Properties of Nanocrystalline Thin Films of Metals and Semiconductors Obtained at the Water-Oil Interface

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Gemma Louise Stansfield
School of Chemistry
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Abstract

The natural world artfully harnesses the interface between immiscible liquids to carry out vital processes such as growing bones and contracting muscles. In contrast, synthetic chemists generally regard such an interface as an intractable barrier to be circumvented by the use of phase transfer reagents. A small number of studies have explored the use of the water-oil interface to synthesize inorganic nanostructures, materials that have assumed great significance in recent times. In these studies, the use of the interface leads to remarkably simple and straightforward routes to complex solids.

This thesis explores the synthetic potential of the water-oil interface. Thin films consisting of Au, Ag and Pt, as well as CdS and ZnS nanocrystals adhered to the interface and spread over very large areas (square centimetres) are obtained in a single step
starting with molecular precursors. The process of transfer of the films from the interface to solid substrates is examined. Further, the properties of the films thus obtained are studied in detail using charge transport measurements.

Charge transport in films of arylthiol-capped Au nanocrystals exhibits strong substituent effects, with electron-donating substituents markedly decreasing conductivity. Detailed analysis suggests that the nanocrystals interact with the ligands by resonance rather than inductive effects. In stark contrast, electron-donating substituents increase conductivity in pyridinyl-capped CdS or ZnS nanocrystal films. Highly uniform films of alloyed Ag-Au nanocrystals are obtained and it is shown that the change in the composition of alloys leads to a regular and reproducible change in transport characteristics of the film, with the initially metallic films turning non-metallic with increasing Au content.

In addition to exploring the electronic characteristics, the interfacial deposits were characterized using Atomic force microscopy, UV-visible spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Scanning and Transmission Electron microscopy.
Declaration

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Part I

Introduction
Chapter 1

Introduction

1.1 What are Nanoparticles?

Particles with a size between 1 and 100 nm are normally regarded as nanomaterials. Figure 1.1 shows the size of nanoparticles in comparison with other small particles.

![Diagram showing typical sizes of small particles. The regime below 0.1 µm corresponds to the dimensions of nanoparticles.]

Nanocrystals can exist in a range of morphologies. They can have globular, plate-like, rod-like or more complex geometries and it is these twinned with both their sizes and structure which lead to their distinctive characteristics. At around one billionth of
a metre in scale, \((10^{-9} \text{ m})\), nanomaterials can display fascinating electronic, magnetic and optical behaviours which, since ancient times, have only been marveled at.

1.2 An Historical Perspective

Nanoparticles are not new. The exploration and exploitation of the properties of nanoparticles have a long and illustrious history, which can be traced back to the Roman period. Colloidal metals were used to dye glass articles and fabrics and as a therapeutic aid in the treatment of arthritis. It was common for the Romans to use silver and gold nanoparticles to colour glass and jewellery and the Lycurgus Cup (Figure 1.2), which has survived intact from the fourth century AD, is beautifully crafted of glass embedded with Au-Ag colloids giving rise to a deep green appearance in normal reflected light but is brilliant scarlet in colour when internally illuminated.

![Lycurgus Cup](image)

Figure 1.2: Lycurgus Cup

In 1865, Andreas Cassius reported that colloids of gold and tin oxide were extremely effective at withstanding high temperatures and so they became fashionable in the 17th and 18th centuries as colourants in glass and ceramics. The Purple of Cassius, formed by reacting stannic acid with chloroauric acid, was a popular purple dye in the olden days. It is actually made up of tin oxide and Au nanocrystals. Faraday gave a groundbreaking lecture in 1857 entitled “Experimental Relations of Gold (and other metals) to Light”, detailing the theories of interactions of light with metal particles.
He described that light has a relation to the matter which it meets within its course, and is affected by it, being reflected, deflected, transmitted, refracted, absorbed and by particles very minute in their dimensions. The particles had not as yet been seen by any power of the microscope which indicates not a lack of knowledge and scientific expertise, but a lack of tools enabling him to develop any real understanding of the unexplained particles.

Despite the early advances, studies of nanoscale particles did not gather momentum in later years and it is only recently, that the unique behaviours of nanoparticles been investigated and understood. Now, the facilities available to scientists have enabled extremely thorough study of nanomaterials and the possible areas of research and applications within the field are endless. Today, it is possible to prepare and study nanocrystals of metals, semiconductors and other substances by various means and advances in both experimental and theoretical methods have led to an understanding of the properties of nanocrystals.

1.3 Properties of Nanocrystalline Materials

It is below a dimension of 100 nm where properties of particles, such as melting point, colour (i.e. band gap and wavelength of optical transitions), hardness and catalytic ability, all vary with size. Nanoscalar materials have properties that are intermediate between those of atomic and bulk matter. Indeed, the surface area to volume ratio in nanoparticulates is smaller than that of individual atoms or molecules, but incredibly larger than that of bulk materials. The dimensions of nanocrystals are so close to atomic dimensions (in the region of Angstroms), that an unusually high fraction of the total atoms are present on their surfaces. For example, a spherical particle consisting of 13 atoms, has 12 atoms on the surface. Such a particle has a surface more populated than the bulk!

Such surface area to volume ratio properties can have a dramatic effect on many of the other properties associated with the material. Indeed, the chemical reactivity of
nanomaterials tends to be much higher than that of the bulk solid, meaning that they can be used as extremely effective catalysts. In recent years, Haruta et al. were able to demonstrate substantial catalytic activity of nanocrystalline gold in CO oxidation,\(^8\) when it had been previously assumed that the catalytic activity of gold was somewhat ineffective due to the relative inertness of bulk gold (Figure 1.3). Following this work, investigations into the catalytic properties of gold nanoparticles are currently developing into an attractive and important field in gold chemistry.\(^9,10\)

Figure 1.3: Figure illustrating that nanoparticles of gold are able to readily catalyze the oxidation of CO and that bulk gold is unable to do so.

### 1.3.1 Electronic Properties

Electronic band theory states that electrons can have energies only within certain ranges of levels of energy, or ’energy bands’. Energetically, these bands are located between the energy of the ground state, the state in which electrons are tightly bound to the atomic nuclei of the material, and the free electron energy state, that describes the energy required for an electron to escape entirely from the material. The energy bands each correspond to a large number of discrete quantum states of the electrons, and most of the states with lower energy are full, up to a particular band called the valence band. Band theory successfully predicts the many physical properties of a solid, such as electrical resistivity or optical absorption.
Atoms have a well-defined structure with discrete energy levels. When two atoms approach each other, the atomic orbitals overlap, leading to a splitting of the two atomic states into two molecular orbitals. When a much larger number of atoms, \( N \), are brought together to form a bulk solid, the number of orbitals becomes exceedingly large and as a consequence, the difference in energies between them becomes very small. Therefore, in solids the levels form continuous bands of energy, rather than the discrete energy levels of atoms in isolation. However, some intervals of energy contain no orbitals, no matter how many atoms are aggregated, thus forming band gaps. Bands have different widths, stemming from the properties of the atomic orbitals from which they arise. Furthermore, bands may overlap, producing a single large band.

Figure 1.4 shows a simplified picture of the bands in a solid that allows three major types of materials to be identified: insulators, semiconductors and metals. The Fermi level is defined as the energy of the highest filled level at absolute zero temperature.

Figure 1.4: Simplified diagram of the electronic band structure of insulators, semiconductors and metals.
1.3. PROPERTIES OF NANOCRYSTALLINE MATERIALS

1.3.1. Insulators

In insulators, the bands of molecular orbitals are such that there is a huge band gap between both the valence band and the conduction band. The band gap is so large that it becomes difficult to promote electrons across the gap with thermal energy alone, causing near zero electrical conductivity. The Fermi level can be found in the middle of the band gap.

1.3.1.2 Semiconductors

Semiconductors characteristically have a band gap between the valence and conduction bands that is smaller than that found in insulators. The ease with which electrons in the semiconductor can be excited from the valence band to the conduction band depends on the size of this band gap, which essentially serves as an arbitrary dividing line between semiconductors and insulators.

For charge to move within a semiconducting material, energy is required to promote electrons from the valence band into the conduction band, across the band gap. As temperature rises above absolute zero, electrons become thermally excited and more of them are promoted into the conduction band. Therefore, the conductivity of semiconductors is strongly dependent upon the temperature of the material. Electrons excited to the conduction band also leave behind unoccupied electron holes in the valence band. The electron-hole pair is known as an exciton. The holes themselves remain stationary, however any surrounding electrons are able to fill this hole, and in this way the holes appear to move. They are essentially behaving as if they were positively charged particles. The 'movement' of the negatively charged electrons twinned with the movement of the positively charged holes both contribute to electrical conduction within semiconductors.

A pure semiconductor is often called an 'intrinsic' semiconductor. The electronic properties and the conductivity of a semiconductor can be changed in a controlled manner by adding very small quantities of other elements, called 'dopants', to the intrinsic material. In crystalline silicon, this is typically achieved by adding impurities of boron or phosphorus to the melt and then allowing it to crystallize. This process is called
1.3. PROPERTIES OF NANOCRYSSTALLINE MATERIALS

"doping" and the semiconductor is 'extrinsic'. This careful control and modification of semiconductor properties makes them very attractive materials for constructing electronic devices.

A n-type semiconductor is produced when the host semiconductor is doped with electron donor materials, generating an excess of negative charge carriers within the materials. An example of this would be doping silicon with phosphorus. Conversely, a p-type semiconductor arises when the semiconductor is doped with substances that accept electrons from the host material thus giving rise to positive holes which are also responsible for conduction, for example, when silicon is doped with boron.

1.3.1.3 Metals

A metallic state is reached when a partially filled band is present, regardless of temperature or when an empty band overlaps with a filled band. The molecular orbitals present in metallic bulk phases have very similar (overlapping) energies and so can be represented by a continuous band. Conduction is strong in metals because electrons are easily excitable across the Fermi level.

However, in metals this is within the valence band and is a decrease in the density of states at the Fermi level, known as the Kubo gap. The Kubo gap has an effect on the properties associated with the material and it is possible to control the Kubo gap which will then in turn cause the system to become metallic or nonmetallic. The electrical conductivity and magnetic susceptibility of a material are also both influenced by the Kubo gap and vary according to the relative size of the gap. It is at this stage that quantum size effects begin to dominate. In metals, quantum size effects are owed to the phenomenon of plasmon resonance.

1.3.1.4 The Nonmetal-to-Metal Transition

When the above diagram (Figure 1.4) explaining band theory for bulk systems is extended and modified for nanoscopic systems, new solid state insights become apparent. For a nanoscopic particle, the density of states within a band is smaller by many
orders of magnitude than in those of macroscopic materials and the energy levels gradually cease to be 'quasi-continuous'. For sufficiently small values of $N$, discrete energy levels can be resolved. Further, the full width of a band may not have developed and there is a subsequent decrease in the density of states at the Fermi level. Bands which would otherwise overlap in bulk metals are now separated by a gap for small clusters, known as the Kubo gap. This has the consequence that nanoscopic amounts of a metal may behave as a semiconductor or as an insulator, depending on the values of $N$ and on the shape of the particle, i.e a 'Size Induced Metal to Insulator transition' occurs (Figure 1.5).

\[
\delta = \frac{4E_f}{3n},
\]

where $E_f$ is the Fermi energy level of the bulk metal and $n$ is the number of valence electrons in the nanoparticle.

Thus, for a 3 nm diameter Ag nanoparticle that contains around $10^3$ atoms, the value...
of $\delta$ would be 5-10 meV. Since at room temperature, $kT \approx 25$ meV, the 3 nm particle would be metallic ($kT > \delta$). At low temperatures, the level spacings especially in small particles, may become comparable to $kT$, rendering them nonmetallic. Because of the presence of the Kubo gap, properties such as electrical conductivity and magnetic susceptibility exhibit quantum size effects. Discreteness of energy levels also brings about changes in the spectral features, especially those related to the valence band.

In semiconductors, cadmium sulphide for example, the presence of the 25 meV Kubo gap is negligible due to the presence of the large band gap of 2.54 eV and so is not readily apparent.

### 1.3.2 Optical Properties

#### 1.3.2.1 Semiconductors

When semiconductor nanoparticles interact with light, the absorption bands observed in the absorption spectra are due to single-electron transitions from the valence band into the conduction band, which occurs at a particular wavelength for a given material. Similarly, fluorescence emission occurs when light of a certain energy interacts with the nanoparticle and excites an electron from the valence band into the conduction band. The electron reaches the lowest energy level in conduction band through heat loss and then eventually returns to valence band, losing the excess energy by emitting light of specific wavelength. The energies associated with these transitions vary with nanoparticle size and consequently the wavelength of the emitted light will also be size dependent. Cadmium selenide is a particularly attractive system to demonstrate the size dependence of the band gap in nanoscopic materials. Colloidal dispersions of this semiconductor of varying sizes display spectacular colour changes associated with their fluorescence, as shown in Figure 1.6.

Spectral characteristics of semiconductor nanocrystals depend on the nature of confinement of the charge carriers (i.e. the diameter of the exciton compared to the diameter of the nanocrystal) and ultimately the sizes of the nanocrystals. Indeed, excitonic absorption can be described by the effective mass approximation\textsuperscript{12,13} (Equation 32 [Equation 32])
1.3. PROPERTIES OF NANOCRYSTALLINE MATERIALS

Figure 1.6: UV Irradiation of CdSe quantum dots results in fluorescent emission at different wavelengths depending on CdSe nanoparticle size.\(^{11}\)

1.1), which reveals that the energy corresponding to the onset of absorption is proportional to \(1/r^2\):

\[
\Delta E = \frac{\hbar^2 \pi^2}{2r^2} \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.786e^2}{\epsilon r} - 0.248 E_{Ry} \tag{1.1}
\]

where \(E_{Ry}\) is:

\[
\frac{e^4}{2\epsilon^2 \hbar^2 (m_e^{-1} + m_h^{-1})} \tag{1.2}
\]

\(r\) is the radius of the nanocrystal, \(m_e\) and \(m_h\) are the effective masses of the electron and the hole respectively and \(\epsilon\) is the dielectric constant of the nanocrystals. The fundamental energy gaps of most semiconductors span the energy range from 0 eV to around 6 eV. Photons of sufficient energy can excite electrons from the filled valence bands to the empty conduction bands and as a result, the optical spectra of semiconductors provide a rich source of information regarding their electronic properties. Optical properties are the basis of many important applications of semiconductors, such as in laser devices,\(^{14}\) light emitting diodes,\(^{15}\) and photodetectors.\(^{16}\)
1.3. PROPERTIES OF NANOCRYSTALLINE MATERIALS

1.3.2.2 Metals

Metallic nanoparticles give rise to absorption spectra that resemble those of semi-conducting nanoparticles, however causes of the resonant absorption bands present are quite different. Inter-band gap excitation of electrons does occur, however, it is mainly due to plasmons associated with the metallic nanoparticles that give rise to their optical spectrum. Plasmons, waves of electrons that ‘flow’ through the material with direction, play a large role in the optical properties of metals. Plasmons that exist at the surfaces of metals are coherent electron oscillations that are able to couple with incoming radiation, resulting in a hybridised excitation known as a surface plasmon polariton. This excited state then propagates along the surface of a metal until energy is lost either via absorption in the metal or radiation into free-space, processes easily monitored using modern spectroscopic techniques.

In bulk conducting metals, light incident upon the surface is propagated as electromagnetic surface waves over a broad range of wavelengths. However, when the dimensions of the metal are reduced to become nanoscalar, then the movement of electrons is effectively ‘confined’ in that dimension in a quantum well, much like the quantum mechanical "particle in a box model". Radiation incident upon the surface of a spherical nanocrystal causes excitation of the bound conduction electrons which then oscillate coherently, resonating with the incident electromagnetic radiation at a sharp bandwidth of frequencies. In the absorption spectrum of metallic nanoparticles, only a single emission peak is observed, since all plasmons oscillate with the same frequency. This collective Localised Surface Plasmon Resonance (LSPR) occurs in metal nanoclusters which are confined in all three dimensions.

The positions, heights and widths of the absorption bands present in the optical spectra of metallic nanoparticles depend on both the nanoparticle size (Figure 1.7), \( r \), and also equally upon the dielectric constant of the medium surrounding the nanoparticles.

The normal position of the plasmon band of Au is around 520 nm. If the size of the Au nanocrystals is increased from 48 nm to 99 nm, the plasmon band broadens and
shifts towards the red end of the spectrum. The most prominent feature of this optical response is the strong presence of the dipolar surface plasmon. Particles above a critical radius should exhibit a red shift of the surface plasmon resonance which increases with $r$ due to phase retardation of the electromagnetic wave in the metal. Very small clusters lose their metallic character as the discreteness of the energy bands causes a fall in the number of free electrons. Collective excitations are therefore suppressed or they obtain increasingly single-electron character so that the term ‘plasmon resonance’ loses its meaning. This is a manifestation of the size-induced metal-insulator transition. In the case of semiconductor and other particles, the number of free electrons is much smaller and the plasmon absorption band is shifted to the infrared region. Therefore, the absorption of visible radiation by semiconductor nanocrystals is due to excitonic transitions.

This thesis is particularly concerned with the nanocrystals of the metals gold, silver and platinum, which can be distinguished by their distinctive colours and sheen. They are particularly favoured for studies regarding nanocrystals due to their easy synthesis, the high intensity of their surface plasmon band and the ease of functionalising the metal surface with ligands such as thiolates.
1.4 Preparative Methods of Nanocrystals

Modern materials science closely intertwines the concepts of physics, chemistry and biology. The emerging importance of nanotechnology and nanomaterials is reflected in the many methods that have been developed in order to synthesize such materials. There are top-down methods, which rely on the continuous breakup of bulk matter and also the bottom-up methods, that involve the building up of nanomaterials from their constituent atoms. The top-down and bottom-up approaches can also be considered to be physical and chemical methods respectively, and have been summarized in the proceeding sections.

Syntheses of nanomaterials by chemical methods are mainly focussed around generating dispersions of nanocrystals in solvents (sols). Therefore, a section outlining the processes of nucleation and crystal growth in solution has been included. Also included is a section detailing the and importance and concepts of self-assembly in the production of nanomaterials.

1.4.1 Physical Methods

Top-down methods are often called 'hard' methods because they require physical interaction to synthesize the required product. Many of the physical methods involve the evaporation of a solid material to form a supersaturated vapor from which homogeneous nucleation of nanoparticles occurs. In these methods, the size of the particles is controlled by temporarily inactivating the source of evaporation, or by slowing the rate by introducing gas molecules to collide with the particles. The growth generally occurs rapidly, in milliseconds to seconds, requiring a precise control over experimental parameters. Several specialized techniques have been developed in the last few decades and they can be classified on the basis of the energy source and whether they make use of solid or liquid (vapour) precursors.\(^{18}\)

Inert gas condensation is very widely used and provides a straightforward means to prepare nanosized clusters, especially of metals. A metal foil or ingot is heated in a
ceramic crucible placed in a chamber filled with an inert gas. The metal vapour cools rapidly losing energy on collision with argon atoms, thereby producing nanoparticles. In spray pyrolysis, small droplets of a solution containing a desired precursor are injected into the hot zone of a furnace to obtain nanoparticles. The droplets are generated by using a nebulizer, generally by making use of a transducer. By controlling the nebulizer energy, the relative vapor pressures of the gases and the temperature of the furnace, the particle size is controlled. Some examples of the use of spray pyrolysis are in the synthesis of Cu\textsuperscript{19} and TiO\textsubscript{2}\textsuperscript{20} nanoparticles. Other physical techniques include laser ablation, Arc discharge methods and ion sputtering. Nanometer-size crystals can also be prepared through high energy ball milling. The large grain boundary area provided by nanocrystallites created in this manner can help provide, along with the disordering energy, the driving free energy for the crystalline-to-amorphous transformation.

### 1.4.2 Chemical Methods

In contrast to the methods above, chemists have attempted to create nanocrystals using a 'bottom-up' approach, that is to say by arranging smaller components into more complex assemblies. Chemical methods have emerged to be indispensible for synthesizing nanocrystals of various types of materials. These methods are generally carried out under mild conditions and are relatively straight forward to perform. Nanodimensional materials in the form of embedded solids, liquids and foam have all been prepared by chemical means and such materials have been in use for some time. One of the earliest chemical methods identified has involved producing metallic nanocrystals through the reduction of metal precursors using various agents. Nanocrystals of Pt\textsuperscript{21} Cu\textsuperscript{22,23} Cr and Ni\textsuperscript{24} amongst many others, have been made through reduction using borohydride. Citrate\textsuperscript{25} and alcohol\textsuperscript{26–28} have also been used to reduce metal salts to produce nanoparticles. Thermolysis routes are related to chemical vapor deposition (CVD) based methods to prepare thin films of nanoparticles. By carrying out thermolysis reactions in high boiling solvents in the presence of capping agents, nanocrystals of various materials, including metals\textsuperscript{29} metal oxides\textsuperscript{30} and semiconductors\textsuperscript{31} can be
obtained. Thermal decomposition provides remarkable control over size and can be easily scaled up to obtain larger quantities of product. Other bottom-up approaches to producing nanoparticles can be solvothermal,\textsuperscript{32} electrochemical,\textsuperscript{33} photochemical\textsuperscript{34} and sonochemical.\textsuperscript{35} Biological syntheses of nanoparticles are also interesting possibilities. The insides of a microorganism can be seen as a tiny reactor as well as a container! Elementary reactions such as reduction are generally mediated by enzymes and so syntheses can therefore be carried out by simply incubating a solution of metal ions in the right microbial culture. The ability of microbes to accumulate inorganic particles such as Au\textsuperscript{36} and ZnS\textsuperscript{37} and magnetite\textsuperscript{38} have all been well documented.

One of the important factors that determines the quality of a synthetic procedure is the monodispersity of the nanocrystals obtained. It is desirable to have nanoparticles of nearly the same size, in order to be able to firmly relate the size with the property under study. Hence, synthetic procedures leading to narrower size distributions tend to be more attractive. The best synthetic schemes today produce nanocrystals with a diameter distribution of around 5%. Other important synthetic issues include the choice of a suitable capping agent and control over nanoparticle shape.

1.4.3 Solution Chemistry

Nanocrystals of materials are generally obtainable as sols, which tend to behave in the same way as classical colloids. For example, the stability of a dispersion depends upon the ionic strength of the medium. Therefore, the main focus of this section is regarding the creation of isolated nanocrystals that are dispersible in solvents (sols). Any chemical reaction resulting in a sol generally consists of three steps: nucleation, particle growth and growth termination by capping.

1.4.3.1 Nucleation

In a supersaturated or supercooled solution, there exists small transient\textit{germs} or clusters of a new phase, that constantly fluctuate in size by desorbing and attaching atoms or molecules. There may be a point when a germ reaches a critical size at which
it becomes stable, i.e. nucleation of a new phase has occurred. In a solution of low concentration (and in the absence of foreign surfaces), nucleation will not take place. The solute concentration must be increased quite considerably over the equilibrium value so that, at some fairly sharp limit i.e. when the solution becomes supersaturated, nucleation can take place.

Classical nucleation theory describes the nucleation process and explains the precipitation of crystals from supersaturated solutions and melts. Gibbs was able to thermodynamically account for this process, and defined the free energy change required for cluster formation ($\Delta G$) as sum of the free energy change for the phase transformation ($\Delta G_v$) and the free energy change for the formation of a surface ($\Delta G_s$). With regards to crystal growth in solution, ($\Delta G$) describes the spontaneous tendency of a supersaturated solution to undergo deposition. Since the solid state is more stable than the liquid, ($\Delta G_v$) becomes negative and thus decreases the Gibbs free energy of the system. On the other hand, introduction of a solid/liquid interface increases the free energy by an amount proportional to the surface area of the cluster. As a result, the growth of clusters depends on the competition between a decrease in ($\Delta G_v$), which favors growth, and an increase in ($\Delta G_s$), which favors dissolution (Figure 1.8).

Figure 1.8: Free energy diagram for nucleation.$^2$

Figure 1.8, shows how the free energy required for nucleation depends on the
radius, \( r \), of the cluster of nuclei. The positive surface free energy (\( \Delta G_s \)) term dominates at small radii, which causes an increase in the total free energy change initially. Thus the smallest clusters in solution typically dissolve. As cluster size increases total free energy passes through a maximum at a critical size (\( r_c \)), above which the total free energy decreases continuously and growth becomes energetically favorable, resulting in the formation of crystal nuclei. Kinetically, the nucleation rate (\( J \)) is defined as the number of nuclei formed over time per unit volume, and can be expressed in the form of an Arrhenius reaction rate equation as:

\[
J = A \exp \left( -\frac{\Delta G_{\text{crit}}}{kT} \right)
\]

where \( k \) is the Boltzmann constant and \( A \) is the pre-exponential factor. This kinetic factor is related to the rate of attachment of molecules to the critical nucleus, thus depends on the molecular mobility. Since the molecular mobility changes rapidly with temperature, the temperature dependence of the pre-exponential factor can be quite significant.

Heterogeneous nucleation takes place at phase boundaries or upon impurities like dust and requires much less energy than homogeneous nucleation. At such sites, the effective surface energy between the nucleus and the other phase is much lower, therefore the free energy barrier for nucleation to occur is greatly diminished. The nature of a surface therefore plays a very important role in heterogeneous nucleation. With heterogeneous nucleation, energy is released due to partial destruction of the previous interface with the presence of the new phases. For example, if a carbon dioxide bubble forms between water and the inside surface of a bottle, the energy inherent in the water-bottle interface is released wherever a layer of gas intervenes, and this energy goes toward the formation of bubble-water and bubble-bottle interfaces.

After the nuclei form in solution, they grow via molecular addition until the concentration drops below a critical level and nucleation stops. The particles will continue to grow via molecular addition until the equilibrium concentration of the precipitated species is reached.
1.4.3.2 Particle Growth

Classical nucleation theory has important implications for the kinetic control of crystal growth in nanotechnology. Once nuclei form in a supersaturated solution they begin to grow by accretion. As a result, the concentration of the solution drops below the critical threshold so that no further nucleation can take place. Existing nuclei grow further until all material is used up. This leads to a relatively monodisperse distribution of crystallite sizes. Thus, if one requires large single crystals, only a few nuclei are needed in solution and the degree of supersaturation should be small. Alternatively, supersaturation should be held at a level where nucleation is unlikely, and a few nuclei can be brought in as seeds and grown to the desired size. In contrast, if one wants to have a large number of very small nanoparticles, one should attempt to reach a high initial degree of supersaturation very quickly. Indeed, Weimarn’s law dictates that the final crystal size is inversely proportional to the initial degree of supersaturation. Monodisperse size distributions, wherein the particles have the same size to within 5%, can be obtained by either; stopping the reaction (nucleation and growth) quickly at the point where all crystallites are roughly of the same size and dispersity; or by supplying a constant reactant source to keep a supersaturated condition during the course of the reaction, so that all nuclei grow at the same rate.

Another important process that must be taken into consideration when investigating particle growth is that of Ostwald Ripening or ‘size defocusing’. Ostwald ripening describes a growth mechanism whereby smaller particles in solution redissolve and release monomers or ions that are consumed by larger particles, the driving force of which is the lower solubility of larger particles. So, when a batch of newly formed particles are kept just above their saturation point, the large particles will grow at the expense of the small ones. Ostwald ripening leads to a broadening of particle size distribution to about 15% of the particle diameter and is not a suitable method for obtaining small monodisperse nanoparticles in solution.

