Surface Plasmon Spectroscopy of Redox Processes on Single Gold Nanocrystals

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Abstract

Gold nanocrystals (Au NCs) are important materials for catalysis, sensing and photonics. Au NCs exhibit strong scattering signals in the visible and near infrared range due to localised surface plasmon resonances. Due to statistical averaging, when measurements are made on ensembles of particles, the precise determination of the effect of gold nanocrystal size, shape and local environment on specific application performance is not feasible. This ensemble problem is overcome by applying a combination of dark field imaging with surface plasmon spectroscopy, enabling the scattering spectra of individual nanocrystals to be measured. This approach allows changes in the electron concentration of a single Au NC to be observed via localised surface plasmon resonance shifts.

In this thesis, the dark field microscopy technique has been expanded to study single gold nanocrystal electrodeposition, gas-phase adsorption, photoreduction, and solid-state charging. The first key objective was to understand how nanocrystal morphology and surface properties influence underpotential deposition. The second key objective was to understand how metal oxide supports influence charge transport during hydrogen adsorption and photoexcitation. These studies clearly demonstrate that the above parameters are crucial to the electrochemical and catalytic properties of Au NCs. By performing the measurements on single nanocrystals, the chemical kinetics and charging rates could be uncovered with detail never before achieved at this scale.
In addition to using standard dark field microscopy techniques in this work, an upgraded laser illuminated dark field system was developed to optically reveal single particle charging rates by measuring electron transfer in real-time. The added sensitivity of this new approach has enabled the optical detection of fewer than 150 electrons as they are transferred to a single gold nanorod. In order to characterise the performance of the laser system, a reliable and reproducible method to rapidly charge single gold nanocrystals was developed. Au NCs were integrated in an ion gel capacitor, enabling them to be charged in a solid, transparent and highly capacitive device, ideal for transmission microscopy.
Declaration

This is to certify that:

i. the thesis comprises of only my original work towards the PhD except where indicated,

ii. due acknowledgement has been made in the text to all other material used,

iii. the thesis is less than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.

Sean S. E. Collins
Preface

The work within is presented as follows: A brief historical introduction with background information regarding the chemistry and physics of metal nanocrystals is presented in Chapter 1, along with three research questions answered in the chapters which follow. This chapter focuses on gold and silver nanocrystals which, owing to their strong plasmon resonance, are most relevant to surface plasmon spectroscopy. Chapter 2 discusses and describes the experimental methods used in the work and justifies their selection. In Chapter 3, the first of the three results chapters, work is presented on the underpotential deposition of silver onto single gold nanocrystals studied by spectroelectrochemistry. In all results presented, and in accordance with theory, when silver deposits on gold nanocrystal surfaces a blue-shift in the scattering spectrum is recorded. It is also shown that the crystal morphology and ligand properties strongly influence the way in which silver is reduced by and deposited onto a gold nanocrystal.

Chapter 4 continues to answer questions pertaining to redox processes on single gold nanocrystals but with a focus on metal oxide support effects. The chapter shows how hydrogen adsorption can be studied on single gold nanorods by monitoring changes in the electron density in real-time. The flexibility of dark field microscopy is demonstrated through the ability to monitor gold nanorods embedded in a variety of metal oxide films. It is shown how the nature of the supporting material strongly influences the adsorption of hydrogen and subsequent
charge transport with gold nanocrystals. Semiconductor supports with added platinum nanocrystals are shown to produce strong plasmon shifts on co-deposited gold nanorods, which is attributed to a spillover mechanism and the reducibility of the oxide. Chapter 4 also examines redox processes on gold nanocrystals in photoexcited metal oxide supports.

Chapter 5 describes improvements in the sensitivity of single particle surface plasmon spectroscopy targeted towards single electron detection. An optical setup was developed to answer specific questions about metal nanocrystal charging and to advance the detection limits of Rayleigh scattering based techniques. The development of a fully transparent quasi-solid state capacitor is initially described, which was used to test the setup’s performance. Charging traces of gold nanorods in the capacitor device are presented and were resolved by employing a supercontinuum laser and photon multiplier tube in conjunction with a transmission dark field microscope. In a straightforward manner, results showing how charging of a gold nanorods by fewer than 150 electrons can be detected using this new approach.

Future directions and conclusions from this body of work are discussed in Chapter 6. Finally, appendices are included at the end of the thesis to provide supplementary information to support findings from the main text where appropriate.

Parts of this thesis were carried out in collaboration with others. The nature and proportion of the contribution of others has been indicated in the footnotes throughout the main text.
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Throughout the course of this PhD project many people have made a significant contribution and without whom this thesis would not have been possible.

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Publications

To date, the work presented in this thesis has been published in the following peer-reviewed journal articles:


Other work carried out during the course of the thesis was published in the following peer-review journal articles:


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7.3 SEM images of a NaBH$_4$ treated Au nanostar before (a) and after (b) Ag deposition, obtained using the same potential sequence carried out in Figure 3.7. (c) Full scattering spectra of the above nanostar at various stages of the deposition process. This figure shows highlights the irregularity of the shifts induced by the shelling process because this nanostar underwent a decrease in scattering intensity with deposited Ag.
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List of Acronyms

Acronyms that appear throughout the text in this order have the following meanings:
NC - nanocrystal
NP - nanoparticle
SPR - surface plasmon resonance
LSPR - localised surface plasmon resonance
NR - nanorod
NIR - near infrared
fwhm - full width at half maximum
DDA - discrete dipole approximation
FDTD - finite difference time domain method
BEM - boundary element method
FEM - finite element method
SPS - surface plasmon spectroscopy
UV - ultraviolet
Vis - visible
SNOM - scanning near-field optical microscopy
SMS - spatial modulation spectroscopy
EELS - electron energy-loss spectroscopy
TIRM - total internal reflection microscopy
DFM - dark field microscopy
PMT - photon multiplier tube
STEM - scanning transmission electron microscopy
CCD - charge coupled device
DLS - dynamic light scattering
SEM - scanning electron microscopy
UPD - underpotential deposition
NaOL - sodium oleate
CTAB - cetyl trimethylammonium bromide
TEM - transmission electron microscopy
ITO - indium tin oxide
FIB - focused ion beam
M - mirror
DFC - dark field condenser
OL - objective lens
L - lens
CMOS - complementary metal oxide semiconductor
PVP - polyvinylpyrrolidone
NS - nanostar
MW - molecular weight
WE - working electrode
PTFE - polytetrafluoroethylene
CE - counter electrode
qRE - quasi-reference electrode
PES - polyethersulfone
CV - cyclic voltammogram
AOTF - acousto-optical tunable filter
[SMS] - poly(styrene)-b-poly(methyl methacrylate)-b-poly(styrene)
ATRP - atom transfer radical polymerisation
BBiB - butylene-\(\text{-}\alpha\)-bromoisobutyrate
MMA - methyl methacrylate
St - styrene
PMDETA - \(N,N,N',N'',N''\)-pentamethyldiethylenetriamine
GPC - gel permeation chromatography
NMR - nuclear magnetic resonance
MPTMS - (3-mercaptopropyl)trimethoxysilane
[EMI][TFSI] - 1-ethyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide
RC - resistor-capacitor
DC - direct current
MM - multimode
TL - tube lens
PH - pinhole
PCL - planoconvex lens
FM - flip mirror
CPU - computer
Chapter 1

Introduction

1.1 Metal Nanocrystals

Metal nanocrystals (NCs) are very small crystalline particles made up of hundreds or thousands of metal atoms with at least one dimension between 1-100 nm. These particles have been prepared by glass makers since the 4th century by the reduction of certain metal salts during glass production.\(^1\) The process led to the formation of nanocrystals, initially gold and silver alloys, distributed in a glass matrix producing a solid sol often referred to as ruby glass. One of the earliest, most cited and stunning pieces of this type of material is the Roman Lycurgus cup pictured in Figure 1.1. It is given incredible optical dichroic properties by gold-silver alloy nanocrystals embedded in the brilliantly sculpted 1600 year old glass chalice. Transmitted light from the cup is red and reflected light appears green. Without any physical understanding of the glass’ optical properties, glass makers continued to develop this art using different metal salts and reaction conditions to create a range of colours which have come to be known as stained glass.\(^2\) Gold salts gave reds and purples, silver salts gave yellows, and chromium salts gave blues. This technology was expanded into inks and pigments which were increasingly
popular during the later half of second millennium. The ruby red solutions of gold nanocrystal ‘sol’ were shrouded in mystique and thought to be an ‘Elixir of Life’ by alchemists of the time.

Figure 1.1 – The famous Lycurgus cup dated from the 4th century on stylistic grounds. a) The dichroic effect displayed by the cup with reflected green light on the right and red transmitted light on the left. b) Transmission electron micrograph of a AuAg alloy nanocrystal inside the glass that is responsible for the effect. ¹

Michael Faraday partly demystified these materials by qualitatively showing in his famous lecture in 1857 that the common properties of the different gold sols were found to be due to “finely divided metallic gold”. ² This is thought to be the first recognition of the properties of very small materials departing dramatically from those observed in bulk materials. Phenomena occurring on the nanoscale are complex because they lie between the classical and quantum realms, i.e. between bulk and atomic behaviour. The departure from bulk material properties has been attributed to spatial confinement, ³ sub-wavelength electromagnetic radiation interaction ⁴ and high surface area to volume ratios. ⁵ Properties of metal nanocrystals rapidly change with only minute variations in size, shape, composition and surface environment. ⁶ The range of unique properties of metal nanocrystals are
beginning to lend themselves to promising applications in the burgeoning field of modern nanotechnology, such as sensing,\textsuperscript{8,9} catalysis,\textsuperscript{10} electronics,\textsuperscript{11} waveguiding,\textsuperscript{12} photovoltaics,\textsuperscript{13} medicine,\textsuperscript{14} textiles,\textsuperscript{15} and coating materials.\textsuperscript{16}

1.2 Optical Properties of Metal Nanoparticles

When considering the general optical properties of a particular metal material, size is the most defining factor. For example, bulk gold appears a lustrous yellow colour to the eye due to having absorption bands with no discrete structure.\textsuperscript{17} The electronic transitions responsible for the photon absorption occur in almost continuous energy levels. On the other hand, atomic gold has very distinct absorption bands due to the quantised structure of electron energy levels. In the range between bulk and atomic, spherical gold and silver nanocrystals display a range of colours depending on their size and shape.\textsuperscript{18}

The interaction of metals with light close to and in the visible region is largely dictated by the free conduction electrons in the metal. The Drude model provides a platform for understanding this interaction, describing the motion of electrons in a solid conductive lattice. By applying this simple model to a metal surface in a dielectric medium, the ‘sea’ of free electrons oscillates 180° out of phase with the driving electric field. This is the basis for the high reflectivity of bulk metals and is the consequence of the negative real part of the dielectric constant of metals. The collective oscillation of electrons coupled to a light wave has been coined a plasmon.\textsuperscript{19} With respect to the nanoscale, the free electron ‘gas’ on a metal nanoparticle (NP) undergoes surface and volume oscillations at distinct resonant frequencies, strongly dependent on size, shape, composition and the surrounding micro-environment. A surface plasmon resonance (SPR) occurs at the interface between a metal and a dielectric material. The surface charge density oscillations
can either propagate as surface plasmon polaritons or be spatially confined in a NP, depending on the structure of the metal. When confined, an SPR is said to be a localised surface plasmon resonance (LSPR) and gives rise to strongly enhanced electric fields around the NP because the resonator is smaller than the wavelength of light itself (represented by the schematic in Figure 1.2). Solutions to Maxwell’s equations have been rigorously applied to explain the light-matter interactions of these plasmonic NPs for more than 100 years.

Figure 1.2 – The origin of the superb chromatic properties of metal nanocrystals is localised surface plasmon resonance - abbreviated to LSPR. The light-matter interaction shown in this schematic occurs when the alternating electric field of an incoming light wave meets the resonant conditions of the nanoparticle in a dielectric medium. The light wave couples to the free conduction electrons on the surface of the particle, causing them to collectively oscillate. The oscillating electron cloud on a nanocrystal is called the localised surface plasmon resonance.

1.2.1 Plasmon Resonance of Spherical Metal Nanoparticles

When a photon strikes a NP it will either be absorbed, scattered or pass through unaffected by the material, i.e. transmitted. In colloid chemistry, the attenuation of light intensity through a solution is commonly expressed with absorbance, as
defined by the well known Beer-Lambert Law. Extinction, on the other hand, is the attenuation normalised by the material’s concentration and path length and is the combined contribution of both absorption and scattering by the solution. Motivated by the mysterious colour of gold, in 1908 Gustav Mie published a complete theoretical explanation of the scattering and absorption contributions of a metal sphere as large as $R \sim \lambda$ ($R$ is the particles radius and $\lambda$ is the incident wavelength of light) to electromagnetic radiation extinction.\textsuperscript{20} He solved Maxwell’s equations with the associated boundary conditions of a sphere and used multipole expansions of the incident electric and magnetic fields to arrive at the origin of the optical extinction.\textsuperscript{21} This theoretical treatment encompassed all ratios of particle diameter to incident wavelength and assumed a material which was homogeneous, isotropic and optically linear.

Mie’s theory uses the frequency dependent dielectric function, $\epsilon = \epsilon' + \epsilon''$, of the bulk metal to calculate the extinction and scattering efficiencies of small particles. A metal NP surrounded by a medium with a dielectric function $\epsilon_m$ will contribute to the extinction of an incident light wave. The wave may encounter many identical particles as it travels through the dielectric medium, \textit{e.g.} many particles impregnated in a glass, dispersed in a liquid, or as an aerosol. The extinction is the difference in intensity between the incident light ($I$) and the transmitted light ($I_0$) and is a sum of both the scattering and absorption of radiation by the particles, according the equation:

$$A = \log_{10} \frac{I}{I_0} = \frac{NC_{ext}}{2.303}$$

(1.1)

where $A$ is the absorbance, $C_{ext}$ is the extinction cross section of a single particle, and $N$ is the number of particles per unit area. This equation assumes a dilute concentration of metal such that interaction between particles can be ignored. By this treatment, $C_{ext}$, and scattering cross section, $C_{sca}$, are given as:\textsuperscript{18}
\[
C_{\text{ext}} = \frac{2\pi}{k^2} \sum ((2n + 1) Re(a_n + b_n)) \quad (1.2)
\]
\[
C_{\text{sca}} = \frac{2\pi}{k^2} \sum ((2n + 1)(|a_n|^2 + |b_n|^2)) \quad (1.3)
\]

where \( k = \frac{2\pi}{\sqrt{\epsilon m}} \) and \( a_n \) and \( b_n \) are the Mie scattering coefficients, and are functions of the radius \( R \) and the wavelength \( \lambda \) in terms of Ricatti-Bessel functions. The absorption cross section can be deduced by the difference between \( C_{\text{sca}} \) and \( C_{\text{ext}} \).

It is often convenient to normalise the extinction cross section and express with unit area dependence:

\[
Q_{\text{ext}} = \frac{C_{\text{ext}}}{\pi R^2} \quad (1.4)
\]

\[
C_{\text{ext}} = C_{\text{abs}} + C_{\text{sca}} \quad (1.5)
\]

The same cross section terms can also be represented by the relation to the particle polarisability, \( \alpha \), by:

\[
C_{\text{sca}} = \frac{k^4}{6\pi} |\alpha(\omega)|^2 \quad (1.6)
\]

\[
C_{\text{abs}} = k \text{Im}[\alpha(\omega)] \quad (1.7)
\]

For metal spheres where \( kR \ll 1 \), which in most cases occurs for particles below 30 nm, only the dipole oscillation contributes significantly to the total extinction. In these circumstances Mie’s theory can be reduced to the dipole approximation, also known as the Rayleigh approximation. This assumes that the electromagnetic phase is constant throughout the metal, resulting in a dipole resonance only. Therefore,
only the first term of the series in Mie’s extinction equation is necessary, and thus the extinction cross section at a specific wavelength, $\lambda$, is written as:

$$C_{\text{ext}} = 24\pi^2 R^3 \frac{\epsilon'' \epsilon_m}{\lambda (\epsilon' + 2\epsilon_m)^2 + \epsilon''^2}$$  \hspace{1cm} (1.8)$$

and likewise, the polarisability can then be written as:

$$\alpha(\omega) = 4\pi R^3 \frac{\epsilon'(\omega) - \epsilon_m}{\epsilon'(\omega) + 2\epsilon_m}$$  \hspace{1cm} (1.9)$$

Note that from the relations using the polarisability term, $C_{\text{abs}}$ scales with $R^3$, and $C_{\text{sca}}$ with $R^6$. Consequently, scattering dominates for large particles, whereas absorption dominates for smaller particles.

The Mie equations are useful theoretical methods to predict the wavelength position of the extinction maximum. However, the model cannot be applied to predict the absolute line shape as it does not take into account all physical processes occurring in small resonating particles or ensemble effects of true solutions. Absorbance measurements of sols containing small gold NCs show that the line width and intensity do not match well with Mie calculations. This is explained by considering the effect of the surface on the plasmon oscillation. Individual electrons can be scattered randomly as they move to the surface of a particle, causing a perturbation of the otherwise coherent plasmon. The probability of electron-surface scattering is higher in small particles and, consequently, the LSPR band width broadens. The plasmon oscillation intensity also decreases more rapidly with decreasing size than predicted by Mie, referred to as finite-size effects.

The free electron behaviour can be used to describe the extinction for many metals up until frequencies equal to that of the bulk plasma value. The dielectric response can therefore be well described by the Drude model, and such the real and imaginary parts of their dielectric functions being written as:
\[ \epsilon'(\omega) = \epsilon_{\infty} - \omega_p^2 / (\omega^2 + \omega_d^2) \]  
(1.10)

\[ \epsilon''(\omega) = \omega_p^2 \omega_d / \omega (\omega^2 + \omega_d^2) \]  
(1.11)

where \( \epsilon_{\infty} \) is the high frequency dielectric constant due to interband and core transitions, and \( \omega_p \) is the bulk plasma frequency:

\[ \omega_p = \sqrt{(Ne^2/m\epsilon_o)} \]  
(1.12)

where \( N \) is now the concentration of free electrons in the metal and \( m \) is the effective mass of the electron. \( \omega_d \) represents the damping frequency which is related to the mean free path of the conduction electrons, \( R_{bulk} \), and the velocity of electrons at the Fermi energy, \( \nu_f / R_{bulk} \), by:

\[ \omega_d = \nu_f / R_{bulk} \]  
(1.13)

This damping frequency term corrects for the perturbation caused by the electron-surface scattering. The mean free path, \( R_{eff} \), becomes size dependent with:

\[ 1/R_{eff} = 1/R + 1/R_{bulk} \]  
(1.14)

which adequately describes noble metals as small as 2 nm diameters. This model predicts a strong LSPR band when \( \epsilon'' \) is small and:

\[ \epsilon' = -2\epsilon_m \]  
(1.15)

By taking the Drude Model into account, together with the core and interband dielectric contributions, the Mie model reflects the true LSPR line shape of small spheres more accurately. However, in particles larger than 30 nm the dipole ap-
proximation breaks down and higher order resonances must also be considered. In this size regime, higher order terms begin to dominate and the peak position consequently shifts to longer wavelengths.\textsuperscript{23,24} Polarisation modes such as quadrupoles arise when the oscillations become inhomogeneous across the space of the metal. Additionally, in larger particles, line width broadening caused by radiation damping is observed, as coherent electron motion is diminished by dephasing of the plasmon. Experimental data demonstrating the LSPR size dependency of Au NCs is displayed in Figure 1.3.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1_3.png}
\caption{(a) Peak-normalised UV-Vis absorbance spectra for various diameters of gold nanoparticle dispersions stabilised in aqueous solution. This figure demonstrates the progressive red-shift that occurs as gold particles increase in size. (b) A plot of the line width for different particle diameters. Increases in full width at half maximum (FWHM) are observed at smaller diameters due to surface scattering and at larger diameters due to radiation damping. Figure adapted from Link and El-Sayed.\textsuperscript{25}}
\end{figure}

1.2.2 Plasmon Resonance for Anisotropic and Complex Metal Nanoparticles

Mie’s equations provide accurate predictions for spheres of various sizes but the model does not apply to other shapes and morphologies. Richard Gans extended
the Mie solution by broadening the dipole approximation in Equation 1.8 to predict the optical properties of ellipsoidal shaped particles.²⁶,²⁷

Ellipsoidal and rod shaped metal NCs exhibit two LSPR bands as shown in Figure 1.4. The transverse band of a gold nanorod (NR) results in an extinction peak around 520 nm, similar to the single peak of a gold nanosphere. The second band observed is the longitudinal band, and the associated peak red-shifts with increasing aspect ratio. The transverse band corresponds to oscillations across the short axis and the longitudinal band is the manifestation of electrons oscillating along the longer axis. The longitudinal band is a lower energy resonance but a rod shaped particle has a higher optical extinction cross section along the longer axis. This culminates in a more prominent band, typically in the red or NIR region of the spectrum for gold rods. The line width and intensity of this longitudinal band is strongly affected by surface scattering and radiation damping.

In general, using the Mie-Gans interpretation of the dipole approximation, a small metal particle of arbitrary shape consists of several plasmon modes which fulfil:

\[(1 - L)\epsilon_m + L\epsilon_{\text{inf}} - L\frac{\omega_p^2 + \Delta\omega_p^2}{\omega^2} = 0 \quad (1.16)\]

when the damping frequency contribution to the real part of the dielectric constant of the metal is ignored, and where \(L\) is the depolarisation or shape factor. The theory describes how the extinction is modified by the splitting of the plasmon modes when isotropy is broken as follows:

\[C_{\text{ext}} = \frac{2\pi R^3 \epsilon_m^{3/2}}{3\lambda} \sum \frac{(1/L^2)\epsilon''}{(\epsilon' + \left[\frac{1-L}{L}\right]\epsilon_m)^2 + \epsilon''^2} \quad (1.17)\]

From the Mie-Gans extension, exact solutions for elongated spheroid particles can be obtained. For real systems such as true NRs, however, their cylindrical
shape and hemispherical ends require a different method such as the commonly used numerical discrete dipole approximation (DDA).\textsuperscript{28} DDA is a convenient method to compute the optical properties of arbitrarily shaped particles.\textsuperscript{29} As there is no restriction on the localisation of cubic lattice sites, the DDA is able to model a particle of arbitrary shape and composition. The structure of interest is made up of cubic array of $N$ individual polarisable elements. The response of the array to an external electromagnetic field is described by an interaction matrix, which then subsequently determines the induced dipole in each element. This information is useful for determining the local electric field at each dipole, $E_{\text{loc},i}$, the basis for studying the near-field response of metal particles.\textsuperscript{30} Each of these electric field terms can be written:

$$E_{\text{loc},i} = E_{\text{inc},i} + E_{\text{dip},i} = E_0 e^{(ikr_i)} - \sum_{j \neq i} A_{ij} P_j \quad (1.18)$$

Figure 1.4 – Peak-normalised UV-Vis absorbance spectra of gold nanorod samples stabilised in aqueous solution with various aspect ratios. As the ratio increases, the longitudinal band progressively red-shifts. The schematic on the right hand side demonstrates the direction of oscillations corresponding to the transverse band (green) and the longitudinal band (red).
where $E_0$ and $k$ are the amplitude and wave vector of the incident electric field, $E_{inc,i}$, respectively. The other contribution to $E_{loc,i}$ is the field radiated by all other induced dipoles, $E_{dip,i}$. $r_i$ is the location of the $ith$ dipole, $P_j$ is the polarisation in each element, and $A_{ij}$ with $i \neq j$ is a $3N \times 3N$ interaction matrix with elements described by:

$$A_{ij}P_j = \frac{e^{ikr_{ij}}}{r_{ij}^3} \left\{ k^2 r_{ij} \times (r_{ij} \times P_j) + \frac{1 - ikr_{ij}}{r_{ij}^2} \left[ r_{ij}^2 P_j - 3r_{ij}(r_{ij} \cdot P_j) \right] \right\}$$  (1.19)

The induced dipole polarisation $P_i$ can be determined from:

$$P_i = \alpha_i E_{loc}(r_i)$$  (1.20)

With $P_i$ in hand, the extinction, absorbance and scattering cross section using DDA can be given as:

$$C_{ext} = \frac{4\pi k}{|E_0|^2} \sum_{i=1}^{N} \text{Im}(E^*_{inc,i}P_i)$$  (1.21)

$$C_{abs} = \frac{4\pi k}{|E_0|^2} \sum_{i=1}^{N} \left\{ \text{Im} \left[ P_i \cdot (\alpha_i^{-1})^* P_i^* \right] - \frac{2}{3} k^3 |P_i|^2 \right\}$$  (1.22)

$$C_{sca} = C_{ext} - C_{abs}$$  (1.23)

where * represents the complex conjugate.

