

Carbon Dioxide Photo-Reduction by a Gold-Ruthenium Cluster Deposited upon Titanium Dioxide

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degree of Master of Philosophy



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Abstract

Solar photo-reduction of CO₂ is emerging as a highly attractive renewable energy source, as it provides both a renewable fuel and a non-atmospheric endpoint for greenhouse gas emissions. Photocatalytic conversion of CO₂ and H₂O to hydrocarbon fuels is well-established to occur using titanium dioxide decorated with metal nanoparticles, however the potential for atomically-precise metal clusters to act as co-catalysts upon TiO₂ for this reaction has been unexplored to date. In this work, a bimetallic Ru₃(μ-AuPPh₃)(μ-Cl)(CO)₁₀ cluster deposited upon TiO₂ (referred to as “AuRu₃-TiO₂”) is demonstrated to heterogeneously reduce CO₂ with water under ultraviolet irradiation. This is the first report of a cluster co-catalyst upon TiO₂ effectively photo-catalysing this reaction, and is found to perform more efficiently than a literature standard of platinum nanoparticle decorated TiO₂.

A range of C₁-C₃ hydrocarbon products are detected from AuRu₃-TiO₂, with molecular hydrogen also evolved from concomitant reduction of water. The dependences of photo-activity upon factors such as reaction temperature and reagent partial pressures are explored. Changing the co-catalyst by a single atom strongly influences both photoactivity and product selectivities. Photo-generation rates of all products of interest decay significantly under repeated testing, with only methane production remaining non-zero after four consecutive tests. Isotopic substitution of D₂O for H₂O shows less than 30% deuterium incorporation into generated hydrogen, but kinetic isotope effects suggest substantial deuteration of hydrocarbon products.

Diffuse reflectance spectroscopy reveals the emergence of a surface plasmon absorption band from AuRu₃-TiO₂ after photocatalysis, highly characteristic of cluster aggregation into larger gold nanoparticles. X-ray photoelectron spectroscopy indicates that the cluster remains intact on heating in vacuum, but forms a ruthenium oxide species on the TiO₂ surface after photo-reduction testing. N₂ adsorption, thermo-gravimetric analysis and temperature-programmed desorption experiments all provide evidence for partial de-ligation of the AuRu₃ cluster on heating in vacuum.

Deposition of de-ligated AuRu₃ upon anatase TiO₂ is modelled by density functional theory, using a Ti₁₄O₄₅H₂₆ model of the anatase (101) surface. In a neutral charge state, the lowest energy structure of AuRu₃ on the surface has octet multiplicity and a pseudo-trigonal pyramid geometry. The cluster inserts filled electronic states into both the TiO₂ valence band and band-gap, but effective orbital overlap occurs only with the former. Binding of H₂O and CO₂ to the surface is found to be weakened by the cluster withdrawing electron density from the adsorbate-surface interactions. CO ligands are bound to both the cluster or the anatase surface in approximately equal strength, and binding of a triphenylphosphine ligand significantly distorts the cluster geometry on the surface. Modelling of Au₁ and Ru₃ clusters on the surface indicates that the gold atom of AuRu₃ is much more weakly bound than ruthenium to both the bare surface and Ru₃-TiO₂, suggesting AuRu₃ likely aggregates on the surface via initial fragmentation into elemental components.

Publications

The publication detailed below is currently in preparation, and will contain some of the work presented in this thesis:

An Atomically-Precise Metal Cluster Co-Catalyst on TiO₂ for Artificial Photosynthesis

Rohan J. Hudson, Jason F. Alvino, Christiaan Ridings, Rohul Adnan, Siriluck Tesana,
Gunther G. Andersson, Vladimir B. Golovko & Gregory F. Metha.

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Abbreviations and Acronyms

AO	Atomic Orbital
AuRu ₃	Ru ₃ (μ-AuPPh ₃)(μ-Cl)(CO) ₁₀
BET	Brunauer-Emmett-Teller
CB	Conduction Band
CEM	Channel Electron Multiplier
CSD	Cambridge Structural Database
CGF	Contracted Gaussian Function
CNC	Computer Numerical Control
DOS	Density of States
DFT	Density Functional Theory
DRIFTS	Diffuse Reflectance Infrared Fourier-Transform Spectroscopy
DRS	Diffuse Reflectance Spectrophotometry
ECP	Effective Core Potential
ESR	Electron Spin Resonance
FID	Flame Ionisation Detector
FTIR	Fourier-Transform Infrared
FWHM	Full-Width Half-Maximum
GC	Gas Chromatograph
GGA	Generalised Gradient Approximation
GHG	Greenhouse Gas
GTO	Gaussian-Type Orbital
HF	Hartree-Fock
IPCC	Intergovernmental Panel on Climate Change
KIE	Kinetic Isotope Effect
LED	Light Emitting Diode
LDA	Local Density Approximation
LSPR	Localised Surface Plasmon Resonance
MO	Molecular Orbital

MS13	Molecular Sieve 13x
NHE	Normal Hydrogen Electrode
O _{2c}	Doubly-Coordinate Oxygen
O _{3c}	Triply-Coordinate Oxygen
PDOS	Partial Density of States
PEC	Photoelectrochemical Cell
PES	Potential Energy Surface
PID	Proportional-Integral-Derivative
RGA	Residual Gas Analyser
Ru ₃	Ru ₃ (CO) ₁₂
Ru ₄	H ₄ Ru ₄ (CO) ₁₂
SCF	Self Consistent Field
STO	Slater-Type Orbital
STEM	Scanning Transmission Electron Microscopy
TCD	Thermal Conductivity Detector
TD-DFT	Time-Dependent Density Functional Theory
TGA	Thermogravimetric Analysis
Ti _{5c}	5-Coordinate Titanium
TOF	Turn Over Frequency
TPD	Temperature-Programmed Desorption
UHV	Ultra High Vacuum
UV	Ultraviolet
VB	Valence Band
XAS	X-Ray Absorption Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
ZPE	Zero-Point Energy

