

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

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**Jason Frankie Alvino**

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*of* ADELAIDE

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School of Physical Sciences

Department of Chemistry

The University of Adelaide

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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  $\text{Au}_6(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_4(\text{NO}_3)_2$ ,  $\text{Au}_8(\text{PPh}_3)_8(\text{NO}_3)$ ,  $\text{Au}_9(\text{PPh}_3)_8(\text{NO}_3)_3$ ,  $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_3$ ,  $\text{Pd}(\text{PPh}_3)\text{Au}_6(\text{PPh}_3)_6(\text{NO}_3)_2$ , and  $\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7(\text{NO}_3)_2$  recorded using synchrotron light. These experiments reveal a series of unique peaks between 50 and  $475\text{ cm}^{-1}$  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  $84.1\text{ cm}^{-1}$  for  $\text{Au}_6$ ;  $165.1$  and  $166.4\text{ cm}^{-1}$  for  $\text{Au}_8$ ;  $170.1$  and  $185.2\text{ cm}^{-1}$  for  $\text{Au}_9$ ;  $173.7$  and  $182.2\text{ cm}^{-1}$  for  $\text{Au}_{11}$ ;  $158.9$ ,  $195.2$ , and  $206.7\text{ cm}^{-1}$  for  $\text{Au}_6\text{Pd}$ ; and  $156.3$ ,  $171.8$ , and  $173.5\text{ cm}^{-1}$  for  $\text{Au}_7\text{Pt}$ . There is also a strong absorption for all clusters near  $420\text{ cm}^{-1}$  that are assigned to P- $\text{Ph}_3$  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,  $\text{Au}_8(\text{PPh}_3)_8(\text{NO}_3)_2$ ,  $\text{Au}_9(\text{PPh}_3)_8(\text{NO}_3)_3$ , and  $\text{Au}_{101}[\text{P}(\text{C}_6\text{H}_5)_3]_{21}\text{Cl}_5$  supported on anatase or P25  $\text{TiO}_2$  nanoparticles are investigated for their activity towards water photolysis and their peak  $\text{H}_2$  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  $\text{Au}_1$ ,  $\text{Au}_2$ ,  $\text{Au}_3$ , and  $\text{Au}_4$  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  $\text{Au}_2$ ,  $\text{Au}_3$ , and  $\text{Au}_4$ . 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.

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## Publications

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

### **Far-Infrared Absorption Spectra of Synthetically-Prepared, Ligated Metal Clusters with Au<sub>6</sub>, Au<sub>8</sub>, Au<sub>9</sub> and Au<sub>6</sub>Pd Metal Cores**

Jason F. Alvino, Trystan Bennett, David Anderson, Baira Donoeva, Daniil Ovoshchnikov, Rohul H. Adnan, Dominique Appadoo, Vladimir Golovko, Gunther Andersson, Gregory F. Metha, RSC Advances, 3, 22140–22149 (2013).

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

David P. Anderson, Jason F. Alvino, Alexander Gentleman, Hassan Al Qahtani, Lars Thomsen, Matthew I.J. Polson, Gregory F. Metha, Vladimir B. Golovko, Gunther G. Andersson, Physical Chemistry Chemical Physics, 15, 3917–3929 (2013).

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

David P. Anderson, Rohul H. Adnan, Jason F. Alvino, Oliver Shipper, Baira Donoeva, Jan-Yves Ruzicka, Hassan Al Qahtani, Hugh H. Harris, Bruce Cowie, Jade B. Atkin, Vladimir B. Golovko, Gregory F. Metha, Gunther G. Andersson, Physical Chemistry Chemical Physics, 15, 14806–14813 (2013).

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

### **DFT Studies of Au<sub>1-4</sub> on the Stoichiometric and Oxygen-deficient TiO<sub>2</sub> Anatase(101) Surface**

Jason F. Alvino, Trystan Bennett, Gregory F. Metha.

## Abbreviations

ADF-STEM	Angular Dark Field Scanning Transmission Electron Microscopy
AO	Atomic Orbital
AuNP	Au Nanoparticle
CEM	Channel Electron Multiplier
CSD	Cambridge Structural Database
DFT	Density Functional Theory
DOS	Density of States
ECP	Effective Core Potential
eV	Electron Volt
EXAFS	Extended X-ray Absorption Fine Structure
FC	Faraday Cup
FCC	Face Centred Cubic
FWHM	Full Width at Half Maximum
GGA	Generalised Gradient Approximation
GTO	Gaussian Type Orbital
HBP	High Binding Peak
HOMO	Highest Occupied Molecular Orbital
HRTEM	High-resolution Transmission Electron Microscopy
LBP	Low Binding Peak
LDA	Local Density Approximation
LSPR	Localised Surface Plasmon Resonance
LUMO	Lowest Unoccupied Molecular Orbital
MO	Molecular Orbital
NBO	Natural Bond Orbital
O <sub>2c</sub>	2 Coordinated Oxygen Atom
O <sub>3c</sub>	3 Coordinated Oxygen Atom
PBC	Periodic Boundary Conditions
PID	Proportional-Integral-Derivative
RGA	Residual Gas Analyser
SCF	Self-Consistent Field
SOMO	Singly Occupied Molecular Orbital
STM	Scanning Tunnelling Microscopy
STO	Slater Type Orbital

TEM	Transmission Electron Microscopy
Ti <sub>4c</sub>	4 Coordinated Ti Atom
Ti <sub>5c</sub>	5 Coordinated Ti Atom
UHV	Ultra High Vacuum
XANES	X-ray Absorption Near Edge Structure
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
ZPE	Zero-point Energy

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