



**Development of New Methods for the  
Synthesis of Plasmonically-Active  
Precious Metal Rods and Shells**

**A thesis presented for the degree of Doctor of Philosophy**

**By**

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## **Dedication**

This thesis is dedicated to my family; past, present and future.

## **Certificate of Originality**

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Jonathan A. Edgar

10/10/2011

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## Abstract

The ability to synthesise metal nanoparticles with various geometries has vastly improved in recent years. The plasmon resonance, the mechanism responsible for the optical response of metal nanoparticles, is highly sensitive to their geometry. This is the primary reason for the current interest in developing syntheses that produce a distinct geometry. In contrast, polydisperse samples of nanoparticles have relatively poorly defined plasmon resonances. Although nanospheres are still the most common geometry of metal nanoparticle synthesised, there is rapidly increasing interest in nanorods and nanoshells on account of their more flexible optical response. Therefore, developing a reliable synthesis for nanorods and nanoshells has been a target of much recent research. Gold is the most popular metal for the synthesis of plasmonically active nanoparticles.

In this thesis I present a development of synthesis methods for plasmonically active nanoparticles and a characterisation of the resulting products. In my work I have synthesised gold nanorods, a mixed dispersion of gold nanorings and hollow gold nanoparticles, silver nanorods and platinum nanospheres. To characterise these nanoparticles I have used a range of techniques including UV-Vis-NIR spectrometry, SEM, TEM, cryo-TEM, SAXS and electrodynamic simulations.

Early in my work I recognised that gold nanorods provided the best opportunities to achieve large scale applications. Some significant drawbacks in the existing methods of synthesis were identified, such as the inefficient reaction of gold. This realisation led me to focus the majority of my efforts on improving the understanding of the mechanisms involved in the synthesis of gold nanorods and, in particular, on the all-important transition from spherical seed particle to anisotropic rod. The nearest competitor to nanorods, with respect to applications, is nanoshells and so I have also compared these two geometries in the literature review.

From the exhaustive work presented in this thesis I present a set of optimum conditions for the synthesis of gold nanorods. Evidence for the disproportionation of gold (I) bromide as the mechanism of gold metal formation in the gold nanorod synthesis is presented. I also show that it is necessary to sacrifice control of the aspect ratio of the nanorods produced in order to improve the efficiency of the reaction. I use a co-reductant to show that the formation of nanorods is dependent on the effectiveness of the reductant that is present after the addition of the gold nanoparticle seeds. It is also apparent that it is possible to achieve a range of aspect ratios as well as particle dimensions by varying the amount of seed particles added to the growth solution.

I have used a range of experimental techniques including cryo-TEM, SEM, UV-Vis spectroscopy and small angle X-ray scattering to probe the physical dimensions and optical properties of gold nanorods at various stages of their growth and from this I have developed a new growth model. Simulations of the optical properties of the intermediate nanoparticle geometries observed support this new growth model.

## Table of Contents

Dedication .....	i
Certificate of Originality.....	ii
Acknowledgements.....	iii
Abstract.....	iv
List of Publications .....	viii
List of Abbreviations .....	ix
List of Figures .....	xii
1 Introduction .....	1
1.1 Trends in Metal Nanoparticle Research.....	5
1.2 Optical Properties of Metal Nanoparticles .....	8
1.2.1 Optical Response of Metals .....	9
1.2.2 Gold Nanorods and Gold Nanoshells .....	12
1.2.3 Modelling Optical Response of User Defined Targets .....	16
1.3 Gold Nanorod Syntheses.....	19
1.3.1 The Development of Gold Nanorod Syntheses.....	19
1.3.2 Kinetics of gold nanorod syntheses .....	28
1.4 Gold Nanoshell Syntheses.....	30
1.4.1 Core – Shell Structures.....	30
1.4.2 Hollow Gold Nanoshells .....	32
1.5 Applications of Gold Nanorods and Nanoshells .....	32
1.5.1 Pigments and colorants.....	32
1.5.2 Spectrally selective coatings .....	33
1.5.3 High density data storage .....	35
1.5.4 Catalysis .....	36
1.5.5 Sensors .....	37
1.5.6 Surface Enhanced Raman spectroscopy .....	39
1.5.7 Use of gold in medical diagnostics.....	41
1.5.8 Therapeutic possibilities for nanoscale gold.....	44
1.6 Motivation.....	46
2 Experimental Methods and Materials .....	48
2.1 Synthesis of H <sub>2</sub> AuCl <sub>4</sub> .....	48
2.2 Precious Metal Nanoparticles.....	48

