GAMMA RADIATION SYNTHESIS AND CHARACTERIZATION OF SILVER AND GOLD NANOPARTICLES IN POLYMER MATRICES

By

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Nanoparticles are referred to nanostructure materials having dimensions in the range of 1 – 100 nm and typically contain few hundred to few thousand atoms. They may compose of single or more elements to form zero-dimensional nanomaterials such as metal nanoparticles, semiconductor quantum dots, colloids, and clusters. Nanoparticles exhibit unusual optical, electronic, magnetic and chemical properties dissimilar to the properties of their molecular and bulk materials due to their quantized nature and large surface area-to-volume ratios. Noble metal nanoparticles such as silver (Ag) and gold (Au) nanoparticles embedded in polymer matrices present high catalytic activity, remarkable optical effects such as light absorption, surface enhanced Raman scattering (SERS), and extraordinary optoelectronic and electronic properties useful for biosensors and electronic devices. The shape, size,
and nanoparticle distribution density of metal nanoparticles and the ambient conditions are crucial parameters to understand the physics and chemistry phenomena of matter at nanometer scales. The potential technological applications depend on our capability to control these parameters during synthesis.

Of various reduction methods including chemical, photochemical, electrochemical, and sonochemical techniques, the radiation-induced production method offers clean, harmless, controllable size, highly pure and stable nanoparticles, and free from reducing agents or impurities. In this works, colloidal Ag and Au nanoparticles were synthesized using gamma-radiation method by reducing silver ions of silver nitrate \((\text{AgNO}_3\) concentration between \(3.7 \times 10^{-4}\) and \(21.0 \times 10^{-4}\) M) and gold ions of tetrachloroauratehydrate \((\text{HAuCl}_4\) concentration between \(1.0 \times 10^{-4}\) and \(7.5 \times 10^{-4}\) M) stabilized by 4.7% poly(vinyl alcohol) (PVA) and 5.6% poly(vinyl pyrrolidone) (PVP). All the samples at different concentrations of silver and gold salts were irradiated with doses of 10, 20, 30, 40, 50, 60, 70 kGy using a \(^{60}\text{Co}\) \(\gamma\)-rays radiation source. Upon gamma irradiation, free electrons, hydrated electrons, and free radicals that are produced able to produce the \(\text{Ag}^+\) and \(\text{Au}^{3+}\) ions into \(\text{Ag}^0\) and \(\text{Au}^0\) atoms prior to an aggregation to form \((\text{Ag}^0)_n\) and \((\text{Au}^0)_n\) nanoparticles respectively. The formation of Ag and Au nanoparticles have been observed by the change in color of the colloidal samples from colorless to golden yellow for Ag nanoparticles and to red for Au nanoparticles. The presence of Ag and Au metals were confirmed by the Energy Dispersive X-ray Spectroscopy (EDX) elemental analysis.

The size of Ag and Au nanoparticles were determined at 90% cumulative distribution of the Photon Cross Correlation Spectroscopy (PCCS) and confirmed by
the Transmission Electron Microscopy (TEM). The average diameter of colloidal Ag and Au nanoparticles decreases with increasing dose and increases with increasing starting salts concentration. The minimum diameters achieved were at 12 and 2 nm respectively for Ag and Au nanoparticles in PVP obtained from the lowest salts concentration and the highest radiation dose at 70 kGy. This radiation-induced nucleation event has been described as a dose-dependent process and the kinetics of nucleation of Ag and Au nanoparticles stabilized in PVA and PVP have been quantitatively studied. At high doses, where the nucleation event is more than the total metal ions, the radiation synthesis produced smaller sizes of nanoparticles following aggregation. On the other hand, at low doses were the nucleation event is less than the total metal ions, the radiation synthesis produced larger sizes of nanoparticles. The shape of Ag and Au nanoparticles were spherical in shape as determined by TEM method.

