

Study of conductance through wires grown dielectrophoretically
from colloidal gold suspensions

by

Christopher Harrower

A Thesis submitted to the Faculty of Graduate Studies of

The University of Manitoba

in partial fulfilment of the requirements of the degree of

MASTER OF SCIENCE

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I. Abstract

Gold nanoparticles have been synthesized by the reduction of tetrachloroauric acid in the presence of stabilized capping agents (citrate, polyvinylpyrrolidone, octadecanethiol) and dispersed in either a polar (water) or a non-polar solvent (dodecane). The size distribution of the nanoparticles was determined to be between 10-15 nm from transmission electron microscope images and through a comparison between Mie extinction theory and the measured extinction. Subsequently the particles were aligned into a wire between two gold electrodes through the action of a non-uniform electric field (dielectrophoresis). Conductance measurements through the dielectrophoretic wires showed non-linear conductance steps at integer multiples of G_0 — an indication of a low-dimensional metallic conductor. Wires grown from PVP and ODT capped gold nanoparticles showed conductance steps at 1, 2 G_0 .

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Costa-Kramer, J.L., "Conductance quantization at room temperature in magnetic and nonmagnetic metallic nanowires", *Physical Review B*, 55(8) R4875 (1997)

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Kretschmer, R., Fritzsche, W., "Pearl Chain Formation of Nanoparticles in Microelectrode Gaps by Dielectrophoresis", *Langmuir*, 20 pp. 11797-11801 (2004)

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VI. List of publications arising from this thesis

- [1] C.T.Harrower, D.R. Oliver (2006) "Electronic transport in dielectrophoretically-grown nanowires" Journal of Materials Science, accepted May 2006 (in press)
- [2] D.R. Oliver, C.T. Harrower (2005) "Electronic properties of wires fabricated via dielectrophoresis of colloidal gold nanoparticles." Key Engineering Materials **314**
- "Electrophoretic Deposition: Fundamentals and Applications" pp.121-126 (2006)

VII. List of Nomenclature

a	Radius [m]
a_j, b_j	Mie extinction theory parameters [dimensionless]
A	Absorbance [dimensionless]
AFM	Atomic force microscope
C_{ext}	Cross sectional extinction parameter [dimensionless]
C	Coulomb
d	Particle diameter [m]
∇	Differential operator $\left[\nabla = a_x \frac{\partial}{\partial x} + a_y \frac{\partial}{\partial y} + a_z \frac{\partial}{\partial z} \right]$
E	Electric field $\left[\frac{F}{m} \right]$
E	Electron energy - Joules [J]
E	Extinction of light [dimensionless]
eV	Electron volt $1\text{eV} = 1.6 \times 10^{-19} \text{ J}$
ϵ_0	Permittivity of Vacuum $8.854 \times 10^{-12} \text{ F/m}$
f	Probability distribution [dimensionless]
F	Force [Newtons]
G	Electronic conductance $\left[\frac{1}{\Omega} \right]$
$G_0 = \frac{e^2}{\pi \hbar}$	Landauer conductance $\sim (12.9 \text{ k}\Omega)^{-1}$

GPIB	General purpose interface bus (IEEE 488 standard communication protocol)
$h = 2\pi\hbar$	Planck's Constant $[6.626 \times 10^{-34} \text{ J} \cdot \text{s}]$
$H^{(2)}(x)$	Hankel function of the second kind
I	Total current [A]
J	Current Density $\left[\frac{\text{A}}{\text{m}^2}\right]$
$J(x)$	Bessel function of the first kind
$K(w)$	Clausius-Mossoti factor (dimensionless)
k	Electron wavevector in reciprocal space $[\text{m}^{-1}]$
k_F	Reciprocal lattice wavevector corresponding to the Fermi surface $[\text{m}^{-1}]$
L	Mean free path [m]
LABVIEW	A graphical programming language from National Instruments
λ	Wavelength [m]
MATLAB	A numerical computational computing environment from Mathworks
m	Ratio of two complex refractive indices $m = \frac{n_m}{n_o}$ [dimensionless]
$m(\omega)$	Polarizability of a particle as a function of radial frequency ω .
m	Meters
m_0	Electron Rest mass $[0.911 \times 10^{-27} \text{ g}]$
n	Complex refractive index of a material $n^* = n + ik$

n	Electron density of a material $\left[\frac{\text{\#electrons}}{\text{m}^3} \right]$
N	Number of particles per unit volume $\left[\frac{\text{\# particles}}{\text{m}^3} \right]$
ODT	Octadecanethiol
PVP	Poly(N-vinyl-2-pyrrolidone)
ρ	Density of electron states $\left[\frac{\text{\#electrons}}{\text{m}^3 \text{J}} \right]$
Q_{ext}	Point extinction parameter [dimensionless]
q_e	Electron charge $[1.602 \times 10^{-19} \text{ C}]$
R	Radius of a particle (m)
R	Resistance $[\Omega]$
s	Seconds
σ	Material conductivity $[\Omega \bullet \text{m}]$
$T(E)$	Electron transmission probability [dimensionless]
TEM	Transmission electron microscope
τ	Average time between collisions [s]
μ_0	Permeability of vacuum $[4\pi \times 10^{-7} \text{ H} \bullet \text{m}^{-1}]$
UV-vis	Ultra violet to visible spectrum, Approximately 300nm – 800nm
v	Velocity $\left[\frac{\text{m}}{\text{s}^2} \right]$
V	Unit of volume $[\text{m}^3]$
V	Voltage [volts]

ω	Angular frequency $\left[\frac{\text{rad}}{\text{s}} \right]$
ψ	Spherical Bessel function
ζ	Spherical Hankel function

1. Introduction

Transistor sizes have been reduced to allow the doubling of the density of devices in integrated circuits approximately every two years.[1] The main motivation behind this reduction is to produce an integrated circuit (IC) that has improved performance and is cheaper. A critical fabrication technique used to build integrated circuits that ultimately limits the size reduction is optical lithography – a process used to fabricate the required small structures. In recent decades, advances in optical lithography have enabled reductions in size, but the technique is still constrained by diffraction limits.[2]

Electronic transport character through a molecule, in the appropriate conditions, may exhibit properties similar to a conductor, or a semi-conductor. It has been conjectured the charge transport character of these molecules may be used to construct a resistor [3], diode [4], or even a transistor [5-6]. One of the major design challenges is the construction of an electrical connection to the molecule without altering the desired transport character [7-8]. Reproducibly attaching a molecule to a metallic surface is difficult [9] but constructing a contact to allow the interrogation of a single molecule is even more difficult.

Ever since the work of Michael Faraday, colloidal chemistry (in particular nanoparticles in solution) has found applications in far reaching fields, including microelectronics. Recent work in colloidal chemistry has demonstrated the possibility of using nanoparticles as building blocks for nanometer-scale structures [10]. A range of construction techniques have been explored and many researches have utilized a self-assembly technique to construct many novel materials and devices [11-12]. Self-assembly techniques are extremely useful in producing periodic structures such as an

inverse opal [13] material but individual control, as required for electrodes, remains relatively unexplored.

Lithographic fabrication techniques produce structures with feature sizes limited by diffraction that restrict feature size to the same scale as the wavelength of the electromagnetic radiation used. Manipulation of nanoparticles into electrically functional structures can also be accomplished through the action of a non-uniform electric field (dielectrophoresis). Since dielectrophoresis constructs structures from smaller particles the feature size of this technique is limited by the smallest attainable particle. Recent studies have illustrated the viability of constructing a molecular contact from the dielectrophoretic deposition of nanoparticles but have not studied their electronic transport character in detail; for example the construction of electrically functional microwires from a solution of gold nanoparticles (colloidal gold) [14].

Electronic transport behaviour of a low-dimensional metallic structure can be studied through a mechanical break junction experiment, in which two gold electrodes are slowly brought into contact and subsequently separated, during which the conductance is monitored. [15]

The objective of this study was to explore whether low-dimensional metallic conductance is observed through wires constructed from the dielectrophoresis of a colloidal suspension. Solutions of the gold nanoparticles were synthesized, concentrated and the size distribution was subsequently characterised. Mechanical break junction experiments were performed in the presence of solutions of the capping agents (ODT, PVP, sodium citrate) used for the gold nanoparticle synthesis to provide a basis of comparison of the conduction observed in the dielectrophoretic growth of the wires. The

results of the mechanical break junction experiments and the conductance observed through wires constructed from nanoparticles is presented in the following sections.

2. Literature Review

This chapter begins with a brief description of the Drude model for metallic conduction [16]. Following this, the Sharvin [17] and Landauer [18-19] semi-classical models for low-dimensional conduction are described. This discussion is followed by an outline of how mechanical break junctions are used to illustrate low-dimensional conductance.

2.1 *Electronic conduction*

In the Drude model a material consists of immobilized positive ions (atomic nuclei) within a ‘gas’ of non-interacting electrons. Upon the application of an electric field a net drift against the field vector is added to the random motion of the electrons. Each electron experiences scattering events that interrupt the acceleration due to the applied electric field. The characteristic time (τ) between each scattering event is a characteristic of the host medium. The current density in response to the field, E , can be expressed as [16]:

$$J = \frac{nq_e^2\tau E}{m} \quad (1)$$

where J is the current density resulting from an electric field, E , applied to an electron gas of density n with each electron having a charge q_e and mass m .

Since $J = \sigma E$ (Ohm’s law) the conductivity of a given material is written as [16]:

$$\sigma = \frac{nq_e^2\tau}{m_e} \quad (2)$$

The average velocity of an electron due to the applied field is defined as v_{drift} and therefore the average distance (mean free path) an electron will travel between scattering events is written as:

$$L = v_{\text{drift}} \tau \quad (3)$$

If the dimensionality of a structure is reduced below this mean free path then the conducting electrons will, on average, move through the structure without experiencing any scattering events. In the absence of scattering, electron conduction through a medium is best modelled as an electromagnetic wave rather than discrete particles.[20].

Landauer conduction theory [18,19] models the electronic conduction through a quantum point contact using the analogy between electronic conduction and electromagnetic wave propagation. In the context of this study, Landauer conduction through a one-dimensional system is considered.

A one-dimensional system can be constructed by considering a system where a low-dimensional region is sandwiched between two macroscopic regions. Electrons are incident from either side and are either transmitted or reflected by the low-dimensional region. The total current that flows from one region to the other region is written as: [17]

$$I = \frac{2q_e}{2\pi} \left[\int_0^\infty \partial E \left(\frac{\partial k}{\partial E} \right) v(k) f_1(k) T(E) - \int_0^\infty \partial E \left(\frac{\partial k'}{\partial E} \right) v(k') f_2(k') T(E') \right] \quad (4)$$

where the transmission probability, $T(E)$, is the probability of an incident electron, with a velocity $v(k)$ and velocity probability distribution $f(k)$ is transmitted through the low-dimensional region. The reverse transmission probability $T(E')$, corresponds to transport in the opposite direction with velocity $v(k')$ and velocity probability distribution $f(k')$.