2.2.1	Gold Nanoparticle Seed Solution .....	48
2.2.2	Gold Nanorod Growth Solution .....	49
2.2.3	Gold Nanorings/Hollow Nanoparticles .....	50
2.2.4	Ag Nanorods.....	50
2.2.5	Platinum Nanoparticles.....	51
2.3	Characterisation and Calibration .....	52
2.3.1	Characterisation of Au(III) species .....	52
2.3.2	Calibration of Au <sup>0</sup> Concentration in Aqueous Solution.....	53
2.3.3	UV-Vis-NIR Spectroscopy .....	54
2.3.4	SEM .....	54
2.3.5	Cryo-TEM.....	55
2.3.6	TEM .....	56
2.3.7	Estimation of nanorod dimensions from a UV-Vis-NIR spectrum .....	56
2.3.8	Small-Angle X-Ray Scattering .....	57
2.4	Simulation of Optical Properties.....	58
2.4.1	DDSCAT .....	58
2.4.2	MiePlot.....	62
2.5	POV-Ray Diagrams of Gold Nanoparticles .....	62
3	Other Precious Metal Colloids .....	64
3.1	Gold Nanorings .....	64
3.1.1	Results and Discussion .....	66
3.1.2	Summary .....	71
3.2	Silver Nanorods.....	72
3.2.1	Results and Discussion .....	73
3.2.2	Summary .....	74
3.3	Platinum Nanoparticles.....	76
3.3.1	Results and Discussion .....	77
3.3.2	Summary .....	78
4	Optimisation of the synthesis of gold nanorods.....	80
4.1	Results and Discussion .....	81
4.1.1	Ag <sup>+</sup> concentration on .....	81
4.1.2	C <sub>16</sub> TABr concentration .....	82
4.1.3	Gold Source .....	83

4.1.4	Mechanism of Reduction .....	84
4.1.5	Sodium Salicylate as a Co-reductant.....	90
4.1.6	Gold Nanoparticle Seed .....	99
4.1.7	Summary .....	113
5	On the Formation of Gold Nanorods .....	115
5.1	Results and Discussion .....	117
5.1.1	UV-Vis-NIR Spectroscopy .....	117
5.1.2	Estimation of nanorod dimensions from a UV-Vis-NIR spectrum .....	121
5.1.3	Small-Angle X-ray Scattering.....	123
5.1.4	Cryo-TEM and SEM .....	127
5.1.5	Simulated Optical Properties for New Growth Model.....	133
5.1.6	Summary .....	138
6	Conclusions .....	140
	Future Work.....	141
	References .....	142
	Appendices.....	162
	Appendix A.....	162
	Appendix B.....	164
	Appendix C.....	169
	Appendix D.....	171
	Appendix E .....	172
	Appendix F .....	173



## List of Publications

Portions of the work presented in this thesis have been published, contributed to or have been submitted for publication. The following is a list of the citations for these publications:

**Jonathan A. Edgar**, Hadi M. Zareie, Martin G. Blaber, Annette Dowd, Michael B. Cortie

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**Jonathan A. Edgar**, Michael B. Cortie

“Nanotechnological Applications of Gold Nanoparticles”

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“Transmitting hertzian optical nanoantenna with free-electron feed”

