# A Study into the Kinetic Formation and Oxidation States of Gold Nanoparticles Produced via Laser Ablation Synthesis in Solution

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*A thesis submitted in total fulfilment of the requirements for the degree of Doctor of Philosophy*

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# AFFIDAVIT

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# ABSTRACT

Nano-sized gold particles are generated by exploiting the laser ablation synthesis in solution technique (LASiS) from gold metal disc. We report on the kinetics of gold nanoparticle (AuNP) production during LASiS and the resulting size distributions. Studies were conducted as a function of laser irradiation in pure water samples, with anionic surfactants, sodium dodecylsulphate (SDS), and cationic surfactants, cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC), in water. Our investigations provide a mechanistic insight into the laser-induced formation kinetics involved in AuNP production via 1064 nm laser irradiation in aqueous solution. This has been achieved by developing a kinetic model involving three different AuNP size regimes. Specifically, we have found that there is no apparent influence of the SDS concentration around the surfactant critical micelle concentration (CMC) on particle size during AuNP production. This is in contrast to results observed for size reduction via 532-nm irradiation where a clear CMC effect has previously been observed. [Yamada et al, *J. Phys. Chem. B*, 2006, 110, 11751-11756] In addition, we also explore the surface oxidation states of produced AuNPs in various surfactants using X-ray photoelectron spectroscopy (XPS). Our investigations shows the $Au^{III}$ chemical oxidation state was present in produced AuNPs in high concentrations of CTAB and CTAC, but absent in those produced in pure water and SDS solution.

Prior to XPS investigations on the LASiS prepared AuNPs, a study to observe the behavior of gold during irradiation of X-rays was performed. We report on the time evolution of the Au oxidation state in sodium tetrachloroaurate $NaAuCl_4$ as a function of soft X-ray exposure time. Our investigations provide mechanistic insight into the photoreduction kinetics from $Au^{III}$ to $Au^{I}$ and then subsequently $Au^{I}$ to $Au^{0}$.We unambiguously show that XPS photoreduction occurs in stepwise fashion via the $Au^{I}$ state.

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# PUBLICATIONS TO DATE

**Laser-Based Formation and Properties of Gold Nanoparticles in Aqueous Solution: Formation Kinetics and Surfactant-Modified Particle Size Distributions.**

Fong, Y. Y.; Gascooke, J. R.; Visser, B. R.; Metha, G. F.; Buntine, M. A. *J. Phys. Chem. C* **2010**, *114*, 15931-15940.

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Fong, YY; Visser, BR; Gascooke, JR; Cowie, BCC; Thomsen, L; Metha, GF; Buntine, MA; Harris, HH *Langmuir* **2011**, *27(13)*, 8099-8104.

**Influence of Surfactant Concentration on Laser-Based Gold Nanoparticle Formation and Stability**

Fong, Y. Y.; Gascooke, J. R..; Metha, G. F.; Buntine, M. A.*Aus. J. Chem **2011**, 65(2),* 97-104.

# ABBREVIATIONS

| | |
|---|---|
| AS | Australian Synchrotron |
| Au | Gold |
| $Au^0$ | Zero oxidation state of gold |
| $Au^I$ | First oxidation state of gold |
| $Au^{III}$ | Third oxidation state of gold |
| AuNP | Gold Nanoparticles |
| $AuNP_{(small)}$ | Small gold nanoparticles |
| $AuNP_{(med)}$ | Medium gold nanoparticles |
| $AuNP_{(large)}$ | Large gold nanoparticles |
| $AuNP_{(bulk)}$ | Bulk gold nanoparticles |
| CMC | Critical micelle concentration |
| FWHM | Full width half max |
| $HAuCl_4$ | Tetrachloroauric acid |
| Hz | Hertz |
| $K_{sol}$ | Solubility constant |
| $k_l$ | Rate constant for forward reaction of large particle |
| $k_{-l}$ | Rate constant for reverse reaction of large particle |
| $k_m$ | Rate constant for forward reaction of medium particle |
| $k_{-m}$ | Rate constant for reverse reaction of medium particle |
| $k_s$ | Rate constant for forward reaction of small particle |
| $k_{-s}$ | Rate constant for reverse reaction of small particle |
| $k_{ml}$ | Rate constant for forward reaction from medium to large particle |
| $k_{lm}$ | Rate constant for reverse reaction from medium to large particle |
| $k_{sm}$ | Rate constant for forward reaction from small to medium particle |
| $k_{ms}$ | Rate constant for reverse reaction from small to medium particle |
| $k_{sl}$ | Rate constant for forward reaction from small to large particle |
| $k_{ls}$ | Rate constant for reverse reaction from small to large particle |
| $k_1$ | Rate constant for forward reaction from $Au^{III}$ to $Au^I$ |
| $k_{-1}$ | Rate constant for reverse reaction from $Au^{III}$ to $Au^I$ |
| $k_2$ | Rate constant for forward reaction from $Au^I$ to $Au^0$ |
| $k_{-2}$ | Rate constant for reverse reaction from $Au^I$ to $Au^0$ |

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|---|---|
| LASiS | Laser ablation synthesis in solution |
| $NaAuCl_4$ | sodium tetrachloroaurate |
| nm | nanometre |
| SD | Standard Deviation |
| SDS | Sodium dodecylsulphate |
| Si | silicon |
| SPB | Surface plasmon band |
| TEM | Transmission electron microscopy |
| XPS | X-ray photoelectron spectroscopy |
| $\lambda$ | Wavelength |
| $\sigma$ | Standard deviation |

# TABLE OF CONTENTS

The END

# LIST OF FIGURES

# LIST OF TABLES