At very low temperatures the conduction is dominated by bound electrons and the integral in equation 4 is performed over all the electrons up to the Fermi level (u_1 and u_2 in each of the macroscopic reservoirs) as:

$$I = \frac{2q_e}{2\pi} \left[\int_0^{u_1} \partial E \left(\frac{\partial k}{\partial E} \right) v(k) f_1(k) T(E) - \int_0^{u_2} \partial E \left(\frac{\partial k'}{\partial E} \right) v(k') f_2(k) T(E') \right] \quad (5)$$

Where the velocity and the probability distribution of the electrons is $v(k)$ and $f(k)$ respectively. The distribution of electrons in one reservoir $f_1(k)$ is equal to the second reservoir $f_2(k)$ since the temperature of each reservoir is assumed to be equal. Also the velocity of the electrons, for a given k , is the same in either reservoir since the material is the same for each of the reservoir. i.e. $v(k)=v(k')$. If the transmission probability is constant from one reservoir to the second reservoir i.e. $T(E) \approx T(E')$, then the current expression may be reduced to:[21]

$$I = \frac{2q_e}{2\pi\hbar} \int_{u_2}^{u_1} \partial E T \Rightarrow I = \frac{q_e}{\pi\hbar} T(u_1 - u_2) \quad (6)$$

Further, if the energy difference across the constriction is $eV = u_1 - u_2$ then [17]

$$G = \frac{I}{V} = \frac{q_e^2}{\pi\hbar} T \quad (7)$$

Thus, the conductance is described by the transmission probability of an electron moving from one macroscopic reservoir to another. While this is intuitive from an electromagnetic wave perspective, it is not as intuitive where an electron gas is concerned. The electromagnetic propagation through a structure can be found from solutions to the Helmholtz equation [22] whereas the low-dimensional conductance is most sensibly found by solutions, in the appropriate form, of the Schrödinger equation. A

comparison between these expressions reveals that the frequency of electromagnetic propagation is analogous to the energy at which an electron propagates through a structure. In nanostructures the electron is greatly affected by the dimensions of the structure. A free electron model with an effective mass yields a reasonable model for electron conduction behaviour through a structure and therefore gives a reasonable expression for the density of states.

Solutions to the Helmholtz equation as applied to electromagnetic propagation through ideal waveguide structures result in discrete frequencies (modes) at which propagation can occur. Perturbations to the ideal structure will cause perturbations in the form of frequency shifts or broadening of the allowable frequencies. Solutions of the Schrödinger equation describing electronic conduction through an ideal conductor also result in electronic conduction at discrete energies (i.e. states) Perturbations to this ideal structure will result in broadening of the discrete energies into a range of energies (sub-band) or by a shift in the discrete energy levels. It should be noted that while there is no occupancy limit to electromagnetic modes, the Pauli exclusion principle defines upper limits to the occupancy of conduction states.

There are four basic structures that can be used to estimate the density of states. i) an infinite structure, a bulk structure that does not constrain the electron motion in any of the three dimensions, ii) a quantum slab, which confines electrons in one dimension but has no constraint in either of the remaining dimensions, iii) a quantum wire, which permits freedom in one direction but confines electrons in the other two dimensions, iv) a quantum dot, this structure confines the electron in all three dimensions.

First, the density of states is calculated for a semi-infinite (three-dimensional) structure with zero potential inside the structure and an infinite potential outside the structure. The density of states equation is then written as: [23]

$$\rho_{\text{DOS}}(E) = \partial E \int_s \frac{\partial s}{\nabla_k E(k)} \quad (8)$$

The unit volume ∂E in a three-dimensional phase space is $(2\pi)^3$. Using this and a parabolic dispersion relation for one sub-band which can be written as: [23]

$E = \frac{(\hbar k)^2}{2m} + E_n$, then the density of states is:

$$\begin{aligned} \rho_{\text{DOS}}(E) &= \frac{1}{4\pi^3} \int \frac{m}{2k\hbar^2} ds = \frac{m}{\pi^2 \hbar^2} k \\ \text{since } k &= \sqrt{\frac{(E - E_n)2m}{\hbar^2}} \\ \rho_{\text{DOS}}(E) &= \frac{1}{\pi^2} \frac{m}{\hbar^2} \sqrt{\frac{(E - E_n)2m}{\hbar^2}} \end{aligned} \quad (9)$$

Secondly, the density of states for an electron confined into a quantum slab structure is described. The two dimensional structure is constructed by a thin sheet of zero potential and an infinite potential everywhere else. The density of states equation for this thin film is a reduction in dimensionality for that of the bulk case as: [23]

$$\rho_{\text{DOS}}(E) = \frac{1}{\pi} \int_s \frac{\partial s}{\nabla_k E(k)} \quad (10)$$

Substituting the dispersion relation [23] $E = \frac{(\hbar k)^2}{2m} + E_n$, equation 10 reduces to:

$$\rho_{\text{DOS}}(E) = \frac{1}{2\pi^2} \int \frac{2m}{2k\hbar^2} ds = \frac{m}{\pi\hbar^2} \quad (11)$$

$$\rho_{\text{DOS}}(E) = \frac{m}{\pi\hbar^2}$$

Since the total density of states is the sum of all density of states for all sub-bands, the density of states is written as: [23]

$$\rho_{\text{DOS}}(E) = \frac{m}{\pi\hbar^2} \sum_n u(E - E_n) \quad (12)$$

Finally, the density of states for an electron within a rectangular wire is considered. The thin wire is constructed from a waveguide with zero potential within the wire and an infinite potential outside the wire. The density of states within the wire is given by: [23]

$$\rho_{\text{DOS}}(E) = \frac{1}{2\pi} \int_S \frac{\partial s}{\nabla_k E(k)} \quad (13)$$

Again using the dispersion relation [23] $E = \frac{(\hbar k)^2}{2m} + E_n$, the density of states is

$$\rho_{\text{DOS}}(E) = \frac{1}{2\pi} \int \frac{2m}{2k\hbar^2} ds = \frac{m}{\pi k \hbar^2}$$

since $k = \sqrt{\frac{(E - E_n)2m}{\hbar^2}}$ (14)

$$\rho_{\text{DOS}}(E) = \frac{m}{\pi\hbar^2} \sqrt{\frac{\hbar^2}{(E - E_n)2m}}$$

As the total density of states is the sum of all density of states for all sub-bands, the density of states is written as: [23]

$$\rho_{\text{DOS}}(E) = \frac{m}{\pi\hbar^2} \sqrt{\frac{\hbar^2}{(E - E_n)2m}} \sum_n u(E - E_n) \quad (15)$$

In summary, the density of state distributions for the three quantum confinement are summarized as follows:

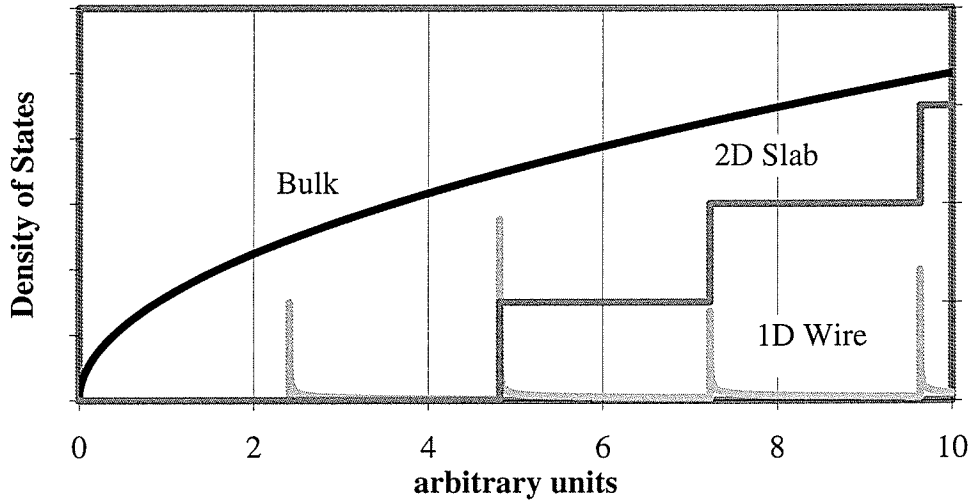


Figure 2.1 - Graph of the Density of States for a Bulk (equation 9), 2D slab (equation 12) and a 1D wire (equation 15) structure.

Another approach to describing electronic conduction through a low-dimensional system is the Sharvin [17] conductance. In this model the electronic conductance is also due to ballistic electrons but these electrons are treated as a gas, similar to the Drude model. As before, the conductance through a low-dimensional structure connecting two large reservoirs of electrons is considered, with the current density from an applied voltage V given by [17]:

$$j(r) = q_e \langle v \rangle \rho(E_F) \frac{q_e V}{2} \quad (16)$$

where ρ is the density of states on either side of the low-dimensional structure at the Fermi level E_F with a velocity v .

In this model, conduction is attributed to electrons at the Fermi level of each of the reservoirs. The density of states and the expected value for the velocity of these electrons is written as: [17]:

$$\rho(E_F) = \frac{mk_F}{\pi^2 \hbar^2} \quad (17)$$

$$\langle v \rangle = \frac{\hbar k_F}{2m} \quad (18)$$

Substituting equations 17 and 18 into equation 16,

$$j = \frac{q_e^2 k_F^2}{4\pi^2 \hbar} V \quad (19)$$

If the conduction is through a cross-section of the low-dimensional connecting region described by a disc of radius a , then the conductance is [17]:

$$G_s = \frac{q_e^2}{\pi \hbar} \left(\frac{k_F a}{2} \right)^2 \quad (20)$$

This expression (20) is known as the Sharvin conductance through a low-dimensional system. The first term of (20), $G_0 = \left(\frac{q_e^2}{\pi \hbar} \right)$, is known as the fundamental property of a reduced dimensional system. The second term, $\left(\frac{k_F a}{2} \right)^2$ depends upon the cross-sectional area taken into account and material properties, such as the radius 'a' and the magnitude of the reciprocal lattice vector corresponding to the Fermi surface, k_F . It has been observed that a low-dimensional metallic system shows non-linear conductance steps at integer multiples of $\frac{q_e^2}{\pi \hbar} (G_0)$ [24]. This observation compared to equation 20 suggests the observed non-linear conductance steps are due to changes in the radius of the

connecting region. Changes in the cross sectional radius may occur during a mechanical break junction experiment where the connecting region is stretched and thinned during separation. Other authors have illustrated that atomic rearrangement (changes in cross section) in the junction results in the non-linear conductance steps [24].

To construct an analogy between Sharvin conductance and the Landauer conductance, equation (16) is modified to account for spin degeneracy of electrons in each state. As a result, the density of states for a one-dimensional system (equation 15), becomes:

$$\begin{aligned}
 I &= q_e \langle v \rangle \rho(E) q_e V \\
 I &= q_e^2 \left(\frac{\hbar k}{2m} \right) \left(\frac{m}{\pi \hbar^2 k} \right) \sum_n u(E - E_n) \\
 \frac{I}{V} &= \frac{q_e^2}{\pi \hbar} \sum_n u(E - E_n)
 \end{aligned} \tag{21}$$

where u is the unit step function and E_n is the lowest energy for every sub-band.

Comparison between (21) and (7) illustrate that the transmission probability T can only take on integer values, i.e. a change in the applied voltage may induce a change in the current and therefore proportional to an integer multiple change of G_0 . This jump in current is a by-product of the low-dimensionality of the system. As such, the presence of conductance steps at integer multiples of G_0 can be thought of as a characteristic conductance through a low-dimensional system.

2.2 Mechanical Point Contact Experiments

Constructing a low-dimensional conductance structure can be achieved through a mechanical point contact experiment in which two metallic electrodes are brought into contact and slowly retracted from one another. During retraction the atoms will re-

arrange into strings between the two electrodes. Further retraction of the electrodes elongates the metallic string to a thickness of only a few atoms, a low-dimensional structure. Upon further separation the wire will rupture while maintaining the dangling strings on each end of the electrodes. If the electrodes are slowly brought back into contact, these dangling strings will come back into contact and re-form a nanometer-sized wire. During the breaking and making of the nanometer sized-wires (nanowire) a small voltage is applied between the electrodes, the resulting current is measured so that the conductance may be calculated [25-32].

Data from the conductance traces (Figure 2.2a) are combined to form histograms that illustrate the frequency at which conductance plateaus occur, illustrated by peaks in conductance (Figure 2.2b). Histograms are compiled from assigning data from the conductance traces (Figure 2.2a) to bins that correspond to the minimal observable conductance. Each bin within the histogram corresponds to the amount of time that the conductance trace remains within the conductance range ascribed to the bin. Many conductance traces are used to compile the histogram to illustrate the reproducibility of the conductance among many conductance traces.