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## List of Abbreviations

$^1\text{H-NMR}$	nuclear magnetic resonance spectroscopy
$\text{A}^*$	ascorbate radical
$\text{Ag}$ or $\text{Ag}^0$	silver metal
$\text{Ag}^+$	silver ion
$\text{AgBr}$	silver bromide
$\text{AgNO}_3$	silver nitrate
AMMRF	Australian microscopy and microanalysis research facility
AR	aspect ratio
$\text{Au}$ or $\text{Au}^0$	gold metal
$\text{Au}_2\text{S}$	gold sulphide
$\text{Au}^{3+}$	gold (III) ion
$\text{AuBr}_2^-$	gold (I) bromide
$\text{AuBr}_4^-$	gold (III) bromide
$\text{AuCl}_2^-$	gold (I) chloride
$\text{AuCl}_4^-$	gold (III) chloride
BDAC	hexadecyl-benzyltrimethyl-ammonium chloride
$\text{BH}_4^-$	borohydride
$\text{Br}^-$	bromide
BSA	bovine serum albumin
BT	bow-tie
$\text{C}_{16}\text{TABr}$	hexadecyltrimethylammonium bromide
$\text{C}_{16}\text{TACl}$	hexadecyltrimethylammonium chloride
$\text{C}_{16}\text{TASBr}$	$\text{AgBr}$ - $\text{C}_{16}\text{TABr}$ complex
$\text{C}_{16}\text{TEABr}$	hexadecyl-triethylammonium bromide
CBT	conically-capped bow-tie
CC	conically-capped cylinder
CCG	complex conjugate gradient
$\text{CdSe-ZnS}$	cadmium selenide - zinc sulphide
CM	Clausius-Mossotti
CMC	critical micelle concentration
cryo-TEM	cryogenic transmission electron microscopy
DDA	discrete dipole approximation
DHA	dehydro-ascorbic acid
DNA	deoxyribonucleic acid
EM	electromagnetic
et alii	and others'
EXAFS	extended X-ray absorption fine structure
fastSPS	fast single-particle spectroscopy
FCC	face centred cubic
FE-SEM	field emission - scanning electron microscope
FFT	fast Fourier transform
FOM	figure of merit
FTIR	Fourier transform infrared spectroscopy

GM	Göppert-Mayer units
GS	growth solution
H <sub>2</sub> A	ascorbic acid
H <sub>2</sub> PtCl <sub>6</sub>	hexachloroplatinic acid
HA <sup>-</sup>	ascorbate anion
HAuBr <sub>4</sub>	tetrabromoauric acid
HAuCl <sub>4</sub>	tetrachloroauric acid
HCl	hydrochloric acid
HDT	hexadecanethiol
HNO <sub>3</sub>	nitric acid
ICP-MS	inductively coupled plasma - mass spectrometry
IR	infrared
ITO	indium tin oxide
KBH <sub>4</sub>	potassium borohydride
LDR	lattice dispersion relation
LSP	localised surface plasmon
MRI	magnetic resonance imaging
Na <sub>2</sub> S	sodium sulphide
NaBr	sodium bromide
NaOH	sodium hydroxide
NaSal	sodium salicylate
NiPAAm	N-isopropylacrylamide
NIR	near infrared
NP	nanoparticle
OCT	optical coherence tomography
OH	hydroxide
PC	personal computer
PTFE	polytetrafluoroethylene
PVA	poly-vinyl alcohol
PVP	polyvinylpyrrolidone
QDs	quantum dots
RIU	refractive index unit
rpm	revolutions per minute
SALDI-MS	surface-assisted laser desorption/ionisation time-of-flight mass spectrometry
SAXS	small angle X-ray scattering
SC	spherically-capped cylinder
SEM	scanning electron microscopy
SERS	surface enhanced Raman scattering
SHE	standard hydrogen electrode
SiO <sub>2</sub>	silicon dioxide
SPIO	super-paramagnetic iron oxide
SPP	surface plasmon polariton
TC <sub>12</sub> ABr	tetradodecylammonium bromide

TC <sub>8</sub> ABr	tetraoctylammonium bromide
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TPL	two-photon induced luminescence
UPD	underpotential deposition
UV	ultraviolet
Vis	visible
WAXS	wide angle X-ray scattering
XPS	X-ray photoelectron spectroscopy