A general scheme for preparing monodisperse nanocrystals, therefore usually requires a single, temporarily short nucleation event followed by slow and consistent
growth upon the existing nuclei.

1.4.3.3 Termination & The Importance of the Capping Agent

Nanoparticles are generally too small to become sufficiently thermodynamically stable in solution, owing to the strong interactions between the tiny nanoparticles that causes them to aggregate. In order to form a stable sol, surface protecting agents, typically organic ligands or capping agents, can be used to facilitate arrest of the nanoparticles during the growth reaction by adsorbing onto their surfaces. Without the ligand shell, the particles continue to grow and then tend to aggregate to form bulk species that flocculate or settle down in the dispersing medium.

Capped nanocrystals are stabilised in one of two ways, depending upon the nature of the dispersing medium (Figure 1.9);

- In aqueous media, nanoparticles become charge-stabilized (Figure 1.9a). Coulombic interactions between charged ligand species lead to forces of repulsion, and an electrical double layer forms. This formation acts as an effective barrier and counteracts the van der Waals attractions between the tiny grains, thus preventing aggregation. Sols produced in aqueous media are known as hydrosols.
1.4. PREPARATIVE METHODS OF NANOCRYSTALS

- In organic media, nanoparticles become sterically stabilized (Figure 1.9b). Ligands, as they become attached to the surface of a nanoparticle, lose their conformational freedom and as a result there exists an apparent local increase in ligand concentration. Osmotic repulsion develops between the two nanoparticles, since the dispersing medium acts to 'dilute' or disperse the ligands in order that equilibrium concentrations of ligand are reestablished. The nanoparticles therefore become separated. Sols produced in organic media are known as organosols.

It is important that the correct capping agent forms a complete dense layer around the surface of the nanoparticle for effective particle stabilisation. The capping ligand must also have sufficient length and adsorb uniformly enough to screen the attractive interactions between the particles. The choice of solvent is also important to ensure optimum stabilisation.

In addition to giving immense stabilization to nanoparticles in solution, the ligand shell surrounding a nanocrystal acts as the interface for interaction of nanoparticles with the environment. It can have a huge influence on the properties of the nanocrystals. The surfaces of nanoparticles, for example their state and charge, can be further adjusted by controlling adsorption/desorption of the capping ligands. For instance, hydrophobic nanoparticles can be slightly positively charged if they are capped with oleic acid and conversely they can be slightly negatively charged when capped with tri-n-octylphosphine oxide. Murray and co-workers have explored new synthetic routes that functionalise nanoclusters using simple ligand exchange reactions. Many interesting and desirable properties have been introduced onto the surface of nanoparticles by either partially or completely exchanging alkanethiols for more functionally complex thiols.

The nanoparticles present in sols can be easily precipitated by various means, then filtered and redissolved again in another solvent, owing to the nature of their capping ligands. Redispersibility of the particles is an important characteristic of great utility. Furthermore, metal nanocrystals in a sterically stabilized sol, can be dispersed in high concentrations. Solubilization of nanocrystals is the basis for many chemical and physical studies on nanocrystals and it is possible to transfer nanocrystals from aqueous to
1.4. PREPARATIVE METHODS OF NANOCRYSTALS

organic medium and vice versa by changing the ligands at the surface of the nanocrystal. For example, Au\textsubscript{55} nanoparticles were easily transferred from dichloromethane into water by simply displacing triphenylphosphine at the surface of the nanoparticles with triphenylphosphine sulfonate.

1.4.4 Self Assembly

Just as atoms and molecules crystallize into different structures, capped nanocrystals spontaneously organize themselves into ordered aggregates that are held together by non-covalent (hydrophobic, electrostatic, magnetic or capillary) interactions. The interactions responsible for the formation of the self-assembled system act on a strictly local level, in other words, the nanostructure builds itself.

As nanoparticles are brought closer together in solution, attractive forces grow between them, yet there is increased repulsion arising from steric crowding of ligands. This twinning of forces results in a cooperative assembly of nanoparticles. To bring about large scale organization, the correct balance of forces is essential. It is therefore vital that the nanocrystals are monodisperse and that a suitable ligand molecule covers the surface of the nanoparticles. Ligands such as long chain thiols,\textsuperscript{3} amines,\textsuperscript{42} phosphines\textsuperscript{43} or fatty acids\textsuperscript{44} have served as good candidates for bringing about a cooperative assembly.

Many techniques have been developed and used to assemble nanoparticles into ordered arrays. External forces have been utilized and exploited in order to promote and assist self assembly of nanostructures, including shear forces,\textsuperscript{45} electric-fields,\textsuperscript{46} magnetic-fields\textsuperscript{47} and gravitational-fields.\textsuperscript{48} Templates can also be used to assist self-assembly. The pores present within alumina can help give rise to one dimensional polymeric chains, nanowires and nanotubes of many materials. Aggregates of ZnS nanoparticles have been organised into linear arrays using virus templates.\textsuperscript{49}

Two dimensional lattices of metallic and semiconducting nanocrystals have been obtained through the simple evaporation of a suitably functionalised dispersion of nanocrystals upon a hydrophobic surface.\textsuperscript{50} As the solvent is removed due to volatility, the re-
maining solute molecules become more and more concentrated, leading ultimately to their self-assembly. Films of Ag\textsubscript{2}S\textsuperscript{51} and Ag\textsuperscript{52} nanoparticles have all been produced through evaporation induced assembly.

Chemically assisted assembly of nanoparticles exploits covalent as well as non-covalent interactions between the surface ligands of nanoparticles to create highly ordered and specific nanoassemblies or patterns.\textsuperscript{53,54} This approach is powerful and is the backbone of most nanoparticle assembly techniques. Regimes such as chemical templating\textsuperscript{55} and self-assembled monolayers\textsuperscript{56} are all well known approaches. Many groups have reported the layer-by-layer deposition of uniform nanocrystalline films using an electrostatic approach,\textsuperscript{57,58} a schematic representation of which has been shown in Figure 1.10. The properties of layer-by-layer films, such as composition, thickness and function can be readily tuned by simply varying the types of species adsorbed, the number of layers deposited and the conditions employed during the assembly process.

![Figure 1.10: Schematic illustration showing layer-by-layer assembly of charged nanoparticles and oppositely charged poly-electrolyte.](image)

Organization of nanoparticles in general can be finely tuned by simply adjusting certain parameters. The particle sizes, shape and the interparticle separation between nanoparticles can all be modulated. For example, through increasing the chain length of an alkanethiol capping ligand, the distance between metal nanoparticles in the self-
assembled state effectively increases. Dodecanethiol-capped Ag nanocrystals have been shown to self-assemble into two-dimensional arrays with an interparticle separation distance of 1.5 nm (Figure 1.11). Because the length of a dodecanethiol chain is much longer than 1.5 nm, one can deduce that the alkane chains projecting out of neighboring nanocrystals are interdigitated.

Bawendi and co-workers first reported that superlattices of CdSe nanospheres could be obtained by selectively evaporating a mixed octane/octanol solution of CdSe nanocrystals under reduced pressure. Advanced multicomponent superlattices, such as Fe₃O₄/Fe₃Pt, PbSe/Fe₂O₃, and PbSe/Pd, with tunable sizes have also been produced.

### 1.4.4.1 Self-Assembled Monolayers

The formation of self-assembled monolayers (SAMs) provides an elegant method by which to assemble nanoparticles into thin films with controlled surfaces. Ligands that contain head groups with an affinity for a certain substrate spontaneously chemisorb onto it.

Figure 1.12 shows a schematic representation of a SAM. Thiol groups can readily adsorb from solution onto a gold surface, creating a dense monolayer, and there have been many theoretical and experimental studies conducted into such assembly.
1.4. PREPARATIVE METHODS OF NANOCRYSTALS

Figure 1.12: Schematic diagram showing a self assembled monolayer. Shaded circles are chemisorbing headgroups. Open circles correspond to endgroups that can be incorporated into the ligand with a variety of functionalities.

Schiffrin and co-workers\textsuperscript{61} have developed a method whereby noble metals are easily reduced to form organosols. Aqueous metal ions are transferred into a toluene layer using tetraoctylammonium bromide, a phase transfer catalyst which is also capable of acting as a stabilizing agent. The Au complex is then reacted with alkanethiols to form polymeric thiolates. Aqueous borohydride is added to this mixture to bring about the reduction that is modulated by the interface of toluene and water. The thiol molecules also serve as capping agents.

1.4.4.2 Thiols Adsorbing onto Gold

Thiols bind to bulk gold surfaces, as well as curved gold nanoparticle surfaces with a high affinity,\textsuperscript{60} by spontaneous adsorption from either the liquid or gaseous phase. A widely used method for preparing SAMs on gold, silver and other materials is to immerse a freshly prepared or clean substrate into a dilute (~1-10 mM) ethanolic solution of thiols for around 12 - 18 hours at room temperature.\textsuperscript{62,63} Dense thiol coverages can be obtained in minutes using even millimolar concentrations of the adsorbate. However, timescales on the order of hours are generally adopted for slow reorganization of thiols in order to maximize the density of molecules and minimize the defects in the monolayer. The chemistry involved in the chemisorption of thiols onto gold is very straightforward, mostly owing to the resistance of gold to oxidation or reaction with
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most chemicals. However, it is the nature of the metal-sulphur bond and the spatial arrangement of the thiol groups upon the gold lattice that continue to drive many experimental and theoretical studies to date.

It is generally accepted that alkanethiols adsorb onto bulk Au(111) surfaces and adopt a $(\sqrt{3} \times \sqrt{3})R30^\circ$ (R = rotated) overlayer structure\textsuperscript{64–67} (Figure 1.13).

![Figure 1.13: Crystallographic details of the thiol adsorption on the Au(111) surface](image)

Figure 1.13: Crystallographic details of the thiol adsorption on the Au(111) surface

The geometric arrangement of alkanethiols on the surface and the nearest-neighbor distances between the metal atoms at the surface are factors that determine the maximum density of molecules on the surface. Further stabilization is achieved within the monolayer as the ligands adopt conformations that allow high degrees of van der Waals interactions\textsuperscript{68} (and in some cases hydrogen bonds\textsuperscript{69}) with the neighboring molecules. The thiol molecules tilt at a 30° angle relative to the gold surface. Not all thiols adopt the same orientations as n-alkanethiols and other organizations have been seen, such as for aromatic thiol ligands\textsuperscript{70–72}. 
1.5 The Liquid-Liquid Interface

Although many chemical and physical methods have been used to synthesise nanoparticles and nanostructured thin films, it has often been difficult to obtain robust films of nanocrystals through self assembly. Meanwhile, producing nanocrystalline films using methods such as molecular beam epitaxy and other physical methods tends to be tedious and equipment-intensive. The development of a greener, more efficient and cost effective method is always attractive in nanotechnology and this has now materialised into the interface between two immisible liquids, where self assembly of nanoscopic structures can readily occur.

1.5.1 Advantages Associated with Using the Liquid-Liquid Interface

During the past decade, designing and synthesising high performance nanomaterials using more environmentally-friendly routes has become an interesting and important topic in nanoscience. Green chemistry has evolved into a modern day philosophy that encourages the design of products and processes that minimize the use and generation of hazardous substances. Minimizing waste and preventing pollution are also important principles to consider when developing safer synthetic methods. Compared with other methods, the liquid-liquid interface is very characteristic of a "green" chemical technique.

The method typically involves an organic liquid containing a metal precursor coming into contact with an aqueous layer containing a suitable reagent for reduction, hydrolysis or sulphidation. With appropriate selection of the reaction parameters, the reaction will proceed at the interface and isolated nanocrystals can be obtained as well as ordered arrays of nanoparticles. In addition to this simplicity, the water-oil interface offers a multitude of advantages over its contemporaries. The method requires very few materials and can easily be adapted to give metallic and semiconducting nanocrystalline films, as well as alloyed films. Films can be easily doped with virtually any element.
1.5. THE LIQUID-LIQUID INTERFACE

by simply adding it to the cationic solution. Furthermore, the nature and properties of interfacial deposits can be varied by simply controlling parameters such as deposition temperature, growth time and precursor concentrations.\textsuperscript{73} To adapt the film thickness and the particle sizes one merely needs to adjust the deposition parameters. No stabilizing additives are necessary for film formation, which occurs free from the presence of any substrate, thus giving a lower defect content.

Interfacial deposition provides a remarkably low-cost and green route to complex solids and the deposition scheme itself requires little or no energy input. Deposition of films can also be carried out at relatively modest temperatures. No specialist equipment is required and interfacial reactions are easily scalable - important features in the opinion of any industrial chemist.

1.5.2 Structure of the Liquid-Liquid Interface and Site of Reaction

When two immiscible liquids meet, an interface results and to an extent, molecules of each liquid will interact with each other in the vicinal regions of this interface. Small oil droplets are formed and dispersed throughout the water, and vice versa, forming stationary layers of water/oil and oil/water emulsions on either side of this boundary. Eventually the droplets will coalesce in order to decrease the amount of energy within the system. However, both Pickering and Ramsden discovered that when solid particles are introduced into the system, they become bound at the interfacial region and prevent the emulsion droplets from coalescing, thus causing the emulsions to be more stable. Challenges have therefore arisen in understanding the deposition and self assembly of solid materials at fluid interfaces.

Consider a system wherein a toluene solution of a metal complex, M\textsuperscript{2+}, is layered atop an aqueous solution of chalcogenide ions, X\textsuperscript{2−}. A large concentration difference between the two phases induces several changes including the diffusion and mixing of the ions. Firstly, an emulsion of toluene in water (and an emulsion of water in toluene) will be formed, accompanied by interfacial turbulence. The turbulence lasts for several minutes, leaving a band of emulsion near the interface. Secondly, taking into account
the diffusion effect, so-called stagnant layers will be formed between the toluene/water and water/toluene emulsion layers due to changes in the concentration of the metal complex and chalcogenide ions. Figure 1.14 shows the concentration profile of the metal complex across the toluene-water interface.

In the synthesis of nanoparticles at the water-toluene interface, it is believed that the stagnant layer is the site of the reaction and that the product exists only at the interface. The nucleation stages in these stagnant layers is presumed to be more homogeneous than heterogenous. Indeed, Johans and co-workers have presented a model for diffusion-controlled nucleation at the liquid-liquid interface, wherein the nucleation process is shown to be exclusively homogeneous.

1.5.3 Interfacial Tension

Molecules within a bulk liquid are surrounded by neighboring molecules and thus experience intermolecular forces from all sides. These consist of short range van der Waals attractive forces. Molecules present at the surface of the liquid, however, are not
surrounded and experience attractive forces only from neighboring particles below, and not from above. As a consequence, molecules at the surface are subject to forces that essentially pull them back into the bulk of the liquid. They become thermodynamically less stable than those molecules in the bulk and the "excess" cohesive energy on the surface is known as surface tension.

When two immiscible liquids meet, molecules at the interface experience an imbalance of forces, which leads to an accumulation of free energy at the interface. The excess energy is called surface free energy or interfacial tension, the common units for which are dynes/cm or mN/m, as a force per unit length. The adsorption of particles at the water-oil interface is chiefly determined by the interfacial tension.

1.5.4 Interfacial Adsorption of Nanocrystals

Interfacial assembly of nanoparticles is dictated by a minimization of the interfacial tension, or surface energy.\(^7\) Introducing a nanoparticle to a liquid-liquid interface will decrease the entropy, and so the energy change, \(\Delta E\), in KJmol\(^{-1}\), must be negative to reduce the total free energy at the interface. Interfacial energy comprises the sum of energies arising from the particle-oil interface \((\gamma_{PO})\), the particle-water interface \((\gamma_{PW})\), and the oil-water interfaces \((\gamma_{OW})\). \(\Delta E\), upon assembly of a single particle at the oil-water interface, is given by:\(^7,7\)

\[
\Delta E = \frac{\pi r^2}{\gamma_{OW}} \times [\gamma_{OW} - (\gamma_{PW} - \gamma_{PO})]^2
\]

Because \(\Delta E\) depends on \(r^2\), the energy gain is smaller and the assembly is less stable for smaller nanoparticles than for larger ones. Consequently, thermal energy is sufficient to induce a displacement of the particles from the interface. The weak energy associated with the assembly of the nanoparticles at the interface gives rise to a thermally activated escape. The residence time of the nanoparticle at the interface increases with increasing particle size. Thus, unlike larger, micrometer-sized particles that are strongly held at the interface, it is possible for smaller nanoparticles at an interface to
be preferentially displaced with the larger ones.

High interfacial energy decreases with the progressive adsorption and assembly of solid nanoparticles at the interface. Once at the interfacial region, the nanoparticles experience a number of forces from both liquids that determine whether or not they will self-assemble into ordered structures or whether they will desorb. The energy required for particle desorption depends upon the interfacial energy of the fluid interface, nanoparticle size and also the three-phase contact angle between the solid, water and the organic fluid. It is estimated that for particles with diameter greater than 20 nm, for contact angles measured through water in the range 10° - 170° and for interfacial tensions higher than 20 mN/m, the desorption energy is many orders of magnitude greater than thermal energy, and so particles become irreversibly trapped at the fluid interface. From a thermodynamic perspective, the energy required for particles to desorb from the interface is simply far too high.

The Gibbs energy ($\Delta G$) of particle adsorption at the liquid-liquid interface is given by Equation 1.3:

$$\Delta G = -\pi d/2 \gamma_{L/L} (1 \pm \cos \theta)^2$$

where $d$ is the particle diameter, $\theta$ is the contact angle, and $\gamma_{L/L}$ represents the tension of the liquid-liquid interface. $\Delta G$ for nanoscalar particles can be comparable to thermal energy ($k_B T$, $k_B$ is the Boltzmann constant), where the contact angle consequently exerts a strong effect on the adsorption of nanocrystals at liquid-liquid interfaces.

Once at the interface, interparticle forces exist between both the particles themselves and also by forces that are exerted upon them from the surrounding media, including gravitational forces, capillary attractions, long range repulsions and van der Waals interactions. Nanoparticles still possess lateral movement when present in the interfacial region, and so interparticular forces must be well balanced in order to contribute to film formation. It is important to use the correct combinations of precursors and deposition parameters such as temperature and concentrations of the precursors, in
1.6. TRANSPORT PROPERTIES IN NANOCRYSTALLINE THIN FILMS

order to obtain films at the interface successfully.

Many experimental and theoretical studies have brought us closer to understanding the true properties and behaviour of the liquid-liquid interface, and many materials have now been produced using this interfacial route.

1.5.5 Recent Studies Involving the Liquid-Liquid Interface

The interface and its immediate environments possess features well suited for synthesis of a range of solids with reduced dimensions. Over the years, the method has been very successfully adapted by Schiffrin as well as others for the synthesis of metal nanocrystals such as Au,$^{80}$ Ag,$^{81}$ Pt$^{82}$ and Pd.$^{83}$ More recently, a myriad of materials of contemporary interests have been obtained using this scheme, including: single crystalline scrolls of CuO,$^{84}$ nanoscopic pyramids of crystalline PbS with a large proportion of an highly reactive and open 331 surface,$^{85}$ hierarchical anisotropic Cd(OH)$_2$ nanowire structures.$^{86}$ Rao and co-workers have shown that assembly at fluid interfaces, particularly the water-oil interface, can prove a facile route in the production of nanocrystalline clusters at near room temperature.$^{87}$ Furthermore, there is good control over sizes of the nanocrystals, associated narrow size distributions and the thin films are easily transferrable from the liquid to a substrate.$^{88}$ Dryfe and co-workers have reported the template-controlled synthesis of Pd nanoparticles by electrodeposition at the liquid-liquid interface.$^{89}$ Two immiscible liquids were able to take the place of the metallic substrate that is typically employed in electrodeposition.

1.6 Transport Properties in Nanocrystalline Thin Films

Understanding the fundamental properties of nanomaterials is of critical importance for the design of nanoparticle-based architectures with tuneable optical and electronic properties. One of the properties that is of fundamental and practical interest is charge transport.

Energy required for charge transport in bulk materials is equal to the bulk work
1.6. TRANSPORT PROPERTIES IN NANOCRYSTALLINE THIN FILMS

function. However, in molecular systems there exist separate energies for adding charge to a molecule (electron affinity, EA) and removing charge from a molecule (ionisation potential, IP). As alluded to earlier, the properties of nanocrystalline materials fall somewhere between those of bulk and molecular materials. So, when a bulk system is "shrunk down" and reduced to nanoscalar dimensions, there exists fewer electrons (or even no electrons), and the electronic behaviour becomes very different.

Nanocrystals possess both electron affinities and ionisation potentials, the values of which are nearly equal to the bulk work function, but not entirely. The difference between the IP and the EA is the charging energy, \( \epsilon_c \), which is equal to \( \frac{e^2}{C} \), where \( e \) is the fundamental unit of charge and \( C \) is the capacitance of the particle.\(^{90}\) Equation 1.4 shows that the capacitance of a nanocrystal is size dependent,

\[
C(r) = 4\pi\epsilon_0\epsilon r \tag{1.4}
\]

where \( \epsilon_0 \) is the permittivity of a vacuum and \( \epsilon \) is the dielectric constant of the material surrounding the particle. Charging energies are Coloumbic states, and are not equivalent to the electronic energy level spacings found in nanocrystals.

In a thin film, nanocrystals are brought together and the film can be said to comprise discrete units or "islands", each with their own specific charging energy, which are separated by a dielectric medium. The nanocrystalline solid has an electrical equivalent circuit as shown in Figure 1.15, as each metal particle is capacitatively coupled, either strongly or weakly, to each of its nearest neighbours.

The possible mechanisms of electron transport through this nanocrystalline matrix can be described using theoretical models of tunneling and hopping. Figure 1.16 shows the two possible conduction mechanisms along with their characteristic current, temperature and voltage dependencies.\(^{91}\)
1.6. TRANSPORT PROPERTIES IN NANOCRYSTALLINE THIN FILMS

Figure 1.15: The electrical equivalent circuit of a close-packed array of nanocrystals

Figure 1.16: Possible conduction mechanisms within nanocrystalline films. $J$ corresponds to conductance.

1.6.1 Charge Transport Mechanisms in Nanocrystalline Films

Tunneling

Quantum tunnelling refers to the quantum mechanical phenomenon whereby an electron tunnels through a barrier that it classically could not surmount. To help visualize the tunneling process, it is convenient to imagine the nanocrystals as closely-spaced, one dimensional metal electrodes, that are either very weakly coupled to each other, or not coupled to each other at all. When the system is subjected to a potential energy difference, the quantum tunneling phenomenon enables charge to flow between the electrodes. An electron approaching the surface of an electrode will polarise that surface, thus creating an "image" of opposite charge. This "image" then exerts an at-
1.6. TRANSPORT PROPERTIES IN NANOCRYSTALLINE THIN FILMS

tractive force on the electron, and facilitates its accommodation within the electrode. A free electron wavepacket is able to transmit freely through the surrounding insulating media and from electrode to electrode, and the initial and final energies of the tunneling electron are equal. This results in an extremely high conductance of the material and it is important to note that the tunneling process does not depend on temperature.

The energy of an electron at room temperature is generally $\sim 25 \text{ meV} = k_B T$, significantly lower than the typical barriers that need to be surmounted for tunneling to take place. Therefore, except at high temperatures or voltages, charge transport between electrodes is forbidden classically. Quantum tunneling through the unsurmountable barrier can take place however, the probability of which decays exponentially with an increase in distance between the two electrodes. Typically, voltages of about $10^6 \text{ Volts}$ are required in order for tunneling to occur from one electrode to the other across a short distance. A Scanning Tunneling Microscope is based on the concept of quantum tunneling; when a conductive microscopic tip is brought very near to the surface to be examined, a potential difference applied between the two can allow electrons to tunnel through the vacuum between them, resulting in a tunneling current. Information is acquired by monitoring the current as the tip position scans across the surface, and is usually displayed in image form. A number of studies have demonstrated the importance of tunneling in films of weakly coupled nanocrystals.

**Activated Hopping**

In the tunneling mechanism described above, nanocrystals do not interact with each other and the transfer of electrons is independent of temperature. However, when nanocrystals in the nanocrystalline solid are coupled with each other and are able to interact with one another, electrons are able to hop from one electrode to another when induced by temperature. The mechanism of activated hopping can be used to describe the electron transport process in such a system.

Activated hopping is similar to most chemical reactions in that it is an activated process and can be described by a rate equation similar in form to the Arrhenius equa-
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tion. There is an exponential dependence on activation energy, $E_a$, a pre-exponential term and the process occurs through a transition state from reactants to products. The rate constant associated with activated hopping, $k_{ah}$, can be expressed in the form of an Arrhenius equation (Equation 1.5):

$$ k_{ah} = k^0 \exp\left(-\frac{E_a}{K_B T}\right) $$ (1.5)

where $k^0$ is the pre-exponential term and $E_a$ is the activation energy. The difficult problem of calculating the pre-exponential factor and activation energy has been solved by Marcus, for which he received a Nobel Prize in Chemistry. The general description is that electron transfer takes place from an electron donor to an electron acceptor whilst surrounded by an external polarisable medium.

Richardson and co-workers have recently proposed a simple model of activated electron hopping between metal cores. The electrical conductivity ($\sigma$) in films of metallic nanocrystals can be represented by Equation 1.6.

$$ \sigma \propto e^{-2\delta \beta} e^{-E_a/kT} $$ (1.6)

where $\delta$ is the core-core separation, $\beta$ is a constant associated with electron tunnelling between two metallic cores separated by a dielectric media and $E_a$ is the activation energy associated with the charging of two neutral particles giving rise to the electron hopping process that has been extensively reported.

It can be seen from the expression that the activated hopping is dependent upon temperature and also upon the distances between the nanocrystals. The nature of the dielectric medium surrounding the nanocrystals is captured in the $\beta$ term and can also have an effect upon the charge transport characteristics of a nanocrystalline film.

The expression derived by Richardson is purely phenomenological and describes no system in particular. However, if the characteristics of a nanocrystalline system are known, the model can be used to predict the charge transport behaviour of the solid, before any experiments are carried out. Indeed, in this thesis, behaviour that has been
1.6. TRANSPORT PROPERTIES IN NANOCRYSTALLINE THIN FILMS

experimentally observed has been suitably "matched" to that model of charge transport described by Richardson.

1.6.2 Factors Affecting Charge Transport through Nanocrystalline Films

1.6.2.1 Nanoparticle Diameter

The electrical resistances associated with nanocrystalline solids has been found to depend upon the diameter of the constituent nanocrystals. Murray and Brust have extensively investigated the electronic behaviour of nanocrystals of different sizes. Rao and co-workers have studied electronic transport properties of nanocrystalline films obtained at the water-oil interface. The group were able to vary the particle diameters by simply performing the interfacial reaction at different temperatures. Charge transport measurements carried out upon the films showed that the electronic properties of the Au films differed when the constituent nanocrystal diameters were changed. Films produced at 30°C comprised smaller nanocrystals, had high resistances of MΩ magnitude and behaved as semiconductors. Those produced at 70°C comprised larger nanocrystals, had resistances of only a few Ohms in magnitude and metallic behaviour was observed.

1.6.2.2 Disorder

Studies have suggested that the disorder in nanocrystalline arrays can significantly decrease the conductivity of the film.