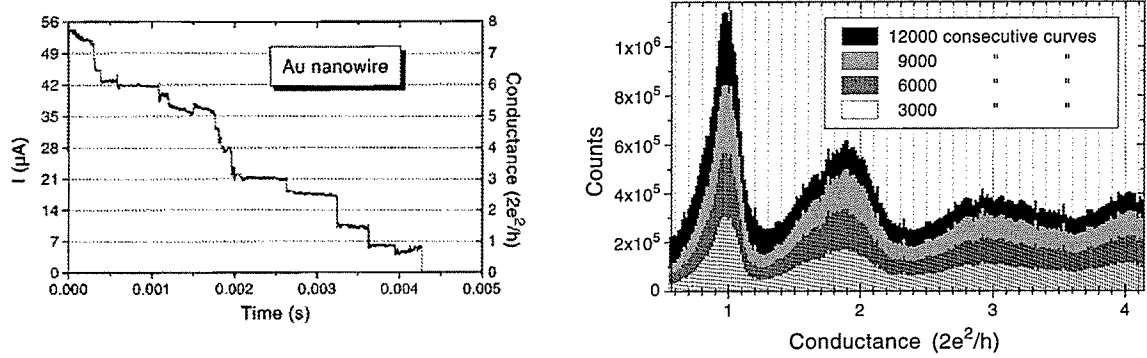


Figure 2.2 - a) Conduction plot and b) histogram plot of point contact of gold wires performed in air at room temperature. Reprinted with permission from [32] Copyright (1997) by the American Physical Society

Mechanical break junction experiments rely on the plastic deformation of the metallic electrodes into a low-dimensional metallic conductor. During continual stretching (retraction) of the electrodes, the cross section of the low-dimensional region will reduce until the wire ruptures. Non-linear conductance steps observed may be due to changes in the cross sectional area as modeled by the Sharvin conductance (20). If an ac voltage is applied to the junction to measure the conductance through this low-dimensional system then the non-linear conductance may also be due to changes in the voltage across the junction (21).

Conductance measurements in a mechanical break junction can be thought of having three regimes of operation, the bulk metallic conductor, metallic low-dimensional conductor, and conductance due to tunnelling after the rupture of the wire. Each regime of operation can be identified by a characteristic noise spectrum, as the transport character of each are vastly different. For the bulk case, noise power spectrum is described by the Johnson-Nyquist (thermal) expression $S = 4kT\Delta f$ [33], where k is Boltzmann's constant, T the temperature, and Δf the frequency bandwidth. The tunnelling

regime incorporates both thermal noise and shot noise, $P = (q_e V_i R) \coth\left(\frac{q_e V_i}{2kT_i}\right)$, where T is the temperature, V is the junction voltage and R the resistance [34]. The final regime of conductance is the metallic low-dimensional conductor in which the power spectrum for noise results from shot noise. Shot noise in a metallic low-dimensional conductor is dependent upon the transmission probability of electrons through the reduced dimensional junction described by Landauer theory [35,36]. The conductance peaks shift to a lower value as the conductance integer multiple is increased. Compilation of the noise into histogram analysis will illustrate the conductance is dependent upon transmission probability as a histogram is a measure of the transmission probability. The thermal noise present in a point contact is related to the power of the noise, $P_{\text{thermal}} = 4kTG$ [37]. This means the noise power present in any bulk or tunnelling conductance trace will increase linearly with an increase in temperature.

Conductance of mechanical break junctions are expected to exhibit conductance peaks at integer multiples of G_0 as modelled by Landauer conduction theory. Other authors have illustrated experimentally the presence of conductance peaks at fractional multiples of G_0 [38]. The atomic arrangement of the wire that produced the fractional conductance has been shown to be highly unstable as the conductance tended to drift toward integer multiples. Another study [29] has illustrated that adsorbed molecules may encourage this atomic re-arrangement and lead to broadening and shift in the conductance peaks toward lower values of G_0 from the integer multiples in the histogram. Mechanical break junctions in this dissertation were performed in the presence of solvents or solutions of the capping agents in order to illustrate their contribution to the conductance.

Electronic conductance through the mechanical break junction experiment prior to wire formation or after the breaking of the wire may be due to tunnelling electrons [39]. A transition would exist from the tunnelling regime to the contact regime as the electrodes are brought into or withdrawn from contact. In the tunnelling regime the conductance is exponentially dependent upon the separation distance (z). [5,40]

$$G \propto e^{-(Bz)} \quad (22)$$

where B is a constant dependent upon the work function of the material tunnelled through. As the electrodes come from infinity into contact the conductance will increase from zero (corresponding to $z \approx \infty$) to approximately $1G_0$, where the conductance may be due to a metallic conductor [41]. If the electrodes are retracted at a constant velocity ($z=kt$), then the conductance will exponentially decrease with an increase in time. (i.e. $G \propto e^{-t}$). The histogram analysis reflects the amount of time the conductance remains within a specified bin (conductance) range. As the conductance increases, the amount of time spent within that range will exponentially decrease. Therefore a tunnelling process is likely to be characterized by a histogram with an exponential decrease in the count frequency as the conductance increases [42].

2.3 Dielectrophoretic growth of nanowires

A reduced dimensional structure may be constructed without relying on the mechanical deformation of the metallic conductor through the dielectrophoretic manipulation of nanoparticles dispersed in a colloidal suspension. Previous studies have shown the viability of constructing wires, nanometer sized gaps and other structures [14, 43-52] from colloidal nanoparticles.

Dielectrophoretic growth of nanowires may be undertaken by the application of an alternating voltage on two electrodes immersed in a colloidal solution. In the presence of a non-uniform alternating electric field, uncharged particles will experience a net force towards or away from regions of highest electric field. Particles that are attracted towards the electrodes will aggregate onto the electrodes and extend the electrode. Extension of the electrodes continues until the gap between the electrodes is bridged, forming a wire.

It has been noted that the large current present upon wire formation that in turn may melt the metal particles into a homogeneous metallic wire. The presence of a homogeneous wire ($\sim 20\mu\text{m}$ in diameter) is also indicated by the observation of linear I/V behaviour in dielectrophoretically grown microwires [43-45]. In an effort to limit the rate of particle aggregation, some workers have included a resistor in series with the junction to limit the current through the formed wire. As illustrated in Figure 2.3 (g,h)) parallel wires may be formed between two parallel plate electrodes, accommodating the relatively large current upon wire formation.

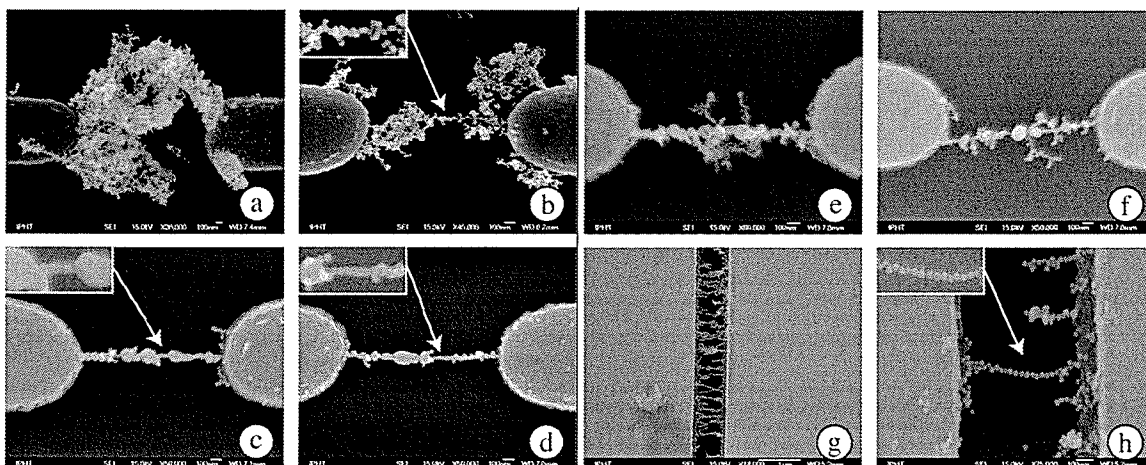


Figure 2.3 - SEM pictures of dielectrophoretically grown nanowires from a colloidal suspension. Each picture is a progression of optimization towards pearl chain formation. Refer to text for further explanations. Reprinted with permission from [47]. Copyright (2004) American Chemical Society.

The formation of wires by dielectrophoresis, as illustrated in Figure 2.3, and the resulting structure of the wire is dependent upon the applied voltage driving voltage, frequency, and electrode geometry. Progression from bulk wire formation to pearl chain formation (Figure 2.3h) was accomplished usually by an increase in the applied frequency, increase in the applied voltage, and utilizing parallel plate-type electrodes.

2.4 Dielectrophoretic Force

Assembling of nanoparticles into functional structures through dielectrophoresis [53] was illustrated in section 2.3. The dielectrophoretic force is imposed on a particle through the presence of an alternating non-uniform electric field and is related to the induced dipole on the particles by [54]:

$$F_{\text{DEP}} = \text{Re}\{[m(\omega) \cdot \nabla] \bar{E}\} \quad (23)$$

in which $m(\omega)$ is the polarizability of the nanoparticle. If the particle is spherical then polarizability is related to the electric field strength by:

$$m(\omega) = 4\pi\epsilon_m R^3 K(\omega) \bar{E} \quad (24)$$

where ϵ_m is the permittivity of the medium, R is the radius of the particle, E is the electric field intensity, and $K(\omega)$ is the Clausius-Mossoti factor defined by [55]:

$$K(\omega) = \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*} \quad (25)$$

Substituting (24) into (23) results in an expression for the average force experienced by the particles:

$$\langle F_{\text{DEP}} \rangle = 2\pi\epsilon_m a^3 \text{Re}\{K(\omega)\} \nabla |E_{\text{rms}}|^2 \quad (26)$$

where ϵ_m^* and ϵ_p^* are the permittivity of the medium and particle respectively. Generally the permittivity of a material is given by:

$$\epsilon^* = \epsilon - j \frac{\sigma}{\omega} \quad (27)$$

where σ and ϵ are the conductivity and the ac capacitivities of a material. As the electric field frequency approaches zero ($\omega \rightarrow 0$), the Clausis-Mossoti factor reduces to:

$$K(\omega) = \frac{\sigma_p - \sigma_m}{\sigma_p - 2\sigma_m} \quad (28)$$

The force imposed on each individual nanoparticle depends upon the gradient of the electric field and the surface conductance (polarizability) of the nanoparticle. In dielectrophoretic growth experiments the applied electric field dominates the interparticle field contributions experienced by the nanoparticles. Thus, equation 26 represents a reasonable first-order approximation to the forces experienced by the nanoparticles.

2.5 Effective dielectric constant of a metallic nanoparticle

In the above consideration of the forces experienced by the nanoparticles it was assumed that the nanoparticles are constructed from a single material. Nanoparticles dispersed into a suspension are non-homogeneous and therefore the permittivity of the particle is not that of a bulk metal and an effective permittivity of the particle must be calculated. In the following discussion, the particles are approximated by a spherical particle stabilized by a capping ligand. This may be described as a particle with a homogenous core surrounded by a homogenous layer as illustrated in Figure 2.4a. A widely-accepted model for the effective permittivity of such a structure is attributed to Irimajiri *et al.* [56-57].

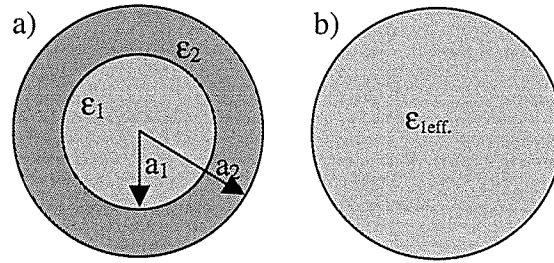


Figure 2.4 - A depiction of the colloidal gold nanoparticles used in the calculation of the effective dielectric constant.