## List of Figures

Figure 1-1 Roman ‘Lycurgus Cup’ from 4 <sup>th</sup> century AD photographed in a) reflected light and b) transmitted light. ....	2
Figure 1-2 Scifinder Scholar analysis for reviews of “metal nanoparticles” subdivided by keyword .....	6
Figure 1-3 Scifinder Scholar analysis for metal nanoparticle research publications refined for precious metals .....	6
Figure 1-4 Scifinder Scholar analysis for a) “gold nanorod(s)” and b) “gold nanoshell(s)” research publications subdivided by keyword.....	7
Figure 1-5 Schematic of a plasmon-polariton dipole resonance in a gold nanoparticle ....	8
Figure 1-6 a) Real and b) imaginary parts of the dielectric function for gold from various sources .....	10
Figure 1-7 A typical gold nanorod absorption spectrum indicating primary features .....	12
Figure 1-8 Gold nanorods in PVA film.....	13
Figure 1-9 Hybridisation model for dipolar resonance modes of a metal nanoshell .....	14
Figure 1-10 Typical spectra of a) large and b) small nanoshells .....	15
Figure 1-11 Structural representation of C <sub>16</sub> TABr.....	20
Figure 1-12 Face-centred cubic crystal bounded by the planes with normal vectors a) < 1 0 0 >, b) < 1 1 0 > and c) < 1 1 1 >. d) Previously proposed crystallographic structure of a single crystal gold nanorod. ....	21
Figure 1-13 Face-centred cubic crystal (10 x 10 unit cells) bounded by the planes with normal vectors a) < 0 2 5 >, b) < 0 5 2 > where c) illustrates the surface atoms of b). d) Currently proposed crystallographic structure of a single crystal gold nanorod. ....	22
Figure 1-14 Cross-section of a gold nanoshell on a dielectric core .....	30
Figure 1-15 Silica – gold (core – shell) nanoshells with increased exposure to growth solution (left to right and top to bottom). Scale bar = 20 nm. ....	31
Figure 1-16 Galvanic replacement of silver nanocubes with a) AuCl <sub>2</sub> <sup>-</sup> and b) AuCl <sub>4</sub> <sup>-</sup> .....	32
Figure 1-17 ASTM E971-88 standard solar spectrum and photo-optic response of the human eye .....	33
Figure 1-18 Demonstration of five dimensional data storage using gold nanorods with wavelength indicated on the left, two-photon luminescence intensity on the right and polarisation indicated below. ....	36
Figure 2-1 Calibration of AuBr <sub>4</sub> <sup>-</sup> extinction in aqueous C <sub>16</sub> TABr solution .....	52
Figure 2-2 Calibration for Au <sup>0</sup> in solution .....	53
Figure 2-3 Nanoparticle cross-sections of the geometries calculated for my new growth model indicating the parameters used to define the structure. a) Bow-tie (BT), b) conically-capped bow-tie (CBT), c) conically-capped cylinder and d) spherically-capped cylinder.....	60
Figure 2-4 Extinction spectra for the intermediate nanoparticle geometries calculated using DDSCAT.....	60
Figure 2-5 Gold nanorod with <052>, <025> and <011> side facets, <110> and <111> end-caps and the growth direction <100> .....	63