The optical properties of Ag and Au nanoparticles were measured by means of UV-Visible absorption spectrophotometer. The presence of Ag and Au nanoparticles was revealed at the absorption peaks between 400 and 425 nm for Ag nanoparticles and between 500 and 550 nm for Au nanoparticles depending on the salts concentration and radiation dose. The maximum absorbance of the colloidal Ag and Au nanoparticles increases with increasing radiation dose, indicating an increase of the nanoparticle distribution density of Ag and Au nanoparticles at higher doses. Exceptional for radiation-induced synthesis, the absorption peaks shifted to lower wavelengths or blue-shift with increasing radiation dose indicating the diameter of Ag and Au nanoparticles decreases with increasing dose. Consequently, this gave a confinement effect on the conduction band of Ag and Au nanoparticles, which
increases with the decrease of nanoparticle diameter. The fundamental characteristics of Ag and Au nanoparticles have been explained in terms of the quantum mechanical description for metal nanoparticles deviating from the more established concept of the surface Plasmon resonance derived from the classical electrodynamics theory.
Zarah-nano adalah merujuk kepada bahan nanostruktur yang mempunyai dimensi 1 – 100 nm dan mengandungi beberapa ratus hingga ribu bilangan atom. Ia terdiri daripada unsur tunggal atau lebih yang membentuk nanobahan dimensi-sifar seperti zarah-nano logam, dot kuantum semikonduktor, koloid, kulstur. Zarah-nano menunjukkan ciri-ciri optik, electronik, magnet, dan kimia yang berbeza dengan sifat molekul dan pukal bahan tersebut kerana ia mempunyai ciri kuantum semulajadi dan nisbah luas-terhadap-isipadu yang tinggi. Zarah-nano argentum (Ag) dan aurum (Au) tersalut dalam matrik polimer menunjukkan aktiviti pemangkinan yang tinggi, kesan optik seperti penyerapan cahaya yang hebat, perningkatan permukaan dalam penyerakan Raman, dan mempunyai ciri-ciri optoelektronik dan elektronik yang
berguna dalam pengesan dan peranti biologi. Bentuk, saiz dan ketumpatan zarah-nano serta keadaan persekitarannya merupakan parameter terpenting untuk memahami fenomena fizik dan kimia jirim dalam skalar nanometer. Kemampuan teknologi bagi menterjemah kegunaannya bergantung kepada kemampuan kita mengawal parameter-parameter tersebut semasa mengsintisis zarah-nano dilakukan. Daripada banyak kaedah-kaedah penurunan termasuk teknik kimia, fotokimia, elektrokimia dan sonakimia, kaedah penurunan induksi sinaran menawarkan yang terbaik kerana ia bersih, tidak mudaratkan alam sekitar, berkemampuan mengawal sais, zarah-nano yang dihasilkan ada tulin, stabil dan bebas daripada agen penurunan dan bahan asing. Dalam penyelidikan ini zarah-nano kodial Ag dan Au telah disentisis dengan menggunakan kaedah sinaran gama secara penurunan ion argentum daripada argentum nitrat (AgNO₃ kepekatan diantara $3.7 \times 10^{-4}$ dan $21.0 \times 10^{-4}$ M) dan penurunan ion aurum daripada tetraklorauratehidrat (HAuCl₄ kepekatan diantara $1.0 \times 10^{-4}$ dan $7.5 \times 10^{-4}$ M) dan distabilkan dalam 5% poly(vinyl alcohol) (PVA) and 6% poly(vinyl pyrolidone) (PVP). Semua sampel dalam kepekatan garam argentum dan aurum berbeza disenarkan dengan dos sinaran 10, 20, 30, 40, 50, 60, 70 kGy menggunakan sumber γ-ray $^{60}$Co. Semasa sinaran gama, pembentukan elektron-elektron bebas, electron-elektron hidrat dan radikal bebas mampu menurunkan ion-ion Ag⁺ dan Au³⁺ kepada atom Ag⁰ dan Au⁰ setelah berlaku pengagregatan dalam bentuk nanopartikel (Ag⁰)ₙ dan (Au⁰)ₙ. Pembentukan zarah-nano Ag dan Au telah dilihat dengan perubahan warna sampel kordial daripada tanpa warna kepada warna emas bagi zarah-nano Ag kepada warna merah bagi zarah-nano Au. Kehadiran logam Ag dan Au telah ditentusahkan dengan menggunakan analisis unsur keadah Energy Dispersive X-ray Spectroscopy (EDX).
Saizizarahan nano Ag dan Au telah ditentukan pada 90% taburan kumulatif kaedah Photon Cross Correlation Spectroscopy (PCCS) dan ditentusahkan oleh kaedah Transmission Electron Microscopy (TEM). Didapati diameter purata zarah-nano kodial Ag dan Au berkurang dengan pertambahan dos dan bertambah dengan pertambahan kepekatan garam. Diameter minimum zarah-nano Ag dan Au yang diperloleh dalam penyelidikan ini masing-masing ialah 12 dan 2 nm pada kepekatan garam terendah dalam PVP dengan dos sinaran tertinggi pada 70 kGy. Disini peristiwa pengnukliusan teraruah oleh sinaran telah dijelaskan sebagai proses bergantung kepada dos dan kenatik pengnukliusan zarah-nano Ag dan Au distabilikan dalam PVP dan PVA telah dikaji secara kuantitif. Pada dos tinggi dimana peristiwa pengnukliusan adalah melebihi jumlah ion logam, sintesis sinaran menghasilkan zarah-nano bersaiz kecil setelah berlaku pengagregatan. Sebaliknya pada dos-dos rendah dimana peristiwa pengnukliusan adalah kurang daripada jumlah ion logam, sintesis sinaran menghasilkan zarah-nano bersaiz besar. Bentuk zarah-nano Ag dan Au adalah berbentuk sfera yang ditentukan dengan kaedah TEM.