The permittivity of a spherical particle containing a homogenous core and covered with another homogeneous spherical layer (Figure 2.4a) can be reduced to a homogenous particle by considering the effective permittivity. If the core and the subsequent layer have a complex permittivity described as: $\epsilon_i = \epsilon_i - j \frac{\sigma_i}{\omega}$, then the permittivity can be calculated as [57]:

$$\epsilon_{\text{leff}}^* = \epsilon_2^* \frac{\left(\frac{a_2}{a_1}\right)^3 + 2 \frac{\epsilon_1^* - \epsilon_2^*}{\epsilon_1^* + 2\epsilon_2^*}}{\left(\frac{a_2}{a_1}\right)^3 - \frac{\epsilon_1^* - \epsilon_2^*}{\epsilon_1^* + 2\epsilon_2^*}} \quad (29)$$

This permittivity then can be used in the calculation of the Clausis-Mossoti factor (equation 25) used in the calculation of the dielectrophoretic force. The Clausis-Mossoti factor illustrates the magnitude of the induced dipole on the nanoparticles depends upon the difference of permittivity of the particle and the surrounding media (solvent). Since the difference in permittivity of the nanoparticle is reduced as a result of the capping ligand, the induced dipole will be reduced, resulting in the reduction of force induced on the nanoparticle. The reduction in force on the nanoparticles would result in the increase in the amount of time required for dielectrophoretic growth experiments.

2.6 Nanoparticle Synthesis

The objective of the nanoparticle synthesis was to create small nanoparticles (<20nm) with as small size distribution as possible. In general, gold nanoparticles are produced as follows: a dilute solution of tetrachloroauric acid $[\text{HAuCl}_4]$ is mixed with a dilute solution of a reducing agent. This reducing agent reduces Au^{3+} to Au^0 until a critical nucleation concentration of Au^0 is reached. Beyond this critical concentration the gold ions will begin to nucleate until the Au^0 concentration falls below the critical nucleation concentration. Following the nucleation process, gold will continually aggregate onto these nucleation sites until the concentration falls below another critical concentration. [58]

Typically, a capping agent is introduced during the reduction process to prevent excessive aggregation of gold onto the gold nanoparticles. A capping ligand achieves this by absorption onto the surface of the gold nanoparticles, preventing further aggregation. The size of the gold nanoparticles depends upon the relative rates of adsorption of the capping agent and aggregation. A higher concentration of capping agents will increase the rate of adsorption and thus can decrease the particle size.

Citrate-stabilized nanoparticles may be synthesized through the reduction of tetrachloroauric acid by sodium citrate. In this process the citrate ion $[C_6H_5O_7]^{3-}$ acts both as the reducing agent and (subsequently) as the capping agent. Citrate adsorbs onto the surface of the gold nanoparticle by [59]:

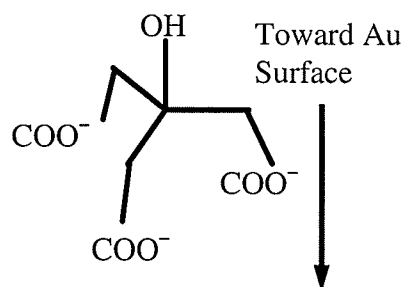


Figure 2.5 - A depiction of citrate adsorption on the surface of a gold particle.

Citrate ions preferentially adsorb onto gold surfaces forming a highly ordered ad-layer of anions [59]. The citrate ions assemble on the surface with the hydrophobic towards the gold surface and the hydrophilic end away from the surface. The negative charge of the citrate molecule will induce an overall net negative charge on the citrate capped gold nanoparticle.

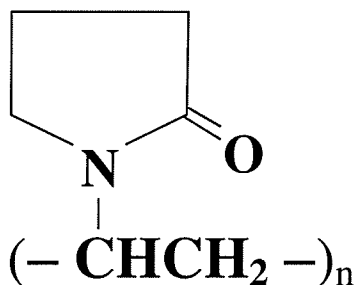


Figure 2.6 - A depiction of PVP (C_6H_9NO)_N that preferentially adsorbs onto the surface of gold

Poly(N-vinyl-2-pyrrolidone) (PVP) covered nanoparticles are synthesized through the reduction of tetrachloroauric acid by sodium borohydride or potassium bitartrate in the presence of the PVP molecule. The PVP molecule prevents further aggregation of gold by adsorbing onto the surface of the gold nanoparticles and the concentration of PVP in solution will decrease or increase the resulting size of the gold nanoparticles. It has been shown that poly(N-vinyl-2-pyrrolidone) (PVP) tends to adsorb onto a gold surface with an estimated film thickness of 10-15 nm [60].

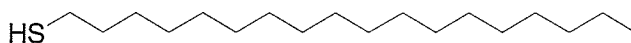


Figure 2.7 - A depiction of octadecanethiol that will adsorb onto the surface of a gold particle

Octadecanethiol (ODT, $C_{18}H_{37}SH$) stabilized nanoparticles can be synthesized through a single-stage or a two-stage synthesis method [61-63]. The one-stage method is accomplished with the reduction of tetrachloroauric acid by a reducing agent (sodium borohydride) in the presence of ODT. Alternatively, gold nanoparticles capped with either PVP or citrate may be synthesized and a ligand exchange reaction can be initiated by the introduction of ODT into the solution. It has been shown the octadecanethiol

adsorbs perpendicular to a gold surface to monolayer coverage with a thickness of 2.0nm [64-65] in up to 800 seconds. As ODT has a relatively slow adsorption rate, the size distribution cannot be easily controlled through changes to the concentration of ODT.

2.7 Characterization of Nanoparticles

Upon completion of nanoparticle synthesis, analysis of particle size distribution was performed. Analysis proceeded by obtaining visible optical absorption spectra of the nanoparticles in suspension and a comparison to the extinction spectra calculated by Mie extinction theory. [66] Images of the nanoparticles obtained from a transmission electron microscope were also analyzed to obtain the particle size distribution.

Extinction spectra of the nanoparticle suspensions were obtained using a spectrophotometer. An extinction spectrum is taken of the solvent and the glass holder to determine the 'background' (a blank sample). This background is then subtracted from the extinction spectrum derived from the colloidal samples.

The theory describing extinction spectra of colloidal suspensions is most frequently attributed by Mie [67]. The colloidal particles could be dielectric particles suspended in air or metallic particles suspended in an aqueous solution.

The extinction of light through a sample is exponentially dependent upon the path length of the beam through the sample,

$$E = ke^{(A(\lambda)z)} \quad (30)$$

where z is the path length through the sample and E is the extinction, or absorbance, of the sample. The extinction (absorbance) is the summation of light scattered or absorbed by the nanoparticle suspension. Extinction spectra are plotted on a logarithmic scale and thus equation 30 can be re-written as

$$\ln(E) = \ln\left(\frac{I}{I_0}\right) = \ln(ke^{A(\lambda)z}) = \ln k + A(\lambda)z \quad (31)$$

where the incident and transmitted intensities are I and I_0 respectively.

The total cross sectional extinction of each nanoparticle is defined as.

$C_{\text{ext}}(d, \lambda)$ For a real solution, the extinction must be written in terms of the particle size distribution as [66]:

$$A(\lambda) = NV \int_0^\infty f(d) C_{\text{ext}}(d, \lambda) dd \quad (32)$$

where N is the number density of particles in the extinction volume V with a probability distribution, with respect to the diameter (d), of $f(d)$.

As a result, equation 32 can be re-written as:

$$\ln(E) = \ln k + NV \int_0^\infty f(d) C_{\text{ext}}(d, \lambda) dd \quad (33)$$

Another parameter that is used is the extinction coefficient Q_{ext} and it is related to the extinction cross section by (assuming a spherical particle)

$$C_{\text{ext}}(\lambda, d) = \pi d^2 Q_{\text{ext}}(\lambda, d) \quad (34)$$

Then Q is related to Mie coefficients a_j , b_j , by:

$$Q_{\text{ext}}(d, \lambda) = \frac{2}{\alpha^2} \sum_{j=1}^{\infty} (2j+1) \text{Re}(a_j + b_j) \quad (35)$$

Mie scattering coefficients, a_j , b_j , are the amplitudes of the scattered electric and magnetic fields respectively. The coefficients a_j , b_j are defined as: [66]

$$a_j = \frac{\alpha \psi_j'(\beta) \psi_j(\alpha) - \beta \psi_j'(\alpha) \psi_j(\beta)}{\beta \psi_j'(\beta) \zeta_j(\alpha) - \beta \zeta_j'(\alpha) \psi_j(\beta)} \quad (36)$$

$$b_j = \frac{\beta \psi_j'(\beta) \psi_j(\alpha) - \alpha \psi_j'(\alpha) \psi_j(\beta)}{\beta \psi_j'(\beta) \zeta_j(\alpha) - \alpha \zeta_j'(\alpha) \psi_j(\beta)} \quad (37)$$

where $\beta = m\alpha$ and $\alpha = \frac{\pi d}{\lambda}$ where m is the ratio of complex refractive index of the particle to refractive index of the surrounding medium. (i.e. $m = \frac{n_m}{n_o}$). In equation 36 and 37, ψ , and ζ are respectively, the spherical Bessel and Hankel functions. These two functions are related to the Bessel and Hankel functions by [67]:

$$\psi_j(x) = \left(\frac{x\pi}{2}\right)^{\frac{1}{2}} J_{j+\frac{1}{2}}(x) \quad (38)$$

$$\zeta_j(x) = \left(\frac{x\pi}{2}\right)^{\frac{1}{2}} H_{j+\frac{1}{2}}^{(2)}(x) \quad (39)$$

The solution to the Bessel function can be solved through a series expansion of equation 38 [68]:

$$J_v(x) = \sum_{k=0}^{\infty} \frac{(-1)^k \left(\frac{x}{2}\right)^{2k+v}}{k! \Gamma(k+v+1)} \quad (40)$$

$$J_{-v}(x) = \sum_{k=0}^{\infty} \frac{(-1)^k \left(\frac{x}{2}\right)^{2k-v}}{k! \Gamma(k-v+1)} \quad (41)$$

Furthermore, the Hankel function can be written in terms of the Bessel function as [68]:

$$H_v^2(x) = J_v(x) - iY_v(x) \text{ where } Y_v(x) = \frac{J_v(x)\cos(\pi v) - J_{-v}(x)}{\sin(\pi v)} \quad (42)$$

If the particles are small compared to the wavelength, then the arguments of the Bessel functions α, β will be small ($x \ll 1$). For this case the first few terms of the expansion may be used and assuming an error $O(x^8)$ is acceptable.

$$\psi_1(x) = \frac{x^2}{3} - \frac{x^4}{30} + \frac{x^6}{840} \quad (43)$$

$$\psi_2(x) = \frac{x^3}{15} - \frac{x^5}{(14)(15)} + \frac{x^7}{(15)(8)(7)(9)} \quad (44)$$

$$\psi'_1(x) = \frac{2x}{3} - \frac{2x^3}{15} + \frac{x^5}{140} \quad (45)$$

$$\psi'_2(x) = \frac{x^2}{5} - \frac{x^4}{(14)(3)} + \frac{x^6}{(15)(8)(9)} \quad (46)$$

$$\zeta_1(x) = -\frac{i}{x} - \frac{ix}{2} + \frac{x^2}{3} + \frac{ix^3}{8} + \frac{x^6}{840} \quad (47)$$

$$\zeta_2(x) = -\frac{i3}{x^2} - \frac{i}{2} - \frac{ix^2}{8} + \frac{x^3}{15} + \frac{ix^4}{8} - \frac{x^5}{210} - \frac{ix^6}{1152} + \dots \quad (48)$$

$$\zeta'_1(x) = \frac{i}{x^2} - \frac{i}{2} + \frac{2x}{3} + \frac{i3x^2}{8} + \frac{6x^5}{140} \quad (49)$$

$$\zeta'_2(x) = \frac{i6}{x^3} - \frac{ix}{4} + \frac{x^2}{5} + \frac{ix^3}{2} - \frac{x^4}{42} - \frac{ix^5}{192} + \frac{x^6}{1080} \quad (50)$$