There are other theoretical techniques for determining both the near- and far-field properties of metal NPs. These include the finite difference time domain method (FDTD),\textsuperscript{31} boundary element method (BEM)\textsuperscript{32} and finite element method (FEM).\textsuperscript{33} A 2008 review discussed the history and application of Mie theory, DDA, FDTD and BEM and, in particular, their usefulness in solving the plasmonic response of gold NPs.\textsuperscript{24} DDA is found to be especially useful for describing individual
particles in complex environments. It is most commonly solved using the freely available Fortran code called DDSCAT.\textsuperscript{34}

Recent studies have applied FEM to model the electromagnetic response of complex metal structures such as nanoshells, nanostars, decahedra \textit{etc}. FEM is a highly accurate method that approximates many partial differential equations of small elements to produce a solution for a much larger object. Not hampered by the geometric limitations of finite-difference methods, FEM is currently the most accurate method for solving frequency domain-problems.\textsuperscript{35} The electromagnetic response of metallic NPs is modelled with FEM by solving the inhomogeneous vector wave equation:

\[
\nabla \times \left[ \frac{1}{\mu_r} \nabla \times \overrightarrow{E} \right] - k_0^2 \epsilon_r \overrightarrow{E} = 0 \quad (1.24)
\]

In the FEM approach, the domain is divided into elements that match the target geometry, enabling irregular geometries and complex structures to be solved. FEM requires a vast number of calculations to solve a problem and has only recently become viable with the development of multicore computer processors and software improvements. The commercial software package most frequently cited in solving the FEM for metal nanostructures is COMSOL Multiphysics. Both DDA (DDSCAT) and FEM (COMSOL) have been used in this thesis to model the expected electromagnetic response of redox processes occurring on single gold nanocrystals. By applying these methods, it is possible to predict how the surface plasmon band may shift by varying physical parameters, such as the dielectric function and charge density.
1.3 Single Particle Measurements

The optical theories described in this introduction simulate the interaction of electromagnetic radiation with a single metal NP. Limited by this simplified model, the calculated spectra of these particles typically do not match the experimental spectra of ensemble measurements. As a consequence of particle inhomogeneity and particle-particle interactions (important in high concentration films), ensemble measurements represent a statistical average of all particles present. These ensemble measurements, like those obtained from a standard UV-Vis absorption spectrometer, result in broader line shapes of LSPR spectra than predicted by theory. Polydispersity, size-dispersity and reproducibility issues continue to plague the field due to the inherently varied nature of crystal nucleation and growth. Despite significant improvements in this area, truly monodisperse final products with 100% yield will perhaps never be achieved without significant advancements in purification.

The study of catalytic processes and redox reactions on metal nanocrystal surfaces is extremely challenging as a result of the same conditions outlined for optical characterisation. Rates of reaction are highly sensitive to a variety of parameters including the particle size and shape, the degree of crystal faceting, the occurrence of underpotential deposition (UPD) and the role of substrate interactions. These factors are all convoluted in ensemble electrochemical measurements. One approach for obviating these problems is to study catalytic and electrochemical redox processes on single metal nanoparticles.

1.3.1 Surface plasmon spectroscopy

Many single particle spectroscopy techniques have emerged over the past two decades to measure the LSPR of metal NCs. Scanning near-field optical microscopy
(SNOM), spatial modulation spectroscopy (SMS), photothermal absorption spectroscopy, confocal microscopy, electron energy-loss spectroscopy (EELS), total internal reflection microscopy (TIRM), and dark field microscopy (DFM) have all been used for this purpose. A recent tutorial review from the Link group covers the state-of-the-art methods for the optical characterisation of single metal nanoparticles and provides an overview of the optical setups and research applications. Several leading techniques are outlined in the following section, including examples of the instruments in Figure 1.5.

Feldmann et al. used SNOM in 1998 to report the first single particle measurement of the homogeneous LSPR line shape for gold NPs. Key discoveries from this research were the surface plasmon dephasing times from near-field spectra, deviations of spectra from one particle to the next due to variations in the nano-environment and double-peaked line shapes caused by electromagnetic coupling between close-lying particles. SNOM utilises a near-field probe and, as such, there are many experimental limitations. One example is that the probe tip itself can interact with the particle under inspection, which may influence its electromagnetic response. Additionally, the tip of the probe cannot always access a NP in a complex environment or embedded in a solid matrix.

Far-field absorbance was quantitatively determined for single metal particles first by Arboeuet et al. and later by Muskens et al. using the spatial modulation spectroscopy technique. The primary advantage of this technique is that it measures absorbance, which is often seen to dominate the extinction expression for small particles. Using SMS, surface plasmon spectra has been measured for particles as small as 5 nm, significantly less than is currently possible for scattering techniques such as TIRM and DFM. However, the frequencies and number of periods required to obtain adequate signal imparts lengthy sample measuring times, disqualifying this technique for many important time dependent experiments.
Figure 1.5 – General schemes for some of the single particle measurement techniques described in the literature. (a) The optical probe of a typical scanning near-field optical microscope taken from Müller et al.\textsuperscript{44} (b) A typical configuration of a total internal reflection microscope as drawn by Sönnichsen et al.\textsuperscript{45} (c) The photothermal absorption spectroscopic setup used by Orrit et al.\textsuperscript{46} The horizontal polarised red probing beam is split into two beams by a Wollaston prism and focussed on the microscope objective by a telecentric lens system. The reflected beams are recombined in the Wollaston prism, and the vertically polarised beam is reflected and sent to the detector. The heating beam is modulated at high frequency by an acousto-optical modulator. It induces a periodic difference between the two beams, giving rise to a modulation of the detected light.

A technique using supercontinuum white-light confocal microscopy yielded similar results to SMS.\textsuperscript{49} By collecting the reflected light from a confocal scan as a function of wavelength, gold particles below 10 nm could be measured with a sensitive photomultiplier tube (PMT) detector. This system collected extinction
spectra, a distinct advantage due to the increased signal over a larger size range. However, it too suffers from the same sampling limitations as SMS.

Photothermal absorption is another sensitive far-field technique that is capable of imaging metal particles as small as 2.5 nm. With the inclusion of a photodiode detector to a photothermal system, spectra of particles as small as 5 nm have been collected. This indirect method combines high-frequency modulation and polarisation interference contrast to eliminate the background scattering effects. The absorption spectrum is indirectly calculated by determining the amount of heat which is non-radiatively transferred from the particle to the surrounding environment. As a result, this technique is not suitable for catalysis and electrochemical studies on single metal NCs as it requires the surrounding volume to be undergoing constant variations in temperature, influencing the redox kinetics.

Novel EELS techniques have recently been developed in conjunction with scanning transmission electron microscopy (STEM). Using EELS, it is possible to probe particles down to 2 nm and extract specific resonances separately, such as the surface and bulk resonances. An additional advantage is the ability to simultaneously characterise the morphology and resonance properties. The inherent differences of EELS as distinct from optical methods are that the measurements are from electron-electron interactions rather than photon-electron interactions, resulting in different ‘selection’ rules of excitation. Currently EELS generated spectra have low signal-to-noise ratios and would not be reliable to measure small changes in the LSPR of single metal NCs. Furthermore, the practical difficulty of operating devices or fluid experiments inside an electron microscope renders EELS unsuitable for many physical chemistry experiments.

TIRM is an effective technique to measure the scattering spectra of individual metal NPs. In TIRM, particles are placed in an evanescent field produced by the total internal reflection of light from a white light source in a prism. The scattered
light from individual particles is collected by a conventional optical microscope and then recorded by a detector coupled to a spectrometer. TIRM was successful in studying different liquids in contact with lithographically fabricated gold discs, confirming the peak shifting effect of changing the local refractive index.45

Other similar Rayleigh scattering techniques based on TIRM are sufficiently sensitive to measure the refractive index change of large single non-adsorbing macromolecules, such as proteins, near the surface of a gold NR.9,52

1.3.2 Dark Field Microscopy

Developed from principles used in TIRM, dark field microscopy was pioneered by Schultz et al. and has since played the biggest role in the study of optical properties of single metal NPs.53 DFM has enabled electron transfer reactions to be observed spectroscopically with unprecedented sensitivity.54 This technique utilises a specialised condenser lens that enables scattered light from individual nano-objects to be collected. DFM is a fast and flexible technique that allows the LSPR spectra of single metal NCs to be measured routinely when combined with a imaging based spectrograph.

In DFM, metal NCs appear as point scatterers on a dark background (Figure 1.6a). The light from the individual points (nanocrystals) is reflected into a spectrometer and the diffracted light focussed onto an array detector to produce a single particle scattering spectrum (Figure 1.6b). The dark background is achieved by illuminating the sample at an oblique angle which ensures only scattered light enters into the objective lens. More detailed technical information about DFM is provided in the Experimental Methods section (Chapter 2) and specific examples of its application toward studying redox processes appear throughout this thesis.

Current DFM systems have severe limitations which, if overcome, would advance this technique and uncover more details about the redox chemistry of metal NCs.
At present, the most significant limitations are sensitivity and the relatively slow measurement rate, which inhibits the investigation of fast time-dependent processes. Thus far, reports of single nanocrystal spectra acquired by DFM have either been of steady-state LSPR measurements, or time-resolved measurements of a slowly shifting LSPR. Two examples of relevant time-resolved measurements are spectra taken of gold nanocrystal growth and gold nanocrystal oxidation of ascorbic acid. Many fast chemical and physical metal NC processes remain unexplored with SPS because there is not yet a tool that can monitor changes of the LSPR fast enough.
1.4 Redox processes on single metal nanocrystals

The optical properties of metal NCs are intrinsically linked to their electrochemical properties. There are many different types of electrochemical processes that can occur on a metal NC but, by definition, all involve the transfer of electrons with their environment. Metal NCs can act as either electron acceptors or donors whilst retaining the same cationic lattice structure. Early work by Grätzel et al. showed that Pt NCs could act as a catalyst in photocatalytic water reduction and Henglein et al. showed that Ag NCs could also store electrons produced from radicals during pulse radiolysis. In this sense they can be thought of as enormously multivalent ‘nanoelectrodes’ or ‘nanocapacitors’. These characteristics enable metal NCs to act as electron transfer mediators, more traditionally referred to as catalysts. Reviews by Murray and Scanlon cover all aspects of charging, discharging and electrochemistry of single nanoparticles. In the following section, aspects relating to optical studies are the focus.

All gold NCs in this thesis are greater than 4 nm in diameter, thus falling under the bulk-continuum voltammetry regime, as opposed to the quantised double-layer charging or molecular-like regimes. In this regime, the following relation describes the simple nature of charging a large metal NC in the bulk-continuum:

$$\Delta E = Ne/K$$ (1.25)

where $\Delta E$ is the electrochemical potential of a NC with double-layer capacitance $K$, and $e$ is the electrical charge of an electron. This continuous change in charge occurs on NCs with sufficiently large capacitance (> 6 aF) even when $\Delta V$ is below $k_B T$, the Boltzmann thermal energy distribution. The first experimental demonstration of bulk-continuum charging on discrete metal NCs was carried out
in 1997 by Mulvaney and co-workers. The LSPR of a colloidal solution of 11 nm Ag NCs was monitored in a transparent spectroelectrochemical cell during a cyclic voltammetry scan. The LSPR peak position of the ensemble of silver particles shifted across a range of 12 nm between 0.8 V and −0.8 V, 391 nm at the cathodic maximum and 403 nm at the anodic maximum. At cathodic potentials, the total absorbance of the LSPR peak increased and a reduction peak was also observed during a cyclic voltammogram. The particles in solution were found to reach an equilibrium of charge density by monitoring the change of absorbance at the original peak position and a ‘reaction rate’ at the working electrode could be calculated. Electrons were transferred from the electrode to the particles by collisions and so the rate correlated well with the predicted diffusion kinetics. The electrophoretic mobility used to calculate this was measured using dynamic light scattering (DLS). The authors calculated the number of electrons transferred per particle, $\Delta N$ (i.e. the change in redox state, or in turn, the change in electron concentration), by making the connection between the change in the LSPR peak position, $\Delta \lambda$, and $\Delta N$ on spherical particles. From Equation 1.12, it is known that the bulk plasma frequency is dependent on the electron concentration. Thus, if there is a change to $\omega_p$, there is also a change to $\epsilon$ through the relationships described in Equations 1.10 and 1.11. When the conditions for Equation 1.15 are met, the following equation can be derived showing that the peak position and electron density are directly related:

$$\begin{align*}
\lambda_f^2 &= \lambda_i^2 N_i/N_f
\end{align*}$$

where $\lambda$ is the mono-modal LSPR peak position, and $i$ and $f$ refer to initial and final, respectively. Thus, an increase in the electron density leads to a blue-shift of the LSPR and a decrease results in a red-shift. So quite simply, if one can observe
a change in colour of a colloidal metal solution corresponding to the LSPR peak, charging and discharging of particles can be quantified accurately.

The electrooptical shifts for anisotropic particles are much stronger per electron. This was first experimentally demonstrated by adding sodium borohydride to solutions of Au NRs. NaBH$_4$ is strongly reducing and resulted in colour changes visible to the eye on Au NR solutions with an aspect ratio above 2. The authors derived a solution for this increased sensitivity using the Mie-Gans treatment of the dipole approximation. It was shown how from Equations 1.12 and 1.16, the Mie-Gans relation can be presented in the following form to describe the electron concentration dependency for small anisotropic particles:

$$\frac{(1 - L)\epsilon_m + L_{\text{erf}} - L\frac{\lambda^2}{\lambda_p^2} \left(1 + \frac{\Delta N}{N}\right)}{1 + \Delta N} = 0 \quad (1.27)$$

where $\lambda_p$ is the bulk plasma metal wavelength. Given $N \gg 1$, it was simplified further so that:

$$\lambda = \lambda_p \left(1 - \frac{\Delta N}{2N}\right) \sqrt{\epsilon + \left(\frac{1}{L} - 1\right)\epsilon_m} \quad (1.28)$$

and the LSPR peak shift, $\Delta \lambda$, can be calculated by:

$$\Delta \lambda = -\left(\frac{\Delta N}{2N}\right) \lambda_p \sqrt{\epsilon + \left(\frac{1}{L} - 1\right)\epsilon_m} \quad (1.29)$$

For rods, this interpretation predicts blue-shifting of both the transverse and longitudinal bands, a response that was also found experimentally. The longitudinal resonance is roughly 10 times more sensitive to electron density, with the exact value dependent on the metal element, $\epsilon_m$, and the aspect ratio. To reach the charge densities required to produce $> 40$ nm shifts observed in this study, the Au NRs required a surrounding environment that could produce a large $K$ at the
surface of the NCs. Compared to an air-colloid interface, a water-colloid interface

\[ K \text{ for a metal NC in any dielectric environment can be determined from the electrooptical shift using the following equation:} \]

\[ K = \frac{\Delta \sigma}{\Delta E} = \frac{(\lambda_f^2/\lambda_i^2 - 1) a F}{3 V_m \Delta E} \]  

(1.30)

where \( \sigma \) is the surface charge, \( a \) is the radii, \( F \) is Faraday’s constant, and \( V \) is the molar volume. The high \( K \) value of the aqueous medium, in conjunction with the addition of only 0.01 M NaBH\(_4\) resulted in \( \Delta N/N \) up to 11%. The examples presented in this section demonstrate the range of methods previously applied to inject and extract electrons from metal NCs. Further to electron exchanges with radiolytically generated radicals, chemical redox agents, and collisions with polarised working electrodes, the charge of metal NCs can be modulated rapidly by immobilising them directly on an electrode. This can be achieved by binding the nanocrystals to the electrode \textit{via} an amino- or mercapto-terminated self assembled monolayer, either in polymer thin films or simply by van der Waals forces. This situation leads to a modified electrode with nanocrystalline features which, in a simplified model, will all be in Fermi equilibrium. In an electrolyte, \( K \) is determined by the dimensions of the parallel-plate-like capacitor at the interface such that:

\[ K = \epsilon_r \epsilon_0 / d \]  

(1.31)

where \( d \) is the double-layer thickness. Typically, in aqueous electrolytes, \( d \) is in the range of 1-3 \( \AA\) which leads to high \( K \) values around 40 \( \mu F \) for small metal colloids. This approach of charging metal nanoparticles has been reported as a potential plasmonic electrochromic smart window technology.\(^62\)

The first example of electrochemical charging of single metal NCs was achieved
by spectroscopically monitoring the LSPR peak position using DFM in work carried out by Novo et al.\textsuperscript{54} Their work has been summarised in Figure 1.7. Au nanodecahedra were immobilised at low density on glass and placed inside a fluid cell containing an ascorbic acid solution. After the Au NRs were placed in contact with the solution, single particle scattering spectra were collected every minute. The longitudinal band was observed to blue-shift 20 nm as the ascorbate ions were oxidised on the Au surface and, in turn, electrons were injected into the NC nanoelectrode. This development also constituted the first direct measurement of redox rates on single metal nanocrystals, \textit{i.e.} the first measurement of single NC catalysis. In this same study, the kinetics of metallic Au deposition onto a single, pre-existing small Au NC in solution was monitored.

Continuing their work on single metal NCs, Novo and co-workers later demonstrated that by using Au NR modified transparent working electrodes in an aqueous electrolyte, cathodic biases could be applied to blue-shift the LSPR of a single gold nanorod. Blue-shifts of up to 12 nm were reported at -1.6 V against a Ag quasi-reference electrode.\textsuperscript{39} The charging process was reversible and scanning electron microscopy (SEM) proved that the LSPR shifts were not due to morphological changes. Direct morphological correlation of a single metal NC to the spectroelectrochemical behaviour provides the ultimate resolution to study single NC electrochemistry and catalysis without heterogeneity issues. Progress from these initial SPS studies is continuing with rising interest in single particle catalysis. A recent review by Sambur and Chen covers single particle catalysis approaches thoroughly amidst its rapid development.\textsuperscript{63}
Figure 1.7 – First experimental examples of redox processes on single metal nanocrystals by the application of DFM. (a) A sequence of scattering spectra for a single gold decahedron (pictured in the SEM image below (b)) during oxidation of ascorbate ions in solution. As more ions inject charge into the nanocrystal the LSPR blue-shifts. The reaction is complete after 60 min, at which point the nanocrystal discharges and the LSPR returns to its ‘uncharged’ position. (c) DFM image of gold decahedra on glass from the study of Novo et al.\textsuperscript{54} (d) In the same study, results were also presented for the single particle growth kinetics of a Au NR by capturing the scattering spectra at various stages. The figure shows the red-shift of the longitudinal band as the aspect ratio increases during growth. (e) In a subsequent study, the authors presented results for the electrochemical charging of a single Au NR in a transparent electrochemical cell. The potential was swept from 0 V to -1.4 V (vs. Ag qRE) and back. The LSPR peak position was reversible (see inset) with potential and could be shifted > 10 nm. (f) By analysing SEM images before and after electrochemical charging, it was demonstrated that the Au NR remained morphologically unchanged.\textsuperscript{39}
1.5 Open questions

This thesis seeks to answer key questions all with the common thread of how redox processes occur on single Au NCs. Answers are constructed by analysing the scattered light from single Au NCs during redox. The light used to illuminate the Au NCs is used only as a means of probing the redox processes as they proceed, as opposed to promoting redox. Here, the aim is to use the LSPR only as a transmitter of the electron concentration on single NCs. This concept has been summarised in the graphic in Figure 1.8.

Charging and discharging a metal NC modifies its Fermi level and thus its redox potential. Catalysis and electrocatalysis on metal nanocrystals is dictated by the surface energy of exposed facets. If the electron concentration of a metal nanocrystal is increased by an external source or reductant, reduction of another chemical species on its surface may occur at potentials more positive than the standard reduction potential. Increases in the charge of the crystal (the same is true of the oxidation ability under anodic bias) promotes electrocatalysis. This concept is critical to advances in water splitting and synthetic fuel production. When it is applied to the reduction of metal ions onto surfaces to form solid deposits it is referred to as underpotential deposition (UPD). This particular process is important in complex nanocrystal engineering. In addition to facet dependent electrochemical processes, edges and corners between facets play a significant role in the redox chemistry on NC surfaces. Edges and corners consist of low coordinated atoms, and due to their high surface energy, particles with these sites have higher capacitance than spheres when immersed in a electrolyte.

Another important consideration for metal NC catalysis is the support material in which the NCs are embedded in, known to strongly influence the catalytic properties of immobilised particles. Several SPS studies have monitored gas interactions with single supported metallic nanostructures. These studies have,
however, neglected the influence of the support materials and the metal-support dependent reaction mechanisms at the single particle level. Understanding UPD and the role of supporting materials in redox processes is critical to the advancement of rational heterogeneous catalytic design and nanocrystal engineering.

In order to obtain single particle spectra, current DFM systems often use CCD cameras, and hence lack the sensitivity to measure small and rapid electron density changes on single particles. An image of the spectral dispersion is recorded on the device where individual p-doped metal oxide semiconductor capacitors represent each pixel. If the photon flux rate incident on the device is below the threshold, image acquisition cannot occur, even with prolonged exposure times. This is particularly restrictive for detecting scattered light from small particles as the intensity diminishes proportionally to the sixth power of the radius, as described in Equations 1.6 and 1.9. Additionally, small changes in spectra are undetected due to the low signal-to-noise ratio of metal nanoparticle spectra acquired by currently available CCD/spectrometer systems. Even after Lorentzian curve fitting, only shifts of at least a couple of nanometres are discernible. Furthermore, current DFM systems are unable study the fast kinetics of chemical reactions and electron
Figure 1.9 – The four single Au NC redox processes measured by DFM in this work. Green = Au, purple = Ag, grey = indium tin oxide working electrode (ITO WE), light blue = aqueous electrolyte solution, darker blue = metal oxide matrix, pink = ion gel electrolyte. $E_F$ = Fermi level of Au NC, $E_{F,we}$ = Fermi level of WE, $E_{F,eq}$ = equilibrated Fermi level, $E_{F,core}$ = Fermi level of Au core, $E_{F,shell}$ = Fermi energy of Ag shell, $E_F$ = equilibrated Fermi level of Au@Ag NC, $E_{CB}$ = conduction band energy level, $E_{VB}$ = valence band energy level. 

(a) Electrodeposition of Ag$^+$ ($M^+$) onto a Au NC on a cathodically biased WE. (b) Dissociative adsorption of molecular hydrogen and subsequent charge spillover onto the semiconducting oxide support. (c) Photoexcitation of the semiconductor and subsequent electron transfer to the Au NC. (d) Electrochemical charging of a Au NC on electrode in a quasi-solid state capacitor.
transfer rates on metal NC surfaces as several seconds of exposure time are required to obtain a spectrum with sufficient signal to analyse.

With these considerations the key fundamental questions to be answered in this thesis are:

1. How do surface properties and morphology influence underpotential deposition on single gold nanocrystals?

2. What effect do metal-oxide supports have on gas adsorption and charge transfer on single gold nanocrystals?

3. Can the temporal resolution and sensitivity of surface-plasmon spectroscopy be improved to measure rapid and small redox changes on individual gold nanocrystals?

In Chapter 3, Ag was deposited via UPD on single Au NCs in contact with a transparent metal oxide electrode, as shown in Figure 1.9a. The process was spectroelectrochemically monitored with DFM and is the first published work on the electrodeposition of metal onto single nanocrystals. The motivation of studying UPD of silver onto single NCs was to select a catalytic process that would produce a drastic change in the LSPR of the original NC. As shown in this chapter, only very small cathodic potentials are required to deposit Ag on the surface of nanocrystalline gold, and the Ag deposits result in large LSPR shifts. The increased magnitude of the optical shift caused by silver deposition enabled the reducing ability of certain facets, edges and corner sites to be studied in real-time with strong signals.

In Chapter 4, dissociative adsorption of hydrogen and spillover were selected as simple yet important processes to study the influence of metal oxide supports on hydrogen adsorption on single Au NRs. Au NRs were selected as the target metal NCs as they have been identified as highly sensitive catalytic probes. Single Au
NRs embedded in various metal oxide thin films were subjected to hydrogen gas flow while the LSPR peaks of single NRs were recorded and analysed as charge transferred to them (Figure 1.9b). The cooperative effect of adding a co-catalyst, Pt NPs, into the oxide support strongly modified the response, as did the presence of adsorbed oxygen on the nanoparticle film surface. The concept of studying charge transfer in metal oxide thin films is continued in the second part of this chapter where photoexcited charge transfer from ZnO to Au NCs was monitored in real-time (Figure 1.9c).

In Chapter 5, a novel approach to charging single Au NRs in a quasi-solid ion gel film was developed (Figure 1.9d). Several rapidly catalysed reactions discussed in Chapters 3 and 4 had drawn attention to the requirement of improved temporal-resolution in DFM systems. Improved temporal-resolution would allow reaction rates to be fully quantified and compared. An improvement in sensitivity could also allow single particle SPS to monitor processes in the ‘quantum catalysis regime’, where the transfer of just a few or few tens of electrons could be directly detected. In order to achieve this, a reliable and robust device was required, and therefore developed to test the sensitivity of the modified dark field microscope. This charging was achieved in a transparent solid capacitor with short time constants and with small changes in the number of electrons. By implementing a novel DFM system with a powerful white-light laser source and single photon counting photon multiplier tube detector, it was possible to optically monitor the charging of individual Au NRs in the capacitor.

The technical developments in Chapter 5, in conjunction with the previously unexplored redox processes discussed in Chapters 3 and 4, highlight the power and potential of collecting scattered light to understand fundamental chemistry and physics at the single particle level.
References


Chapter 2

Experimental Methods

2.1 Synthesis

Both metal and metal oxide nanocrystals were used extensively in this thesis. All nanocrystals were chemically synthesised using previously reported colloidal routes. Colloidal nanocrystals were exclusively chosen to study redox processes as they have well defined facets and crystal structures compared to other fabrication methods, are cheap to produce, and can be easily cast as well dispersed sub-monolayers or uniform films. Gold nanocrystals were central to this work due to their interesting optical and chemical properties previously described in the introduction section. The synthetic route chosen to produce certain types of gold nanocrystals was an important consideration as NC properties are highly dependent on morphology. Additionally, the various capping agents used in different synthetic routes have a significant influence on the surface properties of nanoparticles.