Figure 3-1 Schematic for the formation of a hollow Au/Ag nanoparticle by the galvanic replacement of a silver nanoparticle template. Modified from [142].....	65
Figure 3-2 Spectra for nanoparticles pre- and post addition of $\text{HAuCl}_4$ .....	66
Figure 3-3 a) Low and b) high resolution TEM images of gold nanorings. Scale bars 50 nm and 10 nm for a) and b) respectively. Images courtesy of Dr A. Dowd. ....	67
Figure 3-4 SEM image of gold nanorings and cages. Scale bar = 50 nm.....	67
Figure 3-5 Gold nanoparticles prepared by galvanic replacement of silver nanoparticles stabilised with citrate and $\text{C}_{16}\text{TABr}$ molecules respectively.....	68
Figure 3-6 SEM images of nanorings prepared from a) citrate stabilised and b) $\text{C}_{16}\text{TABr}$ stabilised silver nanoparticles. Scale bars = 20 nm.....	69
Figure 3-7 Diagrams of gold nanorings with aspect ratios equal to a) 3, b) 4 and c) 5 respectively. d) Corresponding extinction spectra for dispersions of gold nanorings of different aspect ratios calculated with DDSCAT .....	69
Figure 3-8 Gold nanoring oriented in the YZ plane (grey area) with incident EM wave travelling in the +X direction and polarised in the Z axis.....	70
Figure 3-9 Plasmon resonance peaks for an aspect ratio 3 gold nanoring in various orientations. The traces are labelled for the respective plane of orientation and incident polarisation of incident light for a wave propagating in the x direction .....	70
Figure 3-10 Comparison of the imaginary part of the complex dielectric functions for silver and gold. Data from reference [295].....	72
Figure 3-11 UV-Vis spectra of $\text{C}_{16}\text{TABr}$ and tri-sodium citrate-stabilised silver seed particles.....	73
Figure 3-12 Absorbance spectra for silver nanorods a) synthesised in the current work using different volumes of CTAB stabilised silver seed particles and b) literature procedure using citrate stabilised seed particles. ....	74
Figure 3-13 Comparison of the imaginary part of the complex dielectric functions for platinum and gold.....	76
Figure 3-14 Measured extinction spectrum of platinum nanoparticles synthesised in water compared with the MiePlot result for a 1 nm diameter platinum nanosphere and various mixtures of 1 nm and 100 nm diameter spheres, also in water .....	77
Figure 3-15 Measured extinction spectrum of platinum nanoparticles synthesised in toluene compared with the MiePlot result for a 1 nm diameter platinum nanosphere also in toluene.....	78
Figure 4-1 Increasing the silver nitrate concentration in the gold nanorod growth solution produces a proportional shift of the longitudinal plasmon peak. ....	81
Figure 4-2 Varying the $\text{C}_{16}\text{TABr}$ concentration of the gold nanorod growth solution shows a dependence of the sample quality on the elevated concentration.....	82
Figure 4-3 UV-Vis absorbance spectra of Au (III) – $\text{C}_{16}\text{TA}^+$ solutions indicating that the gold species present in the gold nanorod growth solution is $\text{AuBr}_4^- \text{-CTA}^+$ .....	83
Figure 4-4 Absorbance spectra of nanorods prepared with $\text{HAuBr}_4$ and $\text{HAuCl}_4$ .....	84
Figure 4-5 a) Concentration of $\text{Au}^{3+}$ measured by UV-Vis spectrometry for solutions with ascorbic acid approaching 1:1 with respect to initial $\text{Au}^{3+}$ concentration b) Cryo-TEM image of solution of $\text{Au}^{3+}$ - $\text{C}_{16}\text{TABr}$ and ascorbic acid, scale bar = 50 nm.....	85

