The Characterisation, Photocatalytic Performance, and Theoretical Investigation of Small Gold Clusters Supported on Titanium Dioxide Nanoparticles

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

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Declaration

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Abstract

Renewable photocatalytic systems that can use solar radiation to produce chemical fuels are appealing technologies that have garnered much interest over the last few decades. The development of novel gold-based heterogeneous photocatalysts has the potential to drive this new form of green chemistry. In this thesis, ligand-protected, atomically precise gold clusters supported on titanium dioxide nanoparticles are characterised by various surface science techniques and their photocatalytic potential for water photolysis is investigated. Given the difficulty associated with acquiring experimental data in the incredibly small size regime of clusters, complementary density functional theory calculations are also performed to match with experimental data and to help elucidate the interactions occurring between gold atoms and the titanium dioxide surface.

The characterisation of these gold clusters begins with the far infra-red absorption spectra of isolated \( \text{Au}_6(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_4(\text{NO}_3)_2, \ \text{Au}_8(\text{PPh}_3)_8(\text{NO}_3), \ \text{Au}_9(\text{PPh}_3)_8(\text{NO}_3)_3, \ \text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_3, \ \text{Pd}(\text{PPh}_3)\text{Au}_6(\text{PPh}_3)_6(\text{NO}_3)_2, \ \text{and Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7(\text{NO}_3)_2 \) recorded using synchrotron light. These experiments reveal a series of unique peaks between 50 and 475 cm\(^{-1}\) that are assigned to specific vibrational modes by comparison with density functional theory calculations. The distinct peaks for each cluster can be assigned to the calculated cluster core vibrations: 80.4 and 84.1 cm\(^{-1}\) for \( \text{Au}_6; \) 165.1 and 166.4 cm\(^{-1}\) for \( \text{Au}_8; \) 170.1 and 185.2 cm\(^{-1}\) for \( \text{Au}_9; \) 173.7 and 182.2 cm\(^{-1}\) for \( \text{Au}_{11}; \) 158.9, 195.2, and 206.7 cm\(^{-1}\) for \( \text{Au}_6\text{Pd}; \) and 156.3, 171.8, and 173.5 cm\(^{-1}\) for \( \text{Au}_7\text{Pt}. \) There is also a strong absorption for all clusters near 420 cm\(^{-1}\) that are assigned to P-Ph\(_3\) vibrations.

Characterisation is continued with the use of Synchrotron X-ray and TEM techniques to investigate the full effect of treatments that are undertaken to remove the organic protective ligands after the gold clusters are supported upon titanium dioxide. These experiments show an increase in particle size and loss of ligands with successively harsher post-treatments. Acidic pre-treatment and the form of the titanium dioxide support are shown to have a strong impact on the severity of agglomeration and ligand loss. These results are also supported by X-ray absorption near edge structure and extended X-ray absorption near edge structure analysis of complementary X-ray absorption experiments.
The photocatalytic potential for water photolysis by these catalysts is also investigated using a new experimental apparatus designed and built during the project. It consists of a heterogeneous gas-phase reactor operating near ambient conditions that can deliver constant and controlled samples of gas to a residual gas mass spectrometer for analysis of the gas composition over time. Using this apparatus, Au₈(PPh₃)₈(NO₃)₂, Au₉(PPh₃)₉(NO₃)₃, and Au₁₀₁[P(C₆H₅)₃]₂Cl₅ supported on anatase or P25 TiO₂ nanoparticles are investigated for their activity towards water photolysis and their peak H₂ production rates are quantified. Anatase-supported samples are found to increase in activity with successively harsher post-treatment conditions, suggesting that increasing the size of the gold particles is beneficial for photocatalytic activity. In contrast, samples prepared on acid-washed P25 or acid-washed anatase show evidence of an ideal gold particle size and ligand coverage after relatively gentle post-treatment conditions.