Various routes to produce gold colloids were discovered, both in the solution and gas phase, centuries before modern chemistry. However, it was not until Turkevich et al. reported the straight-forward route to 10-20 nm gold colloids via citrate reduction of gold salt, that the nucleation and growth mechanisms were
identified and investigated.\textsuperscript{1} Further work by Frens led to an improvement in the size tunability and monodispersity of the Turkevich method, and the resulting method is still commonly used today.\textsuperscript{2,3} Subsequent reports of colloidal routes proliferated as the synthetic understanding of nanocrystalline gold improved in parallel with the tools to study them, \textit{e.g.} transmission electron microscopy. Examples now found in the literature include seeded growth,\textsuperscript{4} photochemical,\textsuperscript{5} electrochemical,\textsuperscript{6} green-chemical,\textsuperscript{7,8} and ionic liquid methods.\textsuperscript{9}

Today, the benefits of such a diversity of available routes means that nanocrystals of almost any shape and size can be obtained. Examples of gold nanocrystal shapes include not only spheres, but also rods,\textsuperscript{10} cubes,\textsuperscript{11} triangles,\textsuperscript{12} tetrahedra,\textsuperscript{13} octahedra,\textsuperscript{14} icosahedra,\textsuperscript{15} plates,\textsuperscript{16} cages,\textsuperscript{17} and many others.\textsuperscript{15} Rational precursor selection and reaction condition optimisation have enabled targeted sizes of particles to be achieved and remain stable for long periods of time. Ligand transfer protocols have also given functional tunability to the nanocrystals post-synthesis, which is crucial in biological and electronic applications.\textsuperscript{18,19}

The gold nanoparticles in this thesis are intentionally referred to as nanocrystals in the title and throughout the main text to distinguish them from non-crystalline, poorly defined morphologies. The synthetic materials and methods for gold nanostars and nanocubes appear in Chapter 3 as they are relevant only to that chapter. The gold nanorod materials and methods appear in this chapter as they are relevant to all the results chapters presented. The only other type of metal nanocrystal used in this work is platinum; the synthesis method for Pt nanocrystals appears in Chapter 4. Metal oxide nanoparticles were a significant feature of the work and were exploited as semiconducting support materials in Chapter 4. Syntheses for anatase and zinc oxide nanoparticles are described in Chapter 4, as well as the silica sol-gel preparation used. All other specific material preparation details feature in the chapters that they are used in.
2.1.1 Gold nanorods

Gold nanorod wet chemical synthesis has existed since the 1990’s when solid-template\textsuperscript{20} and electrochemical\textsuperscript{6} techniques were first developed. Nowadays, the seed mediated growth method is the most widely used approach since its induction by Murphy \textit{et al.}\textsuperscript{21} and the improvements made by El-Sayed \textit{et al.}\textsuperscript{22} This approach typically utilises the soft-templating bilayer assembly of cetyl trimethylammonium bromide (CTAB) in conjunction with a low concentration of Ag\textsuperscript{+} ions to break the symmetry of small Au NC seeds.\textsuperscript{23} When a mild reducing agent such as ascorbic acid,\textsuperscript{24} salicylic acid,\textsuperscript{25} or hydroquinone\textsuperscript{26} is added to a seed solution containing Au\textsuperscript{3+} and Ag\textsuperscript{+} ions, the initial nanocrystal growth is uniform. Once the seed crystals grow to 4-6 nm, the growth proceeds along one axis, producing anisotropic gold nanocrystals. The exact growth mechanism remains elusive, although in recent years significant progress has been made towards understanding the role of the halide and silver ions.\textsuperscript{23}

Two methods have been used in this work to produce gold nanorods for single particle spectroscopy. The El-Sayed method\textsuperscript{22} was used in the early stages of the work as a reliable way to synthesise rods with a particular aspect ratio, however, there were some inconsistencies from synthesis to synthesis in the final products. Subsequently, a detailed bisurfactant method reported by Murray \textit{et al.}\textsuperscript{27} in 2013 was adopted due to its reproducibility. This method introduces a small fraction of sodium oleate (NaOL) into the reaction mixture as a secondary surfactant to complement the templating properties of CTAB. Exactly how the oleate ion is arranged within the CTAB\textsuperscript{+} bilayer structure is not clear but, using Fourier-transform infrared spectroscopy, the oleate ion has been shown to be present on the surface of gold nanocrystal even after purification.\textsuperscript{27} Surfactant concentration, temperature, pH and silver ion concentration can be adjusted to yield rods with widths tunable between 16 nm-70 nm and lengths between 88 nm-187 nm, with
aspect ratios between 1.4-7.6. The largest benefit of this method is arguably the ability to increase the width of the gold nanorods. Previous to this report, the target aspect ratio and thus longitudinal LSPR peak position was routinely met, however, absolute dimensions were not. Nanorods with diameters wider than 20 nm were not common before this method was published.

The volume of a nanorod is crucial for monitoring redox processes on surfaces of single gold nanorods. Firstly, scattering signal increases proportionally with volume, as the radius increases and \( L \) decreases (decreasing \( \epsilon/\epsilon_m \)). As a consequence, for time dependent studies, the exposure time can be decreased significantly and more detailed kinetic information can be obtained for nanorods with larger volumes. This is especially important in samples where the rods are embedded in a film which is itself absorbing or scattering. Conversely, larger nanocrystals have lower surface energy\(^{28}\) and plasmonic electric field enhancements,\(^{29}\) which is detrimental to heterogeneous,\(^{30}\) electro-\(^{31}\) and photo-catalytic\(^{32}\) performance. Furthermore, increasing the volume of a nanorod decreases the LSPR sensitivity to electron density.\(^{33}\) The balance of catalytic activity, sensitivity, band position and signal must be considered when selecting a specific gold nanorod size for time-resolved surface plasmon spectroscopy of redox processes.

To meet the sensitivity requirements for redox process experiments on gold nanorods, an aspect ratio of around 3 was selected. Small Au NRs with dimensions of 13 nm \( \times \) 40 nm were chosen in the hydrogen spillover (Chapter 4.3.1) experiments to increase the sensitivity of individual nanorods to hydrogen reduction. The target size for Au nanorods in all other experiments in this thesis was 30 nm \( \times \) 94 nm in order to increase scattering signal without decreasing electron density sensitivity dramatically. All glassware used in the following methods was immersed in fresh aqua regia solution and rinsed thoroughly with water. All water used in the procedure was deionised (MilliQ, 18.2 MΩ).
2.1.1.1 Original seeded growth method

Gold nanorods (Au NRs) were prepared according to the seed-mediated method.\textsuperscript{22} The seed solution was prepared by initially mixing 5 mL of a 0.2 M cetyl trimethylammonium bromide (CTAB, Unilab, 98\%) aqueous solution with 5 mL of a 0.5 mM aqueous solution of gold (III) chloride (HAuCl\textsubscript{4}.3H\textsubscript{2}O, Aldrich, $\geq$ 99.9\%). Under stirring of the mixed solution, 0.6 mL of ice-cold 0.01 M NaBH\textsubscript{4} (Aldrich, 98.5\%) was added and vigorously stirred for a further 2 min. The seed solution was stored at room temperature and used within 4 h of preparation. A growth solution was prepared by adding 5 mL of 0.2 M CTAB to 0.2 mL of 4 mM AgNO\textsubscript{3} (Sigma-Aldrich, $\geq$ 99.0\%) at room temperature. To this growth solution, 5 mL of 1 mM HAuCl\textsubscript{4} was added and, after mixing of the solution, 70 $\mu$L of 79 mM L-ascorbic acid (BDH Chemicals, 98.7\%) was added and vigorously mixed for 5 s. Immediately, 12 $\mu$L of the seed solution was added to the growth solution and vigorously mixed for 5 s. The growth solution was then left in a water bath at 30 $^\circ$C for 16 h. Following this, the solution was centrifuged twice at 8000 rpm for 20 min and 9 mL (\sim 90\%) of the supernatant was removed after each centrifugation. The pellet was redispersed in 9 mL of water once the supernatant was removed in each step. The final solution was diluted 10 times from the as-synthesised concentration. The estimated nanoparticle concentration of the Au NR solution used for spin coating was $2.5 \times 10^{-11}$ M based on yields reported by Orendorff \textit{et al.}\textsuperscript{34} UV-Vis and TEM characterisation of the product is presented in Figure 2.1. The Au NRs had diameters of 13 $\pm$ 4 nm and lengths of 40 $\pm$ 9 nm.

2.1.1.2 Bisurfactant method

Gold nanorods were prepared by following the bisurfactant seeded growth method.\textsuperscript{27} To prepare the seeds, 5 mL of 0.5 mM gold(III) chloride was mixed with 5 mL of 0.2 M CTAB solution. Freshly prepared 0.01 M NaBH\textsubscript{4} solution (0.6 mL) was diluted
Figure 2.1 – (a) UV-Vis absorption spectrum of the aqueous Au NR (aspect ratio of 3:1) solution and (b) transmission electron micrograph of the Au NRs prepared by the monosurfactant method (CTAB). Note that the Au NRs are slightly bone-shaped.

to 1 mL with water and added rapidly to the Au(III)-CTAB solution under stirring at 1200 rpm. The solution was stirred for 2 min. The seed solution was then aged at room temperature for 2 h before use and used as the seed solution for the following growth step. For the growth solution, 9.0 g (0.047 M in the final growth solution) of CTAB and 1.543 g of NaOL (TCI, 97.0%) were dissolved in 250 mL of warm water (∼50 °C). The solution was allowed to cool to 30 °C and, following this, 18 mL of 4 mM AgNO₃ solution was added. The solution was allowed to sit at 30 °C for 15 min, after which 250 mL of 1 mM HAuCl₄ solution was added. The solution became colourless after 90 min of stirring at 700 rpm and 2.1 mL of 32% HCl was then added. After another 15 min of slow stirring at 400 rpm, 1.25 mL of 0.064 M ascorbic acid was added and the solution was stirred at 1200 rpm for 30 s. Then, 0.4 mL of seed solution was rapidly added to the growth solution. The final mixture was vigorously stirred at 1200 rpm for 30 s and left undisturbed at 30 °C for 18 h to allow for nanorod growth. The nanorods were isolated by centrifugation at 7000 rpm for 30 min, followed by removal of the supernatant. UV-Vis and TEM characterisation of the product is presented in Figure 2.2. The Au NRs had average dimensions of 30 ± 3 nm × 94 ± 8 nm.
2.2 Instrumentation

2.2.1 UV-Vis spectrometry

UV-Vis spectrophotometry is a routine technique in nanoparticle characterisation due to low costs, simple sample preparation and value of information. The absorbance spectrum yields information about the size of the metal and semiconducting nanoparticles, as well as giving an indication of the concentration, dispersity and shape.\textsuperscript{35–37} The position of the longitudinal peak determines the mean aspect ratio and the line width can indicate the dispersity of ratios. The relative intensities of the longitudinal and transverse resonances can often indicate yields of non-rod or spherical shapes. In this work, ensemble absorbance spectra were collected with an Agilent 8453 UV-Vis spectrophotometer, between 200-1000 nm.
2.2.2 Spectroscopic ellipsometry

An ellipsometer records changes in polarisation as light reflects or transmits from a material. The polarisation change is represented as an amplitude ratio, $\Psi$, and the phase difference, $\Delta$. The measured values depend on the optical properties and thickness of the subject material. Ellipsometry is primarily used to determine film thickness and optical constants. Ellipsometers can accurately measure nanometre scale thicknesses without causing any damage to the sample.

Optical constants $n$ and $k$ and film thicknesses were evaluated in this work by measuring the variables $\Psi$ and $\Delta$ with a J. A. Wollam V-VASE Spectroscopic Ellipsometer at two angles of incidence ($60^\circ$ and $70^\circ$) in the wavelength range of 300-1500 nm. Optical constants $n$ and $k$ and film thickness were evaluated from $\Psi$, $\Delta$ data using the WVASE32 ellipsometry data analysis software. The data were fitted with Cauchy dispersion and Tauc-Lorentz oscillators in the non-absorbing region and at the UV absorption edge, respectively.

2.2.3 Transmission electron microscopy

Transmission electron microscopy (TEM) is a common microscopy technique that uses electrons instead of photons for imaging. The de Broglie wavelength of a high energy accelerated electron is much smaller than a photon. This enables the morphology of nanoparticles to be resolved well below the diffraction limit of visible light. The electrons can penetrate nanomaterials, sometimes experiencing momentum changes due to interactions with the sample. Transmitted and some diffracted electrons are detected by an array detector such as a CCD. TEM images shown throughout this thesis were acquired on a FEI Tecnai TF20 microscope operating at 200 kV. TEM samples were prepared by drop casting the sample solutions onto copper TEM grids (300 carbon mesh) and drying in ambient conditions.
2.2.4 Scanning electron microscopy

Scanning electron microscopy differs from transmission electron microscopy by detecting surface topography of a sample by raster scanning a focussed electron beam over the field of view. The spatial resolution of SEM is not as high as TEM, however, it still is incredibly useful in determining surface features and 3D morphology of nanocrystals which can be difficult to assess in transmission mode. Furthermore, nanoparticles can be dispersed onto a much wider variety of substrates because they are not required to be transparent to the electron beam. This is particularly useful for single particle spectroscopy as the same substrate can be used in both optical microscopy and electron microscopy. Crucially, this condition enables the optical properties of a nanoparticle to be correlated directly with precisely known morphology. The substrate is required to be conductive, otherwise the scan area rapidly charges and cannot be imaged. Beam damage is a further consideration and occurs when the electrons alter the material they are imaging. Organic molecules are the most susceptible, but beam damage can also cause nanocrystals to become unstable, reshape and even explode. To alleviate this, the beam accelerating voltage and current can be lowered and exposure time reduced.

All SEM was performed on a FEI Nova 200 Nanolab microscope operating between 5 and 10 kV. Samples were either prepared on silicon wafer or indium tin oxide (ITO) coated slides as indicated specifically in each section. Carbon tape was used to make an electrical connection between the sample stub and the substrate. Where large 25 mm × 25 mm ITO slides were used, two standard 10 mm SEM stubs were used to secure the sample, which was essential when tilting the stage. Where specific methods were used, further SEM experimental details appear in the relevant chapters.
2.2.5 Focussed ion beam

Focussed ion beam (FIB) is a technique that is usually carried out within a SEM vacuum chamber and is used in conjunction with the electron beam to etch or dope materials at the nanoscale. A beam of gallium ions is produced from a liquid-metal ion source and focussed with electrostatic lenses. FIB has been used solely in this work as a method to permanently mark areas near to single nanocrystals using the FIB registration method so that direct morphological correlations could be made. The FIB registration method is demonstrated with an example in Figure 2.3.

![Figure 2.3](image)

**Figure 2.3** – Focussed ion beam (FIB) morphology registration method. (a) An SEM image of a single Au NR (from the sample described in Figure 2.2) on an ITO substrate. (b) Monochromatic DFM image of FIB marked array with dispersed Au NRs in the area. The dot circled corresponds to the Au NR imaged to the left and the scattering spectrum to the right. The bright white horizontal dashes are 5 µm long FIB markings (c) Single particle scattering spectrum of the longitudinal LSPR band of the Au NR (aspect ratio 3:1) in (a) and circled in (b), acquired on the setup described in Figure 2.4.

All FIB was performed on a FEI Nova 200 Nanolab microscope operating at 30 kV and 10 pA with a stage tilt of 52°. Typically, a pair of line-based star marks were made into the ITO layer with a depth of 1 µm and a line length of 15 µm. The marks could be set using the draw function in the FEI software user interface.
The two stars were spaced 50 µm apart. A square array of 5 by 5 line markings were made 200 µm away at a depth of 50 nm and a length of 5 µm. The spacing of the array lines was 50 µm, to give a total array area of 250 nm². The areas selected for the array marking were populated with nanocrystals spaced apart by approximately 5 µm so that single nanocrystal spectra could be isolated on the DFM without signal crosstalk.

2.2.6 Single particle imaging and spectroscopy: Dark field microscopy

Dark field microscopy (DFM) has become the most common method of imaging the far-field signal of single metal nanoparticles. This has occurred because the optics are relatively simple and all required equipment can be purchased ‘off the shelf’. Most modern optical microscopes can be easily configured to image in dark field mode. Additionally, it is very simple to upgrade an optical microscope to have spectroscopic imaging capabilities. Connecting a spectrograph fitted with a mechanical slit and a CCD to the imaging light path can enable the scattering spectra of single metal particles to be collected, provided they scatter significantly more than their surroundings. DFM can be carried out in reflection (i.e. epi-illumination) or transmission.

The two requirements to achieve a ‘dark’ field of view are: an optical condenser which has a centred beam block; and lenses or mirrors which focus the resultant hollow cone of light at an oblique angle with a numerical aperture higher than an objective lens on the optical axis. The objects collected by the objective lens under these conditions are objects that scatter at the sample plane.

The DFM used for measuring all scattering spectra in this work, besides the measurements made using the laser-illuminated dark field microscope described in Chapter 5, was a Nikon TE2000-S Eclipse inverted microscope with a 100 W
Figure 2.4 – Schematic of the dark field microscopy setup used. M = mirror, DFC = dark field condenser, OL = infinity corrected objective lens, L = tube lens, CCD = charge-coupled device.
halogen lamp, a dry dark field condenser (0.8-0.95 NA), and a 40×/0.60 NA dry extra-long working distance objective lens (Nikon CFI S Plan Fluor ELWD 40X) coupled to an IsoPlane SCT 320 imaging spectrometer (Princeton Instruments (150 lines/mm, 500 nm or 800 nm blaze) equipped with a PIXIS 1024 CCD camera, front illuminated and cooled in air at –55 °C. A schematic is provided in Figure 2.4. The background signal was collected from a dark area on the slide (where no nanoparticles or contaminants were present) simultaneously with the single particle spectra. The signal was corrected for the spectral response of the system by subtracting and dividing by the background spectra. To capture colour images/video of single particles, a high resolution colour complementary metal oxide semiconductor (CMOS) camera (Thorlabs DCC1645C) was used in the port above the eyepiece. Further experimental details for DFM are provided in each chapter where they are specifically used for certain experiments.
References


Chapter 3

Spectroelectrochemistry of Silver Deposition on Single Gold Nanocrystals

3.1 Background

Electrodeposition of metallic silver onto gold nanocrystals provides a model system to optically determine influencing factors of under potential deposition (UPD) at the single nanocrystal level. Silver is well suited to these experiments, being a more efficient scatterer of visible light than gold, and with a less damped plasmon resonance than all other noble metals. According to Mie theory, electrodeposition of any metal other than silver would decrease the scattering signal of the Au NC, hindering experimental detection.

UPD refers to the formation of metal adatoms and adlayers at potentials more positive than the equilibrium redox potential. It is an important phenomenon in electrochemistry and has been exploited for decades to grow monolayer metal films.\textsuperscript{1-5} It has also been used in the past as a means to grow core-shell metal
nanocrystals\textsuperscript{6} and is implicated in the formation mechanism of anisotropic gold particles from gold seeds.\textsuperscript{7} Electrochemical nucleation and deposition on a variety of metal electrodes has been shown to generally lead to polydisperse, dendritic particle formation.\textsuperscript{8,9} Indeed, previous groups have shown that the application of large cathodic potentials to ITO electrodes immersed in AgNO\textsubscript{3} solution leads to indiscriminate nucleation and uncontrolled, though spectacular, growth of silver particles on ITO substrates.\textsuperscript{8} Conversely, selective deposition of metal atoms onto gold nanocrystals has not previously been demonstrated without concomitant bulk nucleation and growth on the working electrode. If UPD on different facets could be controlled, the morphology and composition of individual bimetallic nanocrystals could be engineered electrochemically using applied potentials. Additionally, if UPD can provide a pathway to selectively deposit a metal onto a nanocrystal, it would enable the electrochemistry of single metal particles to be studied without optical interference from randomly nucleating crystals.

This chapter shows that selective deposition of a metal onto a nanocrystal via UPD is possible and can be studied with correlated \textit{in situ} dark field imaging spectroscopy and SEM. Real-time spectroelectrochemical measurements of silver deposition on Au NCs adsorbed to conducting ITO substrates was achieved. Voltammetry was carried out at very low silver ion concentrations in a supporting electrolyte and the successful deposition of silver was accompanied by strong LSPR blue-shifts of the gold nanocrystal. Bulk silver formation on the ITO substrate was avoided by applying small cathodic potentials, well below the reduction potential of Ag, in the range where Ag UPD occurs.
3.2 Experimental methods

3.2.1 Materials

Hydrogen tetrachloroaurate (III) trihydrate (HAuCl$_4$.3H$_2$O, 99.999%, Sigma Aldrich), sodium citrate (99%, Sigma Aldrich), poly (N-vinylpyrrolidone) (Sigma Aldrich, analytical grade, M = 10,000 Da), N,N-dimethylformamide (DMF, ≥99.8%, Merck), silver nitrate (ACS reagent, 99%, Sigma-Aldrich), sodium perchlorate, (NaClO$_4$, pa quality), cetyl trimethylammonium bromide (CTAB, Unilab, 98%), NaBH$_4$ (Aldrich, 98.5%), L-ascorbic acid (BDH Chemicals, 98.7%) were used as received. Millipore filtered water (resistivity >18 MΩ/cm) was used for the preparation of all aqueous solutions.

3.2.2 Nanocrystal synthesis

3.2.2.1 Gold nanostars

Gold nanostars (Au NSs) were synthesised following the seed-mediated method developed by Barbosa et al.$^{10}$ Gold seeds were prepared by addition under continuous stirring of 5 mL (1 wt %) sodium citrate aqueous solution to a boiling aqueous solution of HAuCl$_4$ (100 mL, 0.5 mM). After the reaction had proceeded for 15 min, the resulting Au seeds were transferred into ethanol through PVP modification. Thus, 5 mL of a PVP (M = 10,000 Da) aqueous solution containing 0.2 g of PVP was added drop wise to the Au colloid and left to react overnight. The final solution was centrifuged at 4,000 rpm for 90 min, the supernatant removed and the spherical nanoparticles redispersed in ethanol.

For the synthesis of gold nanostars, 82 µL of an aqueous solution of 50 mM HAuCl$_4$ was mixed with 15 mL of 10 mM PVP (M = 10,000 Da) solution in DMF.

*I thank Mariana Chirea for supplying the gold nanostars
To this solution, a certain amount of preformed-seed dispersion was added under continuous stirring and allowed to react until completion of the reaction, whereby there were no further changes in the UV-Vis spectra. The [HAuCl$_4$] : [seed] ratio was 90. The resultant Au NSs were purified by sonication for 1 min, centrifugation at 7,000 rpm for 15 min, and removal of 90% of the supernatant, with the same volume replaced with water. The final solution was sonicated for a further 1 min.

### 3.2.2.2 Gold nanorods and nanocubes†

Gold nanocubes were synthesised using a seeded growth method. For the preparation of the seed solution, 3.75 mL of 0.1 M CTAB solution and 0.0273 mL of 0.05 M HAuCl$_4$ solution were mixed thoroughly. Following this, 0.3 mL of freshly prepared ice-cold 0.01 M NaBH$_4$ solution was added into the same solution with vigorous stirring for 10 min. The resulting seed solution was then kept at 29 °C for 1 h before use.

To grow the seeds into larger nanocubes, 0.1 mL of seed solution was first diluted with 9.9 mL of water. In a separate flask, 3.2 mL of 0.1 M CTAB solution, 0.08 mL of 0.05 M HAuCl$_4$ solution and 1.9 mL of 0.1 M ascorbic acid solution were added sequentially to 16 mL water. The solution was mixed thoroughly after adding each component and, immediately after this, 0.02 mL of the diluted seed solution was added. The final solution was mixed by gently stirring for 1 min and then placed in water bath (30 °C) for 24 h. The resultant product was collected by centrifugation at 7,000 rpm for 15 min, and removal of 90% of the supernatant, with the same volume replaced with water.

The gold nanorod synthesis used in this section has been previously described in the Experimental Methods section of this thesis (see Chapter 2.1).

†I thank Wenming (Simon) Tong for supplying the gold nanocubes
3.2.3 Spectroelectrochemical experiments

The dark field microscopy setup used in these experiments has been outlined in the Experimental Methods section of this thesis (Chapter 2). ITO–coated glass slides (Delta Technologies, $R_s = 8-12\ \Omega/sq$) were used as working electrodes (WE) in all experiments. Samples were marked by using the FIB registration technique (see Chapter 2.2.5), enabling pre and post experimental images of the same nanocrystals to be obtained by SEM. Marked Au nanocrystal modified ITO-coated glass slides were inserted into a purpose built electrochemical cell which adhered to the working distance requirements of the transmission dark field microscope and was connected to a PGSTAT 302N potentiostat (Metrohm AutoLab BV). A schematic of the cell is shown in Figure 3.1 and was enclosed by a steel cage and a polytetrafluoroethylene (PTFE) ring. The electrochemical cell configurations and experimental conditions varied slightly between the NaBH$_4$ treated and non-treated nanocrystal-modified electrodes. For the NaBH$_4$ treated nanocrystal experiments, opportunities to improve the electrochemical cell design were identified which reduced the area of the WE, used smaller amounts of nanocrystals, and increased stability of the qRE, solely to improve the accuracy of the measurements thereafter.