Figure 4-6 Oxidation and degradation pathways for ascorbic acid .....	85
Figure 4-7 Au <sup>3+</sup> - ascorbate complex.....	86
Figure 4-8 Schematic of the disproportionation mechanism of AuBr <sub>2</sub> <sup>-</sup> at the surface of a gold nanoparticle .....	88
Figure 4-9 a) Proportional increase of metallic gold concentration to excess reductant concentration in gold nanorod samples and b) corresponding longitudinal peak positions .....	88
Figure 4-10 Nanoparticle spectra for samples in Figure 4-9 where growth solutions contain 50 μM Ag <sup>+</sup> and ascorbic acid as the sole excess reductant .....	89
Figure 4-11 Nanoparticle spectra for samples in Figure 4-9 where growth solutions contain 100 μM Ag <sup>+</sup> and ascorbic acid as the sole excess reductant .....	90
Figure 4-12 a) Structure of the salicylate anion with intramolecular hydrogen bond indicated, b) probable structure of the salicylate di-anion and c) insertion of the salicylate anion into a C <sub>16</sub> TABr micelle .....	90
Figure 4-13 UV-Vis kinetics data for the interaction of sodium salicylate with AuBr <sub>4</sub> – C <sub>16</sub> TABr at 30°C, dashed arrows indicate increasing time, solid arrows indicate isosbestic points. Inset shows decrease of Au <sup>3+</sup> concentration with time.....	91
Figure 4-14 a) Combinations of NaSal and Au <sup>+</sup> - and Au <sup>3+</sup> -C <sub>16</sub> TABr spectra and b) effect of water on the spectrum of salicylate anion in acetonitrile (arrow indicates increasing concentration of water).....	92
Figure 4-15 Integrated rate law plots for kinetics of the reaction of NaSal and Au <sup>3+</sup> .....	92
Figure 4-16 Nanoparticle spectra for samples in Figure 4-9 where growth solutions contain 70 μM Ag <sup>+</sup> and sodium salicylate as the excess reductant, traces are labelled according to NaSal concentration.....	95
Figure 4-17 By varying the order of addition of reactants for nanorod growth solutions containing H <sub>2</sub> A and NaSal as reductants a dependence of ascorbate as the excess reductant is evident .....	95
Figure 4-18 a) – e) SEM images of nanoparticles formed with a) and b) 0.25 mM, c) 0.50 mM, d) 1.00 mM and e) 2.00 mM NaSal in their respective growth solutions (all scale bars are 100 nm). f) Corresponding normalised absorbance spectra for samples a) – e)	97
Figure 4-19 a) – g) SEM images of nanoparticles formed with a) 5.00 mM, b) 10.00 mM, c) 20.00 mM, d) 50.00 mM, e) 100.00 mM, f) 250.00 mM and g) 500.00 mM NaSal in their respective growth solutions. h) corresponding normalised absorbance spectra for samples a) – g). Scale bars a) – c), f) and g) are 200 nm, d) and e) are 100 nm .....	99
Figure 4-20 Absorbance spectra for seed solutions with a) 0.1 mM and b) 0.5 mM HAuCl <sub>4</sub> and a range of concentrations of C <sub>16</sub> TABr .....	100
Figure 4-21 UV-Vis absorbance spectra of gold nanoparticle seed solutions prepared at different Au <sup>3+</sup> concentrations .....	101
Figure 4-22 a) – f) SEM images for samples prepared using seed solutions with 0.1 mM HAuCl <sub>4</sub> and a) 0.5 mM, b) 1.0 mM, c) 10.0 mM, d) 25.0 mM, e) 50 mM and f) 100.0 mM C <sub>16</sub> TABr respectively. g) Corresponding normalised absorbance spectra for a) – f). h) Nanorod dimensions for a) – f). Scale bars = 200 nm.....	102

Figure 4-23 a) – f) SEM images for samples prepared using seed solutions with 0.5 mM  $\text{HAuCl}_4$  and a) 0.5 mM, b) 1.0 mM, c) 10.0 mM, d) 25.0 mM, e) 50 mM and f) 100.0 mM  $\text{C}_{16}\text{TABr}$  respectively. g) Corresponding normalised absorbance spectra for a) – f). h) Nanorod dimensions for a) – f). Scale bars = 200 nm..... 103

Figure 4-24 a) – e) SEM images for samples a) A1, b) B1, c) C1, d) D1 and e) E1. f) Corresponding absorbance spectra for samples A1 – E1. The inset of f) shows the nanorod dimensions measured from the SEM images. Scale bars = 200 nm..... 105

Figure 4-25 a) – e) SEM images for samples a) A2, b) B2, c) C2, d) D2 and e) E2. f) Corresponding absorbance spectra for samples A2 – E2. The inset of f) shows the nanorod dimensions measured from the SEM images. Scale bars = 200 nm..... 107

Figure 4-26 a) – e) SEM images for samples a) A3, b) B3, c) C3, d) D3 and e) E3. f) Corresponding absorbance spectra for samples A3 – E3. The inset of f) shows the nanorod dimensions measured from the SEM images. Scale bars = 200 nm..... 108

Figure 4-27 a) – e) SEM images for samples a) A4, b) B4, c) C4, d) D4 and e) E4. f) Corresponding absorbance spectra for samples A4 – E4. The inset of f) shows the nanorod dimensions measured from the SEM images. Scale bars a), d) and e) are 200 nm, b) and c) are 100 nm..... 109

Figure 4-28 a) – e) SEM images for samples a) A5, b) B5, c) C5, d) D5 and e) E5. f) Corresponding absorbance spectra for samples A5 – E5. The inset of f) shows the nanorod dimensions measured from the SEM images. Scale bar for a) is 50 nm, scale bars for b) – e) are 200 nm ..... 111

Figure 4-29 Apparent quartic relationship for nanorod dimensions prepared from varied seed solutions. Green triangles indicate optimum range A3 – E3..... 112

Figure 4-30 Comparison of optically and physically (from SEM data) determined gold nanorod aspect ratios ..... 112