The first two Mie coefficients with the above estimation and truncating factors above $O(x^7)$ are:

$$a_1 = \frac{\left(\frac{2m}{9} - \frac{2m^3}{9}\right)\alpha^4 - \left(-\frac{m}{45} + \frac{m^5}{45}\right)\alpha^6}{\left(-\frac{2im}{3} - \frac{im^3}{3}\right)\alpha + \left(-\frac{im}{3} + \frac{3im^3}{10} + \frac{im^5}{30}\right)\alpha^3 + \left(\frac{2m}{9} - \frac{2m^3}{9}\right)\alpha^4 + \left(\frac{im}{12} - \frac{7im^3}{120} - \frac{im^5}{42} - \frac{im^7}{840}\right)\alpha^5 + \left(-\frac{2m^3}{45} + \frac{m^5}{45}\right)\alpha^6} \quad (51)$$

$$b_1 = \frac{\left(\frac{m^2}{45} - \frac{m^4}{45}\right)\alpha^6}{im^2\alpha + \left(-\frac{im^2}{6} + \frac{im^4}{6}\right)\alpha^3 + \left(\frac{im^2}{24} + \frac{im^4}{20} - \frac{im^6}{120}\right)\alpha^5 - \frac{m^5}{45}\alpha^6} \quad (52)$$

$$a_2 = \frac{\left(\frac{m^2}{75} - \frac{m^4}{75}\right)\alpha^6}{\left(-\frac{i3m^2}{5} - \frac{i2m^4}{5}\right)\alpha + \left(-\frac{im^2}{10} + \frac{im^4}{14} + \frac{im^6}{35}\right)\alpha^3 + \left(\frac{im^2}{40} + \frac{im^4}{35} - \frac{im^6}{360} - \frac{im^8}{1260}\right)\alpha^5 + \left(\frac{m^2}{75} - \frac{m^4}{75}\right)\alpha^6} \quad (53)$$

$$b_2 = \frac{1}{-im^3\alpha + \left(-\frac{im^3}{10} + \frac{im^5}{10}\right)\alpha^3 + \left(-\frac{im^3}{120} + \frac{im^5}{84} - \frac{im^7}{280}\right)\alpha^5} \quad (54)$$

Equations 51-54 are the first two terms of the Mie coefficients used in the extinction calculations described in equation 35. Further calculation of the extinction proceeded by performing the calculations in MATLAB.

2.8 TEM Image processing

The Hough transform [69] is a method usually used to identify and extract a line, circle, or any regular shape from a binary image. Identification of the objects proceeds by a mapping of the original image to a parameter space where the objects can be easily identified. For example a line can be drawn on an x,y grid from knowing its slope and x intercept. i.e. $y=mx+b$. After the construction of the image, the slope and x intercept are lost and the plotted point x,y are what remains. The Hough transform proceeds by examining every possible value of m and b and examines the likelihood of these parameters forming the line.

For the case of a circle with radius r drawn on a (m by n pixel) binary image, each pixel, with coordinates (x,y) is described by the equation: $(x-a)^2 + (y-b)^2 = r^2$, where x,y are the pixel coordinates of each element and a,b are the co-ordinates of the center of the circle. In a real image the coordinates (x_i, y_i) of each edge point are known and the parameters a,b,r, are unknown. The Hough transform algorithm begins by setting up a three-dimensional accumulator matrix for all possible values of a,b,r in all the circles to be determined. Each cell of the accumulator matrix is incremented through all values of (x_i, y_i) that satisfy the equation $(x_i - a)^2 + (y_i - b)^2 = r^2$. If any pixel value corresponds to

a value of 2π then the circle of radius r is determined to be in the original image, centered at (a,b) with radius r .

Size distributional analyses such as dynamic light scattering and x-ray powder diffraction may have been performed on the colloidal gold solutions. Dynamic light scattering exploits the time-dependent light scattering fluctuations as a result of the nanoparticle Brownian motion [70]. Typically a stable laser is directed at the particles of interest and the scattered light is captured using a fast device capable of counting individual, usually with the aid of a photo-multiplier tube. Fluctuations in the intensity of the scattered light are analysed by a photon correlator. In the polydisperse case the correlation function will be given by: $|g^{(1)}(\tau)| = \int_0^\infty e^{-\pi\Gamma} G(\Gamma) d\Gamma$ [71]. Where

$G(\Gamma) = G(q^2 D)$ is the normalized linewidth distribution function, q is the momentum transfer in the scattering experiment, and D is the diffusion constant calculated from

$$D = \frac{kT}{6\pi\eta r}$$

where k is Boltzmann's constant, r the radius of the particles, and η the

viscosity coefficient, and T the temperature. The main challenge presented by this method is to calculate the distribution function from the correlation function obtained experimentally. Usually, a distribution is assumed and fitted to the correlation function.

X-ray powder diffraction takes a sample of the powdered material (dried nanoparticles) and is illuminated with a beam of x-rays at a fixed wavelength. The transmitted light intensity of the resulted diffracted radiation is measure with respect to the diffraction angle. The size distribution of the particles may be estimated by: [72]

$$D \approx \frac{0.9\lambda}{\beta \cos(\Theta)}$$

where D is the average particle diameter, λ is the wavelength of the

incident x-rays, β (in terms of 2Θ) is the full width half maximum angle difference from the peak intensity at the angle Θ . Typically an x-ray powder diffraction machine will introduce noise into the measurements by smearing out the peak intensity. This smear results in an error in the estimation for the nanoparticle size distribution especially for small particles ($<5\text{nm}$) where the peak tends to be broad and a low peak intensity.

Neither dynamic light scattering nor x-ray diffraction based facilities that routinely handled this type of analysis are available locally. Analysis of TEM images, while imperfect, was used to obtain a reasonable estimate of the mean particle size distributions synthesized.

3. Experimental

In this chapter the steps and methodologies required to produce gold wires dielectrophoretically from a solution of gold nanoparticles are presented. Following discussion of the synthesis methods studied, the analytical methods used to characterize the particle distribution (extinction spectra and image analysis) is described. The design and construction of the apparatus for dielectrophoretic growth concludes this chapter.

3.1 *Nanoparticle Synthesis*

Suspensions of gold nanoparticles were synthesized for use in dielectrophoretic growth of wires. The nanoparticles needed to be stable in air at room temperature to allow ease of handling and concentration of the solutions for use in the growth experiments. Several synthesis methods were explored and these methods are described below.

The materials used in the production of nanoparticles were obtained from commercial vendors and were used as purchased. Tetrachloroauric (III) acid trihydrate (HAuCl_4) was purchased from Acros Organics BVBA or hydrogen tetrachloroaurate (III) solution ca. 30-wt% solution in dilute HCl (99.99%) was purchased from Sigma-Aldrich. The tetrachloroauric acid solution allowed for ease of storage compared to the hydrophilic tetrachloroauric salt as the hydrophilic salt absorbed moisture over time. Poly(N-vinyl-2-pyrrolidone) (PVP), α -cyclodextrin were purchased from Matheson Coleman and Bell. Sodium citrate, potassium bitartrate and octadecanethiol were purchased from Fisher Scientific while sodium borohydride and tetraoctylammonium

bromide were purchased from Sigma-Aldrich. Of the remaining reagents 1-propanol and toluene were purchased from Fisher Scientific.

Carbonate-capped gold nanoparticles were synthesized by a method outlined by Slot and Geuze [73]. 4 ml of 1 wt% tetrachloroauric acid and 4ml of 1.4 wt% of potassium carbonate was mixed with 25 ml of deionized water and placed in an ice bath. Separately, 4 ml of 0.7 wt% of sodium ascorbate was mixed and added to the mixture. Immediately after the addition of the sodium ascorbate the mixture turned from a pale yellow to a dark purple, indicating nanoparticle formation. Another 63 ml of deionized water were added, and the mixture was then heated to reflux. Once the solution turned to a wine-red (indicating further aggregation of the nanoparticles), the solution was cooled to room temperature and stored at room temperature in a capped bottle.

Citrate-capped gold nanoparticles were produced following the method outlined by Frens [74] , a method that has been developed and studied by later authors[73,75-77]. 50ml of aqueous 23mM tetrachloroaurate(III) solution was heated to 100 °C and 1 ml of 1 wt% sodium citrate was added to the hot solution while stirring vigorously. Within 2 minutes the solution changed colour from pale yellow to orange-red indicating nanoparticle formation. After a further 5 minutes stirring (to ensure completion of the reaction) the solution was concentrated in a rotary evaporator operating at 40 °C.

Thiodipropionic-acid capped gold nanoparticles were synthesized by a method outlined by Tan *et. al.*[77]; 20 ml of a 4 mM solution of thiodipropionic acid and 20 ml of a 1 mM solution of tetrachloroaurate(III) acid solution were mixed and brought to reflux. Separately, 20 ml of 0.5 wt% of potassium bitartrate were heated to 60 °C and quickly

added to the solution. Within two minutes the solution changed from a pale-yellow to light grey.

α -Cyclodextrin-capped gold nanoparticles were synthesized by a method outlined by Liu *et al* [78]. 4.4 ml of 1wt% of tetrachloroauric acid and 2.98g of α -cyclodextrin was added to 85 ml of deionized water. The solution was brought to reflux at which point 10 ml of 1wt% of sodium citrate were quickly added. Within 10 seconds the solution turned colour from a pale yellow to a light grey. Within another 2 minutes the solution turned to a burgundy red, indicating nanoparticle formation. The solution was boiled for a further 15 minutes to ensure completion of nanoparticle formation.

Poly(N-vinyl-2-pyrrolidone)(PVP)-capped gold nanoparticles were synthesized by two different methods. Firstly, an adaptation of Tan *et al* [77], 20 ml of 1 mM aqueous tetrachloroaurate(III) solution containing 1.6 g of PVP was brought to reflux. 20 ml of 0.5 wt% potassium bitartrate that had (separately) been heated to 100 °C was added quickly while stirring vigorously. After 2 minutes the combined solution colour changed from yellow to a deep wine-red, indicating nanoparticle formation. After stirring for another 5 minutes (to ensure completion of the reaction) the nanoparticles were completely dried in a rotary evaporator operating at 40 °C and a pressure of 460 mmHg. The resulting deposit was then re-dissolved in 1-propanol as the potassium bitartrate was negligibly soluble in 1-propanol. After separation from the potassium bitartrate residue the 1-propanol solution was used as a host solution for the colloidal particles, or the nanoparticles were dried in a rotary evaporator and re-dissolved in deionized water to form an aqueous colloidal suspension.

A second synthesis method for PVP-capped gold nanoparticles followed that of Catotenuto and Nicolais [79]. A solution of 4 g of PVP and 5 mg of hydrogen tetrachloroaurate(III) was mixed with 21 ml of ethylene glycol. The solution was continually stirred for two days to allow the formation of nanoparticles. The solution turned from a pale-yellow to a brown-red solution, indicating nanoparticle formation. After an hour of no further observable colour changes, it was assumed that the reaction was completed. Subsequently, 250 ml of acetone were added and the solution agitated in an ultrasonic bath for 5 minutes to dissolve the ethylene glycol into the acetone. The ethylene glycol/acetone solution was then decanted from the brown precipitate (gold nanoparticles). This process was repeated several times (~3 times) until no more ethylene glycol was dissolved in the acetone, as the acetone would remain clear upon mixing with the nanoparticle solution. Upon completion of the washing steps, the solution was dried in a rotary evaporator and later re-dissolved in deionized water. This method of completely drying and re-dissolving the particles was significantly easier than terminating the concentrating procedure at the appropriate concentration in the dielectrophoretic wire growth experiments.