3.2.3.1 Non-treated gold nanostar-modified electrode

Prior to use, the ITO–coated glass slides were washed by sonication in absolute isopropanol, MilliQ water and dried under a stream of nitrogen. Diluted (10×) aqueous solution of washed gold nanostars (150 $\mu$L) was spin coated at 3,000 rpm for 1 min on freshly cleaned 25 mm × 25 mm ITO-coated glass slides. The ITO slide was then placed inside the cell. Through the PTFE ring, a coiled Pt wire and a straight Ag wire were inserted and used as counter (CE) and quasi-reference electrodes (qRE), respectively. A second Ag wire, protected from contacting the electrolyte solution by PTFE tape, was used to connect the particle-containing ITO-
coated glass slide, the WE, to the potentiostat. The Pt CE was cleaned by polishing on micro cloth pads with diamond suspension (0.3 \( \mu \text{m} \)), sonicated in MilliQ water for 5 min, and dried under a stream of \( \text{N}_2 \). The cell was filled with a filtered (0.22 \( \mu \text{m} \) PES membrane) 0.1 M \( \text{NaNO}_3 \) electrolyte aqueous solution (approximately 1.3 mL) with a \( \text{AgNO}_3 \) concentration of \( 6.7 \times 10^{-7} \text{ M} \) and covered with a cover slip to minimise evaporation and eliminate meniscus lensing. Spectroelectrochemical measurements were carried out on nanostars in the middle of the WE.

### 3.2.3.2 Treated gold nanostar, nanorod, and nanocube-modified electrodes

A standard photolithography step was carried out on a 25 mm \( \times \) 25 mm ITO-coated microscope slide using AZ4562 photoresist. Sufficient photoresist to cover the slide was spin coated on the ITO surface and then heated face-up on a hot plate at 100 °C for 5 min. The slide was then placed in a UV-exposure box on top of a mask and turned on for 90 s. A mask with the dimensions in Figure 3.2a was used. Following the exposure, the slide was dipped into a 40 mL of 0.15 M sodium hydroxide aqueous solution for 1 min. After that, a wet etching step was carried out to remove the UV-exposed ITO in HCl acid (37%), the slide was etched in 2:1 solution of
HCl (37%) : H₂O for 8 min. The remaining AZ4562 photoresist was then removed by sonicating the slide in acetone for 15 s. The patterned ITO glass slides were washed further by sonication in absolute isopropanol, then water, and dried under a stream of N₂. Diluted (10×) aqueous solution of washed gold nanostars, nanorods, or nanocubes (20 µL) was spin coated at 500 rpm for 10 min onto the end of the 12 mm T-shape protrusion which makes up the WE. The other side of the pattern, the U-shape, was the CE electrode. Before mounting in the electrochemical cell, the slide was immersed in 40 mL of 0.04 M NaBH₄ solution for 15 min to remove the ligands. The slide was then rinsed repeatedly with water, and dried in a stream of N₂, before being placed inside the cell. Through the PTFE ring, a 0.5 mm diameter platinum/polypyrrole (Pt/PPy qRE (preparation reported by Ghilane et al.)) was inserted with the end positioned <1 mm from the end of the WE. A second Ag wire and a Pt wire, protected from contacting the electrolyte solution by PTFE tape, were used to connect the particle-containing WE (T-shaped ITO) and CE (U-shape ITO) to the potentiostat, respectively. The electrode configuration of the cell is illustrated in Figure 3.2b. The cell was filled with a filtered (0.22 µm PES membrane) 0.1 M NaNO₃ electrolyte aqueous solution (approximately 1.3 mL) with a AgNO₃ concentration specified in the results sections of this chapter, and covered with a cover slip to minimise evaporation and eliminate meniscus lensing. Spectroelectrochemical measurements were carried out on nanocrystals near the end of the WE.

3.2.4 Scanning electron microscopy

The deposition of silver onto the surface of nanocrystals was followed using electron microscopy. Scanning electron microscopy was carried out on single particles before and after the spectroelectrochemical experiments. The particles were only exposed to the electron beam once prior to, and once following the silver deposition.
Figure 3.2 – (a) UV-lithography mask dimensions for patterning ITO working and counter electrodes and (b) cell dimensions and electrode configuration used in the treated nanocrystal experiments.

Identical SEM beam conditions were used to ensure a consistent electron exposure, the settings were 10 kV, 0.54 nA, with a 10 µs dwell time. The magnification used was 250,000× in immersion mode with a 5 mm working distance.

3.2.5 Theoretical modelling

COMSOL was used to simulate the nanostar structure. All calculations were performed in an effective embedding medium $n = 1.515$, to match the experiment. The optical constants of gold were taken from Johnson and Christy. The particle shells were delimited by perfectly matched layers, which prevented any unwanted reflections through absorbing the scattered light from the particles. For theoretical modelling, an ‘average’ nanostar was chosen. From electron microscopy characterisation, the average size of the nanostar core was 57 nm, with a 27 nm tip length, a 23 nm width at the base of tip, a 2.5 nm radius of tip apex, and 8 tips. Theoretical modelling was performed by applying these average parameters to generate optical spectra of both gold nanostars and silver coated/deposited gold nanostars on ITO and immersed in an aqueous environment.

I thank Xingzhan Wei for carrying out the COMSOL modelling.
3.3 Results

3.3.1 Gold nanostars

3.3.1.1 PVP coated gold nanostars

Gold nanostars were selected for initial studies of the metal deposition process due to their many different crystal facets and sharp needle-like structures, which were hypothesised to promote metal deposition. They also exhibit sharp, intense surface plasmon resonances in the visible or NIR regions of the spectrum. Furthermore, the polyvinylpyrrolidone layer that colloidally stabilises the Au NSs forms complexes with Ag\(^+\) ions in solution, and this may facilitate the deposition of Ag adatoms and adlayers.\(^\text{11}\) Gold nanostars and other nanoparticle morphologies have previously been employed as plasmon binding sensors,\(^\text{10,14-16}\) however, reports on electrochemical properties of nanostars at the single particle level are not present in the literature.

In Figure 3.3a, the LSPR peak position (red markers) of a single Au NS is plotted as a function of time during an applied cathodic potential sequence ranging between 0 mV and -100 mV (blue trace). This peak position corresponds to the strongest peak in the Au NS scattering spectrum which is in the NIR (Figure 3.3b, red spectrum on right-hand side). The potential was initially held constant at 0 mV relative to the quasi-Ag reference electrode for five min prior to the application of the potential step sequence. During this time, the LSPR peak position was stable (\(\pm 1\) nm), indicating that there was no silver ion reduction at this potential. After the initial pre-conditioning of the system at 0 mV, a series of increasingly cathodic potential steps was applied. Scattering spectra were collected at each potential. Note that each spectrum required a 30 s acquisition time and the potential was

held constant at each value for at least 60 s to enable two spectra to be acquired. It is evident that at 0 mV and -20 mV, the LSPR peak position and scattering intensities remained unchanged (red and orange spectra, start potential in Figure 3.3b,d). At -40 mV, a blue-shift of the LSPR from 861 nm to 810 nm was observed over 60 s, implying that silver was being readily reduced and was depositing on the surface of the Au NS. There was a concomitant 45% increase in the scattering intensity in this period (green spectrum in Figure 3.3b). At -60 mV and -80 mV, the blue-shift of the LSPR continued and by -100 mV, there was a 122 nm total blue-shift of the LSPR and the scattering intensity had increased to 2.6 times the original value (purple spectrum in Figure 3.3b). The stable position of the LSPR peak when the potential was returned back to 0 V (Figures 3.3a,c) strongly suggests that the silver was not readily re-oxidised. The spectroelectrochemical data for another single gold nanostar on the same electrode is shown in Figure 3.3c and d. The same trends are apparent in this spectra, that is, a blue-shift and increase in intensity of the LSPR, although for this nanostar the changes were more pronounced, featuring a 148 nm blue-shift and a 325% increase in $I/I_0$.

The colour change during the deposition on Au NSs could be easily observed by eye and was captured by a colour camera (Figure 3.4). The scattered light from individual Au NSs changed from initially being in the near infrared to a final colour of red or orange. This blue-shifting and scattering intensity increase was possible due to the deposition of silver; silver has a higher bulk plasma frequency than gold and is the only material which has a less dampened plasmon resonance than gold, and hence a higher scattering efficiency. SEM morphology correlation was undertaken to strengthen the evidence for silver deposition.

Two very different types of electrochemical behaviour for single Au NSs were observed spectroscopically, those that had been imaged by the SEM and those that had not been. Gold nanostars that had been imaged in the SEM prior
Figure 3.3 – (a,c) Position of the surface plasmon band peak of single gold nanostars as a function of both time (red circles) and the applied potential (blue line), measured during electrodeposition of metallic silver from $6.7 \times 10^{-7}$ M AgNO$_3$ and 0.1 M NaNO$_3$ aqueous solution. (b,d) Selected Rayleigh scattering spectra of the same gold nanostars collected at various applied potentials during the deposition process. The nanostars were coated with PVP.
Figure 3.4 – Colour micrographs of individual gold nanostars before (top left) and after (top right) silver deposition. The bottom schematic illustrates the single particle electrodeposition process in a simplified manner.
to voltammetry measurements did not undergo silver deposition whereas gold nanostars unexposed to the electron beam prior to reaction did undergo silver deposition. In the case of pre-imaged Au NSs, it is highly likely the electron beam carbonises the PVP coating, resulting in a carbon shell that passivates the Au surface and prevents silver deposition from occurring. The Au NSs shown in the SEM images in Figure 3.5 had been exposed to the electron beam prior to electrochemical silver deposition. They did not undergo silver shelling and surface plasmon shifts were not observed on these particles.

Contrarily, on gold nanostars not previously exposed to the SEM electron beam, there is a change in shape from star to a more flower-like structure with thicker cores and tips (Figure 3.6). The passivation effect of the SEM rendered the collection of
images of the same individual nanostars before and after electrochemical coating impossible under these experimental conditions.

### 3.3.1.2 PVP-free gold nanostars

To circumvent the electron beam imaging issue, a protocol for removal of the PVP coating was developed. The Au NSs were spin coated onto the ITO WE (updated electrochemical cell design described in the Experimental Methods of this chapter) and pre-treated with a 0.04 M sodium borohydride solution for 15 min in order to remove the PVP.\(^\text{17}\) Silver electrodeposition on these ‘bare’ Au NSs was performed using \(5 \times 10^{-7}\) M AgNO\(_3\) and 0.1 M NaNO\(_3\) aqueous solution. The deposition process was slower under these conditions, as evident by the smaller blue-shifts occurring at a much slower rate. As before, there were no evident changes in spectra at the open circuit potential or at 0 mV applied potential. Following this, small -20 mV cathodic steps were applied to the ITO for 60 s. From Figure 3.7, it can be seen that the gold nanostar underwent a very slight blue-shift of 2 nm at -20 mV. A slight increase in relative deposition rate occurred when the potential
Figure 3.7 – Single nanostar spectroelectrochemical data of $\lambda_{\text{max}}$ against time and potential from the NaBH$_4$ treated nanostar-modified electrode experiment (red plot) accompanied by data obtained under the same conditions except without the addition of any silver to the electrolyte solution (green plot). The slight blue-shift ($\sim$3 nm) in this control can be attributed to focal drift.

was changed to -160 mV and the LSPR peak blue-shifted 5 nm. After the potential was held at -160 mV for 8 min, the applied potential was further reduced to -180 mV (8 min), -200 mV (8 min), and -220 mV (1 min). At each new potential, the rate of blue-shift initially increased again, then slowed but never stopped. This indicates that there was a steady-state flux of silver to the nanostar at each of these potentials and electrochemical equilibrium was never achieved.

In Figure 3.8, the final scattering spectrum of the Au NS after the total 40 min sequence is shown (blue line) as well as the initial spectrum (red line). The total blue-shift in the scattering spectrum of this single nanostar over the 40 min sequence was 31 nm and there was a 30% increase in the scattering intensity. A control experiment was carried out under the same experimental conditions
Figure 3.8 – Full scattering spectra of a single, NaBH$_4$-treated nanostar at the open circuit potential before (red) and after (blue) electrodeposition of metallic silver from $5 \times 10^{-7}$ M AgNO$_3$ and 0.1 M NaNO$_3$ aqueous solution at potentials varying from 0 mV to -220 mV.

without any added AgNO$_3$ to confirm that the LSPR shift was caused by the silver ions (green plot, Figure 3.7). In the absence of Ag$^+$ ions, the LSPR position was relatively unchanged from the initial value.

The blue-shifts in the scattering spectra occur at very small cathodic potentials. However, such blue-shifts may also be due to double-layer charging or potential-induced shape changes to the particles. To resolve these contributions, again SEM was carried out on the nanostars before and after chronoamperometry to determine whether they retained their star-like morphology.

In Figure 3.9, two images of the same gold nanostar before and after the electrodeposition process are presented. The nanostar had been treated with NaBH$_4$ before SEM imaging and the post-deposition image clearly exhibits a
change in morphology due to the deposited silver. This is the same particle for which the optical data shown in Figure 3.7 and 3.8 were obtained. In this case, the silver appears to have deposited predominantly on the tips as spheres or agglomerates,\textsuperscript{18,19} with only a small change in the overall size of the particle compared to the PVP coated stars. SEM images and DFM spectra of additional Au NSs that had undergone silver deposition are presented in Appendix A (Figures 7.2 and 7.3). Furthermore, indiscriminate nucleation of Ag on the adjacent ITO surface was not observed. From the SEM images shown in Figure 3.10, it is clear that no ‘free’ silver nucleation was present on the ITO. This figure also demonstrates that particles exposed to, and not exposed to the e-beam prior to Ag deposition undergo almost identical Ag deposition on NaBH$_4$ treated particles. This was not the case for untreated particles.
Figure 3.10 – SEM images of NaBH$_4$-treated Au nanostars (not previously imaged by the electron beam) after Ag deposition, obtained using the same potential sequence carried out in Figures 3.7-3.9. Note the absence of any indiscriminate Ag nucleation on the surrounding ITO. Silver deposition occurred exclusively on the nanostars.

Ag deposition on Au nanostars$^{20}$ and nanorods$^{21}$ stabilised in solution occurs via epitaxial growth on low energy crystal facets due to the presence of surfactants and halide ions.$^{22}$ The AuNSs in the experiments in this chapter are adsorbed to a surface, so colloidal stability was not a consideration of the chosen electrolyte solution. Conversely here, the dominant factor controlling the spatial distribution of the deposited silver is the local electrical double-layer at ‘bare’ metal nanostar tips, which possibly enhanced the reduction potential of Au NSs. However, it should be noted that the chemical deposition of silver on gold crystals is highly dependent on other factors such as temperature, pH of solution and reducing agent.$^{20-23}$

A further consideration was made in the interpretation of the data to determine whether interdiffusion of Ag atoms into the Au lattice was occurring. It has widely been reported that Au-Ag alloying of nanospheres leads to a single LSPR while core-shell structures will create two resonances.$^{20,24}$ If the silver shell is very thick, the gold LSPR will be masked by the high extinction of the silver. The optical properties
become more complicated for complex and anisotropic Au-Ag nanocrystals. Because of this complexity, the data obtained does not allow the unambiguous determination of alloying, especially due to the low sensitivity of the detector below 470 nm. However, work carried out by Meisel and co-workers demonstrated that the extent of spontaneous interdiffusion of Ag into Au nanocrystals strongly decreases with increasing Au core size due to the increase in melting temperature and lower relative occurrence of surface vacancies. Since the lattice structure and lattice constant for Au and Ag are identical, distinguishing them in TEM is extremely difficult and atomic imaging cannot resolve down to the 1-3 monolayers of possible interdiffused atoms. All the Au NCs studied in this chapter were relatively large in regards to the nanocrystals studied by Meisel, therefore the assumption that no interdiffusion occurred during deposition was made.

3.3.1.3 Simulations

Calculations are presented in Figure 3.11a of the predicted spectral shifts of the nanostar LSPR during silver deposition. The nanostars were simulated as spheres with eight projecting conical protuberances, to match the SEM images shown in Figure 3.5. COMSOL was used to calculate the scattering cross section of the particles for even coatings of silver on the surface. A homogeneous dielectric constant of $\varepsilon_m = 1.78$ for the environment was assumed. The COMSOL simulations predict a blue-shift of 120 nm with a 5 nm silver shell, which is close to the experimentally observed shifts of 122 nm for PVP stabilised nanostars that had not been exposed to the electron beam. Figure 3.11b illustrates the surface charge distribution on a silver-coated gold nanostar during illumination at 729 nm, corresponding to the major scattering peak. These charge distributions reveal that the major LSPR is a dipolar resonance. Figure 3.11c shows the relationship between the increase in relative scattering intensity and blue-shift matches for the theoretical
Figure 3.11 – (a) Calculated scattering spectra using COMSOL of a gold nanostar with different homogeneous Ag shell thicknesses, assuming $\epsilon_m = 1.78$. Dielectric data for gold is from reference 13. (b) Calculated surface charge distribution at the major, dipolar scattering peak $\lambda = 729$ nm. Diameter of the gold sphere core, 57 nm; tip length, 27 nm; length of tip base, 23 nm; radius of tip apex, 2.5 nm; refractive index of the surrounding medium, 1.33. (c) Plot of the relative intensity of the LSPR peak as a function of the peak wavelength of the LSPR band during silver deposition. Diamond-shaped markers represent experimental data and the continuous line is data fitted to COMSOL simulated results.

and experimental data. This close match enables a prediction of the silver shell thickness throughout the deposition process. The thicknesses are calculated using a range, starting from a monolayer of approximately 0.2 nm and increasing up to 5 nm thick coatings similar to the conditions employed in these experiments. From the particle volume changes determined by the modelling, it is estimated that there is deposition of $1.8 \times 10^6$ silver atoms in 150 s. Assuming that the flux is controlled by the interfacial transfer rate and that the particle is a sphere for simplification, it may be written $J \ (\text{mol/s}) = 4\pi R^2 k_{et} [\text{Ag}]$. Inserting $R = 28.5$ nm and $[\text{Ag}] = 6.7 \mu\text{M}$ yields $k_{et} \sim 1 \text{ cm/s}$, which corresponds to a moderate heterogeneous rate constant, but still below the diffusion limit of $> 1\times10^5 \text{ cm/s}$. Under these conditions, the spatial distribution of silver will be controlled by the double-layer structure as assumed above.
3.3.2 Gold nanorods and nanocubes

The motivation for using gold nanostars in single particle electrodeposition experiments was outlined at the beginning of this chapter. However, gold nanostars are fundamentally challenging structures to study due to their irregular morphologies. To understand how UPD proceeds on different facets, edges, and corners of nanocrystalline materials, well-defined and uniform nanocrystals are required. In this section, the electrodeposition onto single gold nanorods and nanocubes is reported.

Gold/silver bimetallic nanorod and nanocube syntheses have been reported on several occasions in the literature using surfactant-templating methods.\textsuperscript{27–32} The reaction conditions control the Ag growth on the Au NR surface, and the deposited silver can form near-homogeneous shells,\textsuperscript{33} dumbbells,\textsuperscript{34} cuboids,\textsuperscript{30} and exclusively tip extended growth.\textsuperscript{22} These overgrowth processes have been studied in real-time but not at the single particle level. This is likely due to the experimental challenges involved, such as morphology correlation. The resultant nanocrystals have been shown to be promising materials for catalysis,\textsuperscript{35} photonics,\textsuperscript{36,37} and surface enhanced Raman spectroscopy.\textsuperscript{38,39}

In Figure 3.12a, the LSPR changes recorded on a single 30 nm × 94 nm Au NR are displayed during a voltammetric staircase in which silver was electrodeposited. In an electrolyte solution containing $5 \times 10^{-7}$ M of AgNO$_3$, the cell was initially left at the open circuit potential to ensure silver was not spontaneously depositing onto the gold surface. Spectra of multiple particles were collected every 30 s. After two min, a 0 V potential was applied to the cell and negligible changes to the LSPR signal were detected. The applied potential was reduced by 20 mV every 1 min. UPD was initiated on the Au NR surface at -140 mV (applied potentials correspond to the black trace), as was illustrated by the blue-shift of $\lambda_{max}$ (red trace) and increase in $I/I_0$ (green trace). The potential was held at -140 mV for 4
min, in which time the $\lambda_{\text{max}}$ blue-shifted 19 nm, with the biggest change occurring within the first minute. The potential was then reduced to -160 mV for another 4 min and then to -180 mV for 16 min. The net changes to the scattering signal were a blue-shift of 58 nm, increase of fwhm of 18 nm, and an increase of $I/I_0$ of 2.4. The initial and final spectra taken are plotted in Figure 3.12b to highlight the magnitude of the changes. Interestingly, the fwhm was observed to increase at potentials more positive than -140 mV, suggesting that there may have been some adsorbate damping occurring at more positive potentials, for example, Br$^-$ from the residual ligands or NO$_3^-$ from the electrolyte. Furthermore, at -140 mV, the fwhm drops suddenly which potentially indicates the chemical adsorbates on the Au surface are being displaced by the first Ag layer. Chemisorbed species have been shown to cause LSPR damping in a previous electrochemical study, however, NO$_3^-$ was shown not to adsorb within the potential range used.

Ferro/ferricyanide redox couple calibration of the electrochemical cell was carried out to determine whether the potential at which deposition first occurred was more positive than the standard reduction potential of Ag$^+$. Fresh ITO electrodes and electrolyte (same [NaNO$_3$], with 4.8 mM potassium ferrocyanide) were used to preserve the electrode and particles from further changes during the calibration cyclic voltammogram (CV). The calibration CV is shown in Appendix A, Figure 7.1. The calibration gives $E^\circ$ (ferro/ferricyanide couple) = 0.14 V vs Pt/PPy qRE. Assuming the $E^\circ$ (ferro/ferricyanide couple) = 0.37 V vs NHE, $E$(Pt/PPy) = $E$(NHE) + 0.23 V. i.e. Pt/PPy qRE lies at more positive potentials than the NHE. Ag deposition appears on Au NRs at -0.14 V vs Pt/PPy qRE, which means it is depositing at about 0.09 V vs NHE. $E$(Ag$^+$/Ag) = 0.799 V + 0.059log[Ag$^+$] $\approx$ 0.43 V for 500 nM Ag$^+$. This would therefore correspond to an overpotential of 0.34 V required for bulk deposition. However, if the silver is complexed, then the active concentration may be lower, and $E$ may be more negative than 0.43.
Figure 3.12 – (a) Full spectroelectrochemical results from the LSPR analysis of a single 30 nm × 94 nm Au NR scattering spectra measured during electrodeposition of metallic silver from $5 \times 10^{-7}$ M AgNO$_3$ and 0.1 M NaNO$_3$ aqueous solutions. The black trace plots applied potential, the red trace plots $\lambda_{\text{max}}$, the blue trace plots fwhm, and the green trace plots $I/I_0$, all against time on the horizontal axis. (b) Initial and final single Au NR scattering spectra corresponding to the adjacent data.

V. Furthermore, the charge on the ITO may affect the potentials; the small gold particles are on large flat ITO plates and the negative potential on the ITO can reduce the flow of silver ions to the gold. For example, Ag$^+$ may adsorb to the ITO, reducing the concentration near the gold particle. The potential is more negative than expected for UPD, although $E$ is very difficult to determine at nM concentrations for these reasons.

SEM imaging of the Au NRs before and after Ag deposition was performed to determine if size and morphology changes could be resolved. To increase time efficiency, direct spectrum-to-morphology correlation was not carried out. Rather,
many rods within the same area on the WE were imaged before and after where spectra were taken during the deposition process. The particles were sized from the SEM images before and after electrodeposition and the results for length, width, and aspect ratio are summarised by the histograms in Figure 3.13a-c, respectively. The before (top four) and after (bottom four) images of Au NRs in the process described above have been shown in Figure 3.13d. Note that the Ag deposited is smooth, but not highly homogeneous, on each individual particle, resulting in slightly irregular shells. Some tend to grow out from the centre of the \{520\} facet on the single crystal rods\textsuperscript{22} and others have more silver at one end. Overall, there is a significant decrease of aspect ratio of the nanorods as a result of a thicker silver shell on the sides rather than the ends. The average aspect ratio shifted from 3 to 2.2 for the 20 particles measured, which corresponds to an average Ag shell thickness of 8 nm on the sides and 4 nm on the ends of the Au NRs.

Gold nanocubes have significantly different faceting and surface energy to Au nanostars and nanorods.\textsuperscript{41} They consist of six \{100\} faces with 90° angle edges and corners. High resolution TEM and XRD measurements reported in the literature have shown that the corners and edges of the cubes exhibit small areas of the higher surface energy\{111\} and \{110\} faces, respectively.\textsuperscript{42} Similar to the tips of the nanostars, the increased surface energy of the atomically-low coordinated edges and corners may assist in the UPD of silver. The presence of one dominant crystal facet provides a more simple single particle system to study electrodeposition. To assist the post deposition morphology characterisation, spectroelectrochemical measurements of gold nanocubes were carried out in higher concentrations of AgNO\textsubscript{3} than the nanostar and nanorod experiments. At higher concentrations, the deposits of silver could be imaged easily on the SEM. The concentration selected to do the spectroelectrochemical experiments on nanocubes was 5 × 10\textsuperscript{-5} M AgNO\textsubscript{3}, with all other experimental conditions described in Chapter 3.2.3.2.
Figure 3.13 – Histograms of Au NRs width (a), length (b) and aspect ratio (c), before (red) and after (blue) silver deposition. (d) Scanning electron micrographs of Au NRs before (top row) and after (bottom row) electrodeposition of metallic silver. Scale bars are all 100 nm.
In Figure 3.14, the top two sets of images show the morphology of the same gold nanocube above (a) and distorted cuboid below (b), before (left) and after (right) the voltammetric staircase was applied. From an initial voltage of 0 mV, the voltage was reduced by -40 mV every 4 min. The final voltage of -340 mV was held for 4 min, at which point the cell was switched off and the sample was rinsed and dried. The 80 nm gold nanocube in the above set of images transformed into a much larger structure with the silver deposits preferentially depositing on the corners of the cubes. Each large spherical deposit can be seen to be protruding from the corner sites. This was also observed for distorted nanocubes (Figure 3.14b), where each corner produced a favourable site for silver nucleation at reduction potentials above where it would be reduced on the \{100\} face. This result provides unequivocal evidence, in conjunction with the nanostar results, that UPD is strongly influenced by nanocrystal morphology. The large volume of metallic silver that formed on the gold nanocube surface resulted in enormous changes to the spectra. The graph in Figure 3.14c shows one spectrum at each potential applied to the cube in Figure 3.14a during the experiment. The initial LSPR peak at 740 nm began to decrease in scattering intensity when -120 mV was applied, which is likely to be the point at which silver UPD was initiated on the corners of the cubes. At this same potential, a new peak was seen to emerge at shorter wavelengths, which was likely to be higher energy resonances arising from the sphere-like silver formations on the corners. This peak progressively red-shifted and increased in intensity as the potential became more negative. Based on the SEM images, the silver deposits reached their final diameter of about 90 nm at -340 mV. The final LSPR peak position of this bimetallic structure was 740 nm, with a second wavelength peak of half the intensity positioned at 600 nm.