Figure 4-31 a) Real and b) imaginary parts of the dielectric data for gold from Palik and CRC Handbook of Chemistry and Physics ..... 113

Figure 5-1 UV-Vis-NIR spectroscopy of the reaction kinetics of gold nanorods. Density plots for gold nanorods with a) 0.60 mM and b) 0.65 mM  $\text{H}_2\text{A}$  in the growth solution respectively. The scale of these plots has been normalised to the maximum absorbance of the 0.65 mM dataset. Time-dependent, two-dimensional absorbance plots indicating the transition of the longitudinal resonance peak for gold nanorods with c) 0.60 mM and d) 0.65 mM  $\text{H}_2\text{A}$  in the growth solution respectively. The insets in c) and d) are an enlargement of the earliest traces for each respective dataset. The arrows indicate increasing time..... 117

Figure 5-2  $\text{Au}^0$  concentration as a function of time for growing gold nanorod solutions with 0.60 mM and 0.65 mM  $\text{H}_2\text{A}$  in the growth solution respectively. .... 119

Figure 5-3 Second order autocatalytic growth model applied to the measured optical absorbance data for the growth of gold nanorods..... 121

Figure 5-4 Physical properties of growing gold nanorods interpreted from UV-Vis spectra a) volume and b) length (L) and width (W)..... 122



Figure 5-5 Particle dimensions estimated from optical data for the growth of gold nanorods with 0.60 mM H<sub>2</sub>A in the growth solution using a 2 nm (2 nm D) or 3 nm (3 nm D) diameter nanoparticle seed. .... 122

Figure 5-6 a) Raw SAXS data of a typical gold nanorod growth solution (GS) and during nanorod growth at various times. b) SAXS profiles of the kinetics data using the GS profile as a background signal. .... 124

Figure 5-7 Guinier plots for SAXS data of a growing gold nanorod solution where the profile for the growth solution has been used as a background. .... 125

Figure 5-8 Analysis of SAXS data using  $I(q)q^4$  vs  $q$  plot indicating Porod plateau (green shaded region). .... 126

Figure 5-9 Cryo-TEM images of samples of a growing gold nanorod solution with 0.65 mM H<sub>2</sub>A taken at a) 2.5 min, b) 15 min, c) 25 min and d) 24 hours. Scale bars for a) – c) are equal to 10 nm and d) is equal to 50 nm. Arrows indicate fine gold particles with dimensions expected of seed particles. .... 129

Figure 5-10 Cryo-TEM images of samples of a growing gold nanorod solution with 0.60 mM H<sub>2</sub>A taken at a) 13.5 min, b) 19 min, c) 29 min and d) 38 min. Scale bars for a) – d) are equal to 20 nm. The arrow indicates fine gold particles with dimensions expected of seed particles. .... 130

Figure 5-11 Percentage of metallic gold (with respect to the final concentration) during the growth of gold nanorods with 0.60 mM and 0.65 mM H<sub>2</sub>A, respectively. .... 131

Figure 5-12 SEM images of samples of growing gold nanorods taken at a) 5-7 min, b) 10-12 min and c) 30-32 min. Scale bars = 100 nm. The arrow in a) indicates fine gold particles with dimensions expected of seed particles. .... 133

Figure 5-13 Refinement of the transverse resonance peak in the later stages of a growing gold nanorod solution. The arrows indicate increasing time. .... 134

Figure 5-14 Nanoparticle geometries used for DDA simulations. a) – c) Intermediate nanoparticle geometries modelled from observations in cryo-TEM images. d) Final nanorod geometry. .... 135

Figure 5-15 Volume-normalised, DDA simulated extinction spectra of intermediate nanoparticle geometries modelled on TEM observations. Green dashed arrow indicates growth direction. Black solid arrows link diagrams of nanoparticles with their corresponding extinction spectrum. .... 135

Figure 5-16 a) Experimentally measured absorbance spectrum of a growing gold nanorod solution with 0.65 mM H<sub>2</sub>A in the growth solution. b) Distributions of simulated nanoparticle spectra combined according to several rules to mimic experimental spectra in a). c) Comparison of the peak positions for the experimental and simulated data in a) and b) respectively. .... 137