A finite resistivity in a metal occurs only as a result of imperfections in the crystal or lattice vibrations. Sufficiently disruptive crystal imperfections can cause a metal to become insulating with a resistivity that diverges in the limit of zero temperature. Understanding this so-called "disorder-induced metal-insulator transition" has been a major achievement in the theory of condensed matter.

Brust and co-workers first carried out electronic transport measurements upon
1.6. TRANSPORT PROPERTIES IN NANOCRYSTALLINE THIN FILMS

alkanethiol-stabilized Au nanocrystalline arrays. Insulating behaviour was observed in the arrays over a wide temperature range. Terrill and co-workers also observed insulating behaviour within Au nanocrystalline arrays, which were varied in terms of their particle sizes and interparticle separation distances. In both studies, the Au nanocrystals were polydisperse in size and not organized into close-packed superlattices.

Korgel and co-workers found that arrays of Ag nanocrystals exhibited metal-insulator transitions, when polydisperse nanocrystals were changed to monodisperse nanocrystals. In the polydisperse samples, conductivity rapidly decreased with decreasing temperature. However, in monodisperse samples, the conductivity increased with decreasing temperature until a critical temperature is reached, where the sign of the temperature coefficient of resistance (TCR) changed, i.e. a metal-insulator transition occurred (Figure 1.17).

![Figure 1.17: Conductivity versus temperature data for nanocrystalline Ag arrays, as prepared by Korgel and co-workers (a) shows a size-polydisperse sample; size-monodisperse samples are also shown with diameters of (b) 7.7 nm; (c) 5.5; (d) 4.8; (e) 4.5; (f) 3.5 nm\(^5\)](image)

In nanocrystalline arrays that are only a short distance away from each other, the collective electron wavefunctions of the individual nanocrystals will overlap and hybridize with those of neighboring nanocrystals, resulting in exchange coupling. In Korgel’s study, the electronic coupling in the monodisperse Ag arrays was sufficient to produce a positive TCR. In contrast, polydisperse samples showed a negative TCR.
1.6. TRANSPORT PROPERTIES IN NANOCRYSTALLINE THIN FILMS

The interparticle separation was the same as in the monodisperse sample, and so the energy barrier posed by the organic capping ligands was also the same to overcome in both cases. The metal volume fraction was also above the percolation threshold in both cases. The key difference in TCR behaviour, therefore, must have been due to the amount of disorder within the system.

1.6.2.3 Interparticle Spacing

Ordered arrays of nanocrystals have been prepared at the air/water interface on a Langmuir trough, and this Langmuir technique can be used to continuously vary the interparticle separation distance, thereby tuning the coupling strength between nanocrystals.

In a recent study, Markovich and co-workers showed that a Langmuir monolayer of alkylthiol passivated Ag nanocrystals could be compressed reversibly through a metal-insulator transition under ambient conditions. The film of Ag nanocrystals separated by a distance of 1.2 nm exhibited insulating behaviour, however, when compressed so that the separation distance was halved, metallic behaviour was observed.

1.6.2.4 Nature of the Surface Ligands

There are endless studies that have been carried out regarding surface ligands that encapsulate metallic nanocrystals. Ligands with long hydrocarbon chains that are typically used in the solution state preparation of nanocrystals have been found to form a highly insulating barrier that strongly localize charges. It has been established that ligands with longer chain lengths are more insulating. When long chain ligands are exchanged with crosslinkers consisting of short chains or unsaturation, charge mobility shows remarkable improvements. For example, Pelka and others have found a eight-fold increase in conductivity within films of metallic nanocrystals when the chain length is decreased from nine methyl units to three.

Andres and co-workers have already studied charge transport through their ordered, two-dimensional arrays. In order to stabilize the monolayer surrounding their
nanoparticles, as well as to lower the energy barrier for hopping or tunnelling to occur, the particles in the arrays were linked with long dithiol bridges, which have high electron affinities. Thus, the interparticle tunnelling barrier was significantly lowered.

Kovalenko and co-workers have been able to substitute organic surface ligands with molecular metal chalcogenide complexes of $[\text{Sn}_2\text{S}_6]^{4-}$ with hydrazinium ($\text{N}_2\text{H}_5$) as the counter ion. These ligands give rise to stable and facile electronic communication between nanocrystals. However, owing to the difficulties associated with "exchange chemistry", it has been relatively difficult to directly study the effect the electronic structure of ligands on the charge transport properties of nanocrystalline solids. Murray and co-workers have studied the influence of substituents by careful studies on tiny Au clusters capped different thiophenols. Recently, Nakanishi et. al. have described a class of nanostructured materials that exhibit photoconductance as well as the previously undescribed inverse photoconductance. Remarkably, the sign of the conductivity change is dependent upon the electronic structure of the molecules comprising the SAMs that stabilise the nanoparticles, thus highlighting the effect of ligand structure on the charge transport characteristics through the nanomaterial.

### 1.7 Applications in Nanotechnology

In 1959, the Nobel Laureate Richard Feynman stated that "The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom". Looking to the future, it is believed that virtually everything we use can be reduced in size, particularly in technology. Access to dimensions at the nanoscale is generating products that have previously only been dreamed about, such as thin, flexible organic electronic memory films and materials which can heal themselves. Applications of nanoscalar materials are numerous, and this section summarises only a small selection of their uses.

From a biological perspective, nanoparticles are smaller, or comparable in size to human cells (10 - 100 $\mu\text{m}$), viruses (20 - 450 nm) and proteins (5 - 50 nm), and so are
able to move freely within living organisms. This gives rise to a horizon of applications and advancements in biological fields. Nanoparticles can be functionalised to enable binding to biological entities of interest. Fast-growing tumour tissues are often quite porous and so functionalised nanoparticles can penetrate very easily. Contrast agents currently used in Magnetic Resonance and X-Ray imaging require catheterization and have limited tissue specificity and retention rates, thus requiring immediate imaging. Nanomaterials could prove more useful at lower doses for tissue-specific targeting and retention. More significantly, nanoparticles have the advantage of slow diffusion out of the bloodstream, which could permit imaging of the circulatory system and blood pool, a particularly useful advantage in cases of stroke. Ferromagnetic nanoparticles (usually magnetite, Fe₃O₄, or maghemite, γ-Fe₂O₃) have been used in the targeted delivery of therapeutic drugs, genes and radionuclides. Functionalised magnetic nanoparticles flowing in the circulatory system can become captured and arrested at target sites by simply placing magnets outside of the body. Particles coated with immunospecific magnets have been successfully bound to red blood cells, lung cancer cells, bacteria and Golgi vesicles.

Nanoscalar materials are used to catalyze chemical reactions in a wide range of applications including in fuel conversion, chemical production and in the synthesis of carbon nanotubes. Catalytic activity often takes place at defects that are present on surfaces or on steps and kinks. Hence, the vast surface area of nanoparticles twinned with their irregularity offer a suitable catalytic environment with a rich variety of such defects. In fact, most metal catalysts of modern practical relevance are nanoparticles rather than large single crystal surfaces.

The rising global energy crisis has meant that the production of clean and renewable hydrogen has received much attention and this has recently been achieved through water splitting using photocatalysts. Li and co-workers have achieved high efficiency of photocatalytic H₂ production using graphene nanosheets decorated with CdS nanoclusters as visible-light-driven photocatalysts. Au-Pd core-shell nanocrystals supported on TiO₂ appear to have a high turnover frequency for the oxidation of
alcohols.\textsuperscript{111} The nanocrystals consist of Au-rich cores and Pd-rich shells and it has been indicated that the Au electronically influences the catalytic properties of Pd. The effect of the nanoparticle shape on the catalytic properties has also been investigated. Tetrahedral Pt nanoparticles are better catalysts than spherical Pt nanoparticles for the Suzuki reaction between phenylboronic acid and iodobenzene.\textsuperscript{112} Nanoscalar catalysts with a wide range of various sizes, shapes and compositions are constantly being identified and modern instrumentation now provides an insight into how their structures and compositions determine their catalytic properties.

The production of nanoelectronics, smaller devices which have greater memory and run more efficiently than current, larger-scale devices, dominates much of nanotechnological research. Nanometer-sized semiconductor devices are revolutionizing many areas of electronics,\textsuperscript{113} and in an effort to increase integration, enhance functionality, and reduce energy consumption, the major focus of the development of nanocrystalline devices is on miniaturization. As a result, many semiconductor devices have evolved from millimeter-sized devices capable of manipulating electricity e.g., transistors\textsuperscript{114} into micrometer-sized devices that can handle both electricity and light e.g., light-emitting diodes.\textsuperscript{15} Nanoelectronics holds the promise of making computer processors more powerful than are possible with conventional semiconductor fabrication techniques. A number of approaches are currently being researched, including new forms of nanolithography, as well as the use of nanomaterials such as nanowires or small molecules in place of traditional complementary metal-oxide-semiconductor (CMOS) components.

Computers with faster processing speeds and greater memory are now highly desirable. The best way to increase speeds, i.e. the speeds at which the internal electric charges work within the system, is to decrease the distance over which they have to travel and shrink the inner devices and circuitry. Indeed, Feynman estimated that "all of the information that man has accumulated in all the books in the world, can be written in a cube of material one two-hundredth of an inch wide". Field Effect Transistors (FETs) are transistors that use electric field to control the shape, and hence the conductivity,
of charge carrying channels in a semiconducting material. Most FETs are made with conventional bulk semiconductor processing techniques, using a single crystal semiconductor wafer as the active region, or channel. However recently, techniques are becoming more centred around nanoscalar materials, and they have been made using semiconducting carbon nanotubes and heterostructured semiconductor nanowires.

It is hoped that nanostructured materials can be used to create cheaper and more efficient solar cells that improve upon conventional planar silicon solar cells. Research surrounding nanoparticle based solar devices is intense as it is believed that the invention of more efficient solar energy would have a great effect on satisfying global energy needs.

Thin films of nanocrystalline doped ZnO have already attracted a lot of attention as transparent conducting oxide electrodes. The films can be deposited at low temperatures, are stable against hydrogen plasma processing and are also considerably cheaper than other transparent conducting oxides. Recently ZnO thin films have been used as viable n-type semiconductor alternatives to TiO₂ in dye-sensitized solar cells, extremely thin absorber devices and Schottky barrier solar cells. Sizable photocurrents have been obtained from CdS nanocrystals anchored to Au substrates using dithiols. Solar cells with efficiency comparable to the commercial cells have been made using poly(2-hexylthiophene)-CdSe nanorod multilayers. Organic solar cells have been fabricated using porphyrins and fullerene units along with Au nanoparticles deposited on nanostructured SnO₂ electrodes. HgTe nanocrystals increase photon-harvesting efficiency of hybrid solar cells in the 350-1500 nm regions. Devices fabricated thus far show photon to current efficiencies up to 100% at 550 nm.

Currently available "nano-based" solar cells may not be as efficient as traditionally synthesized ones, however their lower production costs offset this. In the long term, nanoscalar versions should both be lower cost and, using quantum dots, should be able to reach higher efficiency levels than conventional solar cells.
Part II

Experimental
Chapter 2

Experimental

2.1 Deposition of Au Nanocrystals at the Water-Oil Interface

Interfacial Deposition of Au Nanocrystalline Films

A method originally reported by Rao and co-workers\(^87\) for obtaining films of Au nanocrystals at the water-toluene interface has been adapted. In a typical preparation (Figure 2.1), a toluene solution of chlorotriphenylphosphinylgold(I) (Au(PPh\(_3\))Cl), (10 mL, 1.5mM), was layered atop aqueous sodium hydroxide (16 mL, 6.25mM) in a 100 ml beaker (diameter 4.8 cm). To initiate the reaction, aqueous tetrakishydroxymethylphosphonium chloride (THPC) (330 \(\mu\)L, 50 mM) was injected into the lower layer. The beaker was immediately transferred to an oven set at the desired temperature. At the end of the reaction, a film with metallic yellow lustre was seen at the interface between toluene and water.

Film Transfer

The films of nanocrystals obtained at the interface of water and toluene were transferred onto glass substrates, using a transfer process that has recently been adapted and reported.\(^88\) Transfer of the films was accomplished using the following procedure:
2.1. DEPOSITION OF AU NANOCRYSTALS AT THE WATER-OIL INTERFACE

Figure 2.1: (left) Schematic diagram showing typical preparation of Au nanocrystalline films at the liquid-liquid interface and (right) actual photograph of the Au film at the interface.

A glass substrate held in a vertical orientation (relative to the interface) by attachment to a mechanical dipper was made to pierce the film and become completely immersed in the aqueous layer, where it was left for a minute. Transfer of the film to the substrate took place, when the slide was slowly withdrawn across the interface. The rate of transfer could be adjusted by adapting different speeds of substrate withdrawal. However, it was found that different rates of transfer ranging from 0.25 cm/s to 5 cm/s had no discernible effects on the properties of the films produced. The dipping cycle could be repeated several times. It was noticed that the film was not transferred to the substrate during the first dip from the toluene layer. As the glass substrate passed through the toluene column, a thin layer of toluene moved along, preventing the adhesion of the films to the substrate. Indeed, when the substrates were rendered hydrophobic, no transfer took place. Making the surface hydrophilic therefore aided the successful transfer of films. It was believed that as the glass substrate was left to "rest" for a minute in the aqueous layer, the glass lost its toluene coating and became more amenable to transfer.

Charge Transport Measurements

Contacts of Au that were 50 nm in thickness were thermally evaporated onto the Au films on glass substrates using a sputter coater. The substrates were then incorpo-
2.1. DEPOSITION OF AU NANOCRYSTALS AT THE WATER-OIL INTERFACE

rated into a home-built system composed of a closed-cycle He cryostat, Keithley 2400 Series Source-Measure unit and a Lakeshore 325 Temperature Controller. The samples were mounted onto the cold finger of the cryostat and contacts were made to the electrodes using conductive copper wires and conductive silver paint. The sample was held in a vacuum of $10^{-6}$ mbar and cooled down to 15 K, while DC resistance measurements were carried out.

**Ligand Displacement**

The Au films, mounted upon glass substrates, were submersed into 5mL of a 6.5 mM methanolic solution of the desired aromatic thiol. The films were then left to soak for 1 hour during which time ligand exchange occurred. After this time the films were removed from the thiol solution and washed thoroughly with two portions of methanol. The films were then left to dry completely in air.

The following thiols were used as received from Aldrich: 4-Nitrothiophenol, technical grade, 80%; Thiophenol, 97%; 4-Bromothiophenol, 95%; 4-Chlorothiophenol, 97%; 4-Methylbenzenethiol, 97%; and 4-Methoxythiophenol, 97%.

**Monitoring Ligand Displacement using UV Spectroscopy**

An Au film was firmly attached inside a glass cuvette using blu-tack. The cuvette had a pathlength of 1 cm. 2 mL methanol was then added to the cuvette so that the film was completely submersed (See Figure 2.2).

The cuvette was then placed inside of the UV spectrometer so that a UV spectrum could be obtained. 5 drops of a 6.5mM solution of the relevant thiol was then added to the cuvette using a glass pipette, whilst it was still firmly affixed in the spectrometer. Spectra were taken immediately after adding the thiol, and then at time intervals following the addition. The spectra could be overlaid to monitor any progress as a result of the ligand displacement reaction.
2.1. DEPOSITION OF AU NANOCRYSTALS AT THE WATER-OIL INTERFACE

Figure 2.2: Diagram showing how the ligand displacement was monitored in the UV spectrometer. The Au film was attached to the cuvette using blu-tack and then submerged into methanol. The displacement was initiated on addition of thiol into the cuvette and the progress was monitored using UV spectroscopy.

Figure 2.3: The square wave generator circuit used to construct the amine sensing device.
2.2. DEPOSITION OF AG NANOCRYSTALS AT THE WATER-OIL INTERFACE

Fabrication of the Amine Sensing Device

The sensor was constructed using a square wave generator circuit as shown in Figure 2.3. Here, $V_{out}$ was the square wave, read using an oscilloscope. An Op Amp type AD822 with $\pm 1.5$V supply voltage (note: the rated capability of this Op Amp was from $\pm 1.5$ to $\pm 18$ V) and capacitance $C = 3.3$ nF was used. For $R_1/R_2$, a 100 kOhm potentiostat was used. The sample comprising a film of Au nanocrystals was used as resistor R. The frequency, f, of the resulting square wave depended on $C$, $R_1$, $R_2$ and R. The response to the amine vapour was thus measured as a frequency that was inversely proportional to resistance. This measurement was carried out using an AC voltage, and field stress that could result from a DC bias was avoided. Octylamine was cooled to 0°C in an ice bath and the saturated vapours from this vessel were mixed with the desired quantity of $N_2$ gas using mass flow controllers and allowed to flow over the film sensor. The concentration of the amine was determined from estimated saturated vapour pressure. There are no reports of vapour pressure of octylamine at 0°C. However, Steele and co-workers reported saturated vapour pressures at higher temperatures. These data were extrapolated to 0°C using the Clausius-Clapeyron equation. The reference scale exposure fraction (ranging from 0.0 to 1.0) was arrived at by designating the extrapolated saturated vapour pressure at 0°C, 282 ppm as 1.0.

2.2 Deposition of Ag Nanocrystals at the Water-Oil Interface

Synthesis of chlorotris(triphenylphosphine)silver(I)

The complex was prepared following a method previously reported. Briefly, to a stirred dispersion of AgCl (1.43 g, 10 mmol) in dichloromethane (150 ml), a solution of triphenylphosphine (10.97 g, 40 mmol), in dichloromethane (50 mL), was added dropwise and the stirring continued for an hour, during which time the solids almost completely dissolved. The clear liquid obtained was filtered and, to the filtrate, pentane
was added to precipitate a white crystalline solid. The solid was then washed with pentane and then air dried. Elemental analysis (%) found: C, 69.45; H, 4.84; Cl, 4.23; P, 9.69; Ag, 11.02. Calculated: C, 69.71; H, 4.84; Cl, 3.82; P, 10.00; Ag, 11.62.

**Interfacial Deposition of Ag Nanocrystalline Films**

A 10 mL, 1.5mM toluene solution of chlorotris(triphenylphosphine)silver(I), (Ag(PPh\(_3\))\(_3\)Cl) was layered atop 16 mL of 6.25 mM aqueous sodium hydroxide in a 100 ml beaker (diameter 4.8 cm). To initiate the reaction, 330 \(\mu\)L of 50 mM aqueous tetrakis(hydroxymethyl)phosphonium chloride (THPC) was injected into the lower aqueous layer. Almost immediately, a yellow coloration was observed in the lower aqueous layer. The beaker was then quickly transferred to an oven set at the desired temperature and at the end of the reaction, a film with a lustrous grey sheen was seen at the interface between toluene and water. The film was then transferred onto glass substrates for further analysis.

**Film Transfer**

The films of nanocrystals obtained at the interface of water and toluene were subsequently transferred onto glass substrates, using a transfer process that has recently been adapted and reported.\(^8\) Transfer of the films was accomplished using the following procedure: A glass substrate held in a vertical orientation (relative to the interface) by attachment to a mechanical dipper was made to pierce the film and become completely immersed in the aqueous layer, where it was left for a minute. Transfer of the film to the substrate took place, when the slide was slowly withdrawn across the interface. The rate of transfer could be adjusted by adapting different speeds of substrate withdrawal. However, it was found that different rates of transfer ranging from 0.25 cm/s to 5 cm/s had no discernible effects on the properties of the films produced. The dipping cycle could be repeated several times. It was noticed that the film was not transferred to the substrate during the first dip from the toluene layer. As the glass substrate passed through the toluene column, a thin layer of toluene moved along, preventing the
adhesion of the films to the substrate. Indeed, when the substrates were rendered hydrophobic, no transfer took place. Making the surface hydrophilic therefore aided the successful transfer of films. It was believed that as the glass substrate was left to "rest" for a minute in the aqueous layer, the glass lost its toluene coating and became more amenable to transfer.

**Charge Transport Measurements**

Au contacts were thermally evaporated onto the glass substrates containing the Ag films prior to the film being incorporated into the apparatus. Charge transport measurements were carried out using a home-built system composed of a closed-cycle He cryostat, Keithley 2400 Series Source-Measure unit and a Lakeshore 325 Temperature Controller. The sample was mounted onto the cold finger of the closed-cycle cryostat and contacts to the electrodes were made using copper wires and conductive silver paint. The sample was held in a vacuum of $10^{-6}$ mbar, achieved using rotary and diffusion pumps, and then cooled down to 15 K, while DC resistance measurements were carried out.

## 2.3 Deposition of Pt Nanocrystals at the Water-Oil Interface

**Interfacial Deposition of Pt Nanocrystalline Films**

The preparation mimics that of palladium film preparation as performed by Dryfe and co-workers. A 25mL 1mM aqueous solution of potassium tetrachloroplatinate was layered atop 25 mL 2mM solution of decamethylferrocene in dichloroethane in a 100 mL beaker. The beaker was then transferred to an oven set at the desired temperature.
2.3. DEPOSITION OF PT NANOCRYSTALS AT THE WATER-OIL INTERFACE

Transfer of Pt Nanocrystalline Films

The reaction above could be carried out in a sintered glass tap funnel, in order to aid the transfer of the films at the end of the reaction (Figure 2.4). Glass substrates were placed onto the sinter at the start of the reaction.

When the reaction had completed, the tap was used to slowly and easily remove the dichloroethane layer until the film at the interface was lowered onto the glass substrates, where it was left to "rest" for a minute. The upper aqueous layer could then be carefully removed using a pipette, leaving the platinum films mounted upon the glass substrates on the sinter. The films were firstly left to dry in air, and then in a 50°C oven for 1 hour.

Charge Transport Measurements

Au contacts were thermally evaporated onto the glass substrates containing the Pt films prior to the film being incorporated into the apparatus. Charge transport measurements were carried out using a home-built system composed of a closed-cycle He cryostat, Keithley 2400 Series Source-Measure unit and a Lakeshore 325 Temperature Controller. The sample was mounted onto the cold finger of the closed-cycle cryostat and contacts to the electrodes were made using copper wires and conductive silver paint. The sample was held in a vacuum of 10^{-6} mbar, achieved using rotary and dif-
fusion pumps, and then cooled down to 15 K, while DC resistance measurements were carried out.

2.4 CdS and ZnS Deposition Using Thiobiurets

Synthesis of $[\text{M}(\text{C}_{14}\text{H}_{28}\text{N}_{3}\text{OS})_2] \ (\text{M} = \text{Cd or Zn})$

A solution of di-iso-propylcarbamoyl chloride (1.0 g, 6 mmol) and sodium thio-cyanate (0.49 g, 6 mmol) in acetonitrile (25 mL) was heated to reflux with continuous stirring for 1 h, during which time a fine precipitate of sodium chloride formed. This precipitate was removed by filtration. To the cooled reaction mixture, di-isopropylamine (1.49 mL, 12 mmol) was added followed by stirring for 30 min and addition of the corresponding metal acetate (3 mmol). The solution was then stirred for a further 30 min. The thiobiurets were all obtained as fine solids which were collected by Buchner filtration and dried in air. Cd(C$_{14}$H$_{28}$N$_3$OS)$_2$ was obtained as a white powder. Elemental Analysis: Calc (%): C, 49.0; H, 8.1; N, 12.2; S, 9.3; Cd, 16.4 Found(%): C, 49.2; H, 7.8; N, 12.0; S, 9.1; Cd, 15.9.

Zn(C$_{14}$H$_{28}$N$_3$OS)$_2$: Recrystallization from chloroform and methanol yielded white needle-like crystals. Elemental analysis. Calc(%): C, 52.7; H, 8.7; N, 13.1; S, 10.0; Zn, 10.2. Found(%): C, 52.2; H, 8.3; N, 12.7; S, 9.6; Zn, 9.8.

Interfacial Deposition of Nanocrystalline Metal Sulphide Films

A toluene solution of metal thiobiuret (30 mL, 1.8 mM) was allowed to stand in contact with aqueous Na$_2$S (30 mL, 3.8 mM) until the layers stabilised. The reaction was carried out in a 100 mL beaker of diameter 4.8 cm. The beaker was covered and film formation at the water-toluene interface was over a range of temperatures and timescales. Cadmium sulphide thin films were bright yellow and zinc sulphide films appeared bright white. They were transferred onto glass substrates for further analysis.
2.5. ELECTRONIC PROPERTIES OF CDS & ZNS

Deposition of CdS and ZnS Using Simple Salts

Ethylenediamine (1.67 mL) and cadmium nitrate (1.39g) were dissolved in 30 mL water. Separately, CS₂ (1.51 mL) was dissolved in 30 mL hexane. In a 100 mL beaker (diameter 4.8 cm), the hexane layer was then slowly layered atop the aqueous phase to avoid disruption to the interface that resulted between the two liquids. The reaction beaker was then covered and left in the dark for 24 hours, at room temperature. Thin, yellow films were formed at the interface and collected, using glass substrates, for further characterisation.

2.5 Electronic Properties of CdS & ZnS

Charge Transport Measurements

Au contacts were thermally evaporated onto the glass substrates containing the CdS and ZnS films prior to the film being incorporated into the apparatus. Charge transport measurements were carried out using a home-built system composed of a closed-cycle He cryostat, Keithley 2400 Series Source-Measure unit and a Lakeshore 325 Temperature Controller. The sample was mounted onto the cold finger of the closed-cycle cryostat and contacts to the electrodes were made using copper wires and conductive silver paint. The sample was held in a vacuum of 10⁻⁶ mbar, achieved using rotary and diffusion pumps, and then cooled down to 15 K, while DC resistance measurements were carried out.

Ligand Displacement using Pyridines

The CdS/ZnS films, mounted upon glass substrates, were submersed into 5mL of a 6.5 mM methanolic solution of the desired substituted pyridine. The films were then left to soak for 3 hours during which time ligand exchange occurred. After this time the films were removed from the thiol solution and washed thoroughly with two portions of methanol. The films were then left to dry completely in air.
The following pyridines were used as received from Aldrich: 4-Nitropyridine, 97%; Pyridine, 99%; 4-Methoxypyridine, 97%; 4-Picoline, 99%.

2.6 Characterization of Nanocrystals and Nanocrystalline Thin Films

2.6.1 X-Ray Diffraction, XRD

When a compound crystallizes, the molecules form an ordered array and intermolecular forces arise between them. The motion of the molecules within the solid becomes restricted. The diffraction of X-rays by the core electrons within a crystalline solid provides the most useful information regarding the crystallographic structure, crystallinity, crystal size and preferred orientation of the sample.

Within a crystalline solid it is possible to imagine various families of planes which pass through its unit cell at various angles. It is easy to think of the lattice planes within crystalline solids as mirrors, and to model the crystal as a stack of these reflecting lattice planes of separation, d. In order to define the geometry of these planes, Miller indices are used; a set of three numbers (when considering three dimensions) typically labelled h, k, and l, corresponding to the vector normal to the plane(s) they describe (Figure 2.5).

Figure 2.5: An example of Miller indices in two dimensions.
Max von Laue realized that the wavelengths of X-rays were comparable to the separations of the lattice planes and therefore suggested that X-rays might be diffracted when passed through it. When X-rays are incident upon a crystalline solid, the photons will reflect from the atoms in such a way that the crystallographic planes described earlier can be treated as analogous to a set of parallel reflective planes in optics. A set of parallel reflective planes subject to a beam of electromagnetic radiation will act in a manner similar to a diffraction grating, as shown in Figure 2.6.