By demonstrating that silver can be deposited onto individual electrode-immobilised gold nanorods and nanocubes, a route has been established to sys-
Figure 3.14 – (a,b) Scanning electron micrographs of a cube (a) and a distorted cuboid (b), before (left) and after (right) electrodeposition of metallic silver. (c) Plots of the spectral changes that occur on the cube in the top figure (3.14a) during the electrodeposition process in $5 \times 10^{-5}$ M AgNO$_3$ and 0.1 M NaNO$_3$ aqueous solution.
tematically analyse UPD and electrocatalysis on a wide range of well-defined nanocrystalline materials by monitoring the reactions with dark field microscopy. In future works, various metals, shapes, crystal structures, oligomeric arrangements, scan rates, electrolytes, and so forth, could be studied to enable new bimetallic structures to be engineered.

### 3.4 Conclusions

Controlled deposition of silver onto single gold nanocrystals was observed by DFM-based spectroelectrochemistry. The resulting scattering spectrum of the gold-silver particles was tuned over 100 nm by deposition of a 1-5 nm layer of silver. Additionally, it was found that electron beam imaging has a drastic effect on the surface chemistry of gold nanostars by carbonising the PVP ligand. Chemical pretreatment with sodium borohydride removed the PVP but altered the kinetics of Ag electrodeposition with respect to a PVP coated nanostar. The absence of PVP also promoted Ag deposition, primarily on the tips of the Au nanostars to generate unique bimetallic nanostructures. The deposition process was highly dependent on the Au nanocrystal morphology, with significantly different bimetallic structures resulting from Ag deposition on nanorods and nanocubes. This study directly identified how the morphology and ligand properties of Au NCs influences catalytic behaviour.
References


Chapter 4

Redox Reactions on Single Gold Nanorods in Metal Oxide Thin Films

4.1 Background

The oldest known examples of prepared metal nanocrystals were embedded in oxide matrices and were used for colourants in glass, as described in the introduction chapter. The interface between nanosized gold and metal oxide matrices is interesting because electron density on both components can vary depending on chemical\(^1\) and light\(^2\) exposure. The focus of this chapter is the redox processes central to modern applications of gold/metal-oxide nanocomposite materials, such as gas sensing,\(^3\) heterogeneous catalysis\(^4\) and photocatalysis.\(^1\) The results presented demonstrate how surface plasmon spectroscopy can answer fundamental questions about redox processes occurring in these widely studied materials. Section 4.3 describes how single gold nanorods in metal oxide matrices were used as redox probes to understand the chemical mechanism of hydrogen sorption in reducing
and oxidising gases. Section 4.4 describes single particle studies of photoexcitation and subsequent charge transport in zinc oxide films containing gold nanorods.

### 4.1.1 Hydrogen spillover

The first step in heterogeneous gas catalysis usually involves the adsorption of a reactant onto a catalyst surface. A particularly important case is dissociative H$_2$ adsorption, which is well documented to occur on transition metal surfaces producing mobile adsorbed H atoms. Mobile surface H atoms are critical to many catalytic processes such as hydrogenation reactions. Understanding their chemical behaviour is technologically important for high density hydrogen storage and for the development of hydrogen sensing materials. A pivotal discovery for catalysis was that mobile H atoms can migrate from a metal to its surrounding support matrix and then undergo further chemical reactions, depending on the nature of the support and the presence of other sorbed species. This cross material migration process has been coined hydrogen spillover. The goal of the work in this chapter was to show that single particle surface plasmon spectroscopy is a powerful tool for real-time monitoring of catalytic processes and chemical intermediates during surface redox reactions such as hydrogen spillover.

The first evidence of hydrogen spillover was reported by Khoobiar in 1964 when it was observed that WO$_3$ underwent a colour change when it was reduced by H$_2$, but only in the presence of a Pt catalyst. Since this discovery, H$_2$ molecule interactions with metal/oxide surfaces have been studied by a variety of techniques in order to understand spillover: product analysis, electrical conductivity, and infrared, nuclear magnetic resonance, electron paramagnetic resonance, and X-ray absorption spectroscopies. Electrical conductivity measurements have been important in confirming that in Pt/TiO$_2$ materials H atoms can migrate from the Pt to the reducible TiO$_2$ surface, remaining mobile in either the atomic (H*) or
ionic forms (H⁺), with the possibility of both forms coexisting on TiO₂. Roland et al. showed that increases in conductivity occur in TiO₂ films in contact with, but at a suitable distance from, Pt catalysts exposed to H₂. It was postulated that, following chemisorption of hydrogen gas, there is an initial dissociation to form surface H atoms, some of which further dissociate into mobile electrons and protons; the electrons transfer into the conduction band of the titania support, leaving protons bound to surface lattice oxide ions. The reverse reaction occurs in more oxidising conditions, often when the source of hydrogen is removed, and this is known as reverse spillover. However, half a century after the discovery of hydrogen spillover, aspects of both spillover and reverse spillover remain contentious despite thorough investigation via the numerous techniques listed above. Recent review articles by Prins and Roland et al. discussed the challenges and uncertainties that persist in this area, many of which are due to the extreme difficulty of observing spillover directly.

Surface plasmon spectroscopy has emerged as a new tool to study the chemisorption of gases on metal nanocrystal surfaces. The LSPR of Au NPs is sensitive to changes in the dielectric constant of the supporting matrix and to changes in electron density on the metal. Both of these effects can be exploited to glean information about adsorption and desorption events. Initial reports used changes in the absorption spectra of chemically synthesised Au NP ensembles to demonstrate detection and quantitation of reducing gases such as hydrogen and carbon monoxide. Optical shifts in Au NP/metal oxide gas sensors are often considered to be the consequence of electron exchange on the metal at the metal/oxide interface, as well as an effect of dielectric changes in the support. To understand the LSPR changes, it is therefore crucial to consider the separate contributions of modifying the free-electron density on the plasmonic particles and the dielectric function of the supporting medium. Buso et al. and Della Gaspera et al.
concluded that LSPR changes from H\textsubscript{2} reduction of Au/TiO\textsubscript{2} and Au/TiO\textsubscript{2}/Pt films are induced by the production of free electrons and subsequent charge transfer to the Au NPs. This conclusion was supported by the work of Carpenter et al., where it was found that this mechanism was the main driver of LSPR shifts on Au/yttrium-stabilised-zirconia films when exposed to H\textsubscript{2}.\textsuperscript{28,29} In contrast to LSPR charge transfer driven shifts, Larsson et al. attributed changes in gold particle spectra to H\textsubscript{2} induced dielectric function changes of nearby Pt NPs separated by a SiO\textsubscript{2} support.\textsuperscript{30}

Recent studies have shown that gas sorption can be followed at the single particle level by dark field microscopy. DFM was first used to measure the interaction of hydrogen with single metal NPs by Alivisatos et al. who used lithographically fabricated systems of single Pd NPs close to the tip of a Au nanoantenna to monitor dielectric changes of the Pd component during hydrogen exposure.\textsuperscript{31} Further studies by Alivisatos and co-workers revealed the shape dependence of the hydrogen uptake process by studying changes to the dielectric function of a Pd shell on Au cores.\textsuperscript{32} Work by Tittl et al. showed that individual silica coated Au NPs could be used to investigate dielectric changes during hydridation of a Pd film.\textsuperscript{33} However, the fundamental challenge for catalysis is to investigate the more complex problem of the metal catalyst-support interaction.

By measuring electron transfer at the single particle level, in this chapter it is shown that the H\textsubscript{2} adsorption mechanism on Au and Pt NPs strongly depends on the metal oxide support (TiO\textsubscript{2}, ZnO and SiO\textsubscript{2}). The sensitive optical technique applied was enabled by the use of low-scattering, thin films prepared by sol-gel synthesis. While DFM has been used previously to directly measure electron transfer,\textsuperscript{34,35} this is the first example of optically observed charge transfer processes with gas phase reactants on single metal NPs. SPS measurements on single particles have larger signal-to-noise ratios than ensemble measurements. SPS analysis is
simplified by a low metal loading, which removes Au NP-Au NP optical coupling. Furthermore, it enables proximity effects between Au and Pt NPs to be determined in a straightforward manner because a submonolayer of Au NPs on a flat plane has a more uniform three-dimensional environment than a multilayer or a mixed layer. Single particle spectroscopic information is used to unambiguously show that hydrogen is mobile and undergoes spillover from Pt to Au NPs.

4.1.2 Photoexcited gold/semiconductor thin films

TiO$_2$ and ZnO nanoparticles are commonly employed as photocatalysts, particularly for organic molecule oxidation and water splitting.$^{36}$ The oxidation pathway is controlled by the formation of positive holes upon photoexcitation.$^{37}$ TiO$_2$- and ZnO-Au/Ag hybrid nanoparticles and nanocomposite films have been shown to improve the photooxidation rate compared to the semiconducting component alone.$^{38}$ The positive holes are highly reactive and readily oxidise alcohols and organic dyes.$^{39}$ In 2004, Kamat et al. provided the first experimental evidence that the enhancement of ethanol photooxidation on Ag@TiO$_2$ core@shell clusters was due to electron transfer from the titania shell to the Ag core.$^{40}$ Illuminating an ethanolic solution of Ag@TiO$_2$ with UV excitation, where the TiO$_2$ absorbs efficiently, resulted in an excess of holes on the TiO$_2$ outer surface, which rapidly converted ethanol to oxidised products. SPS was used to monitor charge flow during the redox processes. A strong blue-shift was reported, in an addition to an increase in absorbance of the colloidal solution at the LSPR position, which is congruent with an increase of electron density on the metal according to the Drude model.

It is fundamentally important to understand the role of noble metals in photocatalytic systems and how the charge transport and reactivities of composite systems are influenced by the relationships between metal, semiconductor, shape,
size and crystal structure. For the same reasons cited in the Section 4.1.1, single particle SPS has been utilised to study the photoredox kinetics of individual Au NRs in ZnO thin films. Synthesis, film preparation and experimental setup has been reported in Section 4.1 and 4.2. In this section, the electron transport between a single Au NR and ZnO is reported when UV illumination is sequentially switched on and off under exposure to different gas phase components.

4.2 Experimental methods

4.2.1 Gold nanorods

Au NRs with diameters of $13 \pm 4$ nm and lengths of $40 \pm 9$ nm (see Figure 2.1) were prepared according to the seed-mediated method reported by Nikoobakht et al. as described in Chapter 2.1.1.1. This sample of Au NRs was solely used in the films prepared for the hydrogen spillover experiments (Section 4.3). The 30 nm $\times$ 94 nm Au NRs were synthesised according to the method reported by Murray et al. as outlined in Chapter 2.1.1.2.

4.2.2 Platinum nanoparticles*

Platinum nanoparticles (Pt NPs) of 10 nm diameter (see Figure 4.1) were prepared using the polyol method. A 1 mL solution of 80 mM chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6$, Aldrich, 99.9%) was rapidly added to 7 mL of ethylene glycol (Sigma-Aldrich, anhydrous, 99.8%) with 30 mM and 90 mM concentrations of poly($N$-vinylpyrrolidone) (PVP, Aldrich, M = 10,000 Da) and $\text{NaNO}_3$ (Unilab, 97%) respectively, at 160 °C. After 30 min, the NP solution was cooled to room temperature and precipitated with excess acetone (Unilab, AR grade). The solution

*I thank Michela Citadinni for supplying the Pt NPs
was centrifuged at 4,000 rpm for 5 min, the supernatant discarded, and the precipitate redispersed in ethanol to produce a 30 mM sol based on Pt ion content.

4.2.3 Anantase titania nanoparticles†

TiO₂ NPs with 10 nm diameters (see Figure 4.2) were synthesised as previously described⁴⁵ by adding 3.08 g of titanium tetraisopropoxide (Ti(OPr)₄, Aldrich, 97%) into a previously prepared solution containing 1.24 g of water (MilliQ, 18.2 MΩ/cm), 1.78 g of hydrochloric acid aqueous solution (HCl, Ajax Chemicals, 36%) and 7.18 g of methanol (Merck, AR grade). The solution was stirred for 60 min at room temperature and heated in an oil bath at 70 °C for four hours under reflux. The suspension was cooled to room temperature and the particles were precipitated by adding 30.6 g of acetone (Unilab, AR grade). The precipitate was collected by centrifuging the solution at 4,000 rpm for 2 min. After discarding the supernatant,

†I thank Michela Citadinni for supplying the titania nanoparticles
Figure 4.2 – (a) UV-Vis spectrum of the TiO$_2$ NP solution and (inset) transmission electron micrograph of the TiO$_2$ NPs, with a red circle highlighting a particle displaying clear lattice planes. The spectrum shows transparency in the visible range with the absorption edge in the near-UV range. The sharp edge implies monodispersity of NPs without aggregation phenomena, and hence these NPs were suitable for DFM, which requires low background scattering. (b) X-ray diffraction pattern of TiO$_2$ NP powder which shows the typical peaks of tetragonal anatase structure (JCPDS No. 86-1157).  

4.2.4 Silica sol gel‡

A silica sol was prepared by mixing 5.78 g of tetraethyl orthosilicate ((Si(OC$_2$H$_5$)$_4$, TEOS, Aldrich, 98%), 2.58 g of ethanol (Merck, AR grade), 2 g of water and 32 mg of HCl (37%). The mixed solution was left to stir at room temperature for 1 h before deposition.

‡I thank Michela Citadinni for supplying the silica sol gel.
4.2.5 Zinc oxide nanoparticles

ZnO NPs with 10 nm diameters (see Figure 4.3) were synthesised as previously described\textsuperscript{46} by dissolving 500 mg of zinc acetate dihydrate (Aldrich, <98\%) in 22.5 mL dimethyl sulfoxide. Separately, 750 mg tetramethylammonium hydroxide (TMAH, Aldrich, 97\%) was dissolved in 7.5 mL ethanol. The TMAH solution was added dropwise (2 mL/minute) to the zinc solution under vigorous stirring at room temperature. After 10 min the solution was heated at 50 °C for 1 h. The solutions were then cooled down to room temperature, precipitated with 90 mL of methyl ethyl ketone (Ajax Chemicals, AR grade), and centrifuged at 1,500 rpm for 5 min. The supernatant was removed and the precipitate was redispersed in 2.84 mL of ethanol to a final concentration of 0.8 M in molar zinc.

ZnO NPs with 4-5 nm diameters were synthesised as previously described.\textsuperscript{47} Zinc acetate dihydrate (2.95 g, 13.4 mmol) was dissolved in methanol (125 mL) with stirring at 65 °C. A solution of KOH (1.48 g, 23 mmol) in methanol (65 mL) was then added dropwise at 65 °C over a period of 15 min. The reaction mixture was stirred for 2.5 h at 65 °C. After cooling to room temperature, the supernatant

\textsuperscript{8}I thank Michela Citadinni for supplying the 10 nm zinc oxide nanoparticles and Nicholas Kirkwood for assisting with the 4-5 nm zinc oxide nanoparticles preparation

Figure 4.3 – Transmission electron micrograph of ZnO NPs.
was decanted and the precipitate washed twice with methanol (20 mL). *n*-butanol (70 mL), methanol (5 mL) and chloroform (5 mL) were added to disperse the precipitate and produce a ZnO NP solution with a concentration of 6 mg mL\(^{-1}\). Before use, the ZnO nanoparticle solution was filtered through a 0.22 mm PTFE syringe filter to produce a final concentration of 10 mg/mL.

### 4.2.6 X-Ray diffraction\(^\dagger\)

X-ray diffraction (XRD) characterisation was performed with a Philips PW1710 diffractometer on films deposited on Si substrates. The analysis was performed at an incident angle of 3° using CuK\(\text{Ni}\)-filtered radiation at 30 kV and 40 mA.

### 4.2.7 Thin films\(^\dagger\)

Samples were deposited on 1 mm thick fused silica quartz glass slides for DFM measurements and on silicon substrates for ellipsometry measurements. A summary of the various samples prepared for the hydrogen spillover experiments is provided in Table 4.1 in Section 4.3. The gold nanorod solution was diluted 25 times in water after purification before use in the following films.

**Sample A - Au**  The Au sample was prepared by spin coating the aqueous Au NR solution at 3,000 rpm for 30 s and then drying the sample at 70 °C for 10 min.

**Sample B - Au/Pt**  The Au/Pt sample was prepared by spin coating the Pt NPs containing ethanol solution at 3,000 rpm for 30 s and annealing the sample at 150 °C for 10 min. Following this, the aqueous Au NR solution was spin coated at 3,000 rpm for 30 s onto the dried Pt NPs and annealed at 70 °C for 10 min. The

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\(^{\dagger}\)I thank Michela Cittadini for carrying out the XRD characterisation

\(^\dagger\)I thank Michela Citadinni for preparing the thin films
Pt NPs, requiring a high annealing temperature to work effectively as a catalyst, were deposited first, while the Au NRs are known to spheroidise at temperatures higher than 80 °C; this restriction determined the order of the layers.

**Sample C - Au/TiO$_2$**  The Au/TiO$_2$ sample was prepared by spin coating the aqueous Au NR solution at 3,000 rpm for 30 s and then drying the sample at 70 °C for 10 min. Following this, a layer of TiO$_2$ NPs was deposited at 3,000 rpm for 30 s and the sample was annealed at 150 °C for 10 min.

**Sample D - Au/TiO$_2$-Pt**  The Au/TiO$_2$-Pt sample was prepared by spin coating the aqueous Au NR solution at 3,000 rpm for 30 s and then drying the sample at 70 °C for 10 min. Following this, an ethanolic mixture of TiO$_2$ and 8 wt% Pt NPs was deposited at 3,000 rpm for 30 s and the sample was annealed at 150 °C for 10 min.

**Sample E - Au/TiO$_2$/Pt**  The Au/TiO$_2$ sample was prepared by spin coating the aqueous Au NR solution at 3,000 rpm for 30 s and then drying the sample at 70 °C for 10 min. Following this, a layer of TiO$_2$ NPs was deposited at 3,000 rpm for 30 s. A sub-monolayer of Pt NP solution (0.7 mg/mL) was then spin coated on the top of the sample and the sample was annealed at 150 °C for 10 min.

**Sample F - Au/SiO$_2$-Pt**  The Au/SiO$_2$-Pt sample was prepared by spin coating the aqueous Au NR solution at 3,000 rpm for 30 s and then drying the sample at 70 °C for 10 min. Following this, an ethanolic mixture of SiO$_2$ and 8 wt% Pt NPs was deposited at 3,000 rpm for 30 s and the sample was annealed at 150 °C for 10 min.

**Sample G - Au/ZnO**  The Au/ZnO sample was prepared by spin coating the aqueous Au NR solution at 3,000 rpm for 30 s and then drying the sample at 70 °C for 10 min.
°C for 10 min. Following this, a layer of ZnO NPs was deposited at 3,000 rpm for 30 s and the sample was annealed at 150 °C for 10 min.

**Sample G - Au/ZnO-Pt**  The Au/ZnO-Pt sample was prepared by spin coating the aqueous Au NR solution at 3,000 rpm for 30 s and then drying the sample at 70 °C for 10 min. Following this, an ethanolic mixture of ZnO and 8 wt% Pt NPs was deposited at 3,000 rpm for 30 s and the sample was annealed at 150 °C for 10 min.

**Au/ZnO films for photoexcitation experiments**

The Au/ZnO samples used in the photoexcitation experiments were prepared by sequential layer spin coating on ‘base piranha’ cleaned quartz glass slides. ZnO NP solution (140 µL) was spin coated onto the quartz at 3,000 rpm with a 1,500 rpm/s acceleration for 30 s and was repeated for a second layer. Following this, 140 µL of Au NR solution (0.001 M CTAB) was spin coated with the same conditions as the ZnO NPs. A further two layers of ZnO NPs were spin coated onto the sample and the film was then thermally annealed at 100 °C for 5 min. The thickness of the final film was measured on an equivalently prepared silicon substrate and was found to be 100 nm by ellipsometry. Before measurements were taken on the samples, the entire film was exposed to the full output of 100 W Hg lamp for 30 min in air to partially photo-anneal the film.

In all metal oxide films prepared, the Au NR concentration is estimated to be <0.25 wt% based on the average interparticle distance observed on the DFM. All thermal annealing was carried out in air.

**I thank Nicholas Kirkwood for assisting in the preparation of the Au/ZnO films**
4.2.8 Single particle spectroscopy in gas flow

4.2.8.1 Hydrogen spillover experiments

Single particle time-resolved measurements were carried out using the DFM and spectroscopy setup described in the Experimental Methods section (Chapter 2). The samples were placed in a custom made cell (see Figure 4.4) in which the scattering spectra could be collected in transmission under different atmospheres. The measurements were taken at room temperature using 50,000 ppm H$_2$, balanced with N$_2$ (5% H$_2$ in N$_2$), with a flow rate of 5 L/hr. The gases used in these experiments were high purity grade ($<10$ vpm C$_n$H$_m$) with very low water content ($<15$ vpm). All N$_2$-H$_2$ (5% in N$_2$)-N$_2$ and air-H$_2$ (5% in N$_2$)-air cycles were 60 min-30 min-60 min in duration. For simplicity of notation, H$_2$ (5% in N$_2$) is hereafter reported as just H$_2$.

Using the DFM, Au NR spectra were captured every 60 s during four cycles of exposure to 5% H$_2$ in N$_2$, with N$_2$ or air as the alternating gas. The imaging

Figure 4.4 – Schematic view of the purpose-built transmission gas cell with an example thin film on the underside of the top window.
spectroscopy system was able to measure the scattering spectra of multiple, well-distributed Au NRs simultaneously, hence enabling the surface plasmon band position of 3-10 particles to be tracked at the same time. This provided greater statistical certainty about the spectral response of an average particle within a certain sample, and a representative single particle kinetic trace could therefore be selected. An automated image-to-spectrum extraction and Lorentzian fitting procedure was carried out on the data using IGOR Pro software to execute fast and accurate analysis of hundreds of image files that were collected during each experiment (see software procedure in Appendix B). Prior to running the procedure, the pixel rows of a Au NR-free area of the image in close proximity to the Au NRs being analysed were subtracted from the signal to remove the background contribution from the substrate and oxide layer. Examples of the scattering intensity of the background varying with time have been included in Appendix C (Figure 7.8) to illustrate the stability of these signals during the gas cycles. The single particle baseline spectrum of an oxide-supported Au NR did not always reach zero due to the slight inhomogeneity of background scattering caused by the oxide matrix and the Pt NPs. A non-zero baseline could lead to less effective background correction. If the selected background signal had a different level of scattering intensity than the small area the Au NR was situated in, the background correction was not completely effective in removing the scattering contribution of the surrounding matrix from the Au NR signal. Nevertheless, regular, quasi-Lorentzian lineshapes at intensities expected for single Au NRs of these dimensions were measurable and Lorentzian fitting could be effectively applied to the data extracted. Hence, while automation resulted in enormous efficiency gains, there was a small but noteworthy drawback in the accuracy of the baseline level.

The hydrogen spillover experiments typically ran for six hours, resulting in slow long-term drifts in the focal position of the microscope. Over this time, the focal
position could influence the absolute value of LSPR peak position due to chromatic aberrations present in the objective lenses. An additional focal drift correction was made by fitting a trend line to the data and normalising the data to the fit function, where the long-term changes in the data were clearly not due to the introduction of different atmospheres into the gas chamber.

4.2.8.2 Photoexcitation experiments

Single particle measurements in the photoexcitation experiments were made using the same DFM spectroscopy setup and gas flow cell as described in the previous section, with a few modifications. As illustrated in Figure 4.5, the modified setup enabled the sample to be illuminated with both a UV light source for photoexcitation and a white light source for collecting single particle scattering spectra. Two key modifications in this setup were the addition of a 100 W mercury arc lamp and a Nikon UV-2A filter cube. The UV-2A cube consisted of a 330-380 nm excitation bandpass filter, a 400 nm cut-on longpass dichromatic mirror and a 420 nm cut-on longpass barrier filter, which passed the 334 nm and 365 nm Hg emission onto the sample. A flask, which could be filled with MilliQ water or ethanol, was inserted into the gas line allowing air or N₂ to be bubbled through.
Figure 4.5 – Dark field microscopy setup used in the photoexcitation experiments described in section 4.3.2.
4.3 Results and discussion

4.3.1 Hydrogen Spillover between Single Gold Nanorods and Metal Oxide Supports††

4.3.1.1 Sample summary

A range of samples were studied via DFM to systematically determine the mechanism that underpins LSPR changes on single gold nanocrystals in metal oxide supports under reducing and oxidising gas atmospheres. The samples studied are summarised in Table 4.1.