Octadecanethiol-capped nanoparticles were synthesized by two methods. Firstly octadecanethiol-capped gold nanoparticles were synthesized using a process based on that reported by Carotenuto and Nicolais [79] that developed the earlier methods of Brust *et al* [80] with an adaptation presented by Volpe *et al* and Brown *et al* [81-82]. 30 ml of 30 mM aqueous hydrogen tetrachloroaurate (III) solution was mixed with 2.19 g of tetraoctylammonium bromide in 80 ml of toluene. The mixture was vigorously stirred for 15 minutes to ensure that the two immiscible phases were well-mixed. At this time 240

mg of ODT and 25 ml of 0.4 M aqueous sodium borohydride were added causing a colour change from off-white (milky) to brown. After continuous stirring for a further 3 hours (to ensure completion of the reaction), the toluene phase was separated and concentrated to ~10 ml in a rotary evaporator operating at 70 °C and a pressure of 760 mmHg. The concentrate was allowed return to room temperature, at which point 400 ml of ethanol was added. This dissolved the ODT and tetraoctylammonium bromide and dispersed the nanoparticles. The solution was stored overnight in the dark at -18 °C during which time the nanoparticles aggregated (forming a brown precipitate) enabling them to be separated by filtration. Following the completion of this step, the nanoparticles were re-dissolved in dodecane or toluene (as required for wire growth experiments).

Octadecanethiol-capped gold nanoparticles were also synthesized using a second process reported by Carotenuto and Nicolais [79]. Basically synthesis preceded by the reduction of hydrogen tetrachloroaurate (III) trihydrate by ethylene glycol in the presence of PVP, as outlined in the preceding method. After the gold nanoparticles had been dried in the rotary evaporator, they were re-dispersed in 1-hexanol. The solution was stirred continuously for 2 hours to ensure that the ODT/PVP ligand exchange reaction was complete as there was no evident visible colour change for this process. After this, the ODT-capped nanoparticles were separated from the PVP/hexanol solution by using a centrifuge as the nanoparticles would settle out of the hexanol solution. The hexanol/PVP solution was decanted from the ODT nanoparticle precipitate which was then re-dispersed in 1-hexanol. After the second dispersal, the solution was centrifuged and decanted to remove the remaining PVP from the ODT capped gold nanoparticles.

Gold nanoparticles capped with either sodium citrate or PVP were produced using a procedure outlined by Jana *et al* [83]. 20 ml of ice-cold aqueous 0.25 mM tetrachloroaurate (III) and 20 ml of either 0.25 mM of sodium citrate or PVP were mixed. Immediately after mixing of the two solutions, 0.6 ml of sodium borohydride was added to the solution (all at once). The solution quickly turned from pale yellow to a colour in a range from a pale pink to wine red, depending upon the resulting nanoparticle size. The solution was stirred for another 10 minutes to ensure the complete reduction of the hydrogen tetrachloroauric acid in solution. The solution was allowed to warm to room temperature over a period of one hour while being stirred. This solution was concentrated to ~5 ml in a rotary evaporator at 60 °C. No further washing procedure was required as the starting concentrations of the capping agents and reducing agents were low and therefore these concentrations would remain low after completion of synthesis.

Upon completion of nanoparticle synthesis, the colloidal gold suspension was required to be concentrated (approximately 50x-100x) and purified for use in the dielectrophoretic growth of wire. A number of concentration techniques were explored but only a few techniques were viable for use in concentrating the suspensions.

A centrifuge was used where 1 litre of the colloidal gold suspension was placed into centrifuge bottle and spun with a force of 800 g for 1 hour. The excess solvent was decanted and the remaining concentrated solution re-dissolved in fresh solvent (usually water) to reduce the concentration of the excess reagents. This method was very successful at slightly concentrating (~10x concentration) large quantities of the colloidal gold solutions but failed to produce the concentration required for dielectrophoretic wire

growth experiments. It was noted the particles capped with citrate and α -cyclodextrin aggregated once the suspension reached a critical concentration.

A membrane filter (Biomax 100 centrifuge filter with ~3nm pores) purchased from Fisher Scientific was used as a second concentration step in the centrifuge in an attempt to further concentrate and purify the gold nanoparticle suspension. A sample of the partially concentrated colloidal suspension was placed in the top portion of the filter mechanism and forced through the membrane while by the force experience while being spun in the centrifuge. Concentration of the colloidal gold suspension proceeded by concentrating the solution in a centrifuge bottle and then passing the solution through the membrane filter. Some concentration did occur but due to the large starting quantities this method was not feasible for repeated use as the pores quickly clogged.

Vacuum dialysis tubing was used as a method to concentrate the colloidal gold suspension. The water and salt was forced through the dialysis tubing walls (~2nm diameter holes) by the immersion of the tubing into an evacuated flask. During the concentration the nanoparticles were forced through the thin tubing walls and therefore prevented the concentration of the colloidal gold solution.

Freeze drying was also attempted to concentrate the gold nanoparticle suspension. A quantity of colloidal gold was frozen and subsequently placed under vacuum to sublime the frozen water. As a result of the freezing the colloidal gold aggregated and therefore this method was not successful.

Ultimately the colloidal gold synthesis methods were chosen, as stated previously, to permit the concentration of the solutions by means of drying the nanoparticles in a rotary evaporator and re-dispersed to the appropriate concentration. These methods were

deemed viable, as there were no observable differences in the particle size distribution before and after the re-dispersal.

3.2 Characterization of Nanoparticles - Size Distribution

Upon completion of synthesis and concentration of the gold nanoparticle solution, the size distribution was determined through spectra obtained from a spectrophotometer and images obtained from a transmission electron microscope (TEM).

For calculations of extinction, the index of refraction of water was taken to be 1.33 as used by other authors [66] and the bulk index of refraction for gold was obtained from [84] as shown in Figure 3.1.

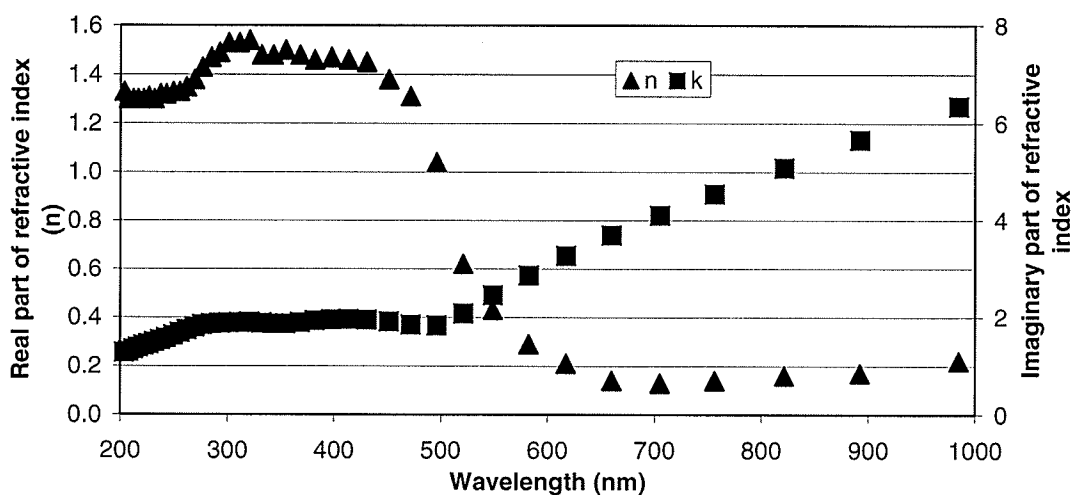


Figure 3.1 - Complex refractive index of gold $n^*=n+ik$ obtained from [84]

To calculate the extinction spectra through the colloidal gold solution a size distribution for the nanoparticles had to be assumed. The calculation was undertaken for both a normal and exponential distribution [85]. The normal probability distribution,

$$f(d) = \frac{1}{a\sqrt{2\pi}} e^{\left(-\frac{(d-u)^2}{2a^2}\right)} \quad (55)$$

included the standard deviation, σ , and mean, μ . The exponential probability distribution,

$$f(d) = \frac{1}{\beta} e^{\frac{(d-\alpha)}{\beta}} \quad (56)$$

included the standard deviation, β , and mean $\mu = \alpha + \beta$.

The location of the extinction peak was affected by changes in particle distribution and was determined by the local maximum of:

$$A(\lambda) = NV \int_{d=0}^{\infty} f(d) C_{\text{ext}}(d, \lambda) dd \quad (57)$$

where the derivative of equation 57 is zero as:

$$\frac{\partial}{\partial \lambda} A(\lambda) = \frac{\partial}{\partial \lambda} \left[NV \int_{d=0}^{\infty} f(d) C_{\text{ext}}(d, \lambda) dd \right] = NV \frac{\partial}{\partial \lambda} \int_{d=0}^{\infty} f(d) [C_{\text{ext}}(d, \lambda)] dd \quad (58)$$

Equation 57 was solved numerically using the Mie scattering coefficients of (51-54) and the peak extinction was found using (58). The code used may be found in Appendix A.

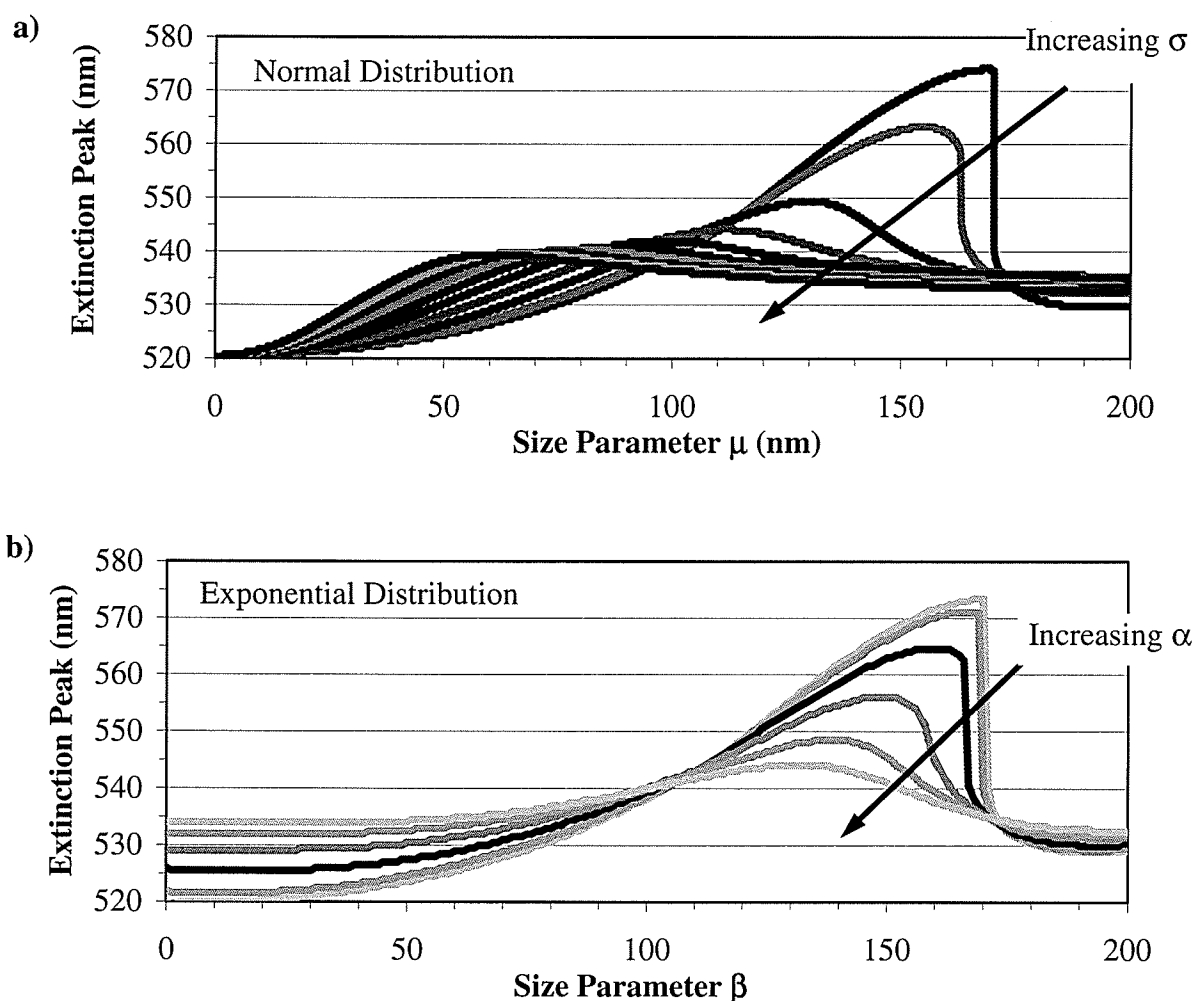


Figure 3.2 - Plot of extinction spectra peak versus size parameter for a) normal distribution (Equation 55) and b) exponential distribution (Equation 56). In a) the arrow indicates increasing values of the distribution parameter σ whereas in b) the arrow indicates increasing values of the size parameter α .