Figure 2.6: A crystal lattice can be shown to cause diffraction via optical analogy to a set of reflective planes.

Incoming electromagnetic radiation reflecting off of different planes within the lattice will result in a path length difference through basic geometry; it is clear from Figure 2.6 that ray 2 will have travelled a greater distance than ray 1, with the difference being equivalent to the length of ABC. It is also apparent that ray 3 will travel the further by the same amount again. Thus when the distance ABC is equal to one wavelength of the incident radiation, the distance DEF (the path length difference between rays 1 and 3) will be equal to two wavelengths, and so on through the crystal. The distance ABC is dependent on the spacing between the planes, \( d \), and the sine of the angle of the incident radiation, \( \theta \). AB and BC are equal, and since:

\[
AB = dsin(\theta)
\]  

(2.1)

it is simple to determine that:
2.6. CHARACTERIZATION OF NANOCRYSTALS AND NANOCRYSTALLINE THIN FILMS

\[ ABC = 2dsin(\theta) \]  

When constructive interference occurs, the path length difference \( ABC \) must be equal to a multiple of the wavelength, \( \lambda \). The Bragg Equation in 2.3 results:

\[ n\lambda = 2dsin(\theta) \]  

The fundamental use of Bragg’s law is in the determination of the spacing between the layers in the lattice for, once the angle \( \theta \) corresponding to a reflection has been determined, \( d \) may readily be calculated. By analysing the diffracted intensity of X-rays over a range of angles, various parameters of the crystal lattice can be determined. Specifically, it is possible to determine which crystallographic planes the faces of the crystals within the sample correspond to, with each peak in X-ray intensity corresponding to a particular plane. This is useful in the characterisation of differing structures of the same substance - for instance, if the sample was formed in a way which results in preferential growth along a specific plane, the diffraction pattern will show this.

X-ray diffraction can be performed upon both single crystalline and powdered samples. In single crystals, a beam of X-rays strikes the crystal, giving rise to scattered beams. The beams land on a photographic film or an area detector with a charge-coupled device (CCD), making a diffraction pattern of spots. Each spot is called a reflection, since it corresponds to the reflection of the X-rays from one set of evenly spaced planes within the crystal. The intensities of the scattered beams and their angles of reflection can be measured as the crystal is gradually rotated. X-ray diffraction data, for a crystal of sufficient purity and regularity, can be used to determine mean chemical bond lengths and angles with remarkable accuracy.

An alternative of this is to use a powdered sample. In this case, the crystals within the sample can be treated as being randomly oriented, and the ratios of X-ray intensities at different angles will directly correspond to the proportions of planes present on the
exposed crystal faces. X-ray diffraction can also be performed on 'textured' samples, i.e. those with some form of preferential orientation, such as thin films. Direct quantitative analysis of the sample is more difficult in this case, as certain planes will be more prevalent in the resulting diffraction pattern. Powder diffraction data are also used to determine phase diagrams, and also for initial determination of the dimensions and symmetries of unit cells.

Methodology

A typical X-ray diffractometer has three key parts; an X-ray source, a sample stage, and a detector. A typical X-ray source will consist of a filament, usually made of tungsten, and an anode, often made of copper, although other elements can also be used. The process of generating X-rays is relatively simple; a current is passed through the filament in order to excite its electrons, which are emitted from the filament inside a vacuum tube. This type of set-up is known as an X-ray tube.

The structure of an X-ray tube will usually consist of the filament and anode at opposite ends of the vacuum chamber, with beryllium windows placed so as to limit the direction of emitted X-rays. The anode is often placed at an angle such that X-rays which pass through the window have all originated from an approximately equal depth within the anode, preventing what is known as 'anode heel effect' - where the X-ray intensity is uneven across the profile of the beam. Along with water being constantly sprayed on the rear of the anode, some X-ray tubes incorporate a rotating anode, such that only a small portion of it is exposed to the electron flux at any one time in order to prevent the anode getting too hot.

Many diffractometers contain a monochromator either between the X-ray tube and the sample stage, or between the sample stage and the detector. The purpose of a monochromator is, as the name would suggest, to remove as much of the unwanted background X-radiation as possible, i.e. the Bremsstrahlung radiation and any characteristic lines other than the $K_{\alpha}$. An X-ray monochromator typically consists of a quartz crystal with a well known diffraction pattern, placed at an appropriate point in order to
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diffract only radiation of the desired wavelength through the remainder of the system.

The monochromator is usually mounted as a part of either the detector or source, one or both of which are themselves mounted on motorised arms. These arms themselves are mounted as part of a circular stage, forming the core of the diffractometer. This arrangement is known as a goniometer (Figure 2.7) - the detector and/or X-ray source moves across the range of angles specified by the user, mapping out the angular distribution of X-rays diffracted from the sample.

![Figure 2.7: Picture of a typical goniometer sample stage.](image)

The user is able to control both the step size between points of data collection and the duration of data collection, allowing the angular resolution of the resultant plot to be controlled up to the limit of the detector. There are several types of detector used in modern diffractometers, however most operate on similar principles. All must consist of an X-ray-sensitive element which, upon interaction with an X-ray, will produce some form of signal proportional to the energy of the X-ray. Many include some form of amplification step between production of this initial signal and output to a computer. One of the most common types of detector used, and an excellent example of the principles, is a scintillation counter. Such a detector consists of a sheet of phosphor attached to a photomultiplier tube. Upon impact by an incident X-ray, the phosphor is excited, be-
fore re-emitting the light in the form of several lower frequency photons. The number of these photons is proportional to the energy of the initial X-ray, and each will subsequently impact upon the cathode of the photomultiplier tube, exciting an electron via the photoelectric effect. This electron then passes through a series of 10 dynodes within the tube, each with a higher potential than the last, which accelerate the electron down the tube. Upon impact with each dynode, the electron will excite more electrons using the kinetic energy gained from its acceleration through the tube, eventually resulting in a pulse of current at the anode. As the number of electrons produced at the photocathode is proportional to the number of photons produced at the scintillator, which is itself proportional to the energy of the original incident X-ray, the final signal is thus proportional to the energy of the incident X-ray.

**Indexing Powder X-Ray Diffraction Patterns**

The spectra obtained during powder X-ray diffraction can be easily imported into many indexing programmes, where it can be compared to a database of powder diffraction patterns. The database consists of .pdf files with a unique code (usually beginning JCPDS...) that contain information about thousands of samples, including their d-spacings, relative intensities of observable diffraction peaks, chemistry descriptions, physical properties and structural classifications. The patterns have been either experimentally determined, or computed based on crystal structure and Bragg’s law. Computer software available now allows chemists to import their obtained spectra into programmes and allows rapid indexing and matching of patterns obtained to those within the database, allowing easy identification of samples.

In this work, X-ray diffraction studies for the characterization of thin films were performed using a secondary graphite monochromatic Cu Kα radiation (40 KV) on a Philips XPert Materials Diffractometer. The data obtained was analysed using the XPert HighScore Plus indexing software.
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2.6.2 UV-Visible Absorption, UV

Ultraviolet-visible (UV-vis) spectroscopy is a tool that is widely used to quantitatively characterize nanoscalar materials. In a typical experiment, a sample is irradiated with electromagnetic waves in the ultraviolet and visible ranges and the absorbed light is analyzed through a resulting spectrum. It can be employed to identify the constituents of a substance, determine their concentrations, and to identify functional groups in molecules. UV-vis spectroscopy therefore has uses in sensing applications.

The visible and ultraviolet spectra of materials are associated with transitions between electronic energy levels. The transitions are generally between a HOMO and a LUMO. The wavelength of the absorption is then a measure of the separation of the energy levels of the orbitals. Two empirical laws have been formulated about the absorption intensity. Lambert’s law states that the fraction of incident light absorbed is independent of the intensity of the source. Beer’s Law states that the absorption is proportional to the number of absorbing molecules. From these laws, the remaining variables give Equation 2.4.

\[ \log_{10} \frac{I_0}{I} = \epsilon l c \]  

(2.4)

\( I_0 \) and \( I \) are the intensities of the incident and transmitted light respectively, \( l \) is the path length of the absorbing solution in centimetres and \( c \) is the concentration in moles/litre. \( \log_{10}(I_0/I) \) is called the absorbance or optical density and \( \epsilon \) is the molar extinction coefficient.

The ultraviolet spectrum is usually obtained from very dilute solutions. A known quantity of the compound is dissolved in a solvent of choice and transferred into a cell. The cell is so made that the beam of light passes through a 1 cm thickness of solution. The cell is then placed into the spectrometer. Liquid samples are usually contained in a cell that has flat, fused quartz faces. Quartz is commonly used as it is transparent to both UV and visible lights. Furthermore, as it operates on the principle of absorption of photons that promotes the molecule to an excited state, it is an ideal technique for determining the electronic properties of nanomaterials. In the spectrum
of nanoparticles, the width of the absorption peak strongly depends on the chemical composition and the particle size. As a result, their spectrum is different from their bulk counterparts.

Equal beams of ultraviolet and visible light are passed through the cell and the intensities of the transmitted beams are observed over a wavelength range. In most spectrometers, a matched cell containing the pure solvent is also prepared and each cell is placed in the appropriate place in the spectrometer. This is so arranged that two equal beams of ultraviolet or visible light are passed, one through the solution of the sample and one through the pure solvent. The intensities of the transmitted beams are then compared over the whole wavelength range of the instrument. In most spectrometers there are two sources, one of 'white' ultraviolet and one of white visible light, which have to be changed when a complete scan is required. Usually either the visible or ultraviolet alone is sufficient for the purpose in hand. The spectrum is plotted automatically on most machines as log_{10}(I_0/I) ordinate and \( \lambda \) abscissa. The unit of \( \lambda \) is almost always m\( \mu \). Strictly speaking, the intensity of a transition is better measured by the area under the absorption peak than by the intensity of the maximum of the peak. For several reasons, most particularly convenience and the difficulty of dealing with overlapping bands, the latter procedure is adopted in everyday use. Spectra are quoted, therefore in terms of \( \lambda_{\text{max}} \), the wavelength of the absorption peak, and the \( \epsilon_{\text{max}} \), the intensity of the absorption peak as determined by Equation 2.4.

The excitation of electrons is accompanied by changes in the vibrational and rotational quantum numbers so that what would otherwise be an absorption line becomes a broad peak containing vibrational and rotational fine structure. Due to interactions of solute with solvent molecules this is usually blurred out, and a smooth curve is observed. In the vapour phase, in non-polar solvents, and with certain peaks, the vibrational fine structure is sometimes observed.

Size dependent properties can also be observed in a UV-visible spectrum, particularly in the nano and atomic scales. These include peak broadening and shifts in the absorption wavelength. Many electronic properties, such as the band gap of a material,
can also be determined by this technique. The molecular electrons are excited to higher energy orbitals by the energies associated with UV-visible ranges. Photons in the visible range have wavelengths between 800-400 nm whereas the near UV range includes wavelengths down to 200 nm.

In this work, a Cary 5000 UV-Vis-NIR spectrophotometer has been used for optical analysis.

### 2.6.3 Scanning Electron Microscopy, SEM

Microscopy has long been an indispensable tool in research - the ability to form images of objects smaller than would normally be visible is invaluable. Optical microscopy has resolution limits that render it unusable for research in many modern fields, however, electron microscopy can greatly surpass these limits allowing for the observation of objects even down to a few angstroms in size.

Conventional (and indeed, electron) microscopy is limited in resolution by several factors, but the effective 'hard' limit i.e. that which cannot be easily circumvented through ingenuity is that of diffraction. For a microscope used for observing waves of wavelength $\lambda$, the smallest resolution achievable, in the absence of other sources of distortion, is given by:

$$d = \frac{0.612\lambda}{n\sin\alpha}$$

(2.5)

where $n$ is the refractive index of the medium through which the wave is travelling, and $\alpha$ is the aperture angle. De Broglie’s famous proposition on wave-particle duality - that electrons have their own, extremely short, wavelengths calculable simply from their energy - would eventually lead to electrons being considered as a potential energy source for use in microscopy, thus greatly reducing this diffraction limit, and allowing much smaller distances to be resolved.

There are two "modes" in which an electron microscope can function; transmission electron microscopy (TEM) is the most analogous to standard optical microscopy,
where electrons pass through a sample and form an image upon a fluorescent screen in a similar manner to photons of light in an optical microscope forming an image on the retina. Scanning electron microscopy (SEM) operates in a substantially different manner, instead relying on electrons scattered from the sample in order to form an image. This has the added advantage of also producing images that appear more three dimensional than by other methods as their enhanced depth of field results in a thicker portion of a sample being in focus at any one time. These capabilities render electron microscopy an extremely useful tool in the analysis of nanometer-scale surfaces.

Figure 2.8: Schematic diagram of the Scanning Electron Microscope. The schematic can be found at www.dileepnanotech.com

While TEM operates in a manner similar to traditional microscopy, SEM relies instead on scattered electrons. A schematic of the SEM is shown in Figure 2.8 Instead of having the beam pass through the sample to be observed and detected on the other side, a SEM will detect the electrons released from the sample as a result of ionisation by the beam, known as 'secondary' electrons. These electrons are used to produce a signal which when plotted against the coordinates from which the electrons were emitted, produces a graph of intensity against position. By translating this data into pixel
2.6. CHARACTERIZATION OF NANOCRYSTALS AND NANOCRYSTALLINE THIN FILMS

brightness, an 'image' of the sample is obtained. An entire sample cannot be imaged in this way instantaneously and the data for each position must be collected separately. The electron beam and detector are synchronised to raster over the surface together, taking data for each point at a time, hence the name 'scanning' electron microscopy. In addition to simple proximity to the detector, the intensity produced from a given point on the sample is increased or decreased by the local topology, that is to say that peaks will produce higher intensities of detected electrons than plateaus or valleys. This is due to the fact that secondary electrons are not just produced from the very surface; the incident electrons interact over a teardrop shaped area known as the interaction volume. Raised areas thus have more of this volume close enough to the surface for electrons to escape, resulting in a higher signal.

As the electron beam is typically very narrow, there is quite a large depth range either side of the beam focus in which it has not yet diverged enough to result in blurring of the image between pixels. Any material within this depth range will therefore appear 'sharp' and as if in focus; this is what causes the large depth of field that SEM can achieve.

During microscopic analysis, electron beams must be focussed and secondary electrons must be captured after emission from a sample, therefore SEM must be performed at high vacuum in order to prevent electron interactions with gas molecules. The basic structure of an SEM will usually consist of a loading chamber for samples and a main chamber kept under high vacuum long-term for this purpose. Electrons are typically produced in the same manner as in an X-ray tube - via thermionic emission from a tungsten filament. The filament is heated by applying a voltage, which causes electrons to be emitted. The resulting electron beam is focused by a condenser lens, which projects the image of the source onto the condenser aperture. It is then focused by an objective lens and rasterscanned over the sample by scanning coils. This is achieved by varying the voltage produced by the scan generator on the scan coils that are energized, creating a magnetic field, which deflects the beam back and forth in a controlled pattern. When the primary electrons hit the sample, they give part of their energy to electrons in
2.6. CHARACTERIZATION OF NANOCRYSTALS AND NANOCRYSTALLINE THIN FILMS

the sample, resulting in the emission of secondary electrons.

Once the electrons have interacted with the sample, the secondary electrons are accelerated towards the detector by a potential applied between it and the sample. The detector itself is often a scintillation counter similar to the one described in Section 1.8.1, albeit with a scintillator material appropriate to the electron beam. The intensity of the secondary electrons is displayed versus the position of the primary beam on the sample. The samples placed in the SEM must be either conducting or covered with a thin metal layer or graphite in order to avoid electric charging. In addition to secondary electrons there are also high-energy electrons, originating in the electron beam (producing X-rays), that are backscattered from the specimen interaction volume. These electrons may be used to detect contrast between areas with different chemical compositions.

A Philips Excel 30 FEG (Field Emission Gun) SEM instrument was employed for the characterization of the thin films in this work. Electrons in the Philips Excel 30 equipment are emitted via a field emission gun (FEG), whereby the electrons are accelerated towards the sample by applying an electric potential.

2.6.4 Energy Dispersive X-Ray Analysis, EDX

Energy-dispersive X-ray spectroscopy (EDS or EDX or EDAX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of an interaction of a some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element’s atomic structure to be identified uniquely from one another.

To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons (see PIXE), or a beam of X-rays, is focused into the sample being studied. This is usually done in situ, whilst the sample is in position under the Scanning Electron Microscope. Scanning electron microscopes are equipped with a cathode and magnetic lenses to create and focus a beam of electrons
and a detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

The EDX analysis in these studied was carried out using the Philips Excel 30 FEG (Field Emission Gun) SEM instrument.

2.6.5 Transmission Electron Microscopy, TEM

In a TEM, a beam of high energy electrons is transmitted through a thin sample to reveal information about its morphology, crystallography, particle size distribution, and its elemental composition. As a gross simplification, the TEM may be compared to a light microscope, however, instead of slides being observed using light sources, specimens in the TEM are "observed" using an electron beam. The TEM can provide atomic-resolution images, as well as giving chemical information at a resolution of 1 nm or better. During operation of the TEM, an electron beam passes through a sample. Only certain parts of it are transmitted, making an amplitude contract image. The image passes through a magnifying lens and is then projected onto a phosphor screen or a charge coupled device (CCD), which allows for quantitative data processing. Information may also be obtained from backscattered and secondary electrons, as well as emitted photons. A simplified TEM set up is shown in Figure 2.9.
2.6. CHARACTERIZATION OF NANOCRYSTALS AND NANOCRYSTALLINE THIN FILMS

Figure 2.9: Schematic diagram showing the components of a Transmission Electron Microscope. The schematic can be found at www.hk-phy.org

The electron gun is essentially cathode that is typically made from materials such as LaB$_6$. It is heated by applying a large current and a stream of electrons is produced, which becomes accelerated down a long column. In operation, electrons are typically accelerated to anywhere from 125 to 300 kV, or higher in some microscopes. High magnification in TEM methods is a result of the small effective wavelengths ($\lambda$) employed. According to Equation 2.6:\textsuperscript{125,126}

$$\lambda = \frac{h}{\sqrt{2mqV}}$$

(2.6)

where $m$ and $q$ are the electron mass and charge, and $V$ is the potential difference. Electrons of 100 keV energy have wavelengths of 0.37 nm and are capable of effectively transmitting through about 0.6 $\mu$m of Si.

The condenser lenses focus the beam to a small and coherent cylinder and there is an aperture present which removes any stray electrons. The beam strikes the specimen on the sample holder, and the majority is transmitted, then focused by the objective
2.6. CHARACTERIZATION OF NANOCRYSTALS AND NANOCRYSTALLINE THIN FILMS

lens. After passing through the projector lenses the beam is enlarged and forms an image upon striking a phosphor or CCD surface.

The versatility and the fact that an individual nanoparticle can be selected and characterized individually makes TEM one of the most powerful characterization techniques for nanoscale materials. A wide variety of materials can be characterized with a TEM, including metals, minerals, ceramics, semiconductors, and polymers. Because electrons must be transmitted through the material it is a requirement that the sample be appropriately thin.

The TEM measurements of thin films in the work to be reported here were carried out using a CM 200 Philips TEM operating at 200 kV.

2.6.6 X-Ray Photoelectron Spectroscopy, XPS

X-ray photoelectron spectroscopy (XPS) is a technique commonly used for the analysis of surfaces. Specifically, XPS can provide us with complex quantitative information about the chemical and electronic states and the proportional presence of elements at the surface of a sample, as well as how these properties vary over the first 2-10 atom layers. As the name would suggest, the process upon which XPS is based is that of X-ray induced photoemission of electrons; by measuring the intensity of emitted electrons over a range of kinetic energies, spectra are produced. A typical XPS spectrum is a plot of the number of electrons detected versus the binding energy of the electrons detected. Each element produces a characteristic set of XPS peaks at characteristic binding energy values that directly identify each element that exist in or on the surface of the material being analyzed. These characteristic peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc.

The production of a 'photoelectron' occurs when photons of sufficient energy incident upon a surface result in the excitation of an electron due to the photoelectric effect. Electrons become emitted from the host matter as a consequence of their absorption of energy from electromagnetic radiation of very short wavelength (Figure 2.10).

The sensitivity of XPS with regard to sampling depth is mostly dependent on the
2.6. CHARACTERIZATION OF NANOCRYSTALS AND NANOCRYSTALLINE THIN FILMS

Figure 2.10: An X-ray about to strike those electrons belonging to an Oxygen atom.

ability of emitted electrons to reach the analyser while having lost little or no energy. Should an electron suffer an inelastic collision while exiting the sample, energy transfer may occur; electrons that have undergone inelastic collisions are known as ‘secondary electrons’ and do not provide useful analytical information, instead forming a part of the background. Those electrons which do not suffer inelastic collisions are referred to as ‘primary’ electrons and it is these that provide the desired signal.

The X-rays used in photoemission experiments are capable of penetrating to depths orders of magnitude larger than the depths from which electrons can escape, and thus there is little change in the X-ray intensity over the thickness of sample from which primary electrons originate. The sample can therefore be considered as an electron source with approximately fixed intensity, $I_0$, originating from beneath a thin layer, $d$, of the sample which acts as attenuation for the emitted electrons. Beer’s Law, can therefore be used to describe the intensity loss over the depth of the sample (Equation 2.7):

$$I_T = I_0 e^{-d/\lambda \cos \theta}$$

(2.7)

where $I_T$ is the transmitted electron intensity, $\lambda$ is the inelastic-mean-free-path, and $\theta$ is the angle between the path of the electron and the normal to the sample surface. Thus the sample depth which may be probed is primarily dependant on the inelastic-
mean-free-path (IMFP) of the electron within the sample, which is heavily dependent on the kinetic energy of the electron.

The main components of a lab-based XPS kit are shown in Figure 2.11. There must be an X-ray source, sometimes with a monochromator, and an analyser. All of these components, along with the sample itself, must be housed within a chamber at ultrahigh vacuum, to allow emitted electrons to reach the analyser without suffering inelastic collisions.

![A typical lab-based XPS experimental set-up.](image)

The types of X-ray source used for XPS are fundamentally the same as those described for use in XRD, above. However, the anodes used are typically made of aluminium or magnesium, rather than copper, and many modern XPS systems utilise what are known as 'dual anodes', whereby one side of a conical anode is plated with aluminium and the other with magnesium. This type of system allows the sample to be analysed using X-rays of two different energies. Monochromators used in XPS are, again, functionally identical to those of an XRD system, operating via diffraction of the X-ray beam from a quartz crystal. XPS detectors are, however, substantially more complicated than the detectors used in XRD as the energy of the electrons must be measured. Most lab-based XPS systems use what is known as a concentric hemispherical analyser (CHA), consisting of two conductive hemispheres concentric to one another, each at a set potential. Electrons are allowed into the space between the hemispheres through a small slit, and become deflected by the potential between them, such that only electrons of a specific energy will traverse the entire analyser to be detected.
2.6. CHARACTERIZATION OF NANOCRYSTALS AND NANOCRYSTALLINE THIN FILMS

and amplified. In order to resolve the energy of incident electrons, an analyser can either operate with a fixed retardation potential and alter the potential of the hemispheres during a scan or the potential of the hemispheres can remain fixed and the retardation potential can be altered.

Synchrotrons are a type of particle accelerator which can be used to accelerate protons or electrons to extremely high velocities. The use of electron synchrotrons holds many advantages over using conventional XPS systems, such as the much greater X-ray intensities, and the ability to select incident x-ray energy from a broad range via the use of a monochromator. Obviously, however, not every lab can contain a synchrotron, and their use is usually competitively allocated.

XPS analysis was carried out in the Earth Sciences Department in the Williamson building at The University of Manchester. In this work, the X-ray source was generated by a dual aluminium and magnesium anode, and was performed under ultra-high vacuum conditions.

2.6.7 Atomic Force Microscopy, AFM

A schematic diagram showing the typical AFM apparatus is shown in Figure 2.12.

![Schematic diagram showing the typical apparatus involved in an atomic force microscope.](image)

Figure 2.12: Schematic diagram showing the typical apparatus involved in an atomic force microscope.

The AFM comprises a cantilever at the end of which is a sharp tip (probe) which is used to "scan" the specimen surface. The radius of the tip is typically of the order of microns or nanometers depending upon the resolution of the image required. When
the tip is brought into contact with a sample surface, the cantilever becomes deflected and moves (according to Hooke’s law) due to the presence of forces between the tip and the sample. Usually, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. In most atomic force microscopes, a feedback mechanism is implemented to prevent contact between the cantilever tip and the sample surface that would possibly cause damage to the sample. This mechanism adjusts the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a true three-dimensional surface profile. Additionally, samples viewed by AFM do not require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample. While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in ambient air or even a liquid environment. This makes it possible to study biological macromolecules and even living organisms.

In this work, a Veeco Explorer Atomic Force Microscope was used.

2.6.8 Charge Transport Measurements

Charge transport measurements in this study were carried out using a home-built system that comprised a cold finger, which was incorporated into a closed-cycle He cryostat. The film to be analysed can be mounted onto the cold finger and copper wires are attached at to the film using a highly conductive silver paint or "glue". A feed through enabled the copper wires to be attached to a Keithley 2400 Series Source-Measure unit, as the cold finger was closed and sealed off from the atmosphere to allow the measurements to be carried out. Finally, a Lakeshore 325 Temperature Controller was included into the set-up in order that the temperature be accurately monitored and controlled throughout the charge transport measurements. A photograph of the charge
2.6. CHARACTERIZATION OF NANOCRYSTALS AND NANOCRYSTALLINE THIN FILMS

Figure 2.13: Schematic diagram showing the home-built charge transport measurement apparatus.

It was necessary to hold the sample in a vacuum of $10^{-6}$ mbar. In many techniques, pressures between $10^{-3}$ and $10^{-9}$ mbar are required, known as high vacuum, typically to minimise interactions between air and whatever particles are used in the technique (e.g. electrons). To achieve suitable vacuum for charge transport measurements, a standard mechanical rotary pump was used initially. At its most basic, a rotary pump consists of an asymmetric vane immersed in oil, with inlet and outlet ports perpendicular to its axis of rotation. This vane acts to compress incoming gases and sweep them towards the outlet. Rotary pumps are often used to initiate pumping down from atmosphere and often, to reinforce other pumps. Once a suitable vacuum level is reached using the rotary pump, a diffusion pump capable of reaching higher vacuum levels, was then used. A diffusion pump operates via means of diffusion. At the top of a diffusion pump is a throat leading to the chamber to be evacuated. Gas molecules diffuse into this throat, where they are caught by jets of hot oil vapour, sprayed downwards from a set of conical openings on a central chimney. This vapour is then cooled and condensed by cooling coils around the outside of the pump; the oil and any captured gas is thus brought to the base of the pump where the oil is reheated by a heater and the gas is
2.6. CHARACTERIZATION OF NANOCRYSTALS AND NANOCRYSTALLINE THIN FILMS

removed by a backing pump. Diffusion pumps will usually have a 'liquid nitrogen trap' at the top of their throat - a region cooled to extremely low temperatures using liquid nitrogen, in order to prevent hot oil vapour from flowing into the chamber. Diffusion pumps are fairly durable, and can under good conditions be used to pump down from $10^{-2}$ mbar to almost UHV conditions.