SEM was carried out on replica films prepared on silicon to ensure the films were uniform and smooth. The SEM micrographs displayed in Figure 4.6 illustrate the uniformity of the films. Pt NPs have a lighter electron scattering contrast to the rest of the film and are apparent in the sample shown in Figure 4.6b and e.

Ellipsometry‡‡ on the replica films on silicon was used to estimate film thickness. The film thicknesses were as follows: 100 nm for all silica-based films; 30 nm for all titania-based films; 30 nm for all zinc oxide-based films.

4.3.1.2 Gold nanorods on glass

Studies were undertaken to understand the effects of hydrogen gas on the surface plasmon modes of single Au NRs dispersed onto glass slides. In Figure 4.7a, the change in LSPR peak position ($\lambda_{\text{max}}$) of a single Au NR is plotted over a 90 min period for both the Au sample (top) and also for the Au/Pt sample (bottom). During this period the gas flow was switched from either N$_2$ (green trace) or air (blue trace) to H$_2$ and back. For the sample that consisted solely of Au NRs on


‡‡I thank Alessandro Martucci for carrying out the ellipsometry measurements.
Table 4.1 – The order of the layers and the material compositions for the eight different samples prepared for optical measurements. Dark blue represents the glass substrate in the schematic, gold represents Au NRs, black represents Pt NPs, grey represents TiO$_2$, light blue represents SiO$_2$, and light green represents ZnO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample name</th>
<th>Composition</th>
<th>Schematic</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Au</td>
<td>Bare Au NRs on glass</td>
<td><img src="image" alt="Schematic A" /></td>
</tr>
<tr>
<td>B</td>
<td>Au/Pt</td>
<td>Au NRs and Pt NPs on glass</td>
<td><img src="image" alt="Schematic B" /></td>
</tr>
<tr>
<td>C</td>
<td>Au/TiO$_2$</td>
<td>AuNRs on glass covered with a TiO$_2$ film</td>
<td><img src="image" alt="Schematic C" /></td>
</tr>
<tr>
<td>D</td>
<td>Au/TiO$_2$-Pt</td>
<td>Au NRs on glass covered with a TiO$_2$ film containing 8 wt% Pt NPs</td>
<td><img src="image" alt="Schematic D" /></td>
</tr>
<tr>
<td>E</td>
<td>Au/TiO$_2$/Pt</td>
<td>Au NRs on glass covered with a TiO$_2$ film with Pt NPs deposited on top</td>
<td><img src="image" alt="Schematic E" /></td>
</tr>
<tr>
<td>F</td>
<td>Au/SiO$_2$-Pt</td>
<td>Au NRs on glass covered with a SiO$_2$ film containing 8 wt% Pt NPs</td>
<td><img src="image" alt="Schematic F" /></td>
</tr>
<tr>
<td>G</td>
<td>Au/ZnO</td>
<td>AuNRs on glass covered with a ZnO film</td>
<td><img src="image" alt="Schematic G" /></td>
</tr>
<tr>
<td>H</td>
<td>Au/ZnO-Pt</td>
<td>Au NRs on glass covered with a ZnO film containing 8 wt% Pt NPs</td>
<td><img src="image" alt="Schematic H" /></td>
</tr>
</tbody>
</table>
Figure 4.6 – Scanning electron micrographs of the (a) Au/TiO$_2$ film, (b) Au/TiO$_2$-Pt film, (c) Au/ZnO film, (d) Au/ZnO-Pt film, and (e) Au/SiO$_2$-Pt film on Si substrates.
glass (Au) there was no detectable change to \( \lambda_{\text{max}} \) during any of the \( \text{N}_2-\text{H}_2 \) or air-\( \text{H}_2 \) transitions. Conversely, a 2-3 nm blue-shift was observed on single Au NRs in the Au/Pt sample when the gas was switched from air to \( \text{H}_2 \), requiring approximately 10 min for \( \lambda_{\text{max}} \) to reach a stable value under each new gas flow. The \( \text{N}_2-\text{H}_2-\text{N}_2 \) trace follows a similar pattern as the air-\( \text{H}_2 \)-air trace for the Au/Pt sample; however, the recovery rate was noticeably slower under \( \text{N}_2 \). From these results, it is concluded that \( \text{H}_2 \) does not dissociate on Au NRs. Figure 4.7b shows typical scattering spectra for a single rod in the Au/Pt sample after 30 min of exposure, first under air flow (red trace) and then under \( \text{H}_2 \) flow (blue trace). A 2-3 nm blue-shift was observed upon switching from air to \( \text{H}_2 \) and was accompanied by an increase of approximately 10% in the peak scattering intensity. Experimental data fitted to Lorentzian functions are also shown. For all samples, peak positions could be calculated to a margin of error of \( \pm 0.2 \) nm.

In Figure 4.7c, traces of \( \lambda_{\text{max}} \), fwhm and relative peak intensity \( (I/I_0) \) are presented as a function of time for a typical single Au NR in the Au/Pt sample over four cycles of air-\( \text{H}_2 \)-air flow. After being exposed to air, the peak position, \( \lambda_{\text{max}} \), blue-shifted repeatedly between 2 nm and 3 nm during \( \text{H}_2 \) exposure, consistent with Figures 4.7a and 4.7b. During cycles 1 and 3, \( \lambda_{\text{max}} \) partially recovered after \( \text{H}_2 \) exposure and during cycles 2 and 4, completely recovered to its original position. There was a consistent increase of 5%-10% in the peak scattered light intensity, \( I/I_0 \) (green trace), under \( \text{H}_2 \) and the scattering intensity reached a stable value at the same rate as \( \lambda_{\text{max}} \). No clear changes occurred in fwhm (blue trace) during any part of the cycle, except following the initial exposure to \( \text{H}_2 \), which resulted in a small but permanent decrease in fwhm from 77 nm to 72 nm. It must be noted that changes to \( \lambda_{\text{max}} \) only occurred for 3 out of the 5 rods measured. Despite the high concentration of Pt NPs deposited onto the glass, it is conceivable that not
Figure 4.7 – Gas interaction results for a typical single particle on glass in the Au and Au/Pt samples. (a) A comparison of $\Delta \lambda_{\text{max}}$ for a single Au NR in the Au sample (top figure) and a single Au NR in the Au/Pt sample in the fourth $\text{N}_2$-$\text{H}_2$-$\text{N}_2$ (green) and air-$\text{H}_2$-air (blue) cycle. (b) A comparison of scattering spectra for a single Au NR in the Au/Pt sample on the fourth air-$\text{H}_2$-air cycle in air (red) and $\text{H}_2$ (blue) after 30 min. (c,d) A full temporal and spectral analysis of $\lambda_{\text{max}}$ (red), fwhm (blue), and $I/I_0$ (green), of a single Au NR in the Au/Pt sample during repeated cycles of air-$\text{H}_2$-air and $\text{N}_2$-$\text{H}_2$-$\text{N}_2$ at room temperature.
all Au NRs were in contact with Pt NPs. A full spectral analysis for Au/Pt during four N₂-H₂-N₂ cycles is also provided in Figure 4.7d.

4.3.1.3 Gold nanorods in titania

The presence of a TiO₂ matrix had drastic effects on the spectroscopic behaviour of the Au NRs. In Figure 4.8a, typical scattering spectra for a single rod in the Au/TiO₂-Pt sample are shown after 30 min of exposure first in air flow (red trace) and then under H₂ flow (blue trace). A much larger 19 nm blue-shift compared to that observed for the Au/TiO₂ sample was exhibited upon switching from air to H₂ in the presence of titania and this was accompanied by an increase of approximately 30% in relative scattering intensity. Figure 4.8b presents a comparison of ∆λ_max for a single Au NR in the Au/TiO₂ sample (top) and a single Au NR in the Au/TiO₂-Pt sample (bottom) during the fourth N₂-H₂-N₂ (green) and air-H₂-air (blue) cycle. Au NRs in the Au/TiO₂-Pt sample exhibited relatively rapid λ_max blue-shifts when the gas flow was changed to H₂ from N₂ or air. In the N₂ experiment, the λ_max blue-shifted 6 nm over the duration of 2 min in H₂ and the λ_max red-shifted upon returning to N₂, although this was markedly slower. During the N₂ phase, the observed peak shifts appear to undergo a two-step process. In the air experiments, the H₂ induced blue-shifts were stronger than in the N₂ experiments, with an observed shift of 19 nm over a time span of 7 min. The red-shift upon returning to air, in contrast to the N₂ experiment, was faster than the blue-shift and reached a stable value in 3 min. For the Au/TiO₂ sample that consisted of Au NRs on glass in a TiO₂ matrix there was no detectable change to λ_max in the N₂-H₂-N₂. However, during air-H₂-air cycles, the λ_max gradually blue-shifted by 9 nm when switched from air to H₂, taking 25 min for λ_max to reach a stable value. The red-shift that occurred when the gas flow was returned to air exhibited a similar kinetic trace to the blue-shift.
Figure 4.8 – Gas interaction results for a typical single particle in the 30 nm thick Au/TiO₂, 30 nm thick Au/TiO₂-Pt, 30 nm thick Au/TiO₂/Pt and 100 nm thick Au/SiO₂-Pt samples. (a) A comparison of scattering spectra for a single Au NR in the Au/TiO₂-Pt sample on the fourth air-H₂-air cycle in air (red) and H₂ (blue) after 30 min. (b) A comparison of ∆λ_{max} for a single Au NR in the Au/TiO₂ sample (top) and a single Au NR in the Au/TiO₂-Pt sample (bottom) in the fourth N₂-H₂-N₂ (green) and air-H₂-air (blue) cycle. (c) A full temporal and spectral analysis of λ_{max} (red), fwhm (blue), and I/I₀ (green), of a single Au NR in the Au/TiO₂-Pt sample during repeated cycles of air-H₂-air at room temperature. (d) A comparison of ∆λ_{max} for a single Au NR in the Au/TiO₂/Pt sample in the fourth N₂-H₂-N₂ (green) and air-H₂-air (blue) cycle.
Figure 4.8c presents $\lambda_{\text{max}}$, fwhm and $I/I_0$ as a function of time for a typical single Au NR in the Au/TiO$_2$-Pt sample during four cycles of air-H$_2$-air flow. The behaviour was generally similar to the sample of Au NRs co-deposited with Pt NPs on glass, however the peak shifts and scattering increases were all substantially larger for rods supported on titania. The fwhm (blue trace) is shown to follow the same kinetic trend as the other two parameters, $\lambda_{\text{max}}$ and $I/I_0$, but exhibited an average decrease of 20 nm during each exposure of H$_2$, and sequentially recovered to its original position in air.

In Figure 4.8d, the crucial role of the matrix during hydrogen dissociation is demonstrated. The Au NRs and Pt NPs were intentionally separated by a 30 nm TiO$_2$ layer to determine the effect of the relative proximity of the Au and Pt nanoparticles on the spectral response. Au NRs in this sample exhibited a blue-shift of 2 nm and 7 nm when changing to H$_2$ from N$_2$ and air, respectively. This indicated that electron transfer to gold nanoparticles occurred, even when the dissociation event was on Pt nanoparticles that were well separated from the gold nanoparticles.

For completion, Figure 4.9 provides typical results for a single Au NR in Au/TiO$_2$-Pt during four N$_2$-H$_2$-N$_2$ cycles, Au/TiO$_2$ during four air-H$_2$-air cycles, and Au/TiO$_2$/Pt during four N$_2$-H$_2$-N$_2$ and four air-H$_2$-air.

### 4.3.1.4 Gold nanorods in silica and zinc oxide

In addition to TiO$_2$, ZnO has been examined as a supporting matrix to address whether Au NRs in other reducible, semiconducting oxide matrices also exhibit LSPR blue-shifts, increases in scattering and fwhm narrowing under H$_2$ pressure. No changes to the spectra of Au NRs in the Au/ZnO sample were observed during air-N$_2$-air cycles (Figure 4.10a), which is in contrast to the Au/TiO$_2$ sample, which blue-shifted upon exposure to H$_2$, even in the absence of Pt NPs (Figure 4.8b).
Figure 4.9 – Additional full analyses of typical LSPR changes (LSPR max position is red, fwhm is blue, relative intensity is green) during either N$_2$-H$_2$-N$_2$ or air-N$_2$-air gas cycles as indicated along the top of each figure. (a) Au/TiO$_2$-Pt, (b) Au/TiO$_2$, (c,d) Au/TiO$_2$/Pt.
There were clear spectral shifts for single Au NRs in the Au/ZnO-Pt sample, demonstrating that ZnO behaves similarly to TiO$_2$. However, the magnitude of the surface plasmon shifts were not as significant as those observed with the TiO$_2$ supported samples. A blue-shift of only 3 nm was observed for a typical Au NR in the Au/ZnO-Pt sample when switching from N$_2$ to H$_2$ (Figure 4.10b). This was approximately half of the shift observed for the TiO$_2$ sample.

In Figure 4.10c, typical scattering responses are presented as a function of time for the Au/SiO$_2$-Pt sample. There was no detectable shift of $\lambda_{\text{max}}$ observed for Au NRs in the Au/SiO$_2$-Pt sample.

4.3.1.5 Source of LSPR changes

The experimental results here demonstrate that spectroscopic changes occur during gas phase redox catalysis. These changes can be used as a method to probe surface reactions. There are two possible explanations for the observed blue-shifts upon exposure to H$_2$. The first of these is a reduction in the refractive index of the matrix, which may have been caused by the conversion of TiO$_2$ to TiOOH. If the observed LSPR changes occur due to this refractive index change, the Au NR would be acting as a dielectric sensor.$^{48,49}$ However, as shown in Figure 4.11, the refractive index of hydrogen-exposed TiO$_2$ films is actually slightly higher than that of TiO$_2$, as determined by ellipsometry. Consequently, a red-shift would be expected, contrary to the consistent observations of the Au NRs on all three different substrates. Furthermore, the increase in refractive index is $<0.01$, which would not explain the magnitude of the shifts. Calculations supporting these findings are provided in Appendix D (Figure 7.9). A second explanation is that the shift is due to an increase in free electron density on the Au NRs. Previously reported$^{28,34,48}$ but not explained, increases in electron density on Au NRs of this size leads to both a blue-shift and an increase in scattering as observed by DFM.
Figure 4.10 – Full spectral analyses of typical LSPR changes ($\lambda_{\text{max}}$ is red, fwhm is blue, relative intensity is green) for (a) Au/ZnO and (b) Au/ZnO-Pt during either N$_2$-H$_2$-N$_2$ or air-H$_2$-air gas cycles as indicated along the top of each figure. (c) Au/SiO$_2$-Pt sample in the fourth N$_2$-H$_2$-N$_2$ (green) and air-H$_2$-air (blue) cycle.
Figure 4.11  – (a) Refractive index ($n$) and (b) extinction coefficient ($k$) of Au/TiO$_2$-Pt film in air and in H$_2$ (5%, balanced with N$_2$) measured by spectroscopic ellipsometry. There is a small increase in refractive index upon exposure to hydrogen gas.

According to the Drude-Rayleigh equations, a blue-shift in the scattering spectrum is predicted for increased electron density on metal NPs. However, some researchers report that this is accompanied by a decrease in the scattering peak intensity,$^{50,51}$ while others report an increase.$^{52}$ These differences can be reconciled by noting that the changes in scattering intensity depend on the particle aspect ratio. In DFM, the scattering from single particles is measured, rather than the ensemble extinction spectrum. To theoretically determine the scattering, it is easiest to consider the cross-section of a single particle. Within the Rayleigh regime, valid for NPs, the intensity of scattered light, $I_{\text{sca}}(\theta)$ at an angle $\theta$ is given by:

$$I_{\text{sca}}(\theta) = I_0 \frac{k^4}{32\pi^2 \epsilon_m^2 r^2} |\alpha|^2 (1 + \cos^2 \theta) \quad (4.1)$$

where $k = 2\pi/\lambda$, $I_0$ is the incident light intensity, $r$ is the distance to the detector, $\epsilon_m$ is the dielectric constant of the non-absorbing medium and the polarisability of the nanocrystal is given by:
Here, $V$ is the particle volume and $\epsilon_p$ is the complex dielectric function of the particle, approximated by the Drude model, which works well for gold and is linearly proportional to the electron density, especially at visible and NIR frequencies. Hence, for gold particles, the product of Equation 4.1 exhibits a peak at almost exactly the same wavelength as the absorption spectrum of an ensemble of particles. Increasing the electron density of the particle increases $\epsilon_p$, leading to a blue-shift in the scattered peak, an increase in the intensity of the scattering signal and a decrease in the fwhm of the scattered light spectra, as shown in Figure 4.12. This is true only for particles characterised by a particle shape factor, $L, < 0.08$, with resonances at wavelengths longer than 600 nm in water. For $L > 0.08$, the LSPR resonance is situated close to the interband transitions. For these particles, an increase in electron density leads to a blue-shift as expected, but, due to the increased damping of the conduction oscillations, the scattering peak decreases in intensity and there is a slight broadening of the spectra.

The trends shown in Figure 4.12 were consistent with experimental observations. A slight decrease in fwhm is predicted and this decrease is observed in Figure 4.8 and 4.9, although the experimental decrease is even larger than predicted and may additionally reflect changes in surface scattering. The possibility that gas adsorption leads to small changes in surface scattering of conduction electrons cannot be excluded. Adsorbate damping would increase the imaginary component of the Drude term in the dielectric function and this in turn would decrease the intensity of the scattering signal. Desorption of water or surface reactions with organic contaminants may have been the cause of the small 5 nm reduction in fwhm of Au NRs in the Au/Pt sample upon the initial exposure to hydrogen. However,
Figure 4.12 – Calculated scattering spectra for ellipsoidal gold rods with polarisation shape factor $L = 0.08$ (a) and $L = 0.15$ (b) in a medium with refractive index $n = 1.36$, for different relative charge densities, $N$. Dielectric data taken from Olmon et al.\textsuperscript{53} For longer rods (a) where the imaginary part of the dielectric function increases with increasing wavelength, a blue-shift leads to less damping and an increase in scattering intensity. However for smaller aspect ratio rods (b), increases in electron density push the surface plasmon resonance towards the interband transitions and this causes increased damping and a decrease in scattering cross section.
this effect alone could not explain the strong blue-shifts and was not observed during subsequent cycles.

With the theoretical scattering behaviour determined above, the spectral shifts observed for the Au NRs in Figures 4.7-4.10 are attributed to changes in electron density. Therefore, in the following discussion the experimental data is described in terms of electron migration between the catalyst and the Au nanoparticles.

4.3.1.6 Irreducible supports

Surface plasmon spectroscopy provides a rapid diagnostic tool for detecting dissociation of hydrogen on nanocrystal surfaces. The lack of a spectral shift in the control experiment of Figure 4.10c clearly indicates that H\textsubscript{2} is not able to adsorb dissociatively on Au nanorods supported on glass at room temperature. This is in agreement with literature reports for gold particles of similar dimensions under the experimental conditions used;\textsuperscript{54} dissociation of H\textsubscript{2} on Au has only been observed on NPs below 5 nm.\textsuperscript{55,56} When Pt NPs are present, the Au NRs undergo clear, reversible spectral shifts on glass (Figure 4.7a). Since the H\textsubscript{2} does not dissociate on the Au NRs, the electrons must be liberated by the Pt particles, however, it is also well established that hydrogen atoms do not migrate on silica. It was therefore deduced that the blue-shift is only possible if the Pt NPs are in contact with, or within a few nanometres of, the Au NRs. Furthermore, the spectrum of the SiO\textsubscript{2} glass supported Au/Pt sample blue-shifted by equal amounts and at similar rates during the H\textsubscript{2} step of the cycle for both O\textsubscript{2} and O\textsubscript{2}-free environments. This result suggests that H\textsubscript{2} dissociation does not involve oxygen and that the rate of dissociation is unaffected by the presence of oxygen. The reactions producing the surface plasmon shifts on the Au NR may be written (also see Figure 4.13, 4.14 and 4.15 for schematic representations):
\[ \text{H}_2 + (\text{Pt}_n)_{\text{SiO}_2} \Leftrightarrow 2 \text{H}\cdots(\text{Pt}_n)_{\text{SiO}_2} \quad [1] \]

(Molecular hydrogen dissociates on Pt surface to form adsorbed H atoms)

\[ 2 \text{H}\cdots(\text{Pt}_n)_{\text{SiO}_2} + \text{SiO}_2 \Leftrightarrow (\text{Pt}_n^{2-})_{\text{SiO}_2} + 2 \text{H}^+\cdots\text{SiO}_2 \quad [2] \]

(H atoms discharge to yield some free electrons with protons bound to surface silica)

\[ (\text{Pt}_n^{2-})_{\text{SiO}_2} + (\text{Au}_n)_{\text{SiO}_2} \Leftrightarrow (\text{Pt}_n)_{\text{SiO}_2} + (\text{Au}_n^{2-})_{\text{SiO}_2} \quad [3] \]

(Electrons migrate between touching Au and Pt NPs to equilibrate the Fermi levels)

Note that because free protons cannot form on the Pt surface, it is likely that atomic hydrogen migrates from the Pt surface and is initially adsorbed to anionic sites on the metal oxide support immediately adjacent to the Pt NP (Reaction 2). Given spillover from Pt to defect-free SiO\(_2\) is energetically impossible,\(^{17}\) the anionic site where H\(^+\) ionosorption occurs is likely to be a lattice O\(^2-\) ion that is bonded to a Si\(^{3+}\) associated with a surface oxygen vacancy (V\(_{O^{2-}}\)).\(^{57}\) The proton-electron pairs produced are not mobile on the insulating SiO\(_2\) support. Delocalised electrons are consequently injected only into those Au NRs that are in direct electrical contact with the Pt. This causes a blue-shift and the observed increase in intensity of the plasmon resonance peak of Au NRs in the Au/Pt sample.

The proposed mechanism in Figure 4.13 is also applicable to the Au/SiO\(_2\)-Pt sample. In this sample, the Pt NPs are dispersed in a three-dimensional matrix so the likelihood of a Pt NP being in contact with a Au NR is strongly diminished. Therefore, although protons and electrons may be produced at V\(_{O^{2-}}\) sites, their transport to the Au NR is prevented, and thus no change to the spectrum is
observed. This result further corroborates the conclusion that dielectric changes to nearby Pt NPs upon Pt-H formation does not contribute significantly to the scattering signals of the rods, otherwise shifts would have been observed in the Au/SiO$_2$-Pt sample, which also had a high concentration of Pt NPs.

### 4.3.1.7 Reducible supports

The results discussed so far have involved Au NRs and Pt NPs in contact with a nonreducible metal oxide support, and these oxides are unable to support hydrogen spillover because the energy required to break a M-H bond is large. Consequently, spillover of atomic H (or radical H*) onto the glass surface does not occur on nonreducible metal oxide supports.\(^{58,59}\) Conversely, TiO$_2$ is known to be active in the hydrogen spillover process.\(^{60}\) The results obtained with Au/TiO$_2$-Pt clearly show an enhancement of the gas interaction compared to all other samples. For the Au/TiO$_2$-Pt sample, it is proposed that when the measurements were performed in the absence of O$_2$, the mechanism of electron transfer followed the sequence in Reactions 1 to 3 (with TiO$_2$ instead of SiO$_2$). The semiconducting matrix enables dissociated hydrogen to produce free conduction electrons, and subsequently the transfer of electrons through the matrix to gold particles.

The results from the Au/TiO$_2$/Pt sample verify that electrons can travel through the semiconductor matrix itself. In this case, the Pt NPs were spatially separated.
Figure 4.14 – Reaction scheme for Equations 1 to 3 for Au/TiO$_2$-Pt.

from the Au NRs by a titania film about 30 nm in thickness. A blue-shift was still recorded for all Au NRs examined in H$_2$ after being in N$_2$ (Figure 4.8d, bottom trace). Therefore, since H$_2$ dissociation was only occurring on the Pt NPs, electrons must be travelling through the TiO$_2$ to reach the Au NR. The magnitude of the shift when the Pt NPs and Au NRs were separated by a TiO$_2$ layer (Figure 4.15) was approximately three times smaller than for the mixed Pt NP and TiO$_2$ sample (Figure 4.14). This suggests there is a limited range over which interparticle electron transfer occurs and it is probably space charge limited, i.e. as electrons accumulate on gold particles, there is a space charge build-up, which slows down further electron transfer. The flux is limited at this point by the surface diffusion of protons from Pt to the Au.

From the results of these experiments it was not possible to directly confirm whether or not mobile protons are reacting with the Au NR surfaces and forming Au-H complexes. The dissociation of H$_2$ and subsequent diffusion onto Au would contribute to the blue-shift observed by also increasing electron density on the Au NRs. Au-H formation has been proposed on large Au nanocrystals with diameters greater than 5 nm based on SPS measurements made on gold nanoparticle films. However, measurements of this proposed Au-H formation were observed at high temperatures, or when the energy used to illuminate the gold nanoparticles was sufficiently high enough that hot-electron generation could drive direct H$_2$ dissociation on the Au surface. The measurements in this thesis were made at
Figure 4.15 – Reaction scheme for Equations 1 to 3 for Au/TiO$_2$/Pt.

room temperature and were shown to be independent of hot-electron processes. Nevertheless, it is still possible that the energy barrier has been lowered enough for Au-H formation to occur when mobile protons on TiO$_2$ come into contact with edge or corner sites of large Au NRs, which could be contributing to the blue-shifts. To confidently report this addition to the proposed mechanism, further SPS studies into distinguishing between electron and proton interactions with gold nanoparticles would be required.