Ciri-ciri optik zarah-nano Ag dan Au telah diukur dengan menggunakan spektrometer penyerapan ultraunggu-cahaya tampak. Kehadiran zarah-nano Ag dan Au dipaparkaan pada puncak-puncak penyerapan diantara 400 dan 425 nm bagi zarah-nano Ag dan diantara 500 dan 550 nm bagi zarah-nano Au bergantung kepada kepekatan permulaan garam dan dos sinaran. Intensiti penyerapan maksimum zarah-nano kodial Ag dan Au bertambah dengan pertambahan dos sinaran, menunjukkan bilangan zarah-nano Ag dan Au bertambah dengan dos sinaran. Istimewa bagi sintesis sinaran ialah puncak-puncak penyerapan beranjak kepada panjang gelombang lebih rendah atau anjakan-biru dengan pertambahan dos sinaran menunjukkan
diameter zarah-nano Ag dan Au berkurangan dengan pertambahan dos. Seterusnya, ini memberi kesan kepada tenaga jalur konduksi zarah-nano Ag dan Au yang bertambah dengan pengecilan saiz zarah-nano. Ciri-ciri asas zarah-nano Ag dan Au telah dibincangkan secara menurut kaedah mekanik kuantum yang menyimpang daripada konsep lazim resonan Plasmon permukaan menurut teori elektrodinamik klasik yang lebih terkenal.
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I certify that a Thesis Examination Committee has met on 10 March 2011 to conduct the final examination of Kazem Naghavi on his Doctor of Philosophy thesis entitled “Gamma radiation Synthesis and Characterization of Silver and Gold Nanoparticles in Polymer Matrixes” 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 PhD of Science in Nanoscience. Members of the Examination Committee were as follows:

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xi
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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.