The sample was then cooled down to 15K using a closed-cycle He cryostat, a device used to maintain very low temperatures. The closed-cycle cryostat consisted of a chamber through which cold helium vapour was pumped. An external mechanical refrigerator extracted the warmer helium exhaust vapour, which was then cooled and recycled. Closed-cycle cryostats consume a relatively large amount of electrical power, but need not be refilled with helium and can run continuously for an indefinite period. The nanocrystalline film samples in this study were cooled by attaching them to a metallic coldplate inside the vacuum chamber which was in thermal contact with the helium vapour chamber.

Once the sample was sealed inside the vessel, DC measurements were carried out as the vessel temperature was lowered. A voltage was applied via the copper wires and the resulting current was then obtained. The Labview programme enabled the measurements to be both plotted and stored as a filetype that could be imported into many graphical analysis packages to be processed further.
Part III

Metallic Nanocrystals
Chapter 3

Investigating the Influence of Surface Ligands upon Charge Transport in Nanocrystalline Films of Gold

3.1 Introduction

Nanocrystalline solids, made up of inorganic nanocrystals sheathed by organic ligands, are useful building blocks for opto-electronic devices including nanolaser devices and solar cells\textsuperscript{128,129}, chemical\textsuperscript{130,131} and biological\textsuperscript{132} sensors as well as plasmonic devices\textsuperscript{133}. Much of the attraction in these solids is due to the profound changes to electronic, optical and thermodynamic properties accompanying the acquisition of nanoscopic dimensions by the inorganic crystallites\textsuperscript{129,134}. However, our efforts to exploit ensuing benefits are limited by surface ligands that present a strong barrier for movement of charges across nanocrystals solids. Ligands with long hydrocarbon chains commonly present in these solids are particularly effective at stifling charge transport. Exchange with shorter bifunctional crosslinking ligands produces markedly improved conductivity. For example, an eight fold increase in conductivity has been obtained when the chain length is decreased from nine methyl units to three\textsuperscript{100}. Particularly robust and conductive arrays of nanocrystals have been obtained using metal chalcogenide
3.2. RESULTS AND DISCUSSION

complex crosslinkers featuring ions such as $\text{Sn}_2\text{S}_6^{1-}$.

Another paradigm is to employ non-crosslinking ligands with a single tether for better charge transport. Such ligands are potentially compatible with a wider variety of target nanocrystals, easier to synthesize and feature easier exchange chemistry. Yet such ligands are rarely studied as non-crosslinked films are mechanically less stable and reliable results are difficult to obtain. The potency of this method was recently illustrated by Nakanishi et. al. who showed that the photoconductivity of Au nanocrystal films can be switched from normal to inverse by simply changing the end functional groups of single tether surface ligands. Herein, it has been found that that Au nanocrystals grown at the water-toluene interface yield films of sufficient quality to permit what is possibly the first solid state measurement of the effect of substituents on the the charge transport characteristics of nanocrystalline films. Underpinning this study is the growth of Au nanocrystal films using molecular precursors at the water-toluene interface, faithful transfer of the film from the interface to a substrate and labile phosphinyl surface ligands that can be easily replaced with a family of para-substituted thiophenols.

3.2 Results and Discussion

Film Transfer Process

The films of nanocrystals obtained at the interface of water and toluene appeared to be "skin-like", and thin and very elastic. They were easily transferred onto substrates of glass or mica, using a novel transfer process that has recently been adapted. A substrate was held in a vertical orientation (relative to the interface) by attachment to a mechanical dipper. The substrate was made to pierce the film and become completely immersed in the aqueous layer, where it was left for a minute. Transfer of the film to the substrate took place, when the substrate was slowly withdrawn across the interface (Figure 3.1). The rate of transfer could be adjusted by adapting different speeds of substrate withdrawal. However, it was found that different rates of transfer ranging from 0.25 cm/s to 5 cm/s had no discernible effects on the properties of the films produced.
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Figure 3.1: Schematic diagram showing how Au films are transferred onto solid supports.

The dipping cycle could be repeated several times. It was noticed that the film was not transferred to the substrate during the first dip from the toluene layer. As the glass substrate passed through the toluene column, a thin layer of toluene moved along, preventing the adhesion of the films to the substrate. Indeed, when the substrates were rendered hydrophobic, no transfer took place. Making the surface hydrophilic therefore aided the successful transfer of films. It is believed that as the glass substrate was left to "rest" for a minute in the aqueous layer, the glass lost its toluene coating and became more amenable to transfer.

Film Properties

Figure 3.2 is a photograph showing uniform films spread over areas of several square centimetres. The films have been mounted upon mica substrates and are reddish-brown in colour with a metallic sheen. Sputtered electrical contacts of gold can also be seen on the surfaces of the films.

Energy-dispersive X-ray (EDX) analysis carried out upon the films reveal dominant peaks that can be attributed to Au (Figure 3.3). Oxygen, potassium and silicon
3.2. RESULTS AND DISCUSSION

Figure 3.2: Nanocrystalline films of Au on mica substrates. The films were prepared at 50°C over 180 minutes. Evaporated contacts of gold can also be seen on the surfaces of the films. The peaks present in the spectrum are due to those elements being present in the mica substrate.

Figure 3.3: EDX Analysis carried out upon films of nanocrystalline Au mounted onto mica substrates.

The reducing agent employed in the reaction is tetrakishydroxymethylphosphonium chloride (THPC). Previous studies have suggested that, in aqueous solutions, THPC hydrolyses in the presence of NaOH to yield HCHO and also possibly H$_2$\textsuperscript{135–137} (Equations 3.1 and 3.2).
3.2. RESULTS AND DISCUSSION

\[
\text{PCl}(CH_2OH)_4 + NaOH \rightarrow P(CH_2OH)_3 + HCHO + NaCl \quad (3.1)
\]

\[
P(CH_2OH)_3 + NaOH \rightarrow O = P(CH_2OH)_3 + H_2 \quad (3.2)
\]

The nascent formaldehyde and hydrogen are both able to release and reduce the Au(I) ions present in toluene\textsuperscript{138,139}. Other products of the reaction include tetrakishydroxymethylphosphine (THP), triphenylphosphine (TPP) and possibly a small quantity of tetrakishydroxymethylphosphine oxide (THPO), which are all capable of binding and stabilizing Au nanocrystals\textsuperscript{138,139}. The continued growth of reduced ions into large crystallites is prevented by the capping abilities of the phosphine based ligands and nanocrystals of Au(0) therefore result. The nanocrystals obtained possess high chemical potential and become adsorbed at the interface, leading to the deposition of a thin film. Previous studies suggest that the room temperature adsorption energies of such nanoparticles at the water-oil interface are of the order of a few millielectron volts\textsuperscript{140,141}. Nanocrystals with irregular surface structures consisting of labile ligands lack robust interparticle repulsion and would normally be incapable of forming extended structures. In the present case, a superstructure is formed at the interface of water and toluene, actively aided by the medium. The assembly is initiated by adsorption of the suitably capped nanocrystals at the liquid-liquid interface. The initial adlayer reduces interfacial tension and aids the growth of multilayered films at the interface of water and toluene. It should be emphasized that it is necessary to adopt the facile transfer process described in order to relocate the interfacial superstructure onto solid substrates with minimal disruption and obtain films with uniform electronic properties.

As previously stated, the Au nanocrystals in the films are capped with triphenylphosphine, tris(hydroxymethyl)phosphine and other phosphine based ligands\textsuperscript{87,142–144}, the presence of which has been confirmed by X-ray photoelectron spectroscopy\textsuperscript{88} (Figure 3.4).

The X-ray photoelectron spectrum taken of Au films mounted upon mica sub-
3.2. RESULTS AND DISCUSSION

Figure 3.4: XPS spectra of the as prepared Au films. (a) shows the entire spectrum and (b) is a zoomed in image of the Au 4f peak.

strates is representative of contaminated thick gold coating and it should be noted that no mica substrate peaks are present, thus showing that the Au coating is complete and thicker than 60 Angstroms.

The X-ray photoelectron spectrum allowed the elemental compositions present to be determined. Atomic Concentrations were detected as follows: O(1s) - 8.206%, C(1s) - 44.685%, Au(4f) - 43.666% and P(2p) - 3.443%.

The very intense Au(4f) peak at 84.15 eV is compatible with those peaks in database that correspond to metallic Au$^0$ at 83.8 eV.$^{143}$ The results on the structure and composition of these films are broadly in agreement with previous studies on Au nanocrystal layers grown at the water-toluene interface.$^{87,142-144}$ There are two rather broad 4f$_{7/2}$ peaks at 84.0 and 88.1 eV (Figure 3.4), corresponding to the binding energy ranges of Au$^0$ and Au$^+$ respectively. This indicates the coexistence of both Au$^0$ and Au$^+$. The broadened nature of the Au 4f$_{7/2}$ peak likely reflects the presence of a distribution of Au species with varying local coordination, including surface and defect species in the nanoparticulate sample. Moreover, the narrow metallic peak component at 83.8 eV can be identified as the fully coordinated bulk-like Au sites in the core of the nanoparticles, in line with a very similar interpretation of XPS data for PPh$_3$ capped
3.2. RESULTS AND DISCUSSION

Au\textsubscript{55} clusters\textsuperscript{145,146}.

The P 2p responses are centered at a binding energy of approximately 131.7 eV, which is within the binding range previously reported for the P 2p emission from PPh\textsubscript{3} ligands in Au(PPh\textsubscript{3})Cl and other organometallic compounds\textsuperscript{147,148}.

SEM images (Figure 3.5) reveal that the nanocrystalline films produced at 50°C and over a time period of 180 min are uniform and continuous, spanning many millimetres. The films obtained after 180 minutes consist of around 10 layers of nanoparticles and are about 100 nm thick.

![Figure 3.5: Scanning electron microscopic images of Au nanocrystalline films produced at 50°C over 180 minutes](image)

Folds (a) and cracks (b) are seen in the film, possibly as a result of the transfer from the interface to the substrate. The resulting nanocrystalline films have a hierarchical structure, with spherical nanocrystals (diameter \(\sim\) 10 nm) aggregating to form larger clusters (\(\sim\) 70 nm) that coalesce to produce a dense layer, resembling a bunch of grapes. Higher-resolution SEM images reveal irregular clusters with diameters of \(\sim\) 70 nm. These clusters can be resolved by atomic force microscopy (Figures 3.6 and 3.7) to be aggregates of spherical particulates. The AFM images beautifully illustrate the resemblance to a "bunch of grapes".

Transfer of the films (obtained over the standard growth period of 180 minutes) directly from the water-toluene interface onto holey carbon grids for analysis by TEM was not feasible. Films obtained over 180 minutes were found to be too thick to allow transmission of the electron beam through the sample and analysis could not take.
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Figure 3.6: AFM tapping mode image of Au films made at 50°C and over 180 mins. The image clearly shows clusters of Au particles. The resolution is 1.5µ x 1.5µ.

Figure 3.7: AFM tapping mode images of AU films made at 50°C and over 180 mins. The films are shown to comprise irregular aggregates of individual Au nanocrystals. The resolution in (a) is 1 mm x 1 mm and in (b) resolution is 250nm x 250 nm.

At shorter growth times (45 minutes), thinner (and more fragile) films suitable for direct imaging by TEM were obtained and the images revealed a dense monolayer of nanocrystals with uniform separation distance.

Transmission electron microscopic (TEM) images on dispersions of Au nanocrystals, created by ultrasonically agitating the films, reveal nanocrystals with diameters of around 10 nm (Figure 3.8). The tendency of the Au nanocrystals to aggregate forming rafts with uniform interparticle spacing is apparent in the image.

In films produced interfacially, the diameters of the nanocrystals are not very uniform, nor is the structural order comparable to self-assembled arrays. Nevertheless, it is
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Figure 3.8: TEM images showing aggregation of spherical Au nanocrystals to form clusters. The Au film was formed at the interface at 50°C for 180 minutes and was transferred onto a glass substrate. This was then added to toluene and sonicated for 5 minutes to disperse the nanocrystals. One drop of this was applied to a holey TEM grid and analysed.

It can therefore be concluded that the films deposited at the interface consist of large microscopic spheroidal aggregates of Au nanocrystals. Similar mesoscalar structures with hierarchy have been observed in films of Bi$_2$S$_3$, Cd(OH)$_2$ and Pd grown at the water-toluene interface, however, at present, there is insufficient understanding of the factors that cause such assembly.

The structure of the films was investigated using X-Ray diffraction (Figure 3.9). It revealed a pattern typical of Au albeit with slightly broader peaks that is characteristic of nanocrystals. A degree of orientation along (111) is apparent from the pronounced intensity of the peak at 38.1 degrees relative to the others. The four most intense peaks
at $2\theta = 38.19^\circ$, $44.93^\circ$, $64.58^\circ$ and $77.55^\circ$ in the XRD pattern can be attributed to (111), (200), (220) and (311) peaks of cubic Au (JCPDS 00-004-0784).

Figure 3.9: Powder X-Ray Diffraction Pattern for Au films made at 50$^\circ$C over 180 mins. The broad peaks are characteristic of nanocrystalline materials and the high intensity Au(111) peak suggests there is a small degree of orientation along the (111) plane in the gold film.

The broadening of X-ray diffraction peaks provides a rough estimate of crystallite size through analysis with the Debye-Scherrer Equation 3.3:

$$\text{Size}_{\text{crystallite}} = \frac{k \lambda}{\delta \cos \theta}$$

where $\lambda$ is the wavelength of the X-ray, $\theta$ is the Bragg angle, $\delta$ is the full width at half maximum of the diffraction peak, and $k$ is a constant and taken as 0.9. The crystallite diameters calculated from the (111) reflection are 15 nm and those calculated from the (200) peak are 7.8 nm, which indicates that the as-prepared interfacial deposits are nanocrystalline, however they may be polydisperse. The value of 7.8 nm correlates well with the 10 nm diameters for the spherical particles that were estimated using
3.2. RESULTS AND DISCUSSION

TEM. However, the different calculated lengths obtained from the (111) and (200) peaks could also suggest there is elongation of the nanocrystals along the (111) crystal plane, meaning that the Au nanocrystals are adopting a rod-shaped morphology.

Figure 3.10 shows the absorption spectrum of Au nanocrystalline films prepared over 180 minutes at 50°C. The plasmon resonance band of the pristine Au nanocrystalline films is centered around 705 nm. This value is significantly red shifted when compared with the plasmon band of isolated nanocrystals in solutions (around 530 nm) with comparable dimensions. Peak shifts into the red end of the spectrum are indicative of increased interactions between particles. Nanocrystals that are self assembled into thin films become coupled together, allowing overlapping of their individual metallic wavefunctions and a "superposition" or broadening and shifting of the collective plasmon band.

Figure 3.10: The absorption spectrum of Au nanocrystalline films mounted upon glass substrates.

The conductivity of the Au films were then measured. Measurements were car-
ried out upon Au films obtained from the same beaker, and that had room tempera-
ture electrical resistance values (obtained using a multimeter) that were within 10% of eachother. The conductivity of the interfacially deposited Au nanocrystalline films shows clear non-metallic behaviour with a negative temperature co-efficient of resistance throughout (Figure 3.11). Such behaviour is typical in films consisting of islands of metal nanocrystal interspersed by long to medium length organic ligands96,100,152.

Figure 3.11: Plot showing the variation of conductivity ($\sigma$) with temperature for pristine Au nanocrystalline films.

Overall, the conductivity decreases by around 10% as the films are cooled from room temperature to 15 K. The conductivity ($\sigma$) can be modeled, following a model of activated hopping proposed by Neugebauer and Webb153, according to which,

$$\sigma \propto e^{-2\delta \beta} e^{-E_a/kT}$$  \hspace{1cm} (3.4)

Here, $\delta$ is the separation between the nanocrystals; $\beta$, the constant associated with tunneling between the nanocrystals separated by a dielectric medium; $E_a$, the activation energy for hopping of electrons between nanocrystals. For nanocrystals with a defined organic surface layer, $\delta$ and $\beta$, maybe assumed to be constant at various temperatures.
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(neglecting thermal expansion) giving:

\[
\sigma = A e^{-E_a/kT}
\]  \hspace{1cm} (3.5)

The activation energy is given by:

\[
E_a = \frac{1}{4\pi \epsilon_0 \epsilon_r} \frac{e^2}{r}
\]  \hspace{1cm} (3.6)

Where, \(\epsilon_0\) is the vacuum permittivity, \(\epsilon_r\) is the dielectric constant of the medium surrounding the nanocrystals and \(r\), the radius of the nanocrystals. The activation energy has also been defined via Coulomb energy expression\(^{101}\) as well as more sophisticated formulations based on Marcus’ theory\(^{154}\). Regardless of the model used for \(E_a\), substituents placed onto the capping ligands that surround the Au nanocrystals can be expected to affect both \(E_a\) and \(A\) in Equation 3.5.

Analysis of transport data reveals that four distinct regimes of conductivity are present in the Au films. The transitions at which these regimes change are centered around temperatures of 50 K, 100 K, and 200 K and within each of these domains, plots of \(\ln \sigma\) vs \(1/T\) (Figure 3.12) are linear suggesting that the classical Arrhenius type activated hopping mechanism defined in Equation 3.5 adequately describes the transport characteristics right across the temperature range studied.

The equations of the lines fitted to each of the charge transport domains (as in Figure 3.12) have been obtained, which have allowed activation energy values and pre-exponential parameters associated with charge transport within that particular domain to be determined. According to the Arrhenius-type expression in Equation 3.7 a plot of \(\ln \sigma\) vs \(1/T\) will give a straight line, the gradient of which will relate to the activation energy for charge transport with the y-intercept relating to the pre-exponential term, \(\ln G_0\).

\[
\ln \sigma = \left( \frac{-E_a}{k_B} \right) \left( \frac{1}{T} \right) + \ln G_0
\]  \hspace{1cm} (3.7)

Figure 3.13 shows the activation energies and pre-exponential terms associated with charge transport within the Au film, for each of the four temperature domains identified.
3.2. RESULTS AND DISCUSSION

Figure 3.12: Plot of $\ln \sigma$ vs $1/T$ for pristine Au nanocrystalline films. Straight line fits to two of the conductivity regimes are shown.

In each of the regimes, a different mechanism of conductivity operates in the films. Typically, as the temperature is lowered, the activation energy falls in steps reaching values less than 10 meV at the lowest temperature regime. At the same time, there is a small decrease in the pre-exponential term, perhaps signalling a change in the conduction mechanism within the film. However, these changes are extremely minor, and activated hopping continues to persist even at the low temperatures. Other studies on disordered films of metal nanocrystals report a switch to variable range hopping or tunneling mode of conductivity at low temperatures since cooling causes localization of charge carriers\textsuperscript{155}. Herein, larger Au nanocrystals, strong interparticle coupling as well as regular interparticle spacing effectively overcome the localization effect.

In addition to the linearity associated with the plots of $\ln \sigma$ vs $1/T$ and their conformation to the Arrhenius-type activated hopping mechanism, \textit{linear} (ohmic) I-V curves were obtained at various temperatures, reinforcing the applicability of the activated
3.2. RESULTS AND DISCUSSION

Figure 3.13: Plot of $\ln \sigma$ vs $1/T$ for pristine Au nanocrystalline films showing 4 temperature domains. Equations for lines fitted to each domain are shown. Activation energies (in eV) and pre-exponential terms (a dimensionless scaling factor) associated with charge transport have also been determined.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$m$</th>
<th>$c$</th>
<th>$E_a$ (eV)</th>
<th>$\sigma_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298-200K</td>
<td>-31.645</td>
<td>8.27</td>
<td>$2.72 \times 10^{-3}$</td>
<td>3892</td>
</tr>
<tr>
<td>199-100K</td>
<td>-13.164</td>
<td>8.17</td>
<td>$1.13 \times 10^{-3}$</td>
<td>3544</td>
</tr>
<tr>
<td>99-50K</td>
<td>-1.6207</td>
<td>8.08</td>
<td>$1.40 \times 10^{-4}$</td>
<td>3229</td>
</tr>
<tr>
<td>49-13K</td>
<td>-0.017</td>
<td>8.05</td>
<td>$1.46 \times 10^{-6}$</td>
<td>3136</td>
</tr>
</tbody>
</table>

A batch of Au films were also prepared at 40$^\circ$C to see how the charge transport properties were affected (Figure 3.15). Both films still possess a negative temperature coefficient of resistance that is characteristic of semiconductors. However, the room temperature conductivity of films produced at 50$^\circ$C is much higher ($3500 \text{ Ohms}^{-1}\text{m}^{-1}$) than those produced at 40$^\circ$C ($120 \text{ Ohms}^{-1}\text{m}^{-1}$). Reactions performed at 40$^\circ$C give rise to nanocrystals with smaller diameters, and as the temperature is raised those diameters increase. Smaller nanocrystals will have much larger charging energies, and nanocrystals interact with each other to a lesser extent, thus making them less amenable to charge transport. This can account for the thirty-fold decrease in conductivity when the reaction is performed at lower temperatures.

The results described above mirror those reported by Rao and co-workers$^{144}$, who
produced ultrathin nanocrystalline films of gold at the water-toluene interface and found that through altering the reaction conditions, the particle sizes produced and therefore the electronic properties of the films could be carefully controlled. Films produced at 30°C had high resistances of MΩ magnitude, and behaved as a semiconductor. Remarkably, those films produced at 70°C gave sheet resistances of a few Ωs magnitude and metallic behaviour was observed, i.e. a size induced metal-insulator transition had occurred.

Influencing Charge Transport using Aromatic Thiols

Soaking of the as obtained films in ethanolic solutions of thiophenol and its associated para substituted derivatives (Figure 3.16) results in the simple and clean replacement of phosphinyl ligands with the arylthiols.

SEM and AFM images of Au films, prepared at 50°C over 180 mins, that have had their phosphinyl ligands displaced with toluenethiol, reveal no discernable changes
3.2. RESULTS AND DISCUSSION

Figure 3.15: Plot showing the conductivities of films of Au films prepared at both 40°C and 50°C versus temperature.

Figure 3.16: Range of aromatic thiols used in the ligand displacement of phosphinyl ligands.

in the structure of the films following the replacement of surface ligands (Figure 3.17) The hierarchy within the Au film and the tendency of the nanocrystals to adopt a "bunch of grapes" type structure is especially noticeable in the AFM image.

However, the surface structure has been probed more closely. X-ray photoelectron spectroscopic measurements carried out on Au films before and after thiol derivatisation indicate that the P(2p) peak present initially vanishes, and is replaced by S(2p) features (Figures 3.18 and 3.19).

Percentage coverages of those elements detected in tolenethiol coated Au films were calculated as follows: O(1s) - 9.350%, C(1s) - 47.962%, K(2p) - 0.489%, S(2p) -
3.2. RESULTS AND DISCUSSION

Figure 3.17: (a) and (b) are SEM images of Au films prepared at 50°C over 180 minutes. The films have had their phosphinyl ligands displaced with toluenethiol. (c) AFM image of the same Au films prepared at 50°C over 180 minutes. The image resolution is 560nm x 560 nm.

3.142% and Au(4f) - 39.057%. Coverages in nitrothiophenol coated films were: Na(1s) - 1.707%, O(1s) - 16.226%, N(1s) - 6.147%, C(1s) - 55.273%, S(2p) - 1.478% and Au(4f) - 19.169%.

There is no trace of phosphorus upon the surface of either thiol-derivatised film, proving that clean replacement of the phosphinyl ligands has taken place. In both spectra, peaks corresponding to S and C have increased whilst the peak corresponding to Au has reduced, indicating that a thin sulphur-containing organic coating is now present, which was not present in those spectra for uncoated samples (Figure 3.4). Importantly, the presence of a peak corresponding to N(1s) in the nitrothiophenol coated sample should also be noted.

The number of thiolate molecules present upon the surface of the Au nanocluster can be predicted using XPS data. Studies involving metallic nanocrystals have shown that Au nanoclusters adopt an icosahedral structure with five-fold symmetry.\textsuperscript{156–158}

The total number of atoms in a perfect Au icosahedron composed of number of shells, K, corresponds to:

\[
n = \frac{10}{3}K^3 - 5K^2 + \frac{11}{3}K - 1
\]

When the total number of atoms present in the gold cluster has been calculated, both the diameters (D) and the number of atoms present at the surface of the clusters can be
3.2. RESULTS AND DISCUSSION

Figure 3.18: X-ray photoelectron spectra obtained from films of Au nanocrystals that have undergone ligand displacement with both (a) toluenethiol and (b) nitrothiophenol.

determined and this has been shown in Table 3.1.

TEM images indicated that nanocrystals formed in this study are of approximately 10nm diameter. Using Table 3.1, it can be approximated that 3242 (15%) atoms are on the surface of the Au clusters.

In the arylthiol capped films, the Au:S ratios obtained from XPS data indicate that there are between 0.27 - 0.31 thiolate species per surface Au atom. This ratio is lower that what is typically seen on curved surfaces, where saturation coverage is expected to yield 0.40 thiolate species per Au atom for spherical nanocrystals with 10 nm diameter. It is believed that thiophenol forms a slightly disordered surface layer, with less than the expected saturation coverage. The propensity of thiophenol and it derivatives to form such a monolayer on flat Au substrates has been previously reported\textsuperscript{159}.

UV-Visible spectroscopy has also been used to monitor the displacement of phosphinyl ligands by the aromatic thiol moiety. The plasmon resonance band of the untreated Au nanocrystal films is centered around 705 nm\textsuperscript{144}. Upon ligand exchange with aromatic thiol, the intensity and position of the peak exhibited clear substituent effects following ligand exchange (Figure 3.20).

Exchange of the phosphinyl moiety with 4-nitrothiophenol results in a red shift of
3.2. RESULTS AND DISCUSSION

Figure 3.19: Superimposed segments of X-ray photoelectron spectra showing (a) the absence of the S(2p) peak in untreated films of Au, (b) the presence of the S(2p) peak in Au films treated with tolenethiol and (c) the presence of S(2p) in Au films treated with nitrothiophenol.

the peak from 706 nm to 731 nm, a shift of 25 nm. In addition, small changes to peak width and intensity are seen. As previously mentioned, shifts towards the red end of the spectrum are indicative of increased interaction between the particles (or enhanced conductivity). In contrast, 4-methoxythiophenol and other thiophenols strongly dampen the peak, causing about 50% intensity loss. The dampening of the peak intensity is possibly due to a reduction in the number of carriers forming the plasmon.

Striking changes to the absolute conductivity of the films is seen when different substituents are introduced onto the aromatic thiol capping ligands (Figure 3.21), which has indeed been mirrored in the aforementioned electronic absorption spectra.

Perhaps surprisingly, thiophenols bearing electron donating substituents (methyl
### 3.2. RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th>K</th>
<th>Total No. of Atoms</th>
<th>D (nm)</th>
<th>No. of Surface Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>0.8</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
<td>1.4</td>
<td>42</td>
</tr>
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<td>4</td>
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<td>2.0</td>
<td>92</td>
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<tr>
<td>5</td>
<td>309</td>
<td>2.4</td>
<td>162</td>
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<tr>
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<tr>
<td>22</td>
<td>33153</td>
<td>11.7</td>
<td>4412</td>
</tr>
</tbody>
</table>

Table 3.1: Table showing the total number of atoms present in an Au cluster with K number of shells, calculated using Equation 3.8. The diameter, D, of the clusters and the total number of particles present at the surface of the cluster has also been calculated.