4.3.1.8 Role of oxygen

Large blue-shifts of the LSPR peak occurred under H$_2$ flow for Au/TiO$_2$, in the absence of Pt NPs, but only when the sample was exposed to air flow beforehand. When oxygen was removed from the reaction the spectra underwent no change during gas cycling (Figure 4.7c, top). Since H$_2$ does not dissociate on these gold nanoparticles, which do not have a significant fraction of low-coordination-number surface gold atoms, this experiment demonstrates that H$_2$ dissociates on TiO$_2$ surfaces that have been exposed to oxygen. Reactive oxygen ions are proposed to generate sites that can enable H$_2$ to dissociate. It has been previously observed that oxygen can adsorb to the Ti$^{3+}$ on the surface when there are oxygen vacancies V$_{O^{2-}}$ on the surface. Changes in the electrical resistance of TiO$_2$ have also
been measured at 300 K when switching between O\textsubscript{2} and H\textsubscript{2}\textsuperscript{,45,46} Work carried out by Roland et al. clearly shows that there is no change in resistance of TiO\textsubscript{2} when switching to O\textsubscript{2} and H\textsubscript{2} pressures from vacuum,\textsuperscript{16} while Li et al. have previously reported the enhancement of hydrogen spillover by surface labile oxygen species on Pt/TiO\textsubscript{2} catalysts,\textsuperscript{68} although the reason is not well understood.\textsuperscript{60} Likewise, it is found here that the presence of chemisorbed oxygen is required in order for H\textsubscript{2} to generate an LSPR response on anatase. The conductivity and optical changes can be understood in terms of the following mechanism (also see Figure 4.16):

\[
\frac{1}{2} \text{O}_2(g) + \text{V}_{\text{O}_2^-} + 3 \text{e}^- \rightleftharpoons \text{O}_{(ads)}^{2-} \quad [4]
\]

(Molecules adsorb on TiO\textsubscript{2} where V\textsubscript{O\textsubscript{2}^-} reside on the surface to form oxygen ions)

\[
\text{H}_2(g) + 2 \text{O}_{(ads)}^{-} \rightleftharpoons 2 \text{OH}_{(ads)}^- + 2 \text{e}^- \quad [5]
\]

(H\textsubscript{2} slowly dissociates on the TiO\textsubscript{2} surfaces where reactive oxygen ions are adsorbed)

When this mechanism occurs, hydroxyl groups form on the surface of the titania and free conduction electrons are generated.

### 4.3.1.9 Hydrogen spillover on ZnO

The Au/ZnO and Au/ZnO-Pt samples behaved similarly to the equivalent TiO\textsubscript{2} samples, however, ZnO was not as effective as TiO\textsubscript{2} at facilitating spillover. Fewer electrons were injected into the Au NRs when surrounded by a ZnO matrix. Without any Pt NPs present, even in an O\textsubscript{2} rich environment, Au NRs in a ZnO matrix did not undergo any LSPR changes. The results from the air-H\textsubscript{2}-air cycles suggest that
the ZnO cannot lower the reaction pathway enough to allow Reaction 4 to occur at a measurable level. This could also imply that due to the unfilled $d$ orbitals, the Ti$^{3+}$ sites are more acidic than the Zn$^+$ sites.

4.3.2 Redox reactions on single gold nanorods in photoexcited zinc oxide thin films

The previous section discussed how the LSPR of a single Au NR can be used to monitor fundamental gas adsorption processes that play important roles in heterogeneous catalysis mechanisms. The redox processes on the Au nanocrystals were driven by gas phase reactants with different redox activities. Noble metal-metal oxide nanocomposites, such as the thin films prepared in section 4.3, are increasingly becoming important materials for efficient photocatalysts$^{69}$ and photovoltaics.$^{70}$ The hybridisation of semiconductor and metal nanocrystals produces a junction where the direction of charge transfer between particles can be controlled effectively by the wavelength of incident light. This control is critical for photodriven surface redox chemistry$^{71}$ and solar cell enhancement.$^{72}$

In Figure 4.17, plots of the $\lambda_{max}$, fwhm and relative peak intensity $I/I_0$ as a function of time for a typical single Au NR in ZnO are presented over four
cycles of the UV light source being switched on and off every 10 min. When the Au/ZnO sample was first exposed to UV illumination, the $\lambda_{max}$ blue-shifted 10 nm (Figure 4.17a). When the UV illumination was turned off in N$_2$ flow, the $\lambda_{max}$ red-shifted back 7 nm. For the following three on-off cycles, the $\lambda_{max}$ value blue-shifted 7 nm during the on step, and red-shifted back 7 nm on the off step, with equal rates. A rate constant for the photoreaction can be calculated by fitting a first order exponential to the curve and is given by $k = 0.024$ s$^{-1} \pm 0.002$ s$^{-1}$. From analysis of the final cycle, the $\lambda_{max}$ appeared to stabilise after about 10 min. The fwhm consistently alternated between about 49 nm and 43 nm when the UV lamp was switched off and on, respectively. The $I/I_0$ value immediately dropped by 10% when the UV source was turned on but recovered back to its original value after 5 min. Following this, when the lamp was turned off, the $I/I_0$ increased by 10% and then decayed back to 1. Figure 4.17b shows the results for the equivalent experiment in air flow. The results were very similar, with the only noteworthy difference appearing in the $\lambda_{max}$ data. When the UV light was switched off, the initial UV-triggered blue-shift appeared to be about 2 nm stronger and the red-shifts back were 2 nm weaker. The final $\lambda_{max}$ positions were permanently more red-shifted than observed in a N$_2$ environment. The calculated reaction rate constant was slightly lower at $k = 0.017$ s$^{-1} \pm 0.001$ s$^{-1}$.

From these results, the proposed mechanism is one that is driven by electron transfer to the Au NR under UV illumination. When the ZnO film absorbs a 334 nm photon from the Hg lamp, the resultant electron transfers across the fermi-equilibrated junction$^{73,74}$ to the gold and the holes remain on the oxide. The fate of the holes during this time is not clear from the data; they may have stabilised at hole trap sites or reacted with residual organics in the sol gel film. The first UV exposure created a permanent red-shift of $\lambda_{max}$, which suggests that further photoannealing processes occurred even after the 30 min pre-anneal in UV light. It
Figure 4.17 – Single Au NR $\lambda_{\text{max}}$, fwhm and relative peak intensity ($I/I_0$) as a function of time in ZnO over four cycles of the UV light source being switched on and off every 10 min in (a) N$_2$ and (b) air flow.
is most likely that, on the ZnO surface, holes were reacting with acetate ions that were not removed during annealing. The final red-shift was about 50% stronger indicating that the oxidative process was enhanced by the presence of oxygen. It is not clear whether the permanent shift was a change to the local refractive index of the ZnO matrix or a change in the electron density of the gold. However, the shift is unlikely to be caused by desorption or degradation of chemical species on the gold surface because the fwhm always recovered back to its original value, inferring that the surface damping of the plasmon remained unchanged. The narrowing of the fwhm is consistent with the proposed mechanism and discussion in section 4.3. The relative intensity changes observed from increased electron density are also explained in the section 4.3 discussion.

The effects of water and ethanol vapour exposure on the UV-generated LSPR changes for the Au/ZnO sample are shown in Figure 4.18. Figure 4.18a exhibits almost identical data to Figure 4.17a, and hence shows that water vapour has little to no effect on the photogenerated electron transport mechanism. The rate constant calculated was the same as the photoreaction in dry N\textsubscript{2}. Conversely, Au/ZnO exposure to ethanol vapour had an enormous influence on the LSPR response of the nanorod under UV illumination (Figure 4.18b). Within the first few minutes of UV illumination, the \( \lambda_{\text{max}} \) rapidly blue-shifted about 6 nm, a similar observation to all previously discussed photoexcitation experiments. After 2 min, the behaviour deviated significantly from the other experiments; the \( \lambda_{\text{max}} \) began to slowly red-shift about 9 nm, beyond the original position of \( \lambda_{\text{max}} \). When the UV lamp was switched off, the \( \lambda_{\text{max}} \) rapidly blue-shifted back to the original position before the red-shifting observed in the on step (9 nm). The \( \lambda_{\text{max}} \) then red-shifted again about 6 nm, close to the original value. This behaviour repeated for each cycle with a slight change to the final \( \lambda_{\text{max}} \) position after each step and a slight increase in the rate of the red-shift observed when the UV lamp was on. The
average rate constant for the process resulting in the red-shift was calculated to be $k = 0.002 \text{ s}^{-1}$.

From the aforementioned results, it can be concluded that water plays no role in the photoredox behaviour on Au/ZnO. However, in the presence of volatile alcohol, in this case ethanol, there is clear evidence that a photoreaction takes place. From the literature, it is expected that the photogenerated hole would oxidise the ethanol to ethanal and that there would be an increase in electron density in the Fermi-equilibrated Au/ZnO matrix.\textsuperscript{73,75} According to this mechanism, a strong blue-shift is expected, but was not experimentally observed. A series of future experiments are required to understand this interesting process. Firstly, spectroscopic ellipsometry could be carried out to understand whether or not the
refractive index of ZnO is a major driver of the LSPR shifts. Electron conductivity measurements could be carried out to understand the ‘bulk’ flow of charge in the film. Finally, to aid interpretation of the surface plasmon spectroscopy data, either IR spectroscopy or gas chromatography-mass spectrometry could identify the reaction products.

4.4 Conclusions

Further progress towards rational catalysis design will depend on the emergence of new methods for understanding and measuring chemical reactions on the surface of nanoscale heterogeneous catalysts such as noble metal NPs. This work has capitalised on the flexibility of DFM to measure electron transport and catalysis mechanisms in colloidal thin films at the single particle level. Isolating heterogeneous catalysis measurements to a single particle in various matrices has the ability to direct the design of new supported catalyst systems. It was demonstrated that gas dissociation and charge migration between single nanocrystal particles during hydrogen adsorption can be monitored. Furthermore, the crucial role of the metal oxide support matrix was directly observed. In these experiments, Au NRs play no active role in the H$_2$ gas adsorption, only functioning as optical electron transfer probes. It was demonstrated that electrons can be transported from Pt NPs during hydrogen dissociation to single Au NRs via a semiconducting matrix. The matrix also greatly enhanced the number of electrons transferred, as well as accelerating the kinetics of forward transfer and back transfer. The presence of adsorbed oxygen species also drastically increased the number of electrons that were transferred to the gold. Finally, it was shown that photochemical and photophysical processes could be monitored at the single particle level to provide a possible route to understanding complex photocatalysis mechanisms.
While these results have provided much insight into how metal oxide matrices influence the mechanism and kinetics of reaction, in some instances the rate of LSPR change was too rapid to resolve on the standard DFM imaging spectroscopy system. The following chapter presents a new approach to resolving fast and small changes of the LSPR on single metal NCs, enabling the DFM technique to monitor previously inaccessible experiments.
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Chapter 5

Single Gold Nanorod Charge Modulation in an Ion Gel Device

The ability to measure very small and fast LSPR changes on single metal nanocrystals would be extremely useful for catalysis and photonics. Specifically, measuring small numbers of electron transfer events occurring on a single nanocrystal could provide new understanding of shape, size and facet dependent catalysis, as well as detailed reaction mechanisms. Resolving the transfer of individual electrons could unveil new information about kinetics by ‘seeing’ exactly when one molecule reacts on the surface of a nanocrystal, or on the surrounding support matrix. Precision and sensitivity of this scale enters into the so-called ‘quantum catalysis’ regime.\(^1\) Observing individual chemical reactions occurring on single nanoparticles in real-time is an enormously compelling concept and one that could perhaps determine rate limiting steps in complex catalytic processes. For example, in a two-step surface reaction, the electron acceptance or donation from a primary redox species must occur before the secondary reaction can proceed. An example of this is CO oxidation, where oxygen adsorbance is required before CO can be converted to CO\(_2\).\(^2,3\) At the limit of single electron sensitivity, the adsorption of a single
molecule of O\textsubscript{2} would be directly detected, as well as every single CO molecule converted. Very high sensitivity combined with fast (picosecond) time resolution may allow rates of reaction on different facets to be measured in the quantum catalysis regime. A highly sensitive system to measure LSPR as a function of time on a single nanocrystal also could potentially lead to the observation of an optical ‘Coulomb-blockade’ or ‘quantum-staircase’ device. These have been built and measured electronically\textsuperscript{4–7} but are yet to be demonstrated optically. The realisation of such a device could lead to novel methods to control light on the nanoscale, due to the inherent ‘digital’ step-like response of the device, which may be very useful for high density information encoding and storage.

To date, reported measurements of single particle redox processes have been limited by the time resolution of the instrument employed. Examples from this thesis are the rate of hydrogen reduction in the Au/TiO\textsubscript{2}-Pt films and photoexcited electron transfer in the Au/ZnO films in Chapter 4. Additionally, measurement of Ag nucleation, shown in Chapter 3, at the single adatom level may allow formation of Au-Ag and Ag-Ag bonds to be differentiated. Progress towards detection of single electron transfer has been achieved by the step-wise detection of individual proteins binding onto the surface of single Au NRs. A white-light laser illuminated DFM system was used by Sönneichsen \textit{et al.} to detect single 450 kDa proteins\textsuperscript{8} and Orrit \textit{et al.} used a photothermal absorption spectroscopy system to detect molecules as small as 53 kDa.\textsuperscript{9} A scanning confocal epi-illuminated DFM system was employed by Baumberg \textit{et al.} to improve the temporal resolution of the single Au NR growth kinetics\textsuperscript{10} that were first reported by Novo \textit{et al.}\textsuperscript{11} This method was effective in determining the kinetics of single Au NR growth with 8 ms resolution.

In this thesis, a white-light laser illuminated DFM technique was developed. Acousto-optical tunable filters (AOTFs) were used to select a monochromatic illumination band (~2-4 nm linewidth) from a supercontinuum laser to rapidly
monitor the scattered photon flux at a narrow wavelength band. This facilitated faster signal acquisition compared to scanning monochromator or spectral imaging-based techniques, and is ultimately limited only by the signal-to-noise ratio and sampling rate of the photon counting electronics. Additionally, the setup has a much lower photon flux requirement because the full range of resonant energies is not needed in the measurement. Overall, a lower photon flux is important in passive plasmonic studies as the resultant heating at high flux can influence kinetics,\textsuperscript{12} change the local refractive index\textsuperscript{13} and, for anisotropic nanoparticles, even lead to a shape change.\textsuperscript{14}

A robust and reproducible method of reducing or oxidising, \textit{i.e.} charging, single nanocrystals was developed to facilitate reliable characterisation of the setup. A quasi-solid-state device minimised the instabilities and handling difficulties of fluid cells previously used to charge single Au NCs.\textsuperscript{1} Chemically synthesised Au NRs were employed as individual optical elements in an ion gel capacitor. Due to electrical double-layer formation, ion gel capacitors exhibit extremely high charge densities at the electrode interface compared to true solid-state devices.\textsuperscript{15} The ion gel device was highly transparent, enabling the scattered light of individual Au NRs to be monitored using the laser DFM system in transmission. In such a device, the LSPR of a single Au NR can be rapidly switched by periodically modulating the electron density on the nanorod.

5.1 Experimental methods

5.1.1 Gold nanorod synthesis

The gold nanorod synthesis used in this section is previously described in the Experimental Methods section of this thesis (Chapter 2).
5.1.2 Triblock copolymer synthesis

The triblock colpolymer poly(styrene)-b-poly(methyl methacrylate)-b-poly(styrene) ([SMS]) was synthesised via two-step atom transfer radical polymerisation (ATRP) based on previously reported methods.\textsuperscript{16-19}

5.1.2.1 Materials

Butylene-\textit{bis-\alpha-}bromoiso\textit{butyrate} (BBiB) was prepared via the esterification of 1,4-butandiol with \textit{\alpha-}bromoiso\textit{butyrl} bromide and characterised via $^{13}$C and $^1$H NMR spectroscopy. Methyl methacrylate (MMA, 99%, Aldrich) and styrene (St, 99.9%, Aldrich) monomers were deinhibited by passing over a short plug of basic alumina. $N, N', N'', N'''$-pentamethyldiethylenetriamine (PMDETA, >98%, Aldrich) and anisole (>99%, Aldrich) were used as received. Copper (I) bromide (CuBr, >98%, Aldrich) was washed sequentially with glacial acetic acid and ethanol, dried under vacuum, then stored under Ar.

5.1.2.2 Synthesis of Br-PMMA-Br macroinitiator

Difunctional initiator BBiB (12.1 mg, 0.031 mmol), MMA (4.0 mL, 37.55 mmol), and PMDETA (6.5 $\mu$L, 0.031 mmol) were dissolved in 4.0 mL of anisole and the mixture was de-gassed \textit{via} three freeze-pump-thaw cycles in a 25 mL Schlenk tube. CuBr (2.2 mg, 0.016 mmol) was then added under a blanket of Ar. A further three freeze-pump-thaw cycles were performed before the flask was back-filled with Ar, a time zero sample taken, then the flask sealed and placed in a 90 °C oil bath. After 3 h reaction time, the flask was opened to air and a sample was taken for NMR analysis. The crude reaction mixture was dissolved in an excess of tetrahydrofuran and passed through a column of basic alumina to remove any copper species. The eluent was concentrated and precipitated twice into 50 mL of cold methanol. The

* I thank Thomas McKenzie for supplying and characterising the triblock copolymer
collected solid product was dried in vacuo. The dried product was analysed via gel permeation chromatography (GPC), and displayed a unimodal peak of narrow dispersity. $^1$H NMR (400 MHz, CDCl$_3$): 0.8-1.2 ppm (CH$_2$-CH$_3$, t), 1.85 ppm (CH$_2$-C, m), 3.6 ppm (COO-CH$_3$, s), $M_n$(NMR) = 51,660 Da, $M_n$(GPC) = 59,509 Da, dispersity = 1.16. GPC chromatogram of Br-PMMA-Br macroinitiator is shown in Figure 5.1 (black trace).

### 5.1.2.3 Chain extension of Br-PMMA-Br macroinitiator with styrene

The collected Br-PMMA-Br product (0.72 g, 0.014 mmol) was dissolved in 4.0 mL anisole. Styrene (St, 0.8 mL, 6.96 mmol) and PMDETA (5.8 µL, 0.028 mmol) were added and the mixture stirred to dissolve. Three freeze-pump-thaw cycles were performed before the addition of CuBr (4.0 mg, 0.028 mmol) under a blanket of Ar. A further three freeze-pump-thaw cycles were carried out before the flask was back-filled with Ar, a time zero sample was taken, then the flask sealed and placed in a 90 °C oil bath. After 5 days reaction time, the flask was opened to air and a
sample taken for NMR analysis. The crude reaction mixture was dissolved in an excess of tetrahydrofuran and passed through a column of basic alumina to remove any copper species. The eluent was concentrated and precipitated twice into 50 mL of cold methanol. The collected solid product was dried \textit{in vacuo}. The dried product was analysed \textit{via} gel permeation chromatography (GPC), and displayed a unimodal peak of moderate dispersity. $^1$H NMR (400 MHz, CDCl$_3$): 0.8–1.2 ppm (PMMA, CH$_2$-C-CH$_3$, t), 1.5 ppm (PSt, CH$_2$-CH, m), 1.8-2.0 ppm (PSt, CH$_3$-CH/PMMA, CH$_2$-C-CH$_3$, m), 3.6 ppm (PMMA, COO-CH$_3$, s), 6.5 and 7.1 ppm (PSt, aromatic protons, m), $M_n$(NMR) = 75,700 Da, $M_n$(GPC) = 111,600 Da, dispersity = 1.46. GPC chromatogram of chain extended PSt-b-PMMA-b-PSt product is shown in Figure 5.1 (red trace).

\section*{5.1.3 Device assembly and electrical characterisation}

Quartz coated with a 140 nm ITO layer was cut with a diamond scribe to 25 mm x 25 mm and 10 mm x 40 mm. The square piece of ITO was photolithographically patterned to create six separate cathodes with a 2 mm x 10 mm active area (see Chapter 3.2.3.2 for the photolithography procedure). The patterned ITO substrate was then cleaned and hydroxylated in a 6% ammonium hydroxide/6% hydrogen peroxide aqueous solution for 20 min at 80 °C. Following this, the substrate was rinsed with water and completely dried in a stream of N$_2$. The dried substrate was immediately immersed for 4 min in a 25 mL solution of toluene containing 330 µL of (3-mercaptopropyl)trimethoxysilane (MPTMS, 95%, Aldrich) heated to 40 °C. It was then removed, rinsed well with toluene and dried with N$_2$. Au NR solution (200 µL) was spin coated onto the ITO side of the substrate at 2,500 rpm for 2 min.

To prepare the ion gel, 100 mg of SMS and 100 mg of vacuum dried 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMI][TFSI], 99.9%, Merck)
Figure 5.2 – (a) Schematic representation of the transparent ion gel capacitor device structure. Two pieces of quartz glass with 140 nm layers of ITO are sandwiched together with a 145 µm thick ion gel layer in between. The 25 mm × 25 mm bottom piece of ITO was photolithographically patterned to create six separate cathodes with a 2 mm × 10 mm active area. The patterned substrate was functionalised with a monolayer of MPTMS and Au NRs. (b) Plot of $Z''$ (reactance) vs Frequency of the device measured to determine the specific capacitance.

were codissolved by sonication in 1 mL of ethyl acetate. The dissolved gel was filtered through a 0.22 µm PTFE filter before deposition. The gel (200 µL) was deposited onto the centre of the substrate and spin coated at 3,000 rpm with a 1,500 rpm/s acceleration for 60 s. The gel (100 µL) was drop cast onto the unpatterned rectangular piece of ITO. Both substrates were placed in a vacuum oven at 60 °C for 24 h to remove residual solvent. After drying, the two substrates were sandwiched together in a custom 3D-printed holder which secured them in place and connected them to conductive wires creating a RC circuit as shown in Figure 5.2a. The thickness of the gel layer was determined by optical microscopy analysis.

To determine the specific capacitance of the device, impedance spectroscopy analysis was carried out with and without a -1 V DC bias. In Figure 5.2b, the results of $-Z''$ (reactance) against Frequency are displayed. A specific capacitance
value of 5.5 $\mu$F/cm$^2$ was calculated using the specific capacitance equation from Lee et al.\textsuperscript{15} at 1 Hz and -1 V bias.

5.2 Results

5.2.1 CCD-imaging spectroscopy measurements

In Figure 5.3a, the LSPR maximum, $\lambda_{\text{max}}$ (red circles and line), of a single Au NR is presented against an alternating voltage source (blue dotted line) between 0 V and -2 V using a two electrode configuration with a potentiostat. The scattering signal was measured in transmission using the standard dark field imaging spectroscopy technique described in Chapter 2 and a 10 nm blue-shift was observed when the potential was switched from 0 V to -2 V. This significant blue-shift occurred with a sub-second shift rate and, furthermore, the signal appeared stable within a few nanometres. During both charging and discharging stages, the change in $\lambda_{\text{max}}$ occurred at a rate faster than could be resolved reliably on this system. Full scattering spectra for a single Au NR are shown in Figure 5.3b at the two applied voltages. There is an associated increase in the overall scattering efficiency of the Au NR when the electron density is increased upon application of a -2 V potential; at -2 V the peak intensity increased approximately 20%. The explanation for this increase is described in Chapter 4.3.1.5. When the exposure time was below a 600 ms exposure time, the signal-to-noise became prohibitively high to carry out time resolved spectral analysis. The noise is significant across the band at this temporal resolution.
Figure 5.3 – Single particle spectroscopy data acquired with a standard dark field imaging spectroscopy system for a single Au NR in the ion gel device. The CCD exposure time was 600 ms, with a total acquisition time of 1,000 ms for each spectrum. (a) The wavelength position of the longitudinal LSPR maximum of a single Au NR (red trace) against time, during three cycles between 0 V and -2 V displayed on the right hand side y-axis (blue trace). (b) Full scattering spectra displayed for the same single rod with an applied voltage of 0 V (red) and -2 V (blue) at 20 s and 50 s into the sequence, respectively. The lines on top of the data represent the Lorentzian fitted data from which the peak positions are obtained.
5.2.2 Laser spectroscopy measurements

To resolve the optical time constants of the Au NRs, a new modification of DFM was developed that was capable of measuring fast electron transfer processes on single metal nanoparticles. This technique, outlined in the schematic in Figure 5.4, utilised an inverted optical microscope with a supercontinuum light source and a photon multiplier tube (PMT). The increased illumination power of the laser in conjunction with a PMT in single-photon counting mode were implemented to achieve a significant enhancement of the sensitivity compared with the standard dark field imaging spectroscopy technique (typically a 100 W halogen lamp and a scientific grade CCD array are used, for example, the one described in Chapter 2.2.6).

5.2.2.1 AOTF-scan generated scattering spectra

To locate single particles in the device, the multichannel capabilities of the AOTFs were utilised. The white light source from the laser was split into two beams, each leading to a separate AOTF. The AOTFs had eight distinct channels which could pass narrow bands in the visible-NIR range simultaneously. With access to 16 channels, a pseudo white light source was passed through the filter and a CMOS camera was used to identify the longitudinal band of the Au NRs in the NIR. The filtered and collimated laser light entered the dark field condenser off-centre yet along the optical axis, ensuring the light was aligned outside the internal beam block. The beam was incident at the oblique angle required for dark field illumination. The beam spot size diameter was approximately 30 $\mu$m when focussed on the top surface of the device, but was stretched elliptically when focussed onto the bottom electrode surface where the Au NRs were fixed. After a particle of interest was identified, it was centred on the CMOS with a mechanically-driven stage. To isolate the particle from nearby particles and background scattering,
Figure 5.4 – Schematic diagram of the laser spectroscopy setup. AOTF = acousto-optical tunable filter, MM = multimode, M = mirror, DFC = dry dark field condenser (0.8-0.95 NA), TL = tube lens, PH = 100 µm pin hole, PCL = planoconvex lens, FM = flip mirror, PMT = photon multiplier tube, CMOS = complementary metal oxide semiconductor, CPU = computer.
a 50 µm pinhole was inserted into the light path at the first image plane after the microscope tube lens. The scattering spectrum of a Au NR was generated by scanning both AOTFs simultaneously from 600 nm to 850 nm in 1 nm steps at a rate of 0.545 nm/s. At each step, a photon count from the PMT was collected to produce a full scattering spectrum of the longitudinal band of a single particle. The wavelength dependency of the laser, quantum efficiency of the detector, and background signal, were accounted for by repeating each scan in an area free of Au NRs. This background signal was subtracted from the particle signal, and then divided by it to remove the background and normalise the spectrum. An example of a single Au NR scattering spectrum is shown in Figure 5.5. The raw data was fitted by a Lorentzian function and the $\lambda_{\text{max}}$ and half width at half maximum (hwhm) were extracted, 761 nm and 34 nm for this specific particle, respectively.

