



On the Thermal Stability of Ligand-Stabilised Gold Nanoparticles

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

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Certificate of Original Authorship

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.

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List of Abbreviations

AU	arbitrary units
AuNP	gold nanoparticle
BT@AuNPs	1-butanethiol-stabilised AuNPs
CDCl ₃	deuterated chloroform (chloroform-d)
Citrate@AuNPs	tri-sodium citrate-stabilised AuNPs
CTAB	cetyltrimethylammonium bromide
DCM	dichloromethane
DD	n-dodecane
DDT	1-dodecanethiol
DDT@AuNPs	1-dodecanethiol-stabilised AuNPs
DPDI	<i>N,N'</i> -dioleyl-3,4,9,10-perylenedicarboximide
DSC	differential scanning calorimetry
EDS	energy dispersive spectroscopy
fcc	face-centred cubic
FWHM	full width at half maximum
HAuCl ₄	tetrachloroauric acid
HBC	hexabenzocoronene
HBC-acetylene	penta(<i>tert</i> -butyl)-substituted hexa- <i>peri</i> -hexabenzocoronene-acetylene
HCl	hydrochloric acid
HD	n-hexadecane
HDT	1-hexadecanethiol
HDT@AuNPs	1-hexadecanethiol-stabilised AuNPs
HNO ₃	nitric acid
HPB	hexaphenylbenzene
ICP-MS	inductively coupled plasma mass spectrometry
IR	infrared spectroscopy
KMnO ₄	potassium permanganate
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry
LSPR	localised surface plasmon resonance
molecules/NP	molecules per nanoparticle
MS	mass spectrometry
NaBH ₄	sodium borohydride

NaClO	sodium hypochlorite
Na ₂ S ₂ O ₃	sodium thiosulfate
NIR	near-infrared
NMR	nuclear magnetic resonance
OA	oleylamine
OA@AuNPs	oleylamine-stabilised AuNPs
OT	1-octanethiol
OT@AuNPs	1-octanethiol-stabilised AuNPs
Pc	phthalocyanine
PyBuOH	1-pyrenebutanol
PyBuSH	1-pyrenebutanethiol
Py@AuNPs	1-pyrenebutanethiol-stabilised AuNPs
4-py ^t Bu	4- <i>tert</i> -butylpyridine
RGB	red green blue
RuPc	ruthenium phthalocyanine
[RuPc(4-py ^t Bu) ₂]	[(4- <i>tert</i> -butylpyridine) ₂ ruthenium phthalocyanine]
[RuPc(4-py(CH ₂) ₃ SAc)(4-py ^t Bu)]	[(<i>S</i> -[3-(4-Pyridinyl)propyl]ethanethioate)(4- <i>tert</i> -butylpyridine)ruthenium phthalocyanine]
[RuPc(4-pyCH ₂ SAc) ₂]	[(<i>S</i> -[4-Pyridinylmethyl]ethanethioate) ₂ ruthenium phthalocyanine]
SAED	selected area electron diffraction
SEM	scanning electron microscopy
SERS	surface-enhanced Raman spectroscopy
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TOAB	tetraoctylammonium bromide
<i>T</i> _{SE}	temperature of the sintering event
UOW	University of Wollongong
UTS	University of Technology Sydney
UV-visible	ultraviolet visible spectroscopy
XRD	X-ray diffraction

Publications Arising From This Work

- **King, S.R.**; Massicot, J.; McDonagh, A.M. A Straightforward Route to Tetrachloroauric Acid from Gold Metal and Molecular Chlorine for Nanoparticle Synthesis.
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- Dehn, M.H.; Arseneau, D.J.; Buck, T.; Cortie, D.L.; Fleming, D.G.; **King, S.R.**; MacFarlane, W.A.; McDonagh, A.M.; McFadden, R.M.L.; Mitchell, D.R.G.; Kiefl, R.F. Evidence for Magnetism in Thiol-Capped Gold Nanoparticles Observed with Muon-Spin-Rotation.
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Abstract

Gold nanoparticles possess many interesting and useful properties, which have made them the subject of extensive research. The most notable of these are their optical properties, which can be tuned to suit a variety of applications or monitored as conditions change for sensing applications. The thermal stability of gold nanoparticles is also of particular interest, as this affects their sintering behaviour and therefore their utility in applications such as printed electronics, catalysis and sensing. The bulk of the research on thermal stability has focussed on lowering their stability to facilitate the formation of continuous, electrically conducting films at moderate to low temperatures. However, relatively little is known about increasing their thermal stability for applications where it is necessary for their useful properties to be retained at higher temperatures. This thesis presents an investigation into the thermal stability of gold nanoparticles, with a focus on probing the upper temperature limits of stabilising the particles using organic compounds. Firstly, a new method was developed for synthesising gold chloride as a precursor to gold nanoparticle synthesis, using the known reaction of gold metal with chlorine gas. The resulting gold chloride solutions were of high purity and stability, and were used directly for synthesising the nanoparticles used in this project. For the thermal stability studies, a selection of compounds was tested for their ability to delay the onset of nanoparticle sintering upon heating at a constant rate. Samples were analysed using a range of techniques including electrical resistance measurements, SEM, TGA, and XRD. Comparisons were made between stabilisers that were bound to the particles and those that were mixed with the particles without being chemically attached. A number of compounds of high thermal stability and compatible solubility were identified as particularly effective stabilisers, such as a ruthenium phthalocyanine complex, oleylamine, 1-pyrenebutanethiol and a perylenedicarboximide derivative, with sintering of the particles not occurring until more than 300 °C with these stabilisers, up to an unprecedented 540 °C. Important insights were also gained into the interactions between nanoparticles and unbound stabilisers and the qualities required for an effective stabiliser. Some of the highly stable gold nanoparticles were then monitored for changes in their optical and structural properties with temperature using reflection spectroscopy and SEM, with the results having potential applications in high temperature optical sensing and thermal history indicators.