Figure 3.20: Absorption spectrum of Au nanocrystal films with different surface ligands (indicated in the legend). The absorbance has been normalized to that of a pristine film.

and methoxy in the para position) cause large decreases to conductivity, relative to thiophenol capped films. For example, 4-methoxythiophenol reduces the room temperature conductivity from $10000 \, \Omega^{-1}\text{m}^{-1}$ to $100 \, \Omega^{-1}\text{m}^{-1}$, while the electron withdrawing sub-
3.2. RESULTS AND DISCUSSION

Figure 3.21: Substituent effects on the conductivity of films of Au nanocrystals. Functional groups at the para position of the thiophenol coating are shown. The as prepared films containing phosphinyl ligands are labelled PPh$_3$.

A substituent (nitro) causes a sizable increase of conductivity (from 10000 Ω$^{-1}$m$^{-1}$ to 75000 Ω$^{-1}$m$^{-1}$). In all, different substituents produce conductivity changes spanning three orders of magnitude. Bromo and chloro substituted thiophenols act akin to electron donating groups rather than the withdrawing substituents and reduce $\sigma$.

Remarkably, the temperature profile of different films, which is highly sensitive to changes in morphology and structure$^{129}$ is identical and all films exhibit a negative temperature coefficient of resistance (Figure 3.22b). These films seem to have a robust structure that is not particularly affected by the group of thiols employed in this study. I-V curves (Figure 3.22a) obtained from films of 4-methyl-thiophenol coated Au nanocrystals at 250 K and 10 K are also linear (ohmic) suggesting that the mechanism for charge transport is that of activated hopping.
3.2. RESULTS AND DISCUSSION

![Graph](image)

Figure 3.22: (a) I-V curves obtained from films of 4-methyl-thiophenol coated Au nanocrystals at 250 K and 10 K. (b) Plot showing the conductivity of thiophenol capped films versus temperature. The temperature coefficient of resistance is negative.

**Interpretation**

Each aromatic thiol used in this study possesses a unique Hammett para-substituent constant, which enables the substituents to be ranked in terms of their electron-withdrawing and electron-donating capabilities.

The Hammett equation describes the relationship between the rates and equilibrium constants associated with a reaction using two parameters: a substituent constant and a reaction constant. For a set of reactions wherein aromatic reactants differ from each other solely in terms of the type of substituent present, the change in the free energy of activation is proportional to the change in Gibbs free energy. The basic Hammett equation, for a series of reactions involving substituted benzene derivatives, is:

\[
\log \frac{k}{k_0} = \sigma \rho
\]  

which relates the reaction rate, \(k\), for a given reaction with substituent, \(R\), and the reference rate constant, \(k_0\) (when \(R\) is a hydrogen atom) to the substituent constant \(\sigma\) and the reaction constant \(\rho\). A Hammett plot of \((k/k_0)\) versus a range of substituent constants should give a straight line. For the context of this study, the equilibrium reaction in question will be that of charge transport. \(\rho\) is a *sensitivity constant* which describes the
susceptibility of charge transport to substituents, compared to the ionization of thiophenol. The value of $\rho$ gives information on the reaction and the associated mechanisms. If the value of:

- $\rho > 1$, charge transport is more sensitive to substituents than thiophenol and negative charge is built during the reaction (or positive charge is lost).
- $0 < \rho < 1$, the reaction is less sensitive to substituents than thiophenol and negative charge is built (or positive charge is lost).
- $\rho = 0$, no sensitivity to substituents, and no charge is built or lost.
- $\rho < 0$, the reaction builds positive charge (or loses negative charge).

These values can be exploited to elucidate the mechanism of a reaction. As the value of $\rho$ is related to the charge during the rate determining step, mechanisms can be devised based on this information.

Within a series of aromatic molecules containing substituents, two main kinds of static electrical influences predominate, and depending upon the nature of the substituent, will influence in varying proportions:

- resonance (mesomeric) effects: the delocalization of charge within a molecule.

- inductive effects: the electrical influence of a group which is transmitted primarily by polarization of the bonding electrons from one atom to the next.

When the series of thiophenol ligands in this study are attached to the Au films, their effect upon conductivity can be accounted for using the dual substituent parameter equation, a modification of the Hammett equation, according to which:

$$ \log k = \rho_I \sigma_I + \rho_R \sigma_R + h \quad (3.10) $$

where, $k$ is the rate constant (replaced here by conductivity); $\sigma$ denotes the substituent constants corresponding to the inductive($\sigma_I$) and resonance($\sigma_R$) effects of the ligand; $\rho$
3.2. RESULTS AND DISCUSSION

is the corresponding reaction constant and h is a constant. Electrostatic characteristics of a molecule such as dipole moment are captured by \( \sigma_I \) term, while \( \sigma_R \) represents the ability of a molecule to delocalize charges. Conductivity values sampled at 250K, 150K, 75K and 25K roughly corresponding to the mid points of the four regimes of conductivity were fitted to Equation 3.10 using a least squares analysis to obtain the reaction constants and h. In each case correlations \( \geq 0.94 \) were obtained (Figure 3.23).

![Figure 3.23](image)

Figure 3.23: Plot showing the correlation of the substituent characteristics to conductivity of the films. Here, \( \sigma_w = \rho_I \sigma_I + \rho_R \sigma_R \).

Significantly, the \( \rho \) values are positive suggesting that reaction centre is negatively charged in the transition state of the rate determining step. If one assumes that electrons are charge carriers and charge transport occurs via a series of redox reactions, the oxidation of negatively charged Au nanocrystals is the slowest step. These observations strongly contrast those from previous studies that have regularly yielded (the equivalent of) negative \( \rho \) values.

Typical pragmatic interpretations of the results obtained would have suggested that the dipole moments associated with the sequence of aromatic thiols would be responsible for any conductivity changes of the Au films. However, the high values for the ratio \( \rho_R/\rho_I \) suggests that the ligands couple by resonance to the nanocrystals, and
3.2. RESULTS AND DISCUSSION

not through dipolar interactions. It is also important to note that the charge transport findings cannot be easily attributed to changes in the interparticle separation distances, as SEM and AFM studies have indicated that the structure of the Au film and the Au-Au interparticle separation distances are not affected when exposed to each of the thiophenols. Therefore, the chemistry associated with the ligand coupling and with the charge transport process as a whole has been interpreted using the elegant concept of resonance.

A classic test that confirms the nature of interactions is to move the substituents to the meta position, from which overlap by resonance is not possible. In the present case, the halo substituted thiophenols are expected to increase rather than decrease conductivity when moved to the meta position. It was found that this was indeed the case (Figure 3.24).

![Figure 3.24: Plot showing the changes to the transport characteristics of nanocrystalline films derivatized with para- and meta- chloro substituted thiophenols. The substituents are indicated next to the data.](image)

The conductivity of 3-chlorothiophenol derivatized films increases (at room temperature) to $2660 \Omega^{-1}\text{m}^{-1}$ in contrast to the 4-chlorothiophenol derivatized films where conductivity falls to $150 \Omega^{-1}\text{m}^{-1}$. This vividly illustrates that resonance effects indeed bring about the observed conductivity changes.
3.2. RESULTS AND DISCUSSION

In simple terms, electron withdrawing substituents (such as nitro) provide an additional area for delocalization for the Au species in the transition state, thus aiding charge transport. Meanwhile, electron donating nanocrystals (e.g. those capped with methoxythiophenol) actually end up localizing the charge and hindering charge flow. Leaking of electron density from Au surfaces indicated in theoretical calculations perhaps underpins this substituent effect. Intuitively, it is difficult to visualize through bond resonance between metallic Au nanocrystals and substituted thiophenols, but the evidence in terms of the effect of halogenated substituents, the shifts in the electronic spectrum and correlation to dual substituent parameter equation seems unambiguous.

Our interpretation on the basis of resonance is in contrast to Vilan and Cahen\textsuperscript{164}, who found that the barrier for charge transport to occur was directly dependent on the dipoles of molecule that decorated the surfaces of 'model' Au films. They show qualitatively that the organic monolayer present on films increases the current if the dipole is positive (CF$_3$ and CN substituents), and decreases the current for negative dipoles (CH$_3$ and OCH$_3$). These pronounced effects of molecular control over the transport barrier were attributed to the action of electrostatic effects, which are macroscopic in nature. They explained that small defects would be statically screened by their surroundings and would not dominate the net transport, as happens when molecules are directly involved in the transport.

Computational methods, based on previous reports\textsuperscript{165} were used to determine the dipole moments for the thiophenols used. The possible structural isomers used in the calculations have been shown in Figure 3.25 and the calculated dipole moments have been shown in Table 3.2.

Cahen and co-workers, found that molecules with dipoles of greatest magnitude (such as nitrothiophenol in Table 3.2) cause films of nanocrystals to be more amenable to charge transport, and their findings correlate well with the values calculated in the table. However, no such correlation has been found with the Au films synthesised herein.

Similarly, Witte and co-workers\textsuperscript{166} used electronic structure calculations to pre-
3.2. RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th>Thiophenol</th>
<th>Isomer/Structure</th>
<th>Relative Energy</th>
<th>Dipole Moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>0.00</td>
<td>1.06</td>
</tr>
<tr>
<td>II</td>
<td>i</td>
<td>0.00</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>ii</td>
<td>+0.01</td>
<td>2.24</td>
</tr>
<tr>
<td>III</td>
<td>i</td>
<td>+0.23</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>ii</td>
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</tr>
<tr>
<td></td>
<td>iii</td>
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</tr>
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<td></td>
<td>iv</td>
<td>+0.02</td>
<td>2.29</td>
</tr>
<tr>
<td>IV</td>
<td>i</td>
<td>+0.94</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>ii</td>
<td>+0.97</td>
<td>2.42</td>
</tr>
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</tr>
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<td>-</td>
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</tr>
<tr>
<td>VII</td>
<td>36</td>
<td>-</td>
<td>1.33</td>
</tr>
<tr>
<td>VIII</td>
<td>-</td>
<td>-</td>
<td>4.77</td>
</tr>
</tbody>
</table>

Table 3.2: Calculated relative energies (kcal mol\(^{-1}\)) and dipole moments (Debye) of the thiophenols used in this study.

dict that physical dipolar interactions between molecules and an Au surface lead to exchange repulsion and a subsequent lowering of the work function of the Au. They found that the dipolar interactions completely dominated any chemical (resonance) effects.

However, Bredas and co-workers have, on the basis of detailed calculations, proposed two conditions for the observation of strong molecular effects (including resonance effects) on Au surfaces: a surface monolayer with high rather than saturation coverage and the presence of substituents no farther than the first phenyl ring.\(^{167}\) The experiments described herein satisfy both of these conditions. Clearly, more careful attention has to be paid to molecular topology for future studies on substituent effects on electronic properties of metal and semiconductor surfaces.

Previously, Murray and co-workers have investigated substituent effects on the ligand exchange rate as well as redox properties of well-defined Au nanocrystals with Au\(_{38}\) cores.\(^{163}\) These pioneering investigations found direct Hammett correlations to the substituent effects with inductive effects dominating the nanocrystalligand interactions. Similar results were obtained in the case of Au\(_{25}\) core nanocrystals.\(^{163}\) It appears that the larger metallic Au nanocrystals studied herein prefer to interact in a contrasting
3.3 Amine Sensors

The Au films were used by collaborators in Sheffield to construct a working amine sensing device. The sensor was constructed using a square wave generator circuit and the sample comprising a film of Au nanocrystals was essentially used as a variable resistor, R. The response to the amine vapour was measured as a frequency that was inversely proportional to R. The device exhibited a specific response to amine vapours (Figure 3.26).

At an exposure fraction of 0.5 (141 ppm octylamine) for 500s, a frequency change
3.4 Conclusion

In summary, films of Au nanocrystals capped with thiophenols exhibit strong substituent effects. The conductivity of the films can be tuned in the range of 100 - 75000 \( \Omega^{-1} \text{m}^{-1} \) by varying the nature of substituents at the para position of the thiophenol capping ligands. Surprisingly, analysis suggests that resonance effects dominate the interaction between nanocrystals and ligands. This conclusion is generic and widely

Figure 3.26: Response of the amine sensor to amine vapours of different concentrations. The change in resistance is converted to a response in the frequency domain, as outlined in the experimental section. The value 1.0 on the exposure fraction corresponds to a concentration of 282 ppm of octylamine. Black line, frequency versus time; grey line, concentration versus time.

of 0.11 kHz was seen. A similar change was obtained when the concentration was doubled and the exposure time halved. With an exposure of 99 ppm of octylamine for 250 s, a frequency change of 0.04 kHz was observed. Thus, the response of the device is directly proportional to the concentration of the amine. It is believed that the response is due to adsorption of amine molecules to the surface of the nanocrystals that make up the sensor, thus changing their electronic properties.

3.4 Conclusion

In summary, films of Au nanocrystals capped with thiophenols exhibit strong substituent effects. The conductivity of the films can be tuned in the range of 100 - 75000 \( \Omega^{-1} \text{m}^{-1} \) by varying the nature of substituents at the para position of the thiophenol capping ligands. Surprisingly, analysis suggests that resonance effects dominate the interaction between nanocrystals and ligands. This conclusion is generic and widely
3.4. CONCLUSION

applicable across the whole body of nanocrystal solids. For example, it would be of interest to see if this interaction is dependent on the diameters of the Au nanocrystals. Future work has been envisaged to test this hypothesis more extensively. Further, the nanocrystalline films studied herein provide a robust set of nanoscopic electrodes suited for studies of the properties of molecules. The films of Au nanocrystals synthesised in this chapter are directly usable as ingredients of functional devices and this has been shown through the construction of a working amine sensor.
Chapter 4

Deposition Of Ag and Ag-Au Nanocrystalline Films With Tunable Conductivity At The Water-Toluene Interface

4.1 Introduction

Films of Ag and Au nanocrystals possess unique optical and electronic properties due to the reduced dimensions of the crystallites and the dominance of surface plasmons. A number of potential applications have been identified for films of metal nanocrystals. Strong local electrical fields present in nanocrystalline Ag films make them ideal substrates for surface enhanced Raman and related spectroscopic techniques. In order to be harnessed in different applications, uniform nanocrystalline films that are spread over large areas and with strongly interacting nanocrystals acting as robust charge transport networks are desirable. The quest for such films dominates current research in this area. Herein, highly uniform films of Ag and Ag-Au nanocrystals covering areas of several square centimeters have been obtained at the interface
of water and toluene by reducing solutions of chlorotris(triphenylphosphine)silver(I), Ag(PPh$_3$)$_3$Cl, and chlorotriphenylphosphine gold(I), Au(PPh$_3$)Cl, in toluene with aqueous tetrakishydroxymethylphosphonium chloride.

Previously, thin Ag films have been obtained at the aqueous-organic interface by reducing an adduct of AgNO$_3$ and p-methoxybenzoic acid in dichloromethane with aqueous hydrazine, in the presence of different surfactants.$^{173}$ Both Efrima and Rao have reported the synthesis and chemical properties of silver films that have been confined within two immiscible liquids.$^{174,175}$ However, the charge transport characteristics of these films are unknown.

Within this chapter, it is shown that interfacial deposits of Ag nanocrystals with highly reproducible charge transport characteristics can be obtained and that the low sheet resistances of the films are indicative of robust coupling between the constituent nanocrystals. Furthermore, it is shown that the transport characteristics can be systematically varied from metallic to non-metallic behavior by alloying the Ag nanocrystals with Au.

### 4.2 Results and Discussion

The interfacial reaction was carried out using those parameters ascertained in Chapter 3, for the production of Au nanocrystalline films. The novel transfer process$^{88}$ also described in Chapter 3 was used to transfer the Ag film from interface to substrate. The reaction carried out at 50°C and over 180 minutes yielded thin films of Ag nanocrystals at the interface that were silvery-yellow with a lustrous metallic grey sheen (Figure 4.1).

The mechanism of action of the reducing agent, THPC, has previously been explained in Chapter 3. The hydrolysis of THPC in the presence of NaOH is thought to yield both HCHO and H$_2$$^{135–137}$ (Equations 4.1 and 4.2), which are both able to release and reduce the Ag(I) ions present in toluene.$^{138,139}$
4.2. RESULTS AND DISCUSSION

Figure 4.1: Photo showing Ag films on glass substrates. The photo on the left shows the metallic silvery grey sheen and the photo on the right shows the reflective, "mirror-like" nature of the films.

\[ PCl(CH_2OH)_4 + NaOH \rightarrow P(CH_2OH)_3 + HCHO + NaCl \] (4.1)

\[ P(CH_2OH)_3 + NaOH \rightarrow O = P(CH_2OH)_3 + H_2 \] (4.2)

Other products formed during the reactions in Equations 4.1 and 4.2 include tetrakishydroxymethylphosphine (THP), triphenylphosphine (TPP) and possibly a small quantity of tetrakishydroxymethylphosphine oxide (THPO), which are all capable of binding and stabilizing Ag nanocrystals\textsuperscript{138, 139} at the interface.

**Film Properties**

SEM images (Figure 4.2) reveal highly uniform and continuous deposits spanning areas extending over several tens of square microns. Folds and cracks are apparent in the deposits.

At high resolution (Figures 4.2c & d), globular clusters with diameters in the range of tens of nanometers can be seen throughout the deposits. The cluster edges appear jagged due to the presence of smaller particulates. High-resolution images reveal irregular clusters with diameters of 70 nm.

Figure 4.3 is a TEM image of Ag nanocrystals prepared at 50°C over 180 minutes. The particulates from films were dispersed in toluene by sonication. The Ag particulates
4.2. RESULTS AND DISCUSSION

Figure 4.2: SEM images of films of Ag nanocrystals obtained at 50°C over 180 minutes.

Figure 4.3: TEM images show aggregation of spherical Ag nanocrystals to form larger clusters. The films were produced at 50°C over 180 minutes. The Ag film formed at the interface was transferred onto a glass substrate, which was added to toluene and sonicated for 5 min to disperse the nanocrystals. One drop of this was applied to a holey TEM grid and analyzed. Scale bar is 20 nm.

are visible as definite separate entities, suggesting that the organic ligands are present at the surface of these particulates, however, the tendency of the nanocrystals to aggregate is apparent in the image.

The films herein consist of nanocrystals coated with organic ligands aggregating to form spherical clusters with diameters of several tens of nanometers. This hierarchical structure bears similar resemblance to those nanocrystalline films of Au that have been previously described (Chapter 3).

The structure of the Ag films prepared at 50°C over 180 minutes was also inves-
4.2. RESULTS AND DISCUSSION

Figure 4.4: Powder X-Ray Diffraction Pattern for Ag films made at 50°C over 180 mins. The broad peaks are characteristic of nanocrystalline materials and the high intensity 38.119° peak suggests there is a small degree of orientation along the (111) plane in the Ag film.

X-ray diffraction of the interfacial film reveals patterns typical of Ag with broad peaks, characteristic of nanocrystals. A degree of orientation along (111) is apparent from the pronounced intensity of the peak at 38.119 degrees relative to the others. The four most intense peaks at $2\theta = 38.12^\circ$, $44.31^\circ$, $64.45^\circ$ and $77.41^\circ$ in the XRD pattern can be attributed to (111), (200), (220) and (311) peaks of cubic Ag (JCPDS 01-087-0717). Using the Debye-Scherrer equation and the (111) plane, the diameters of the nanocrystals were calculated to be 11.2 nm, which correlates well with those diameters seen using TEM.

Figure 4.5 shows the absorption spectrum of Ag nanocrystalline films prepared over 180 minutes at 50°C. The plasmon resonance band of the pristine Ag nanocrystalline films is centered around 410 nm. A lack of defined shape in the spectrum denotes the ability of the electrons within the Ag film to absorb energy from any wavelength and suggests metallic properties.

The room temperature resistance of Ag films, prepared at 50°C over 180 minutes, and measured using multimeter probes, was found to be in the region of about 10 Ohms per square, which is only slightly higher than bulk Ag. Further, the resistance of the films fell with decrease in temperature, which is characteristic behaviour of metallic...
4.2. RESULTS AND DISCUSSION

Figure 4.5: UV Spectrum of Ag nanocrystalline films mounted upon glass substrates.

Figure 4.6: Plot of resistance versus temperature for Ag films prepared at (a) 50°C over 180 minutes and (b) 40°C over 180 minutes. A positive temperature coefficient of resistance is displayed.

These findings are the opposite of those charge transport characteristics associated with Au nanocrystalline films produced using the same conditions. The resistance of Ag films produced at 40°C over 180 minutes increased by a few Ohms (Figure 4.6b), and can be attributed to the fact that nanocrystals produced at lower temperatures tend to have smaller diameters. Nanocrystals of smaller diameters will have larger charging energies and so the film resistance is expected to increase. Given the low resistance values obtained for resistance (Figure 4.6), it is possible that a large fraction of the measured resistance is due to contact resistance.
It is clear that in films of Ag nanocrystals, the electronic levels of the individual crystallites are able to overlap and hybridize with those of its neighbours, leading to strong exchange coupling and a positive temperature coefficient of resistivity. In contrast to films of nanocrystalline Au synthesized using the same procedure, the presence of the phosphinyl-based surface ligands, disorder in the films (a result of the interfacial synthesis method) and the physical separation between particulates seem only to play a minor role in determining the overall electronic structure.

Alloyed Films of Au and Ag Nanocrystals

In their bulk phases, Au and Ag form alloys in the entire range of compositions. In this study, films of nanocrystalline alloys of Au and Ag have been formed by combining the Ag and Au precursors in different ratios and across the whole composition range. The interfacial reaction was carried out with equimolar solutions of Ag(PPh$_3$)$_3$Cl and Au(PPh$_3$)$_3$Cl, mixed in different proportions. For example, to produce an Au$_{0.7}$:Ag$_{0.3}$ alloy, a toluene layer with 7 ml 1.5 mM Au(PPh$_3$)$_3$Cl solution and 3 ml 1.5 mM Ag(PPh$_3$)$_3$Cl was employed.

Striking differences were seen in the appearance of the films. As the Ag content decreased, the colour of the film became darker, moving from shiny yellow to a brown with a low metallic sheen.

Alloyed Film Properties

SEM images (Figure 4.7) reveal highly uniform and continuous deposits of nanoclusters that span areas extending over several tens of square microns. Folds and cracks are apparent in the deposits. The cluster edges are jagged due to the presence of smaller particulates. High-resolution images reveal irregular clusters with diameters of 70 nm. As was the case with Au nanocrystals in Chapter 3, it is thought that the clusters can be resolved into spherical particulates with diameters of around 10 nm, and so the alloyed films of nanocrystals possess a hierarchical self-assembled structure.

As expected, the alloy nanoparticles were found by PXRD to have a crystal struc-
3.2. RESULTS AND DISCUSSION

Figure 4.7: Low (a) and high (b) magnification SEM images of alloyed films of nanocrystalline gold and silver, which were prepared at 50°C over 180 mins. Cracks and folds can be seen in (b); however, the films are continuous and uniform, spanning many square millimetres (a).

The XRD pattern shows a structure similar to that of silver and gold, with broad peaks. The peak widths are too large to permit definitive assignment to either Au or Ag, whose diffraction lines are close together. A degree of orientation along (111) is apparent from the pronounced intensity of the peak at 38.2° relative to the others. The four most intense peaks at $2\theta = 38.2^\circ$, $44.4^\circ$, $64.5^\circ$ and $77.6^\circ$ in the XRD pattern can be attributed to (111), (200), (220) and (311) peaks of cubic Ag (JCPDS 01-087-0718) and cubic Au (JCPDS 00-004-0784).

A remarkable trend is seen in charge transport properties of the films containing Au-Ag alloys: the film resistance increases nearly exponentially with increasing Au content. A plot of the log of film resistance against percentage silver composition (Figure 4.9) is linear.

Films of Au nanocrystals display a clear negative temperature coefficient of resistance (Figure 4.10) and this observed behaviour is consistent with the hopping of localized electrons from one nanocrystal to another.

Notably here, the films switch from metallic to non-metallic behavior when the percentage of Ag falls below 70%. Regular and tight control over charge transport characteristics, extending to over five orders of magnitude, has clearly been achieved. It is noteworthy that previous studies have been unable to achieve such control. Composition changes leading to such large scale changes to electronic properties have been
Figure 4.8: Powder X-Ray Diffraction Pattern for alloyed Au\(_{0.5}\):Ag\(_{0.5}\) films made at 50°C over 180 mins. The broad peaks are characteristic of nanocrystalline materials and the high intensity 38.2° peak suggests there is a small degree of orientation along the (111) plane in the alloyed film.

virtually unknown in the case of films of metal nanocrystals.

A switch from metallic to non-metallic behaviour can be brought about by a number of factors such as decrease in diameter of the nanocrystals, increasing disorder and separation distance as well as by changes in the nature of interaction with surface ligands. As alluded to earlier, change in composition of the films produces little discernable change to the overall dimensions of nanocrystals. And so evidently, changes in dimensions cannot account for the change to non-metallic behavior. Given the regular trend with change in composition, it is believed that the switch in behavior can be attributed to the differences in interaction between the particulates and the surface ligands.

In the case of Ag rich films, relatively weak binding to surface ligands results in physical contact between neighboring nanocrystals leading to development of conductive pathways which result in overall metallic behaviour. In the case of Au rich films, stronger interactions lead to better defined surface structure and robust interparticle repulsion, resulting in the collapse of conductive pathways, leading to semiconducting
4.2. RESULTS AND DISCUSSION

Figure 4.9: Graph showing charge transport properties of alloyed films of Ag-Au nanocrystals. The films were made at 50°C for 180 min. The resistance values plotted are averages of multimeter readings taken from each film in triplicate. The resistance of the films increases nearly exponentially with increasing Au content. Further, the films switch from metallic to non-metallic behaviour when the percentage of Ag falls below 70%.

behavior.

A useful summary of these findings is made by the overlaid UV-Vis Spectra which were taken of the thin films produced (Figure 4.11).

Ag film absorption shows a peak at 400nm and absorbance of light of this wavelength results in yellow colouration, which was indeed observed, and is typically found in the literature for Ag nanocrystals of dimensions less than or equal to 10 nm due to quantum size effects. Figure 4.11 also displays a small Au absorbance peak at around 700nm, which is a quantitative explanation of the reddish hue of gold due to plasmon resonance effects. It is the shapes of the peaks observed at high wavelengths which convey the ease with which electrons can move within the film. A lack of defined shape in the spectrum for Ag reflects the ability of electrons to absorb energy from any wavelength and suggests metallic properties. Well defined peaks at wavelengths of around 700 nm for both Au and the Au/Ag films clearly states that this is not the case for such films. The alloyed and gold films must display non-metallic properties whereby electrons present are more discerning and only selectively absorb energy at specific
4.2. RESULTS AND DISCUSSION

Figure 4.10: Plot showing the variation in film resistance as a function of temperature for films of: Ag nanocrystals (solid line); Au nanocrystals (dashed line).

wavelengths. This is proof of the veracity of charge transport measurement findings; that the 50:50 Ag/Ag alloy possessed electronic properties more like those of 100% Au and the properties are visibly different from those of 100% Ag.