KAZEM NAGHAVI

Date: 18 February 2011
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vi</td>
</tr>
<tr>
<td>ACKNOLEDGEMENTS</td>
<td>x</td>
</tr>
<tr>
<td>APPROVAL</td>
<td>xi</td>
</tr>
<tr>
<td>DECLARATION</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xviii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xxii</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xxxiii</td>
</tr>
</tbody>
</table>

## CHAPTER

1 **INTRODUCTION**  
1.0 Introduction on nanomaterials  
1.1 Metal nanoparticles  
1.2 Significance of silver and gold nanoparticles  
1.3 Statement of the Problems  
1.4 Significant of the Study  
1.5 Scope of the Present Study  
1.6 Objectives of the Study  
1.7 Thesis Outline  

2 **LITERATURE REVIEW**  
2.1 Nanoscience and Nanotechnology  
2.2 History of nonmaterials  
2.2.1 Classification of Nanostructured Materials  
2.2.2 Significance of nanomaterials  
2.2.3 Influence on properties by "nano-structure induced effects"  
2.3 Nanoparticles  
2.4 Processing of nanoparticles  
2.4.1 Binding mechanisms in nanoparticles  
2.4.2 Dispersion of nanoparticles  
2.4.3 Stabilization of nanoparticles  
2.5 Noble metal nanoparticles  
2.6 Characterization of nanoparticles materials  
2.6.1 Microscopy  
2.6.1.1 Transmission Electron Microscopy (TEM)  
2.6.1.2 Scanning Electron Microscopy (SEM)  
2.6.1.3 Atomic Force Microscopy (AFM)  
2.6.1.4 Photon Cross Correlation Spectroscopy (PCCS): Nanophox  
2.6.2 Chemical Analysis  
2.6.2.1 Electron and X-Ray Diffraction (XRD)  
2.6.2.2 Energy Dispersive X-ray Spectroscopy  
2.6.2.3 X-ray Photoelectron Spectroscopy (XPS)  
2.6.2.4 UV-Visible Absorption Spectroscopy  
2.6.2.5 Electrons Spin Resonance (ESR)  

xv
2.7 Synthesis methods of metal nanoparticles

2.7.1 Chemical reduction method
2.7.2 Electrochemical
2.7.3 Physical vapor deposition
2.7.4 Sonication reduction
2.7.5 Microwave irradiation
2.7.6 UV photochemical reduction
2.7.7 Ionizing radiation reduction method
2.7.8 Laser photochemical reduction

2.8 Applications of metal Nanoparticles

2.8.1 Nano-Electronics
2.8.2 Surface Enhanced Raman Spectroscopy (SERS)
2.8.3 Metal nanoparticles as biosensors
2.8.4 Catalysts
2.8.5 Biomedical
  2.8.5.1 Antimicrobial action of silver nanoparticles

3 THEORETICAL

3.1 Ionizing radiation
  3.1.1 Radiation sources
  3.1.2 γ- radiation sources

3.2 γ-radiation interaction with matter
  3.2.1 Photoelectric absorption
  3.2.2 Compton Scattering
  3.2.3 Pair Production
  3.2.4 Raleigh scattering
  3.2.5 γ-ray attenuation coefficients

3.3 Interaction of γ-rays with aqueous systems
3.4 Electronic transition in molecules
3.5 Optical properties of metal nanoparticles
  3.5.1 Free electron model
  3.5.2 Metallic optical responses at different size scales
  3.5.3 Electronic structure of noble metals
  3.5.4 Surface Plasmon
3.6 Classical electrodynamics theory of metal nanoparticles
3.7 Quantum theory of metal nanoparticles