Table of Contents

Declaration	i
Abstract	ii
Publications	iv
Acknowledgements	v
Abbreviations and Acronyms	vii
Chapter 1. Introduction	
1.1 Motivation and Background	2
1.2 Photocatalytic Solar Fuel Production	4
1.2.1 Principles of Photocatalysis	4
1.2.2 Hydrogen as a Solar Fuel	8
1.2.3 Carbon Dioxide Reduction	9
1.3 Titanium Dioxide Photocatalysts for CO ₂ Photo-Reduction	11
1.3.1 Bare Titania Photocatalysts	12
1.3.2 Co-Catalyst Loaded Titania	15
1.3.3 Doped Titania	18
1.3.4 Titania Composite Materials	21
1.3.5 Effect of Reaction Phase	22
1.3.6 Potential Photocatalytic Reaction Mechanisms	24
1.4 Metal Clusters as Catalysts	28
1.4.1 Nanoparticles and Clusters	28
1.4.2 Chemically-Synthesized, Atomically-Precise Clusters on Titania	30
1.5 The Scope of this Thesis	33

1.6	References	36
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Chapter 2. Experimental Methods and Techniques

2.1	Photocatalyst Synthesis, Deposition and Preparation	69
2.1.1	Cluster Synthesis and Deposition on Anatase Titania	69
2.1.2	Synthesis of Platinised TiO ₂ Nanoparticle Standard	70
2.1.3	Photocatalyst Preparation and Immobilisation	70
2.2	Gas-Phase Photocatalysis	71
2.2.1	Apparatus Description	71
2.2.2	Photocatalytic Testing Procedure	75
2.2.3	Temperature-Programmed Desorption Procedure	76
2.2.4	Data Reduction and Analysis	77
2.2.4.1	RGA Data Analysis	77
2.2.4.2	GC Data Analysis	79
2.3	UV-Visible Diffuse Reflectance Spectrophotometry	81
2.3.1	UV-Vis DRS Procedure	82
2.4	X-ray Photoelectron Spectroscopy	83
2.4.1	XPS Procedure	84
2.5	Brunauer-Emmett-Teller Adsorption Analysis	85
2.5.1	N ₂ Adsorption Procedure	86
2.6	Thermo-Gravimetric Analysis	87
2.7	References	88

Chapter 3. Computational Theory and Procedure

3.1	Density Functional Theory	93
3.1.1	The Schrödinger Equation	93
3.1.2	The Hohenberg-Kohn Theorems	95
3.1.3	Exchange-Correlation Functionals	97
3.2	Basis Sets	99
3.3	Computational Procedure	103
3.4	References	106

Chapter 4. Photocatalytic Studies of AuRu₃ Deposited upon Anatase TiO₂

4.1	Determination of Standard Reaction Conditions	111
4.2	Photocatalytic Benchmarks and Comparisons	114
4.2.1	AuRu ₃ -TiO ₂ , Pt-TiO ₂ & Bare TiO ₂	114
4.2.2	AuRu ₃ -TiO ₂ , Ru ₃ -TiO ₂ & Ru ₄ -TiO ₂	120
4.3	The Oxidation Half-Reaction	124
4.4	Isotopic Labelling Studies	127
4.5	Catalytic Repeatability	130
4.6	Optimisation of Reaction Conditions	132
4.6.1	Reaction Temperature	132
4.6.2	CO ₂ :H ₂ O Ratio	135
4.7	Photocatalytic Efficiencies	139
4.8	Conclusions	142
4.9	References	144

Chapter 5. Surface Characterisation of AuRu₃ Deposited upon Anatase TiO₂

5.1	Diffuse Reflectance Spectrophotometry (DRS)	151
5.2	X-Ray Photoelectron Spectroscopy (XPS)	158
5.2.1	Pure AuRu ₃ and As-Prepared AuRu ₃ -TiO ₂	158
5.2.2	Vacuum-Heated and Post-Catalysis AuRu ₃ -TiO ₂	163
5.3	N ₂ Adsorption Analysis	167
5.4	De-ligation Studies: TPD & TGA-FTIR	169
5.4.1	Thermo-Gravimetric Analysis (TGA)	169
5.4.2	Temperature-Programmed Desorption (TPD)	172
5.5	Discussion and Conclusions	175
5.6	References	178

Chapter 6. Density Functional Theory Modelling of AuRu₃ Deposited upon Anatase TiO₂

6.1	AuRu ₃ on the Anatase Surface	183
6.2	Interactions of Small Molecules with AuRu ₃ -TiO ₂	189
6.2.1	CO ₂ and H ₂ O on TiO ₂ and AuRu ₃ -TiO ₂	189
6.2.2	CO and PPh ₃ Ligands on TiO ₂ and AuRu ₃ -TiO ₂	194
6.3	Modelling Aggregation of AuRu ₃ Clusters on TiO ₂	198
6.4	Conclusions	200
6.5	References	202

Chapter 7. Conclusions and Future Directions 204

Appendix A. Average Photocatalytic Reaction Rates	214
Appendix B. Calculation of Photocatalytic Turn-Over Frequencies (TOFs)	218
Appendix C. Calculations of Photocatalytic Energy Efficiencies	220
Appendix D. Fitted XPS Spectra	222
Appendix E. N ₂ Adsorption Isotherm Fitting and Calculated BET Parameters	230
Appendix F. Cartesian Coordinates and Electronic Energies of the Clusters and Adsorbates on the Anatase (101) Surface Model	233