Conclusion

Highly uniform films of Ag and Ag-Au nanocrystals with phosphinyl surface ligands have been obtained at the water-toluene interface. The films posses a hierarchical structure consisting of large aggregates of 10 nm sized nanocrystals. The ubiquity of this structure across the range of compositions studied suggests that the interfacial medium shapes the films. Remarkable differences were seen in the optical and electronic properties of the films as the composition is varied. Strong electronic coupling between Ag nanocrystals together with weak interaction with surface ligands yields metallic films with resistance of a few Ohms. On the other hand, films comprising of Au nanocrystals exhibit behaviour akin to semiconductors with resistance values in the range of MΩs. The resistance of the films scales exponentially with composition of the films, changing from metallic to non-metallic behavior when the percentage of Ag falls
Figure 4.11: Plot showing the variation in film resistance as a function of temperature for films of: Ag nanocrystals (solid line); Au nanocrystals (dashed line).

below 70%.
Chapter 5

Interfacial Deposition of Nanocrystalline Films of Platinum

5.1 Introduction

Platinum is a highly valuable, scarce material and a major precious commodity. The main use for bulk platinum is in jewellery making, however with an emergence in research directed towards nanoscale technologies, there are numerous non-superficial applications of platinum nanocrystals. Pt, especially in nanostructured form is noted for its powerful catalytic abilities. Somarjai and coworkers have studied the hydrogenation of ethylene using single crystals of platinum with (111) surfaces\textsuperscript{178}. More recently the group have shown that the reactivity and selectivity of platinum nanocrystals depends strongly on their morphology and exposed surface properties\textsuperscript{179}. Hexagonal (111) Pt surfaces are 3-7 times more active than cubic (100) surfaces for aromatization reactions.

As well as being outstanding catalysts, Pt films also show extreme resistance to both oxidation and corrosion by high temperatures and chemical elements. Indeed, they are essential components in the manufacture of pacemakers and their inertness within the body, durability and electrical conductivity have made them attractive in many other biological applications. Due to the antioxidant properties of the platinum nanocrystals, they are the subject of substantial research with applications in a wide variety of areas,
including nanotechnology, medicine and the synthesis of novel materials with unique properties.

Previously, the growth and deposition of Pt films by different techniques have been reported. Pt thin films have been deposited on MgO(100) substrates using pulsed laser ablation deposition\textsuperscript{180} and also by sputtering techniques\textsuperscript{181}. Atomic Layer Deposition has yielded low resistivity Pt thin films\textsuperscript{182}. Porter and co-workers have prepared thin noble metal films as a result of immersing Ge substrates into dilute, aqueous solutions of AuCl\textsubscript{4}\textsuperscript{-}, PdCl\textsubscript{4}\textsuperscript{2-}, or PtCl\textsubscript{4}\textsuperscript{2-}, respectively\textsuperscript{183}. Deposition proceeds via galvanic displacement in the absence of fluoride, pH adjusters, complexing agents, or external reducing agents. Physical vapour deposition methods are commonly used to grow Pt films. However, solution based methods capable of producing smooth, conductive thin films are rare.

Solution phase methods of deposition of metallic nanocrystals involving the reduction of a precursor cation, have been developed from two-phase liquid-liquid\textsuperscript{80} and colloidal systems\textsuperscript{87, 184}. Electrochemical methods have also been employed to reduce metals on solid substrates\textsuperscript{185}, with templates controlling the deposit structure on the nanometer scale\textsuperscript{186, 187}. Two-dimensional films have also been grown electrochemically by bringing a working electrode in close proximity to a liquid-liquid interface\textsuperscript{188, 189}. Herein, a combination of various aspects of the above approaches have been utilised in order to bring about the interfacial deposition of Pt.

The films of Pt have been obtained at both room temperature and a relatively modest temperature of 50°C. Aqueous potassium tetrachloroplatinate(II) is held in contact with a reducing agent, a ferrocene derivative, Me\textsubscript{10}FeC\textsubscript{2} in dichloroethane. A novel transfer process capable to reducing disruption to the film structure and it’s properties is employed. The film obtained has been characterized by X-ray diffraction, scanning and transmission electron microscopy, energy dispersive X-Ray analysis, absorption spectroscopy and charge transport measurements.
5.2. RESULTS AND DISCUSSION

Nanocrystalline films were successfully obtained at the interface of water and dichloroethane at 50°C over three hours. A novel transfer process was adapted and was found to dramatically aid the film transfer from interface to substrate. Figure 5.1 shows a schematic diagram of apparatus used for transfer.

The reaction was carried out in a cylindrical funnel with a diameter of 4.8 cm, containing a sintered glass disc whereupon glass substrates where placed at the start of the reaction. Upon completion of the reaction, the lower dichloroethane layer was simply released from the funnel via the tap thus gently lowering the interfacial film to the glass substrates. After allowing the film to ’rest’ for a few minutes, the upper aqueous layer was then removed using pipettes, thus leaving films of platinum nanocrystals that have been virtually undisturbed.

Visual examination of the reaction vessel indicated that after approximately one hour at 50°C, the lower organic phase changed from a deep green colour to amber. The colour change was accompanied by the appearance of a black film at the interface of the two liquids. It should be noted that Pt films could not be obtained at temperatures lower than 50°C. At room temperature, Pt films only began to form after 48 hours, and so the reaction scheme was modified as detailed later order to facilitate the interfacial
5.2. RESULTS AND DISCUSSION

Figure 5.2: EDX analysis of Pt films mounted upon glass substrates. Very large peaks are observed that can be attributed to platinum. Other peaks in the spectrum are due to elements present in the substrate.

deposition over more realistic timeframes at room temperature. After 180 minutes at 50°C, a black film had formed at the interface between water and dichloroethane. Here, the following reactions take place (5.1):

\[
PtCl_{2}^{2-}(aq) + 2Me_{10}FeCp_{2(DCE)} \rightarrow Pt(s) + 4Cl^{-}(aq) + 2(Me)_{10}FeCp^{+}_{2(DCE)} \quad (5.1)
\]

The film was then transferred onto glass substrates (introduced into the vessel at the start of the reaction) and allowed to dry overnight.

The deposition of Pt was supported by energy-dispersive X-ray analysis on the film (Figure 5.2). As in EDX analysis carried out in Chapter 3, other peaks seen in the spectrum can be attributed to those elements present in the glass substrate.

The Redox Couple

The reaction takes place in those stagnant layers of water-in-dichloroethane and dichloroethane-in-water emulsions close to the interface. There the Pt precursor is reduced to Pt(0) nanocrystals as part of a two-phase-redox reaction as the decamethylferrocene is simultaneously oxidised to decamethylferrocenium ions. The decamethylferrocene and decamethylferrocenium redox couple acts as a driving force for the reaction, and has already been investigated and proven a successful reagent in the reduction of
5.2. RESULTS AND DISCUSSION

Unlike the majority of organic compounds, ferrocene and its derivatives undergo a one-electron oxidation at a very low potential, giving rise to the stable ferrocenium cation. Conversely, ferrocenium salts have been used as oxidizing agents, as the ferrocene product is fairly inert and can be readily separated from ionic products.

Interestingly, the ten electron donating methyl substituents present on the cyclopentadienyl component of decamethylferrocene alter and shift the redox potential in a cathodic direction, making it more negative. In a solution of CH₂Cl₂, the reduction potential for the [Me₁₀FeCp₂]⁺/⁰ couple is -0.59 V compared to a [FeCp₂]⁺/⁰ reference. Thus, decamethylferrocene is much more readily oxidised than ferrocene and subsequently is a more effective reducing agent.

**Kinetic Driving Forces**

It has been noted that films of Pt could not be obtained at temperatures lower than 50°C over realistic timeframes using the experimental set-up described earlier.

From an electrochemical perspective, when two immiscible liquids are brought into contact with each other, an arbitrary potential difference exists across the interface that separates them. In this study, Pt nanocrystals form when the aqueous Pt(I) species and the organic decamethylferrocene species come together at the interface to take part in a two-phase redox reaction. There is a subsequent transfer of electrons across the interface so that the tetrachloroplatinate can be reduced and the decamethylferrocene can be simultaneously oxidised. Electrons flow from the dichloroethane layer of a lower work function to the water layer, which is of a higher work function, until the electrochemical potential of the electrons in the bulk of both phases are equal.

The driving force for electron transfer can be influenced through the introduction of appropriate potential-determining ions that govern the interfacial potential difference, \( \Delta \phi_{ow} \), which in turn determines the position of equilibrium in the two-phase redox reaction. Thus, electron transfer can be induced by generating an electrochemical potential gradient. The kinetics and equilibrium position of a heterogeneous electron-transfer
5.2. RESULTS AND DISCUSSION

process such as in Equation 5.1 are a function of the interfacial potential, $\delta \phi$, of water relative to DCE. A common ion, such as perchlorate, is able to control $\delta \phi$ via Equation 5.2:

$$\Delta \phi = \delta \phi^o + \frac{RT}{zF} \ln \frac{a_i, \text{org}}{a_i, \text{aq}}$$

Equation 5.2 implies that if the aqueous phase perchlorate concentration exceeds that of the organic phase (neglecting ion pairing and the nonideality of the solutions) an increase in the interfacial potential results. Therefore, 5 mL of a 1M solution of lithium perchlorate was introduced to the water layer and 5 mL of a 0.1M tetrabutylammonium perchlorate was introduced to the DCE layer at the start of the reaction.

It was found that, at room temperature, films formed over a time period of 8 hours. Reactions carried out at 50°C also using this perchlorate-ion gradient yielded
5.2. RESULTS AND DISCUSSION

Figure 5.3: UV spectra of Pt films formed at 50°C after 1 hour. Solid line corresponds to the DCE phase containing 0.1 M tetrabutylammonium perchlorate and the aqueous phase containing 1 M lithium perchlorate. The dashed line results when both phases did not contain any perchlorate ions.

Figure 5.3: UV spectra of Pt films formed at 50°C after 1 hour. Solid line corresponds to the DCE phase containing 0.1 M tetrabutylammonium perchlorate and the aqueous phase containing 1 M lithium perchlorate. The dashed line results when both phases did not contain any perchlorate ions.

thicker and continuous films over 3 hours. Given the high overall driving force for Pt deposition, the effect upon deposition was manifested as changes in the rate, rather than the extent, of deposition. This suggestion was demonstrated experimentally; Figure 5.3 shows UV spectra that were taken of films produced after one hour of reaction at 50°C with the perchlorate ion gradient present, and also in the absence of any perchlorate. It should be noted that the broad features present in the absorption spectrum are wholly due to surface plasmon resonance due to Pt. The features corresponding to the film formed over one hour in the absence of any perchlorate was significantly lower in intensity than that of films formed using potential-determining ions. It can therefore be concluded that films form at a faster rate when the interface potential is increased.

Structure and Properties of Pt Films

Figures 5.4 and 5.5 show SEM images of Pt films formed at 50°C and room temperature respectively. At both temperatures, cracks are apparent in the film which can be attributed to the evaporation of water and dichloroethane from the film during the transfer and drying process. Also apparent are small white "starburst" structures upon the surface of the film, which are likely lithium perchlorate depositing from the
5.2. RESULTS AND DISCUSSION

Figure 5.4: SEM images of Pt films prepared at 50°C over 180 minutes. The films were formed using a 1M lithium perchlorate/0.1M tetrabutylammonium perchlorate ion gradient.

Figure 5.5: SEM images of Pt films prepared at room temperature over 10 hours. The films were formed using a 1M lithium perchlorate/0.1M tetrabutylammonium perchlorate ion gradient.

Even at higher resolutions (Figure 5.4d), diameters of nanocrystals or indeed diameters of nanoclusters could not be resolved. This is not the case as was in Chapter 3, as nanoclusters of Au could be easily seen. This may be an early indication that the Pt nanocrystals obtained at the interface are much smaller in size than those of Au obtained in a similar manner. TEM analysis confirmed that this was indeed the case (Figure 5.6). The Pt films were agitated ultrasonically and thus dispersed in toluene. One drop of this toluene dispersion of Pt nanocrystals was applied to a holey carbon grid for analysis by TEM. The images revealed extremely small particulates of around 5 nm in diameter. The tendency of the particles to aggregate is apparent in the image.
5.3 Conclusion

Uniform films of Pt nanocrystals have been deposited at the water-dichloroethane interface using aqueous tetrachloroplatinate ions and decamethylferrocene as the re-
5.3. CONCLUSION

Figure 5.7: A plot of resistance versus temperature for films of nanocrystalline platinum. The films measured were obtained at the interface of water and dichloroethane at 50°C over 3 hours.

Reducing agent in the reaction. The rate of film deposition was slow, and films were only formed at temperatures higher than 50°C over 3 hours. The rate of deposition could be increased by incorporating a perchlorate-ion-gradient across the interface between the two liquids. The increased interfacial potential alluded to the deposition of Pt ions being more favourable, as to decrease the interfacial tension. An important concept that must be noted is that ion and electron transfer across the interface were strongly coupled.

TEM analysis has shown that the films consisted of very small particles of around 4 nm, however whether these particles tended to form larger aggregates in a hierarchical manner, similar to that seen with Au and Ag nanocrystals was unclear as nanoclusters could not be resolved using high resolution SEM.

The miniscule sizes of the particles has perhaps also been fittingly reflected in the charge transport characteristics of the Pt films. Measurements have shown that the Pt films are highly resistive, with a room temperature resistivity coefficient of around 105 nΩm. The resistivity coefficient associated with the platinum films was calculated to be 0.3 Ωm, which is distinctly higher than the value for bulk platinum. This behaviour can be attributed to a weak electronic coupling between Pt nanocrystals together with strong interaction with surface ligands present upon the nanocrystal surfaces.
Part IV

Semiconductor Nanocrystals
Chapter 6

Interfacial Deposition of CdS & ZnS Nanocrystalline Films Using Metal Thiobiurets

6.1 Introduction

The development of a synthesis capable of producing high quality nanocrystalline thin-films of a certain material is a step toward making nanoscopic semiconductor devices a reality. There has been an intense focus on thin film materials, particularly those of II-IV group semiconductors, which display a broad range of band gaps ranging from 0.15 eV in HgTe to 3.68 eV in ZnS. Most of the II-IV semiconductors are important materials for applications in various photoelectric and other kinds of devices.

CdS is a well established photoconductor with several current and many potential uses. Thin CdS films have been used in photoelectronic devices such as window materials in CdS/CdTe solar cells,\textsuperscript{194} as well as in optical filters\textsuperscript{195} and gas sensors.\textsuperscript{196} ZnS exhibits a variety of luminescent properties and has been used in the fields of flat displays,\textsuperscript{197} sensors\textsuperscript{198} and lasers.\textsuperscript{199} ZnS thin films, with the addition of a suitable activator, have been used as a phosphor in many applications, from cathode ray tubes\textsuperscript{200} to "glow in the dark" products.\textsuperscript{201} ZnS can be doped as both a n-type and a p-type
6.2. RESULTS AND DISCUSSION

The water-toluene interface in particular has already proven to be successful in the assembly of arrays of CdS/ZnS nanocrystals into thin films.\textsuperscript{73} Cadmium diethyldithiocarbamate has been used as a successful precursor when dissolved in toluene and held in contact with aqueous sodium sulphide.\textsuperscript{73} The reaction proceeds at the interface and results in bright yellow deposits of cadmium sulphide suspended at the interfacial region. In the same study, thin films of zinc sulphide were also obtained at the interface using a zinc diethyldithiocarbamate precursor.

Here, novel cadmium and zinc thiobiuret precursors are used in the synthesis of CdS and ZnS thin films at the interface between water and toluene. Thiobiuret and dithiobiuret metal complexes have not yet been particularly well studied. Their related compounds have attracted attention as potential chemotherapeutic agents\textsuperscript{202,203} and also because of their possible use in plastics and resins,\textsuperscript{204} however, there were no reports of their use as precursors for metal sulphide thin films or nanoparticles until recently. O’Brien and co-workers have synthesised a range of metal thio- and dithiobiuret complexes including those of Co, Ni, Fe, Zn, Cd, In, and Cu.\textsuperscript{205} All of the complexes were successfully used as single source precursors for the deposition of metal sulphide thin films by Aerosol Assisted Chemical Vapour Deposition (AACVD). They showed the deposition of good quality thin films of CoS, NiS, CuS, FeS, CdS and ZnS.

In the light of the above, it is worthwhile to explore the use of thiobiurets as metal precursors for the synthesis of chalcogenide thin films at the interface of water and oil. In this chapter, the syntheses of thin films of CdS and ZnS are reported.

6.2 Results and Discussion

CdS Films

CdS films were obtained upon layering 30 mL of a 1.8 mM toluene solution of cadmium thiobiuret atop 30 mL of 3.8 mM aqueous sodium sulphide. After a few minutes, a pale yellow coloration was observed at the interface of the two liquids as a
6.2. RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hour)</th>
<th>Temperature (°C)</th>
<th>Outcome</th>
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<tbody>
<tr>
<td>GS075A</td>
<td>5</td>
<td>10</td>
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</tr>
<tr>
<td>GS075B</td>
<td>5</td>
<td>22</td>
<td>very thin film</td>
</tr>
<tr>
<td>GS075C</td>
<td>5</td>
<td>40</td>
<td>very thin film</td>
</tr>
<tr>
<td>GS075D</td>
<td>5</td>
<td>60</td>
<td>thin film formed</td>
</tr>
<tr>
<td>GS070A</td>
<td>24</td>
<td>10</td>
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<tr>
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<tr>
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<td>48</td>
<td>60</td>
<td>very thick film</td>
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</tbody>
</table>

Table 6.1: Varying the reaction conditions in the synthesis of CdS films at the interface of water and toluene. Cadmium thiobiuret and sodium sulphide precursors were used in the synthesis. The concentrations of the reagents were kept constant, with 1.8 mM cadmium thiobiuret and 3.8 mM Na\textsubscript{2}S being used in each case.

result of CdS deposition. The yellow colouration became stronger and deeper as time progressed, however, the liquid phases remained colorless throughout the deposition.

The observations indicated that the following reaction was operative:

\[
[Cd(C_{14}H_{28}N_{3}OS)_{2}] + Na_{2}S \rightarrow CdS + 2(C_{14}H_{28}N_{3}OS)Na
\]  

(6.1)

The optimum parameters required for the synthesis of CdS thin films using a thiobiuret precursor were investigated through the variation of precursor concentration, temperature and timeframe. (Table 6.1 shows the results of these findings). Visual examination was used to identify those films that were smooth and continuous.

Remarkably, cadmium sulphide films formed over all temperatures and timeframes, except in the reaction carried out at 10°C for 5 hours, a short period of time at a cold temperature. It should be noted that at the highest temperature of 60°C and over 48 hours, the film appeared to have disintegrated slightly and there was bright yellow precipitate and film residue had started to form at the bottom of the beaker. However, the fact that films can be formed at ambient temperatures over a relatively
6.2. RESULTS AND DISCUSSION

Figure 6.1: Photograph of CdS films mounted upon glass substrates. The films have been formed over 24 hours at 40°C. The films are bright yellow, characteristic of cadmium sulphide, and span areas of several square centimetres.

Figure 6.2: SEM images of CdS films formed at 10°C over (a) & (b) 24 hours and (c) 48 hours.

A short period of time is extremely advantageous when it comes to thin film production, and this characteristic holds promise when it comes to scaling up the reaction due to decreased energy costs. The films produced were bright yellow, the characteristic colour of cadmium sulphide, they were continuous and spanned many square centimetres (Figure 6.1). The films were transferred to glass substrates by gently lifting the film from the interface using the substrate.

The structure, morphology and characteristics of CdS films were examined in detail using spectroscopic and microscopic techniques.

The nature of the liquid interface is strongly reflected in the macroscopic structure of the films. Regardless of the deposition conditions, the films consist of large
6.2. RESULTS AND DISCUSSION

Figure 6.3: SEM images of films formed at room temperature over (a) & (b) 5 hours, (c) 24 hours and (d) 48 hours.

spheroidal aggregates with jagged edges. At 10°C (Figure 6.2), very thin films are obtained that comprise nanoclusters that are around 150 nm in diameter. After 24 hours, the films are fractious and there are many cracks present in the film, suggesting that it is discontinuous and there has been insufficient time for the film to form across the whole area of the interface. Upon leaving the interfacial reaction for a further 24 hours, the films obtained are much thicker and appear under the microscope to be "overgrown", smooth and individual nanoclusters cannot be resolved.

The deposits obtained at room temperature comprise slightly larger nanoclusters (Figure 6.3), and when they are left over longer time periods they too adopt an "overgrown" appearance. Deposits obtained at 40°C and 60°C are made up of slightly larger and more spherical grains that are much more "well-defined" (Figures 6.4 and 6.5). Over shorter time periods the films are smooth and continuous, however when the interfacial reaction is left to progress over 48 hours, large cracks can be seen in the films
6.2. RESULTS AND DISCUSSION

Figure 6.4: SEM images of films formed at 40°C over (a) & (b) 5 hours, (c) 24 hours and (d) 48 hours.

that are obtained. This observation essentially mirrors that when the films are seen to disassemble and "sink" from the interface to the bottom of the beaker.

Visual examination indicated that those films produced over 40°C and over 24 hours produced the smoothest and most continuous films.

Samples were prepared for high resolution TEM analysis by ultrasonically dispersing a film of nanocrystals (grown at 40°C over 24 hours) in 5 mL toluene for 15 minutes. It was revealed that the nanocrystalline films comprised randomly oriented single-crystalline CdS grains with dimensions in the range of 8 nm (Figure 6.6).

The TEM image also shows the clear tendency of the CdS nanocrystals to agglomerate into larger clusters. Spherical CdS nanocrystals of 8 nm diameter coalesce to form larger aggregates that have a diameter of around 100 nm, as seen in the SEM images. This hierarchical structure and morphology has been observed in those nanocrystalline films of Au and Ag obtained in Chapters 3 and 4, and also in films of Bi₂S₃, Cd(OH)₂ and Pd grown at the water-toluene interface.
X-Ray diffraction patterns revealed that CdS films were composed of hexagonal grains (see Figure 6.7). The three most intense peaks at $2\theta = 26.7^\circ$, $43.9^\circ$ and $52.1^\circ$ could be indexed to the (002), (110) and (112) planes of hexagonal CdS (JCPDS 75-1545). The sizes of the grains in the CdS films were obtained from X-ray diffraction patterns using the Debye-Scherrer Equation 6.2:

$$\text{Size}_{\text{crystallite}} = \frac{k\lambda}{\delta \cos \theta}$$

where $\lambda$ is the wavelength of the X-ray, $\theta$ is the Bragg angle, $\delta$ is the full width at half maximum of the diffraction peak, and $k$ is a constant and taken as 0.9. The crystallite diameters were calculated using the most intense (002) reflection in each pattern. The calculated diameters have been shown in Table 6.2.

It can be seen that the temperature at which the reaction takes place has a distinct effect on the sizes of the CdS nanocrystals obtained. This observation is comparable with studies involving Au, where a tangible change in nanocrystal size from 7 nm to 12
6.2. RESULTS AND DISCUSSION

Figure 6.6: TEM images of films formed at 40°C over 24 hours.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation Temperature (°C)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) CdS_{\text{room temp}}</td>
<td>22</td>
<td>5</td>
</tr>
<tr>
<td>(b) CdS_{40}</td>
<td>40</td>
<td>8</td>
</tr>
<tr>
<td>(c) CdS_{60}</td>
<td>60</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 6.2: Table showing the calculated diameters of CdS nanocrystals formed at different temperatures, using X-Ray diffraction data.

nm is seen with increase in interfacial reaction temperature\(^{87,144}\) from 30°C to 60°C. Fan and co-workers\(^{73}\) have reported the control of sizes of CdS nanocrystals obtained at the water-toluene interface using a cadmium diethyldithiocarbamate precursor by varying the reaction temperature. However the scale of the size changes is much lower than that observed herein. Here, it is clear that deposition temperature controls the sizes of the crystallites. An increase in temperature from room temperature to 60°C almost doubles the nanocrystal diameter from 5.4 nm to 11.9 nm.

The electronic absorption spectrum of a CdS film deposited on glass substrate is shown in Figure 6.8. The absorption onset indicates a band gap of 2.48 eV and is 0.06 eV higher than that of bulk CdS, which is indicative of quantum confinement effects brought about by the small crystallite size in the films. The optical properties of these
6.2. RESULTS AND DISCUSSION

Figure 6.7: X-Ray diffraction pattern for CdS films produced over 24 hours at (a) room temperature (b) 40°C and (c) 60°C.

films compare well with thin films grown by chemical bath deposition. The UV spectra of CdS films produced at different temperatures over 24 hours were then obtained (Figure 6.8). The absorption edges of each film clearly appear at different energies. A model proposed by Viswanatha and Sarma was followed in order to obtain estimates of mean diameters of the nanocrystals using the absorption spectra. This method is based on high-level theoretical calculations and has been shown to provide accurate estimates of experimental diameters for different families of semiconductor nanocrystals such as ZnO and GaN. To apply this method, the position of the peak (E₀), as well as its full width at half maximum (FWHM) are obtained using the first derivative of the curve as shown in Figure 6.9. From these values, E₁ (E₀ - FWHM/2) and E₂ (E₀ + FWHM/2) are obtained.

The mean diameter (d), is obtained by solving Equation 6.3:

\[ \Delta E_g = \frac{1}{ad^2 + bd + c} \]  

(6.3)

where a, b and c are constants that depend on the identity of the semiconductor.
6.2. RESULTS AND DISCUSSION

Figure 6.8: Electronic absorption spectra for (a) CdS films obtained at room temperature, (b) CdS films obtained at 40°C and (c) CdS films obtained at 60°C. All films were obtained over 24 hours.

For CdS, the values of a, b and c are 0.1278, 0.1018 and 0.1821, respectively. Here, \( \Delta E_g \) is the observed shift in the band gap (E_g), given by \( E_0 - E_g \). In order to obtain the diameter distribution \( \Delta D_{real} \), diameters \( d_1 \) and \( d_2 \) are obtained using Equation 6.3 and shifts \( (\Delta E_g) \) corresponding to \( E_1 \) and \( E_2 \). The difference \( (\Delta D_{app} = d_1 - d_2) \) is scaled using Equation 6.4:

\[
\Delta D_{real} = -0.0025 \Delta D_{app}^2 + 0.524 \Delta D_{app} - 1.41 \tag{6.4}
\]

to obtain the true diameter distribution \( (\Delta D_{real}) \). Using the absorption spectra obtained and the above expressions, the average diameters of the CdS nanocrystals formed at different temperatures have been obtained and have been tabulated in Table 6.3.

The values calculated using UV data do not exactly match those values estimated using XRD analysis, however, given the nature of the two methods, the obtained correlation is indeed gratifying.
6.2. RESULTS AND DISCUSSION

Figure 6.9: (a) shows absorption data for CdS nanocrystals and (b) shows the derivative of the top curve, and the positions of \( E_0 \) and the position of the FWHM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation Temperature (°C)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) CdS(_{rt})</td>
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<td>3.2</td>
</tr>
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<td>(b) CdS(_{40})</td>
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<td>5.7</td>
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<tr>
<td>(c) CdS(_{60})</td>
<td>60</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Table 6.3: Table showing the calculated diameters of CdS nanocrystals formed at different temperatures over 24 hours, using UV-Vis absorption data.

