

## DOCTORAL THESIS

### Synthesis, characterization and analytical separation of metal nanoparticles

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**Synthesis, Characterization and Analytical Separation  
of Metal Nanoparticles**

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**A thesis submitted in partial fulfillment of the requirements  
for the degree of  
Doctor of Philosophy**

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## Abstract

This thesis mainly focuses in two parts. The first one is the synthesis and analytical separation of a water-soluble metal nanoparticle, *N*-acetyl-L-cysteine protected gold monolayer protected cluster (Au MPC). The as-prepared product was well characterized by different techniques. The crude Au MPC is a polydisperse spherical product with an average particle size of  $1.7 \pm 0.5$  nm.

Since the synthesized Au MPC product is polydisperse, an effective capillary electrophoretic (CE) technique for separating samples of Au MPC has been developed.

The separation mechanisms of Au MPC in capillary zone electrophoresis suggest that the larger core sizes Au MPC emerge first from the capillary. The electrophoretic separation depends on pH, buffer concentration and organic modifiers. The run buffer containing 20 % *v/v* ethanol provides the best separation for water-soluble Au MPC and it is attributed to the more significant difference in the charge-to-size ratio between the Au MPCs. An increase in applied voltage can reduce the run time of Au MPC separation with the sacrifice of resolution. The proposed CE method provides a powerful tool to evaluate and separate the water-soluble Au MPC products.

In order to efficiently fractionate larger amounts of MPC product, a novel and simple electrolyte-induced fractionation method has been proposed. The effect of electrolyte

concentrations and the lipophilicity of the solution in fractionation were also investigated. Small gold nanoclusters, Au<sub>10</sub>, Au<sub>11</sub>, Au<sub>12</sub> and Au<sub>15</sub>, could be isolated from the Au<sub>10</sub> to Au<sub>50</sub> polydisperse Au MPC product under certain experimental conditions. The core sizes isolation was evaluated by their photophysical properties, migration orders in CE, and mass spectrometry. The electrolyte-induced fractionation assists in the study of the photophysical properties of smaller Au MPCs that are present with the larger Au MPCs in a polydisperse Au MPC product.

The second part is to explore the application and synthesis of a bimetallic core-shell nanoparticle. An easy and simple two-step reaction was employed to synthesize a new type of ligand-protected (homocysteine-protected) gold-coated iron oxide nanoparticle (homocys-Au-Fe<sub>3</sub>O<sub>4</sub>). Fe<sub>3</sub>O<sub>4</sub> nanoparticles were initially prepared and subsequently coated with Au layers under hot citrate reduction of HAuCl<sub>4</sub>. The citrate monolayer of the nanoparticles was place-exchanged with homocysteine molecules to produce the well dispersed homocys-Au-Fe<sub>3</sub>O<sub>4</sub> nanoparticles. These homocys-Au-Fe<sub>3</sub>O<sub>4</sub> nanoparticles have been fully characterized by different techniques. The homocys-Au-Fe<sub>3</sub>O<sub>4</sub> nanoparticles were coated with ultra-thin layers of Au atoms (~0.5 nm) having an average diameter of ca. 12 nm. This investigation provides important insights into the design of new water-soluble bimetallic core-shell magnetic nanoparticles for biomedical, analytical and catalytic applications.

## Table of Contents

<b>Declaration .....</b>	<b>i</b>
<b>Abstract .....</b>	<b>ii</b>
<b>Acknowledgements .....</b>	<b>iv</b>
<b>Tables of Contents .....</b>	<b>vi</b>
<b>List of Figures .....</b>	<b>xii</b>
<b>List of Abbreviations .....</b>	<b>xviii</b>
<b>Chapter 1 Introduction .....</b>	<b>1</b>
<b>1.1 Gold Nanoparticles.....</b>	<b>1</b>
<b>1.2 Synthesis of Gold Nanoparticles.....</b>	<b>2</b>
<b>1.2.1 Physical Methods.....</b>	<b>3</b>
<b>1.2.2 Chemical Methods.....</b>	<b>4</b>
<b>1.2.2.1 Citrate Reduction.....</b>	<b>4</b>
<b>1.2.2.2 Brust-Schiffrin Method.....</b>	<b>5</b>
<b>1.3 Monolayer-protected Cluster.....</b>	<b>7</b>
<b>1.4 Characterization of Nanoparticles.....</b>	<b>9</b>
<b>1.4.1 Core Size and Shape.....</b>	<b>10</b>
<b>1.4.2 Monolayer Shell Analysis.....</b>	<b>12</b>