4 MATERIALS AND METHOD

4.1 Materials
4.2 Preparation of Silver and gold Nanoparticles in polyvinylpyrrolidone (PVP)
4.3 Preparation of silver and gold Nanoparticles in poly (vinylalcohol) (PVA)
4.4 Preparation of composite of Ag-PVA and Au-PVA film samples
4.5 UV-visible spectroscopy and absorbance measurement
4.6 Energy Dispersive X-ray Spectroscopy measurements
4.7 Average size measurement of Ag and Au nanoparticles
  4.7.1 Photon Cross Correlation Spectroscopy (PCCS)
  4.7.2 Transmission Electron Microscopy (TEM)
**RESULTS AND DISCUSSION**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0 Introduction</td>
<td>116</td>
</tr>
<tr>
<td>5.1 Formation of Ag nanoparticles</td>
<td>117</td>
</tr>
<tr>
<td>5.2 Formation of Au nanoparticles</td>
<td>119</td>
</tr>
<tr>
<td>5.3 Energy Dispersive X-ray (EDX) studies</td>
<td>122</td>
</tr>
<tr>
<td>5.3.1 EDX of Ag nanoparticles in PVA</td>
<td>122</td>
</tr>
<tr>
<td>5.3.2 EDX of Au nanoparticles in PVA</td>
<td>126</td>
</tr>
<tr>
<td>5.4 The Average nanoparticles diameter measurement using PCCS</td>
<td>129</td>
</tr>
<tr>
<td>5.4.1 Particle size of Ag nanoparticles in PVP</td>
<td>130</td>
</tr>
<tr>
<td>5.4.2 Particle size of Ag nanoparticles in PVA</td>
<td>134</td>
</tr>
<tr>
<td>5.4.3 Particle Size of Au nanoparticles in PVP</td>
<td>138</td>
</tr>
<tr>
<td>5.4.4 Particle Size of Au nanoparticles in PVA</td>
<td>141</td>
</tr>
<tr>
<td>5.5 Transmission Electron Microscope studies</td>
<td>145</td>
</tr>
<tr>
<td>5.5.1 TEM micrographs of Ag nanoparticles stabilized by PVP</td>
<td>146</td>
</tr>
<tr>
<td>5.5.2 TEM micrographs of Ag nanoparticles stabilized by PVA</td>
<td>152</td>
</tr>
<tr>
<td>5.5.3 TEM micrographs of Au nanoparticles stabilized by PVP</td>
<td>156</td>
</tr>
<tr>
<td>5.5.4 TEM micrographs of Au nanoparticles stabilized by PVA</td>
<td>161</td>
</tr>
<tr>
<td>5.6 The influence of radiation dose and ion concentration on particle size</td>
<td>165</td>
</tr>
<tr>
<td>5.6.1 The average size of Ag nanoparticles in PVP</td>
<td>165</td>
</tr>
<tr>
<td>5.6.2 The average size of Ag nanoparticles in PVA</td>
<td>172</td>
</tr>
<tr>
<td>5.6.3 Mechanism of nucleation and growth Ag nanoparticles</td>
<td>174</td>
</tr>
<tr>
<td>5.6.4 The average size of Au nanoparticles in PVP</td>
<td>176</td>
</tr>
<tr>
<td>5.6.5 The average size of Au nanoparticles in PVA</td>
<td>179</td>
</tr>
<tr>
<td>5.6.6 Mechanism of nucleation and growth Au Nanoparticles</td>
<td>181</td>
</tr>
<tr>
<td>5.7 Optical absorption characteristics</td>
<td>183</td>
</tr>
<tr>
<td>5.7.1 UV-visible absorption spectra of Ag nanoparticles in PVP</td>
<td>185</td>
</tr>
<tr>
<td>5.7.2 UV-visible absorption spectra of Ag nanoparticles in PVA</td>
<td>192</td>
</tr>
<tr>
<td>5.7.3 UV-visible absorption spectra of Au nanoparticles in PVP</td>
<td>199</td>
</tr>
<tr>
<td>5.7.4 UV-visible absorption spectra of Au nanoparticles in PVA</td>
<td>206</td>
</tr>
<tr>
<td>5.8 Conduction band energy Ag and Au nanoparticles</td>
<td>213</td>
</tr>
<tr>
<td>5.8.1 Conduction band energy of Ag nanoparticles in PVP</td>
<td>217</td>
</tr>
<tr>
<td>5.8.2 Conduction band energy of Ag nanoparticles in PVA</td>
<td>222</td>
</tr>
<tr>
<td>5.8.3 Conduction band energy of Au nanoparticles in PVP</td>
<td>226</td>
</tr>
</tbody>
</table>
5.8.4 Conduction band energy Au nanoparticles in PVA
5.9 The influence of PVP and PVA stabilizers on Ag and Au nanoparticles

6 CONCLUSIONS AND FUTURE WORK
6.1 Conclusions
6.2 Future work and recommendations

REFERENCES
BIODATA OF STUDENT
LIST OF PUBLICATIONS