartikel Pt yang disediakan telah sepenuhnya diturunkan dan ia sangat tulen keadaanya yang disahkan oleh penyerapan maksima jalur-dedua mantap dapat dilihat dalam kawasan 215 dan 265 nm, yang beranjakan biru kepada panjang gelombang yang lebih rendah dengan dos yang semakin meningkat disebabkan oleh pengurangan saiz nanopartikel. Penyerapan maksima berasal dari peralihan terkuantum intra-jalur bagi elektron konduksi daripada keadaan tenaga terendah bernombor kuantum $\{ n = 5;\ l = 2$ atau 5d$\}$ ke keadaan tenaga yang lebih tinggi berkuantum nombor $\{ n \geq 6\ ; \Delta l = 0,\ \pm 1\ ; \Delta s = 0,\ \pm 1 \}$ untuk penyerapan maksima 215 nm dan dari keadaan tenaga bernombor kuantum $\{ n = 6;\ l = 0$ atau 6s$\}$ kepada keadaan tenaga yang lebih tinggi bernombor kuantum $\{ n \geq 7\ ; \Delta l = 0;\ \Delta s = 0 \}$ untuk penyerapan maksima 265 nm. Untuk mengkaji kemungkinan ini, kami mengira spektrum penyerapan nanopartikel Pt berbentuk sfera dengan diameter sama dengan yang diperolehi dari eksperimen dalam kawasan 2.7-5.8 nm. Kami mendapati satu persetujuan yang baik diantara jalur konduksi eksperimen dan jalur konduksi teori dengan variasi kurang daripada 1%. Ini menunjukkan bahawa pengujaan terkuantum

intra-jalur bagi elektron konduksi boleh berlaku dalam nanopartikel logam dan teori baru pada asasnya sah untuk menggambarkan fenomena mekanik kuantum penyerapan nanopartikel logam tersebut.

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I certify that a Thesis Examination Committee has met on 25 June 2013 to conduct the final examination of Elham Gharibshahi on her thesis entitled "Theory, Synthesis, and Characterization of Colloidal Platinum 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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DECLARATION

I hereby 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.

ELHAM GHARIBSHAHI

Date: 25 June 2013

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