ZnS Films

ZnS films were obtained by layering 30 mL of a 1.8 mM toluene solution of zinc thiobiuret atop 30 mL of 3.8 mM aqueous sodium sulphide. After an hour at 40°C, or around 10 hours at room temperature, a pale white coloration was observed at the interface of the two liquids as a result of ZnS deposition. The colouration became stronger and deeper as time progressed, however, the liquid phases remained colorless throughout the deposition.

The observations indicated that the following reaction was operative:

\[
[Zn(C_{14}H_{28}N_{3}OS)_{2}] + Na_{2}S \rightarrow ZnS + 2(C_{14}H_{28}N_{3}OS)Na
\]  

(6.5)
6.2. RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hour)</th>
<th>Temperature (°C)</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS076A</td>
<td>5</td>
<td>10</td>
<td>no film formed</td>
</tr>
<tr>
<td>GS076B</td>
<td>5</td>
<td>22</td>
<td>no film formed</td>
</tr>
<tr>
<td>GS076C</td>
<td>5</td>
<td>40</td>
<td>no film formed</td>
</tr>
<tr>
<td>GS076D</td>
<td>5</td>
<td>60</td>
<td>no film formed</td>
</tr>
<tr>
<td>GS077A</td>
<td>24</td>
<td>10</td>
<td>no film formed</td>
</tr>
<tr>
<td>GS077B</td>
<td>24</td>
<td>22</td>
<td>thin film formed</td>
</tr>
<tr>
<td>GS077C</td>
<td>24</td>
<td>40</td>
<td>thin film formed</td>
</tr>
<tr>
<td>GS077D</td>
<td>24</td>
<td>60</td>
<td>thin film formed</td>
</tr>
<tr>
<td>GS078A</td>
<td>48</td>
<td>10</td>
<td>no film formed</td>
</tr>
<tr>
<td>GS078B</td>
<td>48</td>
<td>22</td>
<td>thin film formed</td>
</tr>
<tr>
<td>GS078C</td>
<td>48</td>
<td>40</td>
<td>thin film formed</td>
</tr>
<tr>
<td>GS078D</td>
<td>48</td>
<td>60</td>
<td>thin film formed</td>
</tr>
</tbody>
</table>

Table 6.4: Varying the reaction conditions in the synthesis of ZnS films at the interface of water and toluene. Zinc thiobiuret and sodium sulphide precursors were used in the synthesis and their concentrations were kept constant at all times. 1.8 mM zinc thiobiuret and 3.8 mM Na$_2$S solutions were used.

The optimum parameters required for the synthesis of ZnS thin films using a thiobiuret precursor were investigated through the variation of precursor concentration, temperature and timeframe. (Table 6.4 shows the results of these findings). Visual examination was used to identify those films that were smooth and continuous.

Films were not formed at the colder temperatures of 10°C or over short timeframes of 5 hours. However, over a minimum time period of 24 hours, smooth and continuous films of ZnS were obtained at room temperature as well as at 40°C and 60°C.

The films were carefully lifted from the interface onto glass substrates and left to dry overnight. Figure 6.10 shows bright white films of ZnS that have been mounted upon glass substrates. Interestingly, films formed at room temperature appeared dull and matt white, however as the temperature was increased, the films exhibited a definite shimmer and appeared "glittery" in parts.

The structure, morphology and characteristics of ZnS films were examined in detail using spectroscopic and microscopic techniques.
Figure 6.10: Photograph of a ZnS film, formed at 40°C over 24 hours, on a glass substrate.

The ZnS nanocrystals in Figure 6.12 appear spherical, however upon closer inspection and using the higher resolution images it can be seen that there are jagged and angular edges to the nanoclusters. This indicates that there is a hierarchical organisation of the individual ZnS nanocrystals into clusters. The angular appearance and tendency of the nanocrystals to subtend 60 and 120 degrees, could both be an early indication that the hexagonal form of ZnS has been synthesised.

Using the SEM images, sizes of the nanoclusters that form can be estimated and it is apparent that as the temperature is increased, the sizes of the clusters produced also increases. At room temperature, nanoclusters of around 100 nm are produced. An increase in temperature to 40°C, produces clusters with an average diameter of 150 nm and a further increase to 60°C gives rise to diameters of around 250 nm. Using the SEM images obtained over different timeframes, it can be concluded that the timeframe of the reaction appears to have no bearing upon the sizes of the nanoclusters produced.

TEM analysis was carried out on films dispersed in solution by sonication. As was the case with the CdS films, it was revealed that the ZnS films comprised randomly oriented single-crystalline grains with dimensions in the range of 8 nm (Figure 6.16a). Again, the TEM image clearly shows the ZnS nanocrystals aggregating into larger clusters (Figure 6.16b). The agglomeration of smaller particles into larger clusters has indeed become an emerging theme throughout this thesis and can be attributed
6.2. RESULTS AND DISCUSSION

Figure 6.11: SEM images of ZnS films formed at room temperature (a) over 24 hours and (b) over 48 hours.

Figure 6.12: SEM images of ZnS films formed at 40°C over 24 hours.

to the interfacial reaction procedure. At present, however, there is insufficient information available to rationalise such assembly.

Figure 6.17 shows the X-Ray diffraction patterns of ZnS films formed over 24 hours at various temperatures. The pattern revealed that ZnS films were composed of cubic grains, and that the crystallinity of the films improves with an increase in temperature. The most intense peaks at $2\theta = 28.9^\circ$, $48.1^\circ$ and $56.5^\circ$ could be indexed to the (111), (220) and (311) planes of cubic ZnS (JCPDS 77-2100). The sizes of the grains in the ZnS films were estimated from X-ray diffraction patterns using the Debye-Scherrer Equation, and using the most intense (111) reflection in each pattern. The calculated diameters have been shown in Table 6.5.

It can be seen that the temperature at which the reaction takes place has a distinct effect on the sizes of the ZnS nanocrystals obtained. This observation is comparable
6.2. RESULTS AND DISCUSSION

Figure 6.13: SEM images of films formed at 40°C over 48 hours.

Figure 6.14: SEM images of ZnS films formed at 60°C over 24 hours.

with those results obtained using cadmium thiobiuret in the same system, which has been described earlier. An increase in temperature from room temperature to 60°C increases the sizes of the crystallites from 6 nm to 10 nm.

Figure 6.18A shows the electronic absorption spectrum of a sample prepared at 40°C over 24 hours. The optical band gap of ZnS was estimated to be 3.35 eV, which is close to the expected value for cubic Zns, which is 3.54 eV. The effect of reaction temperature upon the absorption spectrum of the ZnS films was investigated and has been shown in Figure 6.18B.
6.2. RESULTS AND DISCUSSION

Figure 6.15: SEM images of ZnS films formed at 60°C over 48 hours.

Figure 6.16: TEM images of ultrasonically dispersed ZnS films formed at 40°C over 24 hours.

Using Equations 6.3 and 6.4, the sizes of the nanocrystals synthesized at different temperatures can be estimated. They have been calculated and tabulated in Table 6.6.

The calculated diameters using absorption data all come out around 7 nm, which correlates well with sizes estimated using TEM and X-Ray diffraction data. However, the increase in particle size due to a raised reaction temperatures is very slight and not as big an increase as is seen with CdS nanocrystals. Also, the increase in particle size is not as great in magnitude as those values that have been calculated using X-Ray diffraction data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation Temperature (°C)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ZnS_{roomtemp}</td>
<td>22</td>
<td>6</td>
</tr>
<tr>
<td>(b) ZnS_{40}</td>
<td>40</td>
<td>8</td>
</tr>
<tr>
<td>(c) ZnS_{60}</td>
<td>60</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 6.5: Table showing the calculated diameters of ZnS nanocrystals formed at different temperatures, using X-Ray diffraction data.
6.2. RESULTS AND DISCUSSION

Figure 6.17: X-Ray Diffraction patterns obtained from ZnS films produced over 24 hours at (a) room temperature (b) 40°C and (c) 60°C.

Figure 6.18: (A) Absorption spectra of ZnS films produced over 24 hours at 40°C. (B) Absorption spectra of ZnS films made over a range of reaction temperatures showing a distinct variation in band gap.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation Temperature (°C)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ZnS&lt;sub&gt;rt&lt;/sub&gt;</td>
<td>22</td>
<td>6.6</td>
</tr>
<tr>
<td>(b) ZnS&lt;sub&gt;40&lt;/sub&gt;</td>
<td>40</td>
<td>6.9</td>
</tr>
<tr>
<td>(c) ZnS&lt;sub&gt;60&lt;/sub&gt;</td>
<td>60</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Table 6.6: Table showing the calculated diameters of ZnS nanocrystals formed at different temperatures over 24 hours, using UV-Vis absorption data.
6.3 Interfacial Deposition of CdS Nanocrystalline Films Using Simple Salts

In addition to the deposition of CdS using a novel thiobiuret precursor, an hierarchical nanocrystalline film of CdS has been successfully deposited at the interface of n-hexane and water at room temperature. The reaction also involves the use of much simpler reactants and the need for complex organic precursors has been eliminated.

A film of CdS was obtained at the interface using cadmium nitrate as the Cd\(^{2+}\) source and CS\(_2\) as a source of S\(^{2-}\). Ethylene diamine was dissolved in water at the start of the reaction and acted as both a capping agent to arrest the growth of CdS nanocrystals and also as a phase transfer agent. Ethylenediamine coordinates with Cd\(^{2+}\) in the water phase and thus the Cd\(^{2+}\) is carried from the water phase to the water-oil interface due to the solubility of the ethane chain in n-hexane. Similarly, metastable microdroplets of CS\(_2\) in water also form, thus producing two stagnant layers surrounding the interface. After around 8 hours at room temperature, yellow colouration was observed at the interface of the two liquids that became deeper as time passed. After 24 hours, thick and bright yellow films were observed at the interface. The films were then transferred onto glass substrates to be analysed.

Reaction Chemistry

It is thought that the film formed as a result of the following reactions:

\[
H_2NCH_2CH_2NH_2 + CS_2 \rightarrow H_2NCH_2CH_2NHCSSH \tag{6.6}
\]

\[
n(H_2NCH_2CH_2NHCSSH) \rightarrow [-HNCH_2CH_2NHSC-]_n + nH_2S \tag{6.7}
\]

At the start of the reaction, CS\(_2\) was dispersed in n-hexane and ethylenediamine was dissolved in the aqueous phase. Towards the interface of the two liquids, ethylen-
6.3. INTERFACIAL DEPOSITION OF CDS NANOCRYSTALLINE FILMS USING SIMPLE SALTS

Figure 6.19: SEM images of CdS films obtained using the simple salt system over 24 hours at room temperature.

diamine can react with CS$_2$ to generate N-ethylaminocarbamodithioic acid (Equation 6.6). This is then able to polymerize to form poly(N-ethylamino carbamodithioic acid), (PECA) and releases H$_2$S in the process (Equation 6.7). H$_2$S can be easily hydrolysed to release S$^{2-}$, which can then subsequently react with Cd$^{2+}$ at the interface to generate CdS nanocrystals.

**Film Structure**

The surface structure of the films was analysed using SEM. Figure 6.19 reveals nanoclusters of 200 - 300 nm in diameter that have assembled together to give a film with a very rough appearance.

Samples to be analysed by TEM were prepared by ultrasonically dispersing the CdS sample. Dispersed spherical particles were observed (Figure 6.20). It is concluded that the CdS film consisted of spherical subunits, that had aggregated together to form larger clusters. Such hierarchical organisation has been seen in all of the interfacial syntheses described in this thesis, for example, during the synthesis of Au and Ag nanocrystalline films.

Figure 6.21 shows the XRD pattern of the nanocrystalline CdS films obtained. The pattern shows only one very large and broad peak at 44.1° that corresponds to the (110) plane of hexagonal CdS (JCPDS code 75-1545). The broadening of the peak is due to the nanoscalar dimensions of the CdS nanocrystals.
6.4. CONCLUSION

Figure 6.20: SEM images of ultrasonically dispersed CdS films that were formed at room temperature over 24 hours.

The electronic absorption spectrum (Figure 6.22) for the films acts as supporting evidence that it is in fact CdS that has been formed.

The absorption edge is at 501 nm, and the onset indicates a band gap of 2.47 eV which is 0.05 eV higher than that of bulk CdS, which is indicative of quantum confinement effects brought about by the small crystallite size in the films.

6.4 Conclusion

In this chapter, the liquid-liquid interface was used to produce semiconducting films of both CdS and ZnS nanocrystals. It appears that a change in metal precursor structure changes the nature and properties of the film quite dramatically, compared with previously published results on CdS at interface.73

Films of CdS nanocrystals were obtained using a cadmium thiobiuret precursor over 24 hours at extremely modest temperatures of 10°C. XRD and UV analysis have shown that the diameters of the nanocrystals can be systematically varied by simply altering the reaction temperature. Increasing the temperature from 22°C to 60°C almost doubles the nanocrystal diameter from 5 nm to 12 nm. Calculation of nanocrystal size and size distribution from the electronic spectra offers a convenient way to obtain information during the reaction and optimise the reaction conditions.

Using zinc thiobiuret, films of ZnS nanocrystals were obtained at the water-toluene interface. The films could be obtained at room temperature over 24 hours.
6.4. CONCLUSION

Figure 6.21: XRD pattern for CdS nanocrystals that were formed at room temperature over 24 hours.

XRD patterns revealed that the cubic zinc blende (sphalerite) structure of ZnS had been obtained, which is a stable phase at low temperatures for ZnS. The band gap calculated using both the XRD and the UV-Vis spectra is about 3.35 eV, which is close to the value for bulk cubic ZnS (3.54 eV).

SEM images combined with TEM images for both films revealed that the thin films consisted of nanocrystals that had assembled in a hierarchical fashion, that is to say individual metal-sulphide nanocrystals had aggregated together to form larger clusters, which then self-assembled together to form the thin film.

In addition to this, films of nanocrystalline CdS have been produced at the interface of water and n-hexane at room temperature. Only simple metal and sulphide-containing precursors are required along with a small amount of ethylenediamine, which acts as both a capping agent and as a phase transfer catalyst. As with films synthesised throughout the whole of this report, hierarchy is apparent as a result of the assembly process.
Figure 6.22: Electronic absorption spectrum for CdS nanocrystals that were formed at room temperature over 24 hours.
Chapter 7

Electronic Properties of CdS & ZnS Nanocrystalline Thin Films and The Influence of Surface Ligands

7.1 Introduction

Control over the surface chemistry and the electronic properties of semiconducting materials is essential in the construction of semiconductor devices. The surfaces of semiconductor nanocrystals are usually terminated with organic ligands, which are typically organic molecules that can increase solubility and prevent the nanocrystals from aggregating as they are formed. In general, the use of surface ligands leads to greater control over the electronic properties of semiconductor nanocrystals and the chemisorption of small molecules onto the surfaces of semiconductors in order to finely tune the materials charge transport capabilities is emerging as a well-studied and interesting area.\textsuperscript{210,211} It has been found that the nature of the ligand capping layer surrounding semiconductor nanocrystals strongly affects their luminescence properties.\textsuperscript{212}

In this chapter, the charge transport properties of CdS and ZnS nanocrystalline films produced using metal thiobiurets and sodium sulphide (Chapter 6) have been reported. There have been no complex capping agents employed during the interfacial
7.2. RESULTS AND DISCUSSION

Figure 7.1: Plot of conductivity versus temperature for (a) CdS and (b) ZnS films, both formed over 24 hours at 40°C.

synthesis and so the films produced essentially exist as a "blank canvas" that can be decorated with a choice of desired capping ligands. In this chapter, the surfaces of CdS and ZnS films have been modified by adsorbing onto them a range of para-substituted pyridines which vary from one another in terms of their dipole moment and electron-withdrawing/-donating capabilities. The resultant charge transport behaviour has been studied.

7.2 Results and Discussion

The charge transport properties of the as obtained CdS and ZnS films were investigated. Figures 7.1a & b show that the CdS and ZnS films are poorly conducting, with room temperature conductivity of around 25 Ohms$^{-1}$m$^{-1}$, but nevertheless behave as typical semiconductors, exhibiting a clear negative temperature coefficient of resistance.

In Au nanocrystalline films described in this thesis, there were four distinct regimes of conductivity present in the Au films, however with these CdS and ZnS films there are two regimes. A plot of $\ln \sigma$ vs $1/T$ (Figure 7.2) is linear suggesting that the classical Arrhenius type activated hopping mechanism defined in Equation 7.1 adequately describes the transport characteristics across the temperature range studied.

$$\sigma = A e^{\frac{E_a}{kT}}$$  \hspace{1cm} (7.1)
Figure 7.2: Plot of $\ln \sigma$ versus $1/T$ for (a) CdS and (b) ZnS films. Both films have been formed over 24 hours at 40°C. The plots are linear and show two distinct temperature regimes.

<table>
<thead>
<tr>
<th></th>
<th>$m$</th>
<th>$c$</th>
<th>$E_a$</th>
<th>$G_0$</th>
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<tbody>
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<td>CdS 298K - 220K</td>
<td>-445.7</td>
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<td>ZnS 220K - 150K</td>
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<td>3.35</td>
<td>0.0123</td>
<td>28.51</td>
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</table>

Table 7.1: Table showing the activation energies (in meV) and pre-exponential terms (a dimensionless scaling factor) associated with charge transport through films of CdS and ZnS under different temperature regimes.

The equations of the lines fitted to both of the charge transport domains have been obtained, which have allowed activation energy values and pre-exponential parameters associated with charge transport within that particular domain to be determined. According to the Arrhenius-type expression in Equation 7.1, a plot of $\ln \sigma$ vs $1/T$ will give a straight line, the gradient of which will relate to the activation energy for charge transport with the y-intercept relating to the pre-exponential term, $\ln G_0$.

Table 7.1 suggests that in each of the regimes, a different mechanism of conductivity operates in the films. Typically, as the temperature is lowered, the activation energy falls by about half and at the same time, there is a halving of the pre-exponential term, perhaps signalling a change in the conduction mechanism within the film. However, these changes are minor, and activated hopping continues to persist even at the low temperatures. This behaviour was also observed with the films of nanocrystalline Au described earlier in Chapter 3.
7.2. RESULTS AND DISCUSSION

Figure 7.3: A family of substituted pyridines that were bound to the CdS and ZnS films. From left to right: nitropyridine, pyridine, picoline and methoxypyridine.

Influencing Charge Transport Properties using Substituted Pyridines

Just as thiophenol moieties become strongly bound to Au nanocrystals, pyridine molecules are known to effectively cap cadmium sulphide nanocrystals.\textsuperscript{213,214} Tri-n-octylphosphine oxide (TOPO) has been used as a capping/passivating agent in the syntheses of films CdS nanocrystals at temperatures of 120-250°C and it was found that the TOPO cap could be easily replaced by other organic capping agents such as pyridines, in particular, 4-picoline. Soaking of the CdS and ZnS films made using thiobiurets in ethanolic solutions of pyridine and its associated para substituted derivatives (Figure 7.3) results in binding of the pyridines to the metal sulphide surface.

UV-Visible spectroscopy was used to monitor the binding of pyridinyl ligands to the CdS surface. The absorption edge corresponding to CdS is centered around 525nm, however, upon ligand binding by pyridine, the intensity and position of the peak exhibited very subtle substituent effects (Figure 7.4). Binding of 4-nitropyridine results in a very small red shift of the absorption edge by around 10 nm whereas in contrast, 4-methoxypyridine resulted in a very small blue shift of around 10 nm. A similar behaviour was observed with films of ZnS.

More significant changes to the electronic properties of the films, more specifically changes in conductivity of the films is seen when different substituents are introduced onto the pyridinyl capping ligands (Figure 7.5), which has indeed been mirrored in the aforementioned electronic absorption spectra. All films still exhibit a clear negative temperature coefficient of resistivity.
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Figure 7.4: Overlaid absorption spectra of CdS films before and after derivatisation with methoxy and nitropyridine.

These experimental findings and the pattern that can be clearly seen, are wholly opposite to those found when Au films were capped with aromatic thiols with various substituents. When pyridine bore the electron donating methoxy substituent, an increase in the conductivity, relative to pyridine capped films, was observed. In CdS films, 4-methoxypyridine increases the room temperature conductivity from $26 \, \Omega^{-1} \, m^{-1}$ to $58 \, \Omega^{-1} \, m^{-1}$, while the electron withdrawing substituent (nitro) causes a decrease of conductivity from $26 \, \Omega^{-1} \, m^{-1}$ to $6 \, \Omega^{-1} \, m^{-1}$. In ZnS films, 4-methoxypyridine increases the room temperature conductivity from $23 \, \Omega^{-1} \, m^{-1}$ to $30 \, \Omega^{-1} \, m^{-1}$, while the electron withdrawing substituent (nitro) causes a decrease of conductivity from $23 \, \Omega^{-1} \, m^{-1}$ to $8 \, \Omega^{-1} \, m^{-1}$.

Figure 7.6 shows the relationship between the Hammett parameter associated with the adsorbed pyridine ligands\textsuperscript{215,216} and the resistance of the film at 250K.

The plots in Figure 7.6 show that substituent characteristics and the conductivity of the films correlate extremely well, with R squared values calculated to be above 0.96. The trend observed is in stark contrast to that observed by Cahen and co-workers, and indeed to the trend observed with the Au nanocrystalline films produced herein. They absorbed an identical set of molecules, except for a systematic change in one substituent group, onto nanocrystalline films of Ga-As film they found that that when a
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Figure 7.5: Plot of conductivity versus temperature for (a) CdS and (b) ZnS films prepared at 40°C over 24 hours. The films have been soaked in ethanolic solutions of pyridines that vary in terms of their para substituents. The substituents present on the pyridine ligands are indicated next to the plots.

Figure 7.6: Plot showing the relationship between the Hammett parameter associated with the adsorbed pyridine ligand and the resistance of (a) CdS and (b) ZnS films at 250K.

given voltage was applied to the material, the current obtained depended strongly upon the specific molecular substituent. The presence of electron-withdrawing groups, such as CF₃ and CN increased the current, whereas that of electron-donating groups, such as OCH₃, decreases the current.

Herein, capping the films with nitropyridine gives rise to a highly resistive film, and this effect could be viewed in incredibly simple terms. The nitropyridine molecule is electron-withdrawing, and so when bound to a material containing few electrons (CdS or ZnS) the nitropyridine will withdraw electrons from the semiconductor to such an extent that charge transport through the semiconductor will be exceptionally hindered.

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7.3 Conclusion

On the other hand, methoxypyridine, an electron-donating molecule, facilitates electron transport through the semiconducting films. The molecules are able to donate their electron density to the material, hence facilitating charge transport through the material as a whole.

The nature of charge transport through films of semiconducting nanocrystals could serve as an interesting topic for further investigation. Studies should be undertaken to understand how pyridine molecules are able to affect the charge transport flow through CdS and ZnS, in the manner that was observed herein.

7.3 Conclusion

The water-toluene interface, using metal thiobiuret precursors and sodium sulphide, have given rise to films of CdS and ZnS nanocrystals. The electronic properties of these films can be reliably and repeatably measured. Moreover, the conductivity of semiconducting CdS and ZnS nanocrystals can be easily manipulated by adsorbing pyridinyl derivatives to their surfaces in order to affect the nature of the films. In summary, films of CdS and ZnS nanocrystals capped with pyridinyl ligands exhibit strong substituent effects. The conductivity of the films can be tuned in the range of 6 to 60 $\Omega^{-1}m^{-1}$ by varying the nature of substituents at the para position of the pyridine capping ligands. Electron-donating substituents (e.g. methoxy) present on the pyridines make the films more amenable to charge transport, whereas electron-withdrawing groups (e.g. nitro) hinder charge flow through the film. The findings and trends observed in this Chapter are in stark contrast to those observed with Au nanocrystalline films that are capped with para-substituted thiophenols.
Part V

Summary and Suggestions for Further Work
Films of Au nanocrystals with diameters in the range of 5-10 nm were obtained at the water-oil interface using a molecular gold-containing precursor and at temperatures of 40°C and 50°C. The films spanned many square centimetres and could also be directly transferred from the interface onto solid supports. Furthermore, the optical and electronic properties of the films, as well as their structures, have been extensively explored and manipulated. It has been shown that films of Au nanocrystals capped with thiophenols exhibit strong substituent effects. By simply varying the nature of substituents at the para position of the thiophenol capping ligands, the conductivity of the films can be manipulated and tuned in the range of 100 - 75000 Ω\(^{-1}\)m\(^{-1}\). Detailed analysis of the results obtained suggests that resonance effects dominate the interaction between the Au nanocrystals and the surface ligands. Further work could involve seeing if this interaction is dependent on the diameters of the Au nanocrystals, and a wider range of ligands could be explored to test this hypothesis. In addition, it was found that the nanocrystalline films studied herein provided a robust set of nanoscopic electrodes suited for studies of the properties of molecules. The films of Au nanocrystals synthesised were well-suited as ingredients of functional devices and this was shown through the construction of a working amine sensor.

Highly uniform films of both Ag and alloyed Ag-Au nanocrystals with phosphinyl surface ligands were also obtained at the water-toluene interface. Films formed at 50°C consisted of large aggregates of 10 nm sized nanocrystals. A range of compositions of the Ag-Au alloys were studied and remarkable differences were seen in the optical and electronic properties of the films as the composition was varied. Strong electronic coupling between Ag nanocrystals together with weak interaction with surface ligands yielded metallic films with resistance of a few Ohms. On the other hand, films that comprised Au nanocrystals exhibited behaviour akin to semiconductors with resistance values in the range of MΩ. The resistance of the films scaled exponentially with composition of the films, changing from metallic to non-metallic behavior when the percentage of Ag fell below 70%. Further work could involve alloying nanocrystals of other materials and exploring the electronic properties that result.
The electroless deposition of uniform films of Pt nanocrystals at the water-dichloroethane interface has also been reported. Aqueous tetrachloroplatinate ions were brought into contact with a decamethylferrocene reducing agent, and over 180 minutes and at 50°C, a thin black film of diameter platinum nanocrystals was formed. The rate of film deposition was slow, and no films formed below this temperature over realistic timeframes. The rate of deposition was therefore dramatically increased by incorporating a perchlorate-ion-gradient across the interface between the two liquids. A temperature of 50°C and a timeframe of 180 minutes gave rise to Pt nanocrystals of 4 nm in diameter, and the miniscule sizes of the particles was reflected in the charge transport characteristics of the Pt films. The Pt films were extremely resistive and possessed a room temperature resistivity coefficient associated with the platinum films was calculated to be 0.3 Ωm, which is distinctly higher than the value for bulk platinum.

CdS and ZnS nanocrystals have also been formed at the water-toluene interface, using metal thiobiuret precursors and sodium sulphide. It was found that the diameters of the CdS nanocrystals could be systematically varied from 5 nm to 12 nm by simply raising the reaction temperature from 22°C to 60°C.

The electronic properties of these films were also explored. It was found that the conductivity of the CdS and ZnS nanocrystals could be easily manipulated in the range of 6 to 60 Ω⁻¹m⁻¹ by simply adsorbing pyridinyl derivatives to their surfaces. Electron-donating substituents (e.g. methoxy) present on the pyridines made the films more amenable to charge transport, whereas electron-withdrawing groups (e.g. nitro) hindered charge flow through the film, findings that are in stark contrast to those observed with Au nanocrystalline films that are capped with para-substituted thiophenols.
Part VI

Bibliography
Bibliography