Finally, density functional theory investigations are undertaken of Au₁, Au₂, Au₃, and Au₄ clusters bound to the stoichiometric and oxygen-deficient titanium dioxide anatase(101) surface using an atomic-centred basis set approach. Numerous isomers are found within 0.5 eV of the lowest energy structure for Au₂, Au₃, and Au₄. The structural parameters, binding energies, infrared spectra, charge transfer, and density of states for each isomer are described in detail. Key findings include: increased binding energy as the number of Au atoms are increased; strong Au-Au stretching and cluster breathing modes that shift considerably between isomers; charge transfer from the Au clusters to the titanium dioxide surface; and the introduction of numerous occupied gold states at the valence band edge that extend into the band gap. This work provides the foundation for future studies that will use these anatase models to investigate the properties of small Au clusters with photocatalytically relevant molecules and their reaction pathways.
Acknowledgements

First and foremost, the successful completion of this project would never have been possible without the guidance and support of my primary supervisor Prof. Greg Metha. Greg has provided me with a great deal of knowledge, advice, and encouragement throughout the entire project, without which the last few years would have been far less enjoyable. He has also given me many opportunities to perform experiments at the synchrotron and attend conferences to discover new science while meeting new people, for which I am grateful. I'd also like to thank my co-supervisors Dr. Tak Kee and Dr. David Huang for their support throughout the years and constructive critique of my work.

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Big thankyou to Peter Apoefis for building various parts of the experimental apparatus throughout the course of my project, as well as his patience when teaching me about vacuum system design and technical systems. Also thanks to Matthew Bull for helping me with many of the electronics and designing our pulsed nozzle driver. Without their help, construction of the new apparatus simply would not have been possible.

I would like to thank the Australian Synchrotron and their wonderful staff, especially Dr. Dominique Appadooo, who was always willing to come into the lab and help us even in the most ridiculous hours of the night. His hospitality while we were at the synchrotron with the 'Rastonites' was certainly more than one could ever ask for. In addition, Assoc. Prof. Hugh Harris and Dr. Claire Weekley were very helpful back in Adelaide for the analysis and interpretation of our XAS data.

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Last but certainly not least, I would like to thank my family for their love and support throughout my university studies, especially for being patient with what I am sure was a fairly grouchy and difficult Jason after many long hours spent in the lab or while writing my thesis. If it were not for my family encouraging me to head to university when I finished school, I would never have reached this stage of my studies.
Publications

The publications listed below contain some of the work presented in this thesis:

**Far-Infrared Absorption Spectra of Synthetically-Prepared, Ligated MetalClusters with Au₆, Au₈, Au₉ and Au₆Pd Metal Cores**

**Chemically-Synthesised, Atomically-Precise Gold Clusters Deposited and Activated on Titania**

**Chemically Synthesised Atomically Precise Gold Clusters Deposited and Activated on Titania. Part II**

The publications listed below are currently in preparation and will contain some of the work presented in this thesis:

**DFT Studies of Au₁₋₄ on the Stoichiometric and Oxygen-deficient TiO₂ Anatase(101) Surface**
Jason F. Alvino, Trystan Bennett, Gregory F. Metha.
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ADF-STEM</td>
<td>Angular Dark Field Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>AO</td>
<td>Atomic Orbital</td>
</tr>
<tr>
<td>AuNP</td>
<td>Au Nanoparticle</td>
</tr>
<tr>
<td>CEM</td>
<td>Channel Electron Multiplier</td>
</tr>
<tr>
<td>CSD</td>
<td>Cambridge Structural Database</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>DOS</td>
<td>Density of States</td>
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<tr>
<td>ECP</td>
<td>Effective Core Potential</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>FC</td>
<td>Faraday Cup</td>
</tr>
<tr>
<td>FCC</td>
<td>Face Centred Cubic</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalised Gradient Approximation</td>
</tr>
<tr>
<td>GTO</td>
<td>Gaussian Type Orbital</td>
</tr>
<tr>
<td>HBP</td>
<td>High Binding Peak</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>LBP</td>
<td>Low Binding Peak</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localised Surface Plasmon Resonance</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular Orbital</td>
</tr>
<tr>
<td>NBO</td>
<td>Natural Bond Orbital</td>
</tr>
<tr>
<td>O$_{2c}$</td>
<td>2 Coordinated Oxygen Atom</td>
</tr>
<tr>
<td>O$_{3c}$</td>
<td>3 Coordinated Oxygen Atom</td>
</tr>
<tr>
<td>PBC</td>
<td>Periodic Boundary Conditions</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional-Integral-Derivative</td>
</tr>
<tr>
<td>RGA</td>
<td>Residual Gas Analyser</td>
</tr>
<tr>
<td>SCF</td>
<td>Self-Consistent Field</td>
</tr>
<tr>
<td>SOMO</td>
<td>Singly Occupied Molecular Orbital</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunnelling Microscopy</td>
</tr>
<tr>
<td>STO</td>
<td>Slater Type Orbital</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
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</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<tr>
<td>Ti_{4c}</td>
<td>4 Coordinated Ti Atom</td>
</tr>
<tr>
<td>Ti_{5c}</td>
<td>5 Coordinated Ti Atom</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge Structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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<tr>
<td>ZPE</td>
<td>Zero-point Energy</td>
</tr>
</tbody>
</table>
# Table of Contents

