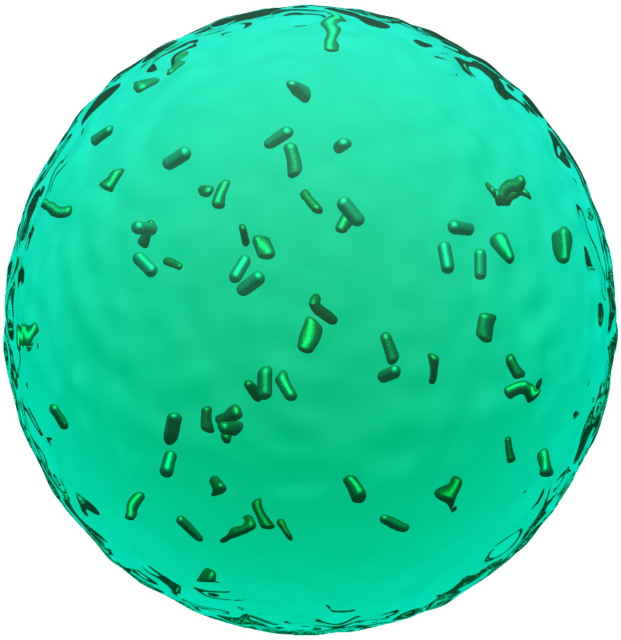

Development of New Methods for the Synthesis of Plasmonically-Active Precious Metal Rods and Shells

A thesis presented for the degree of Doctor of Philosophy

By

Jonathan A. Edgar

B. Sc. Hons. (Nanotechnology): University of Technology, Sydney

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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.

Production Note:
Signature removed prior to publication.

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 electrodynamics 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

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

"Synthesis of hollow gold nanoparticles and rings using silver templates"

2008 International Conference on Nanoscience and Nanotechnology **2008**, 36-39.

Jonathan A. Edgar, Michael B. Cortie

"Nanotechnological Applications of Gold Nanoparticles"

Gold: Science and applications. CRC Press: **2009**; p 369-397.

Andrey I. Denisyuk, Giorgio Adamo, Kevin F. MacDonald, Nikolay I. Zheludev, Matthew D. Arnold, **Jonathan A. Edgar**, Michael J. Ford, Viktor Myroshnychenko, Javier García de Abajo

"Transmitting hertzian optical nanoantenna with free-electron feed"

Nano Letters **2010,** 10, (9), 3250 – 3252

Nicholas L. Stokes, **Jonathan A. Edgar**, Andrew M. McDonagh, Michael B. Cortie

"Spectrally selective coatings of gold nanorods on architectural glass"

Journal of Nanoparticle Research **2010,** 12, (8), 2821 - 2830

Jonathan A. Edgar, Andrew M. McDonagh, Michael B. Cortie

"On the mechanism of formation of gold nanorods"

ACS Nano **2011** submitted

List of Abbreviations

^{1}H-NMR	nuclear magnetic resonance spectroscopy
A*	ascorbate radical
Ag or Ag^0	silver metal
Ag^+	silver ion
AgBr	silver bromide
$AgNO_3$	silver nitrate
AMMRF	Australian microscopy and microanalysis research facility
AR	aspect ratio
Au or Au^0	gold metal
Au_2S	gold sulphide
Au^{3+}	gold (III) ion
$AuBr_2^-$	gold (I) bromide
$AuBr_4^-$	gold (III) bromide
$AuCl_2^-$	gold (I) chloride
$AuCl_4^-$	gold (III) chloride
BDAC	hexadecyl-benzyldimethyl-ammonium chloride
BH_4^-	borohydride
Br^-	bromide
BSA	bovine serum albumin
BT	bow-tie
C_{16}TABr	hexadecyltrimethylammonium bromide
C_{16}TACl	hexadecyltrimethylammonium chloride
C_{16}TASBr	AgBr- C_{16}TABr complex
C_{16}TEABr	hexadecyl-triethylammonium bromide
CBT	conically-capped bow-tie
CC	conically-capped cylinder
CCG	complex conjugate gradient
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_2A	ascorbic acid
H_2PtCl_6	hexachloroplatinic acid
HA^-	ascorbate anion
$HAuBr_4$	tetrabromoauric acid
$HAuCl_4$	tetrachloroauric acid
HCl	hydrochloric acid
HDT	hexadecanethiol
HNO_3	nitric acid
ICP-MS	inductively coupled plasma - mass spectrometry
IR	infrared
ITO	indium tin oxide
KBH_4	potassium borohydride
LDR	lattice dispersion relation
LSP	localised surface plasmon
MRI	magnetic resonance imaging
Na_2S	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_2	silicon dioxide
SPIO	super-paramagnetic iron oxide
SPP	surface plasmon polariton
$TC_{12}ABr$	tetradodecylammonium bromide

TC_8ABr	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

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