

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*

Date: December 2011  
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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<sup>III</sup> 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<sub>4</sub> as a function of soft X-ray exposure time. Our investigations provide mechanistic insight into the photoreduction kinetics from Au<sup>III</sup> to Au<sup>I</sup> and then subsequently Au<sup>I</sup> to Au<sup>0</sup>. We unambiguously show that XPS photoreduction occurs in stepwise fashion via the Au<sup>I</sup> state.

## ACKNOWLEDGMENTS

I would first like to thank my principle supervisor Professor Mark Buntine for granting me an opportunity to study this PhD. His passion and enthusiasm on science has inspired me to become a “great” scientist over the years (it is too memorable). In particular, he has given me all the freedom to pursue new ideas. Moreover, Mark is a generous man who sincerely cares for my colloid project since he is a spectroscopist.

I also thank my co-supervisor Associate Professor Greg Metha for his encouragement that he has given me over the past few years. Especially in the early stage of my PhD, he has never given up on communicating with me due to my poor language skill which is well known as “Mablish”.

Dr Jason Gascooke has been a great mentor and friend throughout my PhD, almost like my supervisor. He has taught me to be patient, advice me on perseverance with my research and encourage me on how to write a logic scientific paper which is my weakness. Without his passion of love in science, I would not have finished my PhD. There are so much to thank him for. In here, I sincerely thank him for everything in my PhD life from the bottom of my heart.

The past and present laser lab members at the University of Adelaide has shared in the joy of working hours in the lab, other activities outside the lab e.g. camping trip, student conferences, barbeques and retreats etc and the core component involved in these activities is “Alcohol”. I specially thank my academic sister, Dr Olivia Maselli, for sharing the joy of discussions and her moral and science support. I also thank Australian Government for granting me the Endeavour Awards to study at University of Tokyo, Japan.

Finally, I sincerely thank my parents, Fook-Cheung Fong and Po-Wah Yam for supporting me morally and financially throughout my life. They specially flow over to Adelaide, Australia from Hong Kong every year to support me. The memorable moment is Mum’s cooking which I missed the most. I also thank my sister (Fiona Fong) and my brother in law (Cyrus Shum) for their loves and cares. My niece (Eleanor Shum) has given me a lot of happiness during her first trip of Oz land. I hope my most adorable pets, JoJo, BB and QuQu, would excuse my absence on their last journey of their lives. The last, during every day of my tough PhD journey, I would like to thank my be-loved cat, GoGo, who always loves me, cheers me up on my good and bad days and be there for me.

## **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.

### **Photoreduction Kinetics of Sodium Tetrachloroaurate under Synchrotron Soft X-ray Exposure**

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 <sup>0</sup>	Zero oxidation state of gold
Au <sup>I</sup>	First oxidation state of gold
Au <sup>III</sup>	Third oxidation state of gold
AuNP	Gold Nanoparticles
AuNP <sub>(small)</sub>	Small gold nanoparticles
AuNP <sub>(med)</sub>	Medium gold nanoparticles
AuNP <sub>(large)</sub>	Large gold nanoparticles
AuNP <sub>(bulk)</sub>	Bulk gold nanoparticles
CMC	Critical micelle concentration
FWHM	Full width half max
HAuCl <sub>4</sub>	Tetrachloroauric acid
Hz	Hertz
$K_{sol}$	Solubility constant
$k_1$	Rate constant for forward reaction of large particle
$k_{-1}$	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 <sup>III</sup> to Au <sup>I</sup>
$k_{-1}$	Rate constant for reverse reaction from Au <sup>III</sup> to Au <sup>I</sup>
$k_2$	Rate constant for forward reaction from Au <sup>I</sup> to Au <sup>0</sup>
$k_{-2}$	Rate constant for reverse reaction from Au <sup>I</sup> to Au <sup>0</sup>

LASiS	Laser ablation synthesis in solution
NaAuCl <sub>4</sub>	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

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