Declaration I  
Abstract II  
Acknowledgements IV  
Publications VI  
Abbreviations VII  

## Chapter 1. Introduction

1.1 Background 2  
1.2 Photocatalysis 4  
1.2.1 Semiconductor Electrodes and Supports 5  
1.2.2 Mechanisms of Photocatalysis 7  
1.2.3 Semiconductor Nanoparticles as Supports 9  
1.3 TiO₂ Photocatalysis 12  
1.3.1 The Structure of TiO₂ Surfaces and Nanoparticles 13  
1.3.2 TiO₂ Defects 15  
1.3.3 Co-catalysts, Lattice Doping, and Dye Sensitisation 16  
1.4 The Catalytic Capacity of Gold Nanoparticles 19  
1.4.1 Gold Nanoparticles Supported on TiO₂ 20  
1.4.2 Growth and Morphology of Gold Nanoparticles Supported Upon TiO₂ 20  
1.5 Particle Size Effects 24  
1.5.1 Clusters versus Nanoparticles 24  
1.5.2 Optical and Electronic Properties of Gold Nanoparticles 24  
1.5.3 Size Effects on Catalytic Activity 26  
1.5.4 Atomically Precise, Ligand Stabilised, Small Gold Clusters 28  
1.6 Gas-Phase Photocatalysis 32  
1.7 The Scope of this Thesis 33

## Chapter 2. Experimental Techniques, Apparatus, and Method

2.1 Catalyst Synthesis and Preparation 37  
2.1.1 Preparation of Ligated Gold Clusters 37
2.1.2 Preparation of TiO₂-Supported Gold Clusters 38
2.1.3 Activation Post-Treatment of Supported Gold Clusters 38
2.1.4 Preparation of Platinised TiO₂ Nanoparticles 39
2.2 Far-IR Spectroscopy 41
  2.2.1 Sample Preparation and Apparatus 42
2.3 X-ray Photoelectron Spectroscopy 43
  2.3.1 Sample Preparation and Apparatus 44
  2.3.2 Peak Fitting 45
2.4 X-ray Absorption Spectroscopy 46
  2.4.1 Sample Preparation and Apparatus 48
  2.4.2 Data Analysis 49
2.5 Transmission Electron Microscopy Studies 51
2.6 Photocatalysis Investigations 52
  2.6.1 Description of the Photocatalysis Experimental Apparatus 52
  2.6.2 Sample Preparation 57
  2.6.3 Experimental Procedure 57
  2.6.4 Residual Gas Analyser and Quadrupole Ion Filter 58
  2.6.5 Data Acquisition 59
  2.6.6 Post-Experiment Data Analysis 60
  2.6.7 Calibration 63
    2.6.7.1 Gas Fractionation 64
    2.6.7.2 Linear Detector Response 65

Chapter 3. Computational Theory and Method 68
3.1 Introduction to Density Functional Theory 68
  3.1.1 The Schrödinger Equation 68
  3.1.2 The Variational Principle 69
  3.1.3 Electron Density Functionals 70
3.2 Basis Sets 73
3.3 Computational Methods 76
  3.3.1 Calculation of Ligated Gold Clusters 76
  3.3.2 Calculation of the Anatase(101) Surface and Au₁₋₄ Clusters 77
Chapter 4. DFT Assisted Characterisation of the Far-Infrared Spectra of Au₆, Au₈, Au₉, Au₁₁, Au₆Pd, and Au₇Pt Clusters

