Synthesis, modelling and characterisation of gold nanoparticle colloidal crystals

A Thesis presented for the degree of

Doctor of Philosophy

by

Nadine Harris

B.E. Eng. (Elec.) (Hons.): University of Technology, Sydney

Institute for Nanoscale Technology

Faculty of Engineering

University of Technology, Sydney

December 2008

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 itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Chapter 1 contains a literature review prepared by myself. Chapter 2 describes the theoretical concepts behind the work presented in this thesis and while this theory is described in many textbooks and journal articles, I have presented it here in order to relate the most salient theoretical concepts appropriate to my research. Chapters 3 – 6 detail work done by me under the supervision of Associate Professor Mike Ford and Professor Michael Cortie along with advice from other colleagues. One exception should be noted. The work using the software package COMSOL in section 4.1 was contributed by Dr Matthew Arnold. Chapter 7 contains my concluding remarks and suggestions for future work.

Nadine Harris

Acknowledgements

Firstly, I would like to thank my supervisor Associate Professor Mike Ford whose guidance, infinite levels of patience, enthusiasm and limitless availability were paramount to this work and my development as a researcher. I've know Mike both professionally and socially during the time it has taken me to complete my PhD. During this time he has taught me how to follow the scientific method, the best way to negotiate a jump on my mountain bike, although I never did get it quite right, and finally how to climb Aunty Jack. I would also like to thank my co-supervisor Professor Michael Cortie for many discussions and support. I am indebted to all of my peers at the University of Technology, Sydney (UTS) in particular Dr Andrew McDonagh for his patience in supplementing my knowledge of chemistry, Dr Chris Poulton for his mathematical guidance, Ms Katie McBean for her help with Scanning Electron Microscopy and Dr Matthew Arnold for all things optical. Fellow PhD students, both past and present, who have helped me during my PhD include Dr Benjamin Soulé de Bas, Dr Rainer Hoft, Ms Dakrong Pissuwan, Mr Burak Cankurtaran, Mr Nicholas Stokes, Mr Michael (Bob) Coutts, and of course Mr Marty Blaber, who is exceedingly generous and has taught me many things during my PhD. In particular, how to program and write scripts which have saved me a considerable amount of time.

This PhD would not have been possible without the financial support of the Australian Research Council (ARC) and the ample computing time provided by the Australian Partnership for Advanced Computing (APAC) and the Australian Centre for Advanced Computing and Communications (AC3).

I have been fortunate enough to have been supported by many researchers external to UTS and I would like to thank Dr Åsa Jamting, Dr Bruce Warrington and Mr Malcolm

Lawn from the National Measurement Institute (NMI) in Lindfield for allowing me to use their particle sizer and laser. Also, thanks to Professor Paul Mulvaney from the University of Melbourne for his advice in both experimental and career matters and Professor Julian Gale from Curtin University for his help with GULP.

Finally, I would like thank my husband Gary and at this point I am lost for words to express how grateful I am for his unparalleled support while I have been working on my PhD. He will know what I mean when I simply say, “cheers mate!”

Contents

List of Figures

List of Tables

Glossary of Acronyms

BCC	Body Centred Cubic
CMR	Clausius Mossotti Relation
CTAB	Cetyltrimethylammonium Bromide
DDA	Discrete Dipole Approximation
DLS	Dynamic Light Scattering
EDS	Energy Dispersive Spectroscopy
ESEM	Environmental Scanning Electron Microscope
FCC	Face Centred Cubic
GULP	General Utility Lattice Program
HCP	Hexagonal Close-Packed
HHDT	16-Hydroxy-1-Hexadecanethiol
ITO	Indium-doped Tin Oxide
LBL	Layer By Layer
LDR	Lattice Dispersion Relation
MD	Molecular Dynamics
MEA	Mercaptoethyl Alcohol
MMA	Methyl Methacrylate
MSA	Mercaptosuccinic Acid
MUOH	11-Mercapto-1-Undecanol
MUTEG	1-Mercaptoundecyl Tetra(Ethylene Glycol)
NAG	N-Acetylglutathion
NIR	Near-Infrared
NNLS	Non Negative Least Squares Fit

PBCGST	Preconditioned BiConjugate Gradient Stabilisation
PIM	Parallel Iterative Methods
pMA	p-marcaptoaniline
PML	Perfectly Matched Layer
PMMA	Polymerised Methyl Methacrylate
SAXS	Small Angle X-ray Scattering
SC	Simple Cubic
SCLDR	Surface Corrected Lattice Dispersion Relation
SEM	Scanning Electron Microscope
SERS	Surface Enhanced Raman Scattering
TEM	Transmission Electron Microscope
T-matrix	Transition matrix
UV	Ultraviolet

Abstract

Three-dimensional, micron-sized colloidal crystals comprised of gold nanospheres have been synthesised directly from a gold nanoparticle/methyl methacrylate (MMA) colloid by application of a 514 nm laser at 480 mW. An array of colloidal crystals can be created by translation of the glass substrate under the laser beam, after two minutes of irradiation at each site. Control experiments and calculations show that plasmon-induced localised heating of the gold nanoparticles contributes to the rapid formation of colloidal crystals.

The effects of particle order and disorder on the optical response of three-dimensional structures containing 15 nm diameter gold nanospheres are investigated using the T-matrix technique. Calculations were performed on structures containing up to 163 particles. The ordered structures produce an additional extinction peak that is not present in the disordered structures. The position of this additional peak depends upon the inter-particle spacing. In the disordered structure this peak is therefore missing because the inter-particle spacing is not well-defined.

The optical response of a simplified array of a one-dimensional chain of 15 nm diameter gold nanospheres in the regime where the near-fields of the particles are coupled is investigated using the T-matrix technique. Calculations are performed with chains up to 150 particles in length and with an inter-particle spacing between 0.5 and 30 nm. For wavevectors perpendicular to the chain axis and longitudinal polarisation the extinction peak red-shifts as the inter-particle spacing is reduced. The magnitude of the peak-shift is inversely proportional to the inter-particle spacing, a result that is consistent with the Van der Waals attraction between two spheres at short range. For a fixed particle gap the

extinction peak tends towards an asymptotic value with increasing chain length, with the asymptotic value determined by the inter-particle spacing.

A nanoshell geometry that produces maximum absorption efficiency is investigated using a formulation of Mie theory. The calculated surface heat flux under sunlight (800 W/m^2) and laser (50 kW/m^2) irradiation is used to determine the temperature of the nanoshell using a convective heat transfer model. For irradiation by sunlight, the resultant heat flux is optimised for an 80 nm diameter nanoshell with an aspect ratio of 0.8, while for irradiation by laser the maximum heat flux is found for 50 nm nanoshells, but with an aspect ratio of 0.9.

A direct comparison between the absorption efficiencies of geometrically varying nanoshells and nanorods is performed using a formulation of Mie theory and the Discrete Dipole Approximation (DDA) technique, respectively. The absorption efficiency produced by nanorods far exceeds that produced by nanoshells for a constant volume of gold.