As illustrated in Figure 3.2 the position of the extinction peak was dependent on the average of the nanoparticle size distribution. It should also be noted that the refractive index of the gold nanoparticles was assumed to be that of bulk gold. This estimate may not be entirely accurate as the attached ligands will modify the refractive index even if the nanoparticles appear to behave like bulk gold. (See Section 2.5)

Samples of the nanoparticle suspension were dried onto a TEM grid (Marivac Inc.: #185, 400 mesh carbon-coated copper) and negatives obtained using a transmission electron microscope. The negatives were scanned into a computer using an EPSON 2500 scanner and image processing was performed to estimate the particle size distribution. As will be discussed in section 4.1 the particle shapes in the TEM images were close enough to circular that a circular edge profile could be assumed. The circular Hough transform [69] was chosen to extract the spherical-shaped particles from the TEM images.

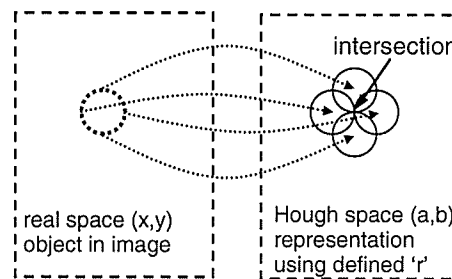


Figure 3.3 - Illustration depicting the circular Hough transform algorithm. Circular images can be identified in Hough space.

The circular Hough transform was implemented by first converting the scanned images to a binary data format (i.e. 1-bit black and white image) and the edge pixels were identified using a built-in edge-finding function [86] in MATLAB software package. In a new image file, the location of each edge pixels was defined to be the centre of a circle of a pre-specified radius. The 'value' associated with each pixel depended on the number of these circles intersecting at that pixel. If the number of intersecting circles at a pixel exceeded 60% of the number of edge pixels for that shape, this intersection was deemed to be the centre of a particle with the radius specified. This process was repeated for radii between 2 and 50nm to compile the size distribution. This technique presumed that most particles were close enough to spherical in shape, aggregations and other structural

formations, such as nanorods, were ignored. The MATLAB code for this above algorithm may be found in Appendix B.

3.3 *Dielectrophoresis Experimental Setup*

A control system was required for the wire growth experiments to reduce the high driving voltage upon completion of wire formation. This lower voltage served to hold the wire together and enabled observations of the conductance through the wire. Preceding the final design of the control system, there were three iterative designs that were used and tested for the wire growth experiments.

Initially, a manual control system was developed in which either a dc or ac voltage source was used to induce dielectrophoresis of the colloidal suspension between the two electrodes. Current measurements were taken by using either a multimeter or an oscilloscope. The operator was required to monitor the voltage and to quickly remove the applied high voltage at the point the current corresponded to a resistance exceeding 20 k Ω . It was noted the wire would rupture or the resulting wire was large and therefore low-dimensional conductance was not measured.

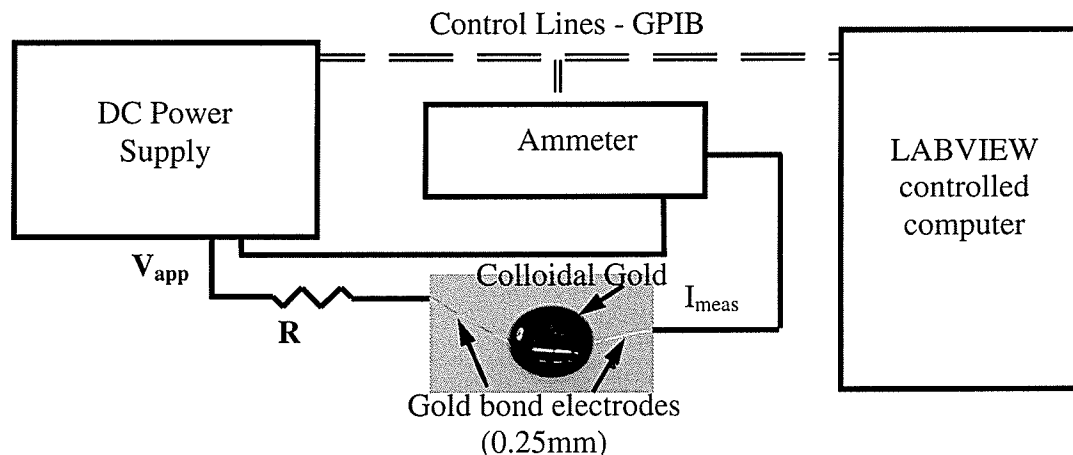


Figure 3.4 - A basic control system using a LABVIEW interface to control and monitor dielectrophoretic growth of wires from a colloidal suspension.

Next, an automated control system was developed using the apparatus shown in Figure 3.4 and used with the aid of a LABVIEW-programmed computer from which control signals were sent to the DC power supply through a GPIB connection. The control system would decrease the applied voltage once the current surpassed a set limit. The response time was greatly improved using this system and less than 100 ms.

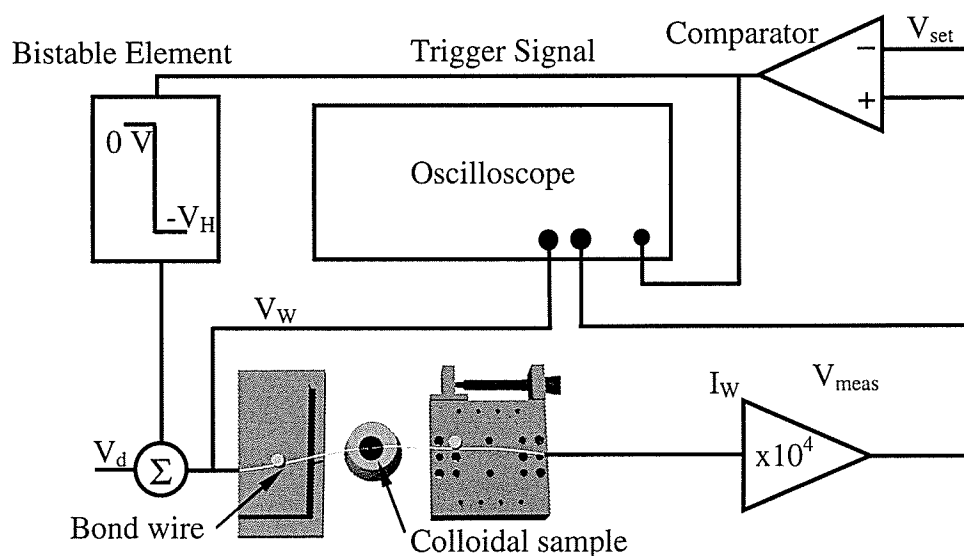


Figure 3.5 - The final control system design using a fully automated analog control system that was implemented on a wire-wrap board.

The third and final control system, as illustrated in Figure 3.5, reduced the voltage on the electrodes once the current through the electrodes passed a preset current limit. Wire growth was accomplished by the application of $V_d = 0.2 + 0.5\sin(10\pi t)$ V to the electrodes. At the point of wire formation the current and therefore V_{meas} increased dramatically. The comparator changed state as V_{meas} surpassed the set voltage (V_{set}). In turn changed the bistable element from 0 volts to $-V_H$, decreasing the voltage between the electrodes by $\sim 90\%$. As a result, the wire growth was slowed and data from which conductance could be calculated was recorded by the oscilloscope.

The technique for mounting and controlling the electrode spacing was also developed iteratively. Initially, it was assumed that the colloidal gold suspension may be used without concentration after completion of the synthesis and that approximately 30 ml of the colloidal gold suspension would be required.

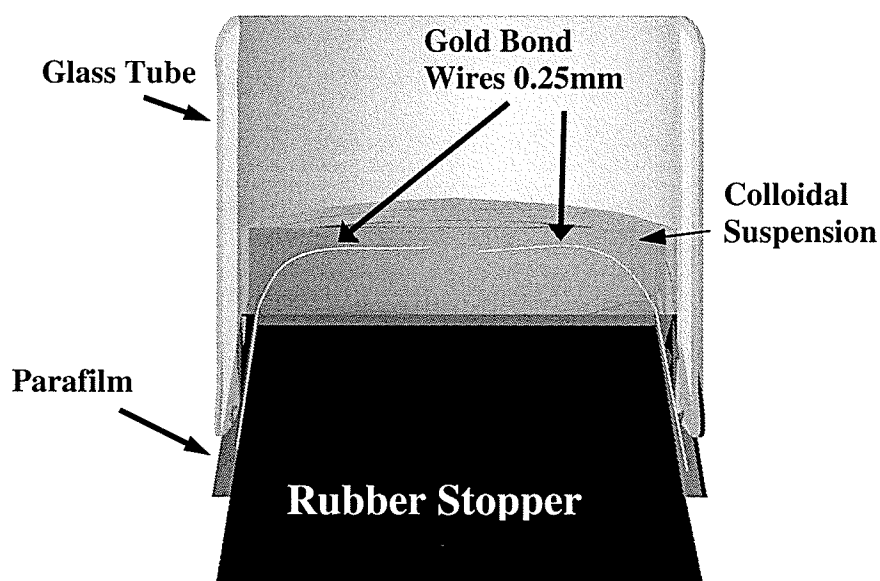


Figure 3.6 - First iteration of the dielectrophoretic growth experimental setup.

As seen in Figure 3.6, a glass tube was used to clamp the bond wires to a rubber stopper covered with parafilm. This provided a vessel for the colloidal solution which was added after the gold electrodes had been positioned with the aid of an optical microscope.

The next design evolved from the realization that a more concentrated colloidal suspension was required for successful wire growth. The large surface tension of the colloidal solution was exploited as a drop (~1ml) could be placed over the two electrodes without any containment. The major drawback with this design was that the electrodes were no longer held firmly in place, which resulted in less control of the electrode spacing.