4.1 Optimised Ligated Metal Cluster Geometries 80
4.2 Far-IR Results and DFT Assignment 81
   4.2.1 AuPPh₃Cl 81
   4.2.2 Au₆ 84
   4.2.3 Au₈ 88
   4.2.4 Au₉ 90
   4.2.5 Au₁₁ 94
   4.2.6 Au₆Pd 99
   4.2.7 Au₇Pt 102
4.3 Charge Population Analysis 106
4.4 Conclusions 108

Chapter 5. X-ray and TEM Characterisation of Au₈, Au₉, Au₁₁, and Au₁₀₁ Clusters

5.1 X-ray Photoelectron Spectroscopy Studies of TiO₂-Supported Gold Clusters 110
   5.1.1 Au₈, Au₉, Au₁₁, and Au₁₀₁ Supported on Acid-washed P25 Nanoparticles 114
      5.1.1.1 Untreated 114
      5.1.1.2 Washed at 100 °C 114
      5.1.1.3 Heated Under Vacuum at 200 °C 116
   5.1.2 Au₈, Au₉, and Au₁₀₁ Supported on Pure Anatase Nanoparticles 117
      5.1.2.1 Untreated 117
      5.1.2.2 Calcined under O₂ at 200 °C 118
      5.1.2.3 Calcined under O₂ followed by H₂ at 200 °C 118
   5.1.3 Comparison Between Supports 119
5.2 X-ray Absorption Near Edge Structure of Supported Gold Clusters 120
   5.2.1 Anatase-Supported Au₉ clusters 120
   5.2.2 Silica-Supported Au₉ clusters 124
5.3 Extended X-ray Absorption Fine Structure Analysis 128
   5.3.1 Unsupported Au₈ and Au₉ 128
   5.3.2 Anatase- and Silica-Supported Au₉ Clusters 131
5.4 Transmission Electron Microscopy Studies of TiO₂-Supported Gold Clusters 136
   5.4.1 Angular Dark Field Scanning Transmission Electron Microscopy 136
Chapter 6. Photocatalytic Studies of Au₈, Au₉, and Au₁₀¹ Supported on TiO₂ Nanoparticles

6.1 Experimental Benchmarks and Preliminary Evaluations
6.1.1 Photocatalytic Performance of Pt-TiO₂ for Water-Splitting
6.1.2 Degradation of Samples and Observed Colour Changes
6.1.3 Effects of Sample Exposure to Vacuum
6.1.4 Production of CO₂ and Consumption of O₂
   6.1.4.1 The Behaviour of Atomic and Gaseous Oxygen Species
   6.1.4.2 Sources of Carbon Contamination
6.2 Photocatalytic Performance of Au Clusters on TiO₂ for Water-Splitting
   6.2.1 Photocatalytic Performance of the Au₈ cluster
   6.2.2 Photocatalytic Performance of the Au₉ cluster
   6.2.3 Photocatalytic Performance of the Au₁₀¹ cluster
   6.2.4 Overall Comparisons of the Photocatalytic Performance Between Clusters
6.2.5 Photocatalytic Performance of Au₈, Au₉, and Au₁₀¹ Compared to Pt-TiO₂
6.3 Conclusions

Chapter 7. DFT Studies of Au₁-₄ on the Stoichiometric and Oxygen-Deficient TiO₂ Anatase(101) Surface

7.1 Optimisation of the Anatase(101) Model
7.1.1 Anatase(101) Model Size Considerations
7.2 Structural Parameters and Binding Energies
   7.2.1 Stoichiometric TiO₂ Anatase(101)
     7.2.1.1 Discussion
   7.2.2 Oxygen-Deficient TiO₂ Anatase(101)
     7.2.2.1 Discussion
7.3 Predicted Vibrational Spectra
   7.3.1 Au₁ on the Stoichiometric and Oxygen-Deficient Anatase(101) Surfaces
   7.3.2 Au₂ on the Stoichiometric and Oxygen-Deficient Anatase(101) Surfaces
   7.3.3 Au₃ on the Stoichiometric and Oxygen-Deficient Anatase(101) Surfaces