1.4.3	Elemental Analysis.....	12
1.5	Analytical Separation of Nanoparticles.....	15
1.6	Gold-coated Magnetic Nanoparticles.....	17
1.7	Aims of the Project.....	20
Chapter 2	Experimental Section.....	23
2.1	Chemicals.....	23
2.2	Synthesis of Metal Nanoparticles.....	24
2.2.1	Synthesis of <i>N</i> -acetyl-L-cysteine-protected Au MPC.....	24
2.2.2	Synthesis of Homocysteine-protected Gold-coated Magnetic Nanoparticle.....	26
2.2.2.1	Synthesis of Iron Oxide Nanoparticles.....	26
2.2.2.2.	Synthesis of Citrate-protected Au-coated Iron Oxide Nanoparticles.....	26
2.2.2.3	Synthesis of Homocysteine-protected Gold-coated Iron Oxide Nanoparticle.....	27
2.3	Characterization of Metal Nanoparticles.....	27
2.3.1	XPS Measurement.....	27
2.3.2	UV-visible Absorption Spectroscopy.....	28
2.3.3	<sup>1</sup> H NMR Spectroscopy.....	28
2.3.4	FTIR Spectroscopy.....	28

2.3.5.	Thermogravimetric Analysis.....	29
2.3.6	Atomic Absorption Spectroscopy.....	29
2.3.7	Magnetic Susceptibility Measurement.....	30
2.3.8	XRD Measurement.....	30
2.3.9	SEM, EDS, TEM and HRTEM Measurements.....	30
2.3.10	Photoluminescence Spectrometry.....	31
2.3.11	MALDI-MS.....	31
2.4	Analytical Separation.....	31
2.4.1	Capillary Zone Electrophoresis.....	31
2.4.2	Fractionation of Au MPC.....	33
<b>Chapter 3</b>	<b>Synthesis and Characterization of Water-soluble N-acetyl-L-cysteine-protected Gold Nanocluster.....</b>	<b>35</b>
3.1	Introduction .....	35
3.2	Result and Discussions.....	36
3.2.1	X-ray photoelectron Spectroscopy.....	36
3.2.2	UV-visible Absorption Spectroscopy.....	37
3.2.3	<sup>1</sup> H NMR Spectroscopy.....	39
3.2.4	FTIR Spectroscopy.....	40
3.2.5	Thermogravimetric Analysis.....	42

3.2.6	Transmission Electron Microscopy.....	43
3.3	Conclusion.....	44
<b>Chapter 4</b>	<b>Capillary Electrophoretic Separation of Water-soluble Gold Monolayer-protected Clusters.....</b>	<b>45</b>
4.1	Introduction .....	45
4.2	Results and Discussion.....	46
4.2.1	Separation and Migration Order of Au MPCs.....	46
4.2.2.	Effect of Buffer Concentration.....	53
4.2.3	Effect of Buffer pH.....	57
4.2.4	Effect of Organic Modifier.....	60
4.2.5	Effect of Applied Voltage.....	68
4.2.6	Application to Au MPC Product Analysis.....	70
4.3	Conclusion.....	75
<b>Chapter 5</b>	<b>Electrolyte-induced Fractionation of Gold monolayer-Protected Clusters Studied by UV-Vis Absorption Spectrophotometry, Capillary Electrophoresis and Mass Spectrometry.....</b>	<b>76</b>
5.1	Introduction .....	76
5.2	Results and Discussion.....	77
5.2.1	Fractionation Under Different Electrolyte Concentrations.....	77



5.2.2	<b>Effect of the Lipophilicity of Organic Solvent on Fractionation.....</b>	84
5.2.3	<b>Photophysical Properties of Au MPC Fractions.....</b>	90
5.2.4	<b>MALDI-MS analysis of Au MPC Fractions.....</b>	97
5.2.5	<b>XPS Analysis of Au MPC Fractions.....</b>	102
5.3	<b>Conclusion.....</b>	103
<b>Chapter 6</b>	<b>Synthesis and Characterization of Homocysteine-protected Gold-coated Magnetic Nanoparticles.....</b>	<b>105</b>
6.1	<b>Introduction .....</b>	105
6.2	<b>Results and Discussion.....</b>	107
6.2.1	<b>X-ray Photoelectron Spectroscopy.....</b>	108
6.2.2	<b>Visible Absorption Spectroscopy.....</b>	111
6.2.3	<b>pH Effect.....</b>	114
6.2.4	<b>Magnetic Property.....</b>	117
6.2.5	<b>FTIR Spectroscopy.....</b>	119
6.2.6	<b>TGA and AAS.....</b>	120
6.2.7	<b>Energy Dispersive X-ray Spectroscopy.....</b>	121
6.2.8	<b>X-ray Diffraction.....</b>	122
6.2.9	<b>SEM, TEM and HRTEM.....</b>	123
6.2.10	<b>Homocysteine-protected Magnetic Au Nanoparticles.....</b>	127

<b>6.3</b>	<b>Conclusion</b>	129
<b>Chapter 7</b>	<b>Conclusion .....</b>	131
<b>Chapter 8</b>	<b>List of References .....</b>	134
	<b>Curriculum Vitae .....</b>	148
	<b>List of Publications.....</b>	149