5.2.2.2 Fast charging measurements

After defining the spectral parameters of a Au NR, $\lambda_{\text{max}}$ and hwhm, fast charging measurements could be conducted. The AOTF channels were tuned to the single
resonance wavelength that generates the largest change in scattering cross section, $\Delta Q_{sca}$, in response to changes in electron density, as predicted by discrete dipole approximation calculations.\(^1\) This resonance position is at the half maximum on the blue side of the peak, where the gradient of the Lorentzian function is steepest. For the Au NR shown in Figure 5.5, this monochromatic excitation wavelength was 727 nm. Figure 5.6a shows the scattering signal of a Au NR as a function of time upon oscillation of the applied potential between 0.0 V and -2.0 V at 0.1 Hz. The initial signal (at 0.0 V) was stable (blue trace) with a value of approximately 2,500 photons/ms. Photons were collected with 1 ms bin time. When the voltage was switched to -2.0 V, the signal level increased by approximately 22%, or 3,100 counts/ms. When the voltage was returned to 0.0 V the signal returned to a similar count as the initial signal, and the stabilised signal level at 0.0 V varied by just 8% over the four cycles. From Figure 5.6a, it can be seen that the signal level for the particle at -2.0 V is slightly more consistent and stable than at 0.0 V. To confirm that the change in signal intensity was due to the blue-shifting of the LSPR, the red flank of the peak was monitored at the half maximum (795 nm) during a repeat of the sequence (red trace). The red trace displays a lower initial signal of $\sim$720 counts/ms, resulting from the lower initial laser power at this relatively long wavelength and the drop of sensitivity of the PMT into the NIR. Monitoring the red trace recorded an 18% decrease in scattering upon switching to -2.0 V, confirming that the changes in signal were indeed due to a blue-shift. This result is consistent with that obtained by the standard DFM technique in Figure 5.3a.

In Figure 5.6b, the second cycle for both the blue flank and the red flank are shown together with fitted exponential functions. The exponential fitted data allowed the optical time constant, $\tau_{NC}$, to be calculated for each cycle. For the specific Au NR in Figure 5.6b, sequential measurements of $\tau_{NC}$ for charging were found to be: 50 ms ± 1 ms, 82 ms ± 2 ms, 119 ms ± 3 ms and 123 ms ± 5 ms.
Figure 5.6 – Time-resolved kinetic charging data acquired using the laser DFM setup. (a) Photon count per millisecond plotted against time of the blue flank at half maximum (blue trace) and red flank at half maximum (red trace), during 4 cycles of 0.0 V (white background) to -2.0 V (grey background). (b) Optical response of charging (dots) with single exponential fits (lines) for the blue and red flanks.

with an average value of 90 ms ± 30 ms. Similar $\tau_{NC}$ values were obtained on the red flank of the resonance (264 ± 7 ms, 151 ± 5 ms, 116 ± 3 ms, 111 ± 2 ms). Applying a simple model of the cathode, and assuming that the Au NRs are charging at the same rate as the entire ITO layer (i.e. their Fermi levels remain in equilibrium at all times), then the electrical RC time constant of the total ion gel capacitor ($\tau_{\text{tot}}$) should be equal to the measured $\tau_{NC}$ of the Au NR. This theory was tested by monitoring the sequence with the potentiostat and fitting exponential functions to the electrical data ($i$ versus $t$ data) in the same way. During charging, the $\tau_{\text{tot}}$ for each cycle were found to be 109 ms ± 6 ms, 89 ms ± 5 ms, 87 ms ± 5 ms and 88 ms ± 5 ms, with an average value of 90 ms ± 10 ms. This average closely matches the average $\tau_{NC}$ of the Au NR under charging. Conversely, during the discharging steps the agreement between $\tau_{\text{tot}}$ and $\tau_{NC}$ is much weaker, 230 ms ± 50 ms for the optical value of the Au NR taken from the blue flank and 71 ± 2
ms for the $\tau_{tot}$ of the device. A longer $\tau_{NC}$ for discharging was observed for multiple particles, suggesting that the Au NRs are not discharging at the same rate as the overall device. Charge retention on the Au NRs may also explain why the $\tau_{NC}$ for charging fluctuates between cycles.

5.2.2.3 High sensitivity measurements

To determine $\Delta Q_{sca}$ over the full range of the longitudinal LSPR band, the AOTFs were set to a single channel and the scattering signal was recorded in 16 nm intervals separately as potential was brought to -2.0 from 0.0 V in 0.5 V steps. After each change in potential, the signal was left for several seconds to stabilise, after which time data was collected over 30 s to determine $\Delta Q_{sca}$. The average values of $\Delta Q_{sca}$ over the full potential change are plotted in Figure 5.7a. Error bars are estimated as the standard deviation of the photon count/s. $Q_{sca}$ increases at shorter wavelengths, below the isosbestic-like point at about 755 nm, and decreases at longer wavelengths. This behaviour occurs due to a blue-shift and an increase in scattering, resulting from an increase in electron density. The asymmetric plot shape about the isosbestic-like point is due to the blue-shift and increase in scattering occurring together. A blue-shift alone would result in equal but opposite amplitude of $\Delta Q_{sca}$ about the isosbestic-like point. A physical explanation for this phenomenon was first published in the work in Chapter 4.3.1.

The method used to determine $\Delta Q_{sca}$ produces uncertainties through high signal-to-noise ratios, which prevent measurement of values below a 5% change in relative scattering signal. For example, a 200 mV modulation resulted in a $\Delta Q_{sca}$ signal-to-noise ratio of approximately 1:1. An averaging technique suitable for digital photon counting applications was applied to overcome this limitation. A square wave function generator was used and the frequency was set to 0.5 Hz, a frequency low enough to allow sufficient time for signal collection. The average
Figure 5.7 – Change in scattering cross section (a) for set wavelengths over the longitudinal band at different applied voltages from a potentiostat and (b) for different applied potentials from a wave function generator using the average $\Delta Q_{sca}$ over 200 square wave cycles at 0.5 Hz.

photon count was calculated after 200 cycles, binning only the last 800 ms of each second. The average $\Delta Q_{sca}$ values for voltages down to 10 mV for a single Au NR are displayed in Figure 5.7b. The averaging technique was shown to be effective in measuring $\Delta Q_{sca}$ values below 0.1%. The response to the voltage applied is relatively linear, an expected response for an ideal capacitor. Supporting data for other Au NRs are provided in Appendix E (Figure 7.10).

From $\Delta Q_{sca}$, it is possible to calculate the average number of electrons transferred during each wave cycle. A change of $\Delta Q_{sca}$ of $\sim0.05\%$ obtained in the low potential range can be converted to a number of electrons by modelling the expected shifts with the finite element method in COMSOL. Spectra of a 30 nm $\times$ 86 nm Au NR in an estimated refractive index polymer environment of 1.45 was simulated with charge density changes ($\Delta N$) between 0%-1% (Figure 5.8). Figure 5.8a shows that there is very little overall change to the LSPR lineshape or position at these low $\Delta N$ values. However, if the $\Delta Q_{sca}$ at the blue flank hwhm position is
Figure 5.8 – Modelling data generated by COMSOL. (a) Calculated scattering spectra of a gold nanorod with different charge densities $\Delta N$, assuming refractive index = 1.45. Dielectric data for gold is from Johnson and Christy. Dotted line represents the blue flank of the hwhm. (b) Plot of $\Delta Q_{sca}$ against $\Delta N$ taken from the generated spectra on the left at the blue flank of the hwhm.

Plotted against $\Delta N$ (Figure 5.8b), a gradient for the relationship between these parameters is obtained and at 0.05% $\Delta Q_{sca}$ the value for $\Delta N$ is 0.0033%. The total number of atoms in the nanorod was calculated to be $3.5 \times 10^6$, using the volume and density of an average gold nanorod from this sample. The number of free electrons is equal to the number of atoms for gold. Using this value, it was calculated that there were 110 electrons ($\pm 10$) on average transferring on and off a single Au NR in each cycle. A change of 110 electrons is equivalent to a 0.02 nm blue-shift, well below the detection limits of CCD imaging-based single particle spectroscopy systems. The uncertainty reported has been estimated from the size distribution of the rods. This is the smallest optically measured number of electrons transferred on a single gold nanocrystal reported to date.
5.3 Discussion

Reporting optical detection of 100 ms RC charging kinetics on a single particle and the detection of close to 100 electrons surpasses previous reports in this field.\textsuperscript{1,11} The method of optically tracking electron transfer introduced in this chapter would be useful for measuring previously undetected surface processes on gold nanoparticles. Two such examples are the detection of small numbers of adsorbing low molecular weight molecules and low activity redox reactions. Another useful prospect for this method is detecting spectral shifts on metal nanocrystals with highly damped LSPR, such as palladium and platinum NCs. Both materials are industrially important catalysts but their catalytic activities are notoriously difficult to study directly using surface plasmon spectroscopy.\textsuperscript{21} The super-continuum laser approach here may enable the detection of very small changes in LSPR lineshape at specific wavelengths, providing a sensitive method toward optical catalyst screening. For this to be true, modifications of the technique will need to be developed so that it is suitable for monitoring a wider range of reaction conditions, particularly when the reaction is not driven by an external source. In the case of the experiments reported here, the averaging technique may not be suitable in the absence of a conductive medium because an external voltage would not periodically modulate the redox state of a Au NR.

The holy grail of surface plasmon spectroscopy is the confident detection of single electron transfer \textit{via} optical plasmonics. The instrument developed in the work of this thesis presents the furthest progress towards this goal to date. Perhaps the most important goal of plasmonic detection is the change of a single particle by one redox state, \textit{i.e.} single electron transfer. Many challenges will be needed to be overcome to achieve this target. Most notably, these include fabricating a device suitable for optical measurements and developing a technique with the sensitivity required to measure such a small change. The source electrode is the most crucial
part of the device design, and is required to scatter less than the metal island which is being charged. This could be achieved through molecular assembly of a rationally chosen tunnelling barrier in a 3D configuration (similar to the device reported in this chapter), or development of a carbon nanotube electrode as reported by Thelander et al.\textsuperscript{4} Using a conductive probe tip\textsuperscript{6} is less likely to succeed with a far-field DFM approach unless the refractive index of the material can be matched to the surrounding environment, avoiding scattering from the probe tip. On the detection side, the sensitivity must be improved from the reported findings from this thesis, and elsewhere. If a scattering approach is used, a stronger light source and more advanced lock-in amplification techniques must be applied. To further compound the difficulties of scattering-based detection, the island diameter must be <17 nm,\textsuperscript{7} and the island cooled to low temperatures to achieve discrete electron transfer.\textsuperscript{5} As $Q_{sca} \propto R^6$, the scattering from the particle will be minuscule. A promising solution could be to functionalise a relatively large gold nanocrystal with a dye molecule. Upon photoexcitation of the molecule, single electron transfer from the molecule to the metal could occur if there was 1:1 stoichiometry between the dye and metal. The small size requirement of current single electron devices could be avoided by creating a single electron barrier, which can be overcome upon photoexcitation, instead of a quantum tunnelling barrier alone, which is strongly dependent on $kT$ and $R$. A further challenge is building a single electron plasmonic device that could measure a $\tau_{NC} < 1$ ns (i.e. GHz frequency). If achieved, this would be a significant breakthrough for applications of gold nanocrystals in nanophotonic information systems. To compete with modern electronics, this GHz frequency is required for an active component (e.g. transistor) response time.
5.4 Conclusions

A spectroscopic laser DFM system was developed to resolve the optical switching constant of individual Au NRs in a novel ion gel capacitor device. The optical switching time constant ($\tau_{NC}$) was found to be less than 100 ms in the device. Less than 0.1% changes in scattering cross section at the flank of the half maximum were detected, corresponding to the transfer of fewer than 150 electrons. These findings exceed the sensitivity of charge-induced changes in any previously reported work on single metal NCs. In the following conclusions section of this thesis, several approaches to single electron charging and detection on a device are introduced. The suggested approaches are suitable for DFM and, if achieved would have significant implications for catalysis research.
References


Chapter 6

Conclusions

Interest in the redox properties of Au NCs has surged since major advances have been made in synthesis and spectroscopy. Much effort has been put towards controlling gold nanoparticle morphology after discovery that intriguing optical properties could be produced by various shapes, sizes and multi-particle arrangements. The effort has also been spurred on by the emergent understanding of gold’s catalytic properties, which are crucially dependent upon morphology and support materials. The electrochemical and optical properties are intertwined as predicted by the Mie model, explaining the link between electron density on a metal particle and its colour. This link has enabled redox processes on Au NCs to be studied spectroscopically, which has yielded electrochemical information yet to be obtained by any other method, particularly at the single particle level.

In this thesis, important redox processes were studied on single Au NCs by spectroscopically recording scattered light from the particles over time. The main objectives laid out in the introduction were to reveal which parameters influence silver UPD, gas adsorption and electron transfer on single NCs, and to develop a high sensitivity DFM that could detect fast and small changes on Au NCs. In this search, electrodeposition of silver onto single Au NCs using applied potentials
was recorded for the first time, as was hydrogen spillover, photoexcited electron transfer and optically detected solid state charging on single Au NCs.

DFM offers an incredibly flexible platform to study diverse redox processes with minimal interference from probe tips, non-radiative heating and hot-electron processes. It can measure the scattering spectra of single Au NCs in complex electrochemical cells, metal oxide films, and solid state electrical devices. It was shown that by upgrading the illumination source from a lamp to a more powerful white-light laser and using a PMT in single photon counting mode, very small changes in electron density can be detected on single NCs and rapid charging rates can be determined.

Silver deposition was initiated on Au nanostars, nanorods and nanocubes immobilised on cathodically-biased ITO electrodes immersed in an electrolyte containing very low concentrations of AgNO₃, and monitored by DFM as described in Chapter 3. Direct morphology was carried out with FIB registration and SEM. This work established that the nature of the NC surface strongly directs the UPD process. For example, it is proposed electron beam carbonised polymer ligands passivate the metallic surface, inhibiting Ag UPD. More importantly, in the absence of ligand capping layer, UPD is favoured on cube corners and star tips over crystal facets.

As with any fundamental study, many questions remain and the possibilities of further single particle UPD experiments are plentiful. Further parameters could be explored, such as studying a wider variety of Au NCs, other types of metal NC surfaces (most notably Ag as it has a strong LSPR signal), other metal ions in the electrolyte solution (Pt, Pd, Cu, etc.) a range of ligand capping layers, and the influence of various supporting electrolyte ions. It may be possible to alter the morphology of UPD layers/deposits. While not the subject of this thesis, plasmonic enhancement of the local electric field could direct deposition to ‘hot-spots’ creating...
new bimetallic structures, *e.g.* depositing silver between two gold nanotriangles in a ‘bow-tie’ dimer configuration while illuminated strongly on-resonance, or alternatively using polarised light to usher UPD along the excited axis. It would seem that to successfully achieve this very challenging proposal, the absolute highest level of electrochemical control would be required as the hot-spot enhanced effect is likely to be quite small.

To answer the second question of the thesis, a new approach to studying redox processes on a DFM was executed. Many important heterogeneous catalytic processes occur in the gas phase and there were previously no experiments at the single particle level to determine the influence of the supporting substrate. In Chapter 4, dissociative hydrogen adsorption and the subsequent spillover of charges on Pt and metal oxides were monitored spectroscopically by co-deposited Au NRs. The strong enhancement of charge transport between catalyst particles within semiconductor matrices was demonstrated. The presence of Pt NPs in the oxide film was shown to increase the rate of hydrogen adsorption and the presence of adsorbed oxygen increased the degree of free electron production in the film.

The redox processes reported in this section are very fundamental and there is a requirement for the technique to be further developed into areas of industrial interest. Adsorption studies of different gas species would be a exciting next step to increase the range of processes that could be explored by DFM. Carbon monoxide oxidation would be a worthy target as the process removes toxic gas from the atmosphere and CO catalytic converters are ubiquitous in the automotive industry, providing economic incentive. However, CO has a significant energy barrier to oxidation so high temperatures are sometimes required making microscopic measurements difficult. Furthermore, Au NCs only really become good oxidation catalysts once their dimensions drop below 5 nm. At this small size scattering strongly diminishes with $\propto R^6$ and the plasmon becomes strongly damped by surface scattering.
Measuring the LSPR of such small particles is a huge challenge in its own right, let alone measuring the small changes as a result of $\Delta N$. This further reinforces the need to advance the sensitivity of DFM.

Improvements in the sensitivity of DFM-based spectroscopy are described in Chapter 5. A ‘single-wavelength’ method was developed to detect charge induced changes on the edges of the longitudinal LSPR of single Au NRs, where the biggest changes were predicted to occur. By only requiring a single wavelength to be monitored, the scattered laser light could be measured with a very sensitive PMT, enabling thousands of photons per ms from a single NC to be detected. By sacrificing the ability to capture the full LSPR that lamp/CCD-based DFM offers, the temporal resolution can be improved significantly. Au NRs within the ion gel device developed to test this system were charged within sub-100 ms time scales, in which the exponential curves of RC charging were easily resolved by the system. Further progress was made when it was demonstrated that by applying an averaging technique, changes in electron density close to 100 electrons could be resolved.

As discussed in Chapter 5, achieving single electron detection is a major challenge but one worth striving to achieve. Measurement of redox processes on single metal nanocrystals is currently restricted to large Au and Ag NCs. The charging behaviour of large crystals are not capable of discrete quantum charging due to their continuum electronic structure. Single particle evaluation of the heterogeneous catalysis of redox processes by SPS also poses equal challenges. Many metal NC catalysed processes require metals with highly damped LSPR bands, or non-distinct LSPR bands buried within the same region as their interband and core transition. Due to this requirement, the sensitivity of any optical technique will be the largest obstacle to directly screening individual catalyst particles. If surmounted, high throughput catalysis screening may become a reality. Large arrays of unique crystals could
be analysed simultaneously using a flexible hyperspectral technique which could rapidly guide smart catalysis design. The improvements to SPS demonstrated in this thesis pave the way for future advancements in the optical analysis of redox processes on single metal NCs.
Chapter 7

Appendices

7.1 Appendix A

Figure 7.1 – CV scan for the calibration of the PtPPy reference electrode used in Chapter 3. The calibration was carried out using 4.8 mM potassium ferrocyanide in 0.1 M NaNO₃.
Figure 7.2 – SEM images of a NaBH₄ treated Au nanostar before (a) and after (b) Ag deposition, obtained using the same potential sequence carried out in Figure 3.7. (c) Full scattering spectra of the above nanostar at various stages of the deposition process. This figure highlights the complex spectra of irregular Au nanostars by the multiple peaks visible in the spectral window.
Figure 7.3 – SEM images of a NaBH$_4$ treated Au nanostar before (a) and after (b) Ag deposition, obtained using the same potential sequence carried out in Figure 3.7. (c) Full scattering spectra of the above nanostar at various stages of the deposition process. This figure shows highlights the irregularity of the shifts induced by the shelling process because this nanostar underwent a decrease in scattering intensity with deposited Ag.
7.2 Appendix B

```plaintext
Macro GetCrossSeries(Signal, Back, PointsAv, WLvsPixel)
  Variable Signal, Back, PointsAv, WLvsPixel
  prompt Signal, "Enter the middle point for signal"
  prompt Back, "Enter the middle point for background"
  prompt PointsAv, "Enter the number of pixel lines to average"
  prompt WLvsPixel, "Display vs Pixel or Wavelength (Wavelength wave named WL)", popup,"Pixel, WL"
  String ImageToUse

  Variable i
  i = 0
  do
    if (Exists("xWave") == 0)
      MakeN=2D "xWave"
    endif
    xWave = (0, 1970)
    if (Exists("yWave") == 0)
      MakeN=2D "yWave"
    endif
    yWave = [Signal, Signal]
    ImageToUse = StringFromList([], (Wavelist(""", "")), "")
    print "name W", ImageToUse, ".ist"
    print ImageToUse
    ImageLineProfile xwave=xWave, yWave=yWave, Width=PointsAv
    Rename W IMAGE_LINEPROFILE, ImageToUse=*_Sig_*num2str(Signal)
    yWave = [Black, Back]
    ImageLineProfile xwave=xWave, yWave=yWave, Width=PointsAv
    Rename W IMAGE_LINEPROFILE, ImageToUse=*_Bkg_*num2str(Back)
    DuplicateO ImageToUse=*_Sig_*num2str(Signal) vs Signal
    ImageToUse=*_Sig_*num2str(Signal) vs _Sca_
    if (WavesPix = 1)
      if (i == 0)
        DisplayW=[10, 10, 400, 360] ImageToUse=*_Sig_*num2str(Signal) vs _Sca_
      else
        AppendToGraph ImageToUse=*_Sig_*num2str(Signal) vs _Sca_
      endif
    else
      if (i == 0)
        DisplayW=[10, 10, 400, 360] ImageToUse=*_Sig_*num2str(Signal) vs Wavelength
      else
        AppendToGraph ImageToUse=*_Sig_*num2str(Signal) vs Wavelength
      endif
    endif
    Label bottom "Wavelength (nm)"
  enddo
  ModifyGraph mirror=2
  ModifyGraph gbn=[0, 0.6224]
  ModifyGraph tick=2.5Style=1, tick=10, ticklen=4
  Label left "Scattering (a.u.)", DelayUpdate
  KillWaves/A/Z
  i = i + 1
while i < RemSize(List(Wavelist(""", "")))
end
```

Figure 7.4 – Igor procedure file (.ipf) macro code used to extract spectra from a series of consecutively numbered .tif image files obtained by single particle SPS. When running the GetCrossSeries macro in Igor Pro v6.36, the user selects signal, background, number of pixel lines to average, and x-axis output type, from the first image to generate a series single particle scattering spectra.

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Figure 7.5 – Igor procedure file (.ipf) function code used to extract peak position for all the spectra produced from the GetCrossSeries macro. Prior to running the Kinetics function in Igor Pro v6.36, the user places A and B markers on either side of the LSPR peak. After running the function, a ‘wave’ labelled VARX is created that contains the all the LSPR peak position values for each peak.

```
Function Kinetics()
    string G tempstr, stringer
    variable k=1
    WAVE w_coef, w_sigma
    make /o/n=0 varX
    make /o/n=0 varSD
    stringer=WaveList("", ",", "WIN:" )
    do
        tempstr=stringfromlist(k,stringer)
        duplicate $tempstr, twave
        CurveFitQ /M=2/N=W=0 lor, twave[xcsr(A),xcsr(B)])/X=Wavelength[xcsr(A),xcsr(B)]/D
        killwaves twave
        redimension /n=(k+1) varX
        redimension /n=(k+1) varSD
        varX[k]=w_coef[2]
        varSD[k]=w_sigma[2]
        k+=1
    while (str2num(tempstr)<-1)
end
```
Figure 7.6 – Igor procedure file (.ipf) function code used to extract peak fwhm for all the spectra produced from the GetCrossSeries macro. Prior to running the Kinetics_FWHM function in Igor Pro v6.36, the user places A and B markers on either side of the LSPR peak. After running the function, a ‘wave’ labelled FWHMX is created that contains the all the fwhm values for each peak.
Figure 7.7 – Igor procedure file (.ipf) function code used to extract relative peak intensities for all the spectra produced from the GetCrossSeries macro. Prior to running the Kinetics_RI function in Igor Pro v6.36, the user places A and B markers on either side of the LSPR peak. After running the function, a ‘wave’ labeled RIX is created that contains all the relative intensity values for each peak.
Figure 7.8 – Background (area with no Au NRs) scattering intensity at 800 nm for the Au/TiO$_2$-Pt sample during air-H$_2$-air (left, small dots) and N$_2$-H$_2$-N$_2$ (right, large dots) cycles. Small changes can be observed in the background signal during air-H$_2$-air cycles which correlate to the gas cycles, however, they are very small and have little impact on the scattering signal of the Au NRs.
7.4 Appendix D

Figure 7.9 – Calculated scattering spectra for ellipsoidal gold rods with polarisation shape factor $L = 0.09$ (top) for different values of $N$ in matrices with refractive indices corresponding to TiO$_2$ and reduced TiO$_2$. Dielectric data taken from Olmon et al.$^1$ In both cases, electron density increases cause a blue-shift and significant increase in scattering cross section. However, the change in refractive index due to H$_2$ does not shift the peaks significantly. Hence, it is concluded that the blue-shifts are due to electron density increases and not to ‘refractive index sensing’ in these experiments.
7.5 Appendix E

Figure 7.10 – Two supplementary $\Delta Q_{sca}$ vs Voltage plots for two different Au NRs.
References

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Author/s:
Collins, Sean

Title:
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