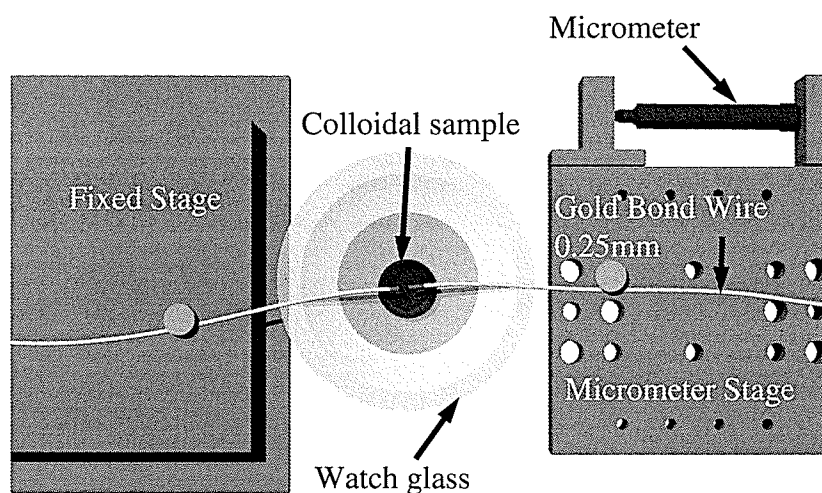


Figure 3.7 - Third iteration of the electrodes in the dielectrophoretic growth experimental setup.

This design was modified (Figure 3.7) to enable control over the electrode spacing and to incorporate a watch glass instead of the parafilm (which dodecane dissolved).

The final two electrode designs were constructed by milling the electrodes onto a copper cladded PCB board and into a thin gold film deposited onto a silicon wafer. These electrodes were constructed in order to control the separation of the electrodes and concentrate the electric field. Electrodes constructed from the thin gold film had a separation distance much smaller than the PCB board and therefore would exhibit higher electric field intensity for a given voltage. Growth of the wires between the PCB electrodes were resulted in wires that were relatively large ($>10\mu\text{m}$) as the wires were measured under an optical microscope. The attempted growth of the wires between the electrodes fabricated on the thin gold film did not result in wire growth. The reason for this is still under investigation. (Appendix D)

4. Results and Analysis

In this chapter the results of the nanoparticle size distribution analysis and the results of the dielectrophoretic wire growth experiments are presented.

4.1 Characterization of the gold nanoparticle suspension

In this section the results of the nanoparticle size distributions obtained from the extinction spectra and transmission electron microscope (TEM) images are described and discussed.

Spectra of the colloidal gold nanoparticles were obtained from UV-Vis spectrophotometer immediately after synthesis, as outlined in section 3.2.

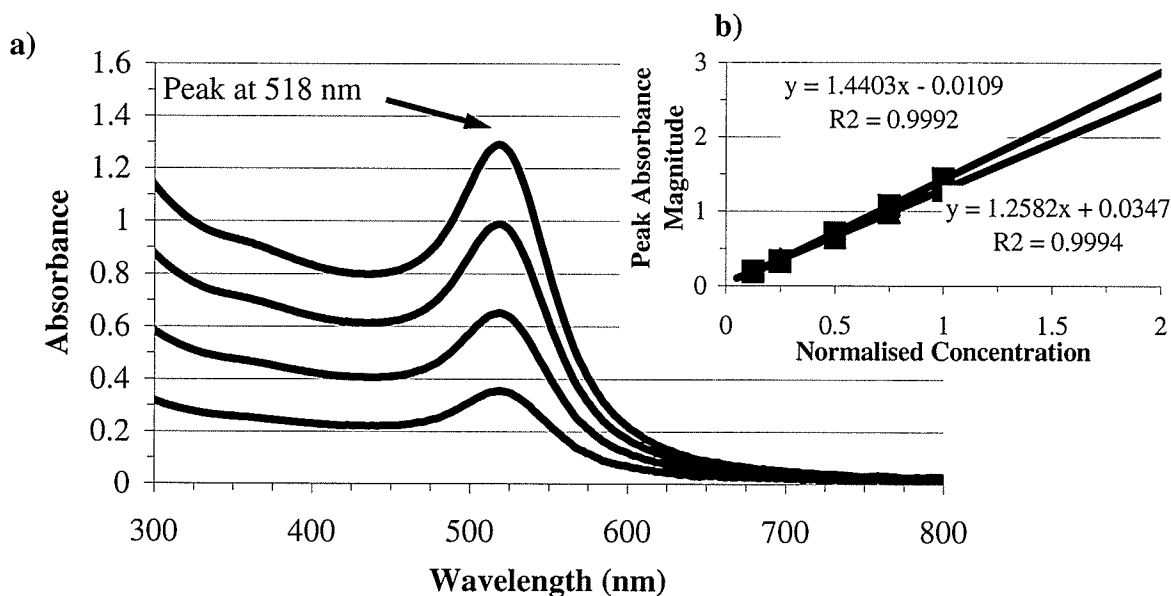


Figure 4.1 - a) Extinction plots of 4 dilutions of the citrate capped gold nanoparticles produced by the reduction by sodium citrate, a method outlined in section 3.1. b) Extinction peak vs. concentration of nanoparticles normalized to concentration at conclusion of synthesis.

Extinction spectra of citrate-capped gold nanoparticles synthesized by the reduction of tetrachloroauric acid by sodium citrate, a method explained in section 3.1 are

shown in Figure 4.1. The extinction peak of the citrate-capped gold nanoparticles occurred at 518nm and by a least square error comparison with the calculated extinction peaks in figure 3.2 indicated an average particle diameter in the range of 10-30 nm. The extinction peak absorbance displays a linear relationship with the particle concentration within the range presented (Figure 4.1b). This relationship was used to verify the concentration of particles after the concentration steps had been taken. A sample of the concentrate was taken and re-diluted to allow measurements to be taken by the spectrophotometer, as the extinction due to concentrated solutions was too large for measurement purposes.

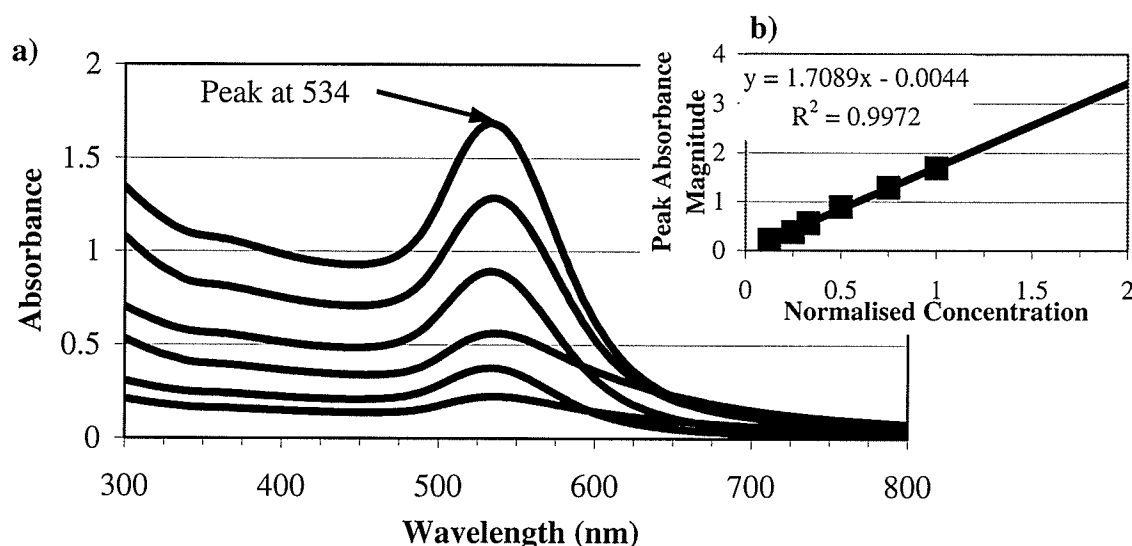


Figure 4.2 - a) Extinction plot of α -cyclodextrin capped nanoparticles. b) Extinction peak vs. concentration normalized to concentration at conclusion of synthesis.

Extinction spectra of α -cyclodextrin-capped gold nanoparticles and the relationship of extinction peak vs. concentration are illustrated in Figure 4.2. The extinction peak of the α -cyclodextrin-capped particles occurred at 534 nm and by a least square error comparison with the calculated extinction in Figure 3.2 suggested the

average particle diameter was between 20 and 80 nm. Again, the linear relationship between extinction and concentration was used to determine the solution concentration.

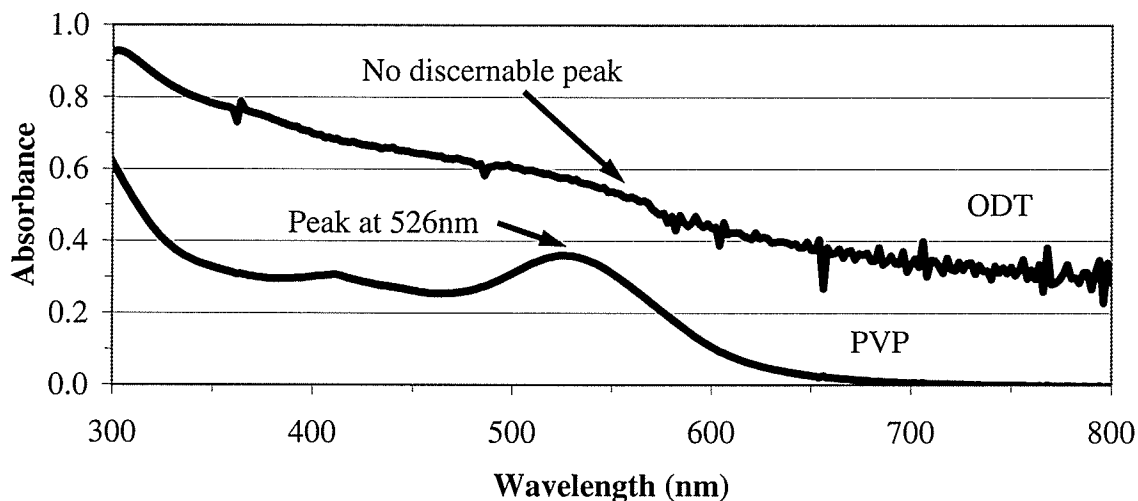


Figure 4.3 - Absorbance of PVP capped nanoparticles disperse in deionized water and ODT capped nanoparticles dispersed in dodecane.

Absorbance spectra of ODT and PVP capped gold nanoparticles are illustrated in Figure 4.3. The extinction peak of the PVP-capped gold nanoparticles occurred at 526nm. With a least-square error comparison with the theoretical extinction peak (Figure 3.2) indicated the average particle size between 10 and 30 nm. Also an extinction peak that occurred at 526 nm indicated the particles are larger than the citrate-capped particles but smaller than the α -cyclodextrin capped particles.

The extinction peak of the ODT capped gold nanoparticles was not discernable as the peak is not well defined in the data presented in Figure 4.3. The lack of extinction peak may be the result of small gold nanoparticles (diameter < 10 nm) and therefore the extinction peak cannot be discerned from the background extinction. The work of Crespo *et al* [87] has suggested that the Au-S bond localized 5d electrons in the gold

nanoparticles, removing the surface plasmon resonance that is otherwise responsible for the extinction peak at these wavelengths.

The particle size distribution was also measured through solution samples dried onto carbon-coated copper TEM grids and imaged using a transmission electron microscope. Excess capping agents were present in the solutions these were not removed from the solution upon completion of synthesis. Removing these excess capping agents was not feasible when directly concentrating the gold solutions. The capping agents crystallized on the TEM grid, suspending the nanoparticles between the grids. The thickness of the crystallized capping agent altered the contrast of the resulting image and impeded reliable analysis. Synthesis methods involving washing/re-dissolution of the nanoparticles incorporated steps to remove excess capping agents, alleviating this problem.

Images obtained from the TEM represented a two-dimensional representation of the nanoparticles dispersed throughout the thickness of the film. Since the nanoparticles were randomly oriented a false appearance of aggregation could result. The image analysis process ignored aggregated nanoparticles on the presumption that obvious aggregation would have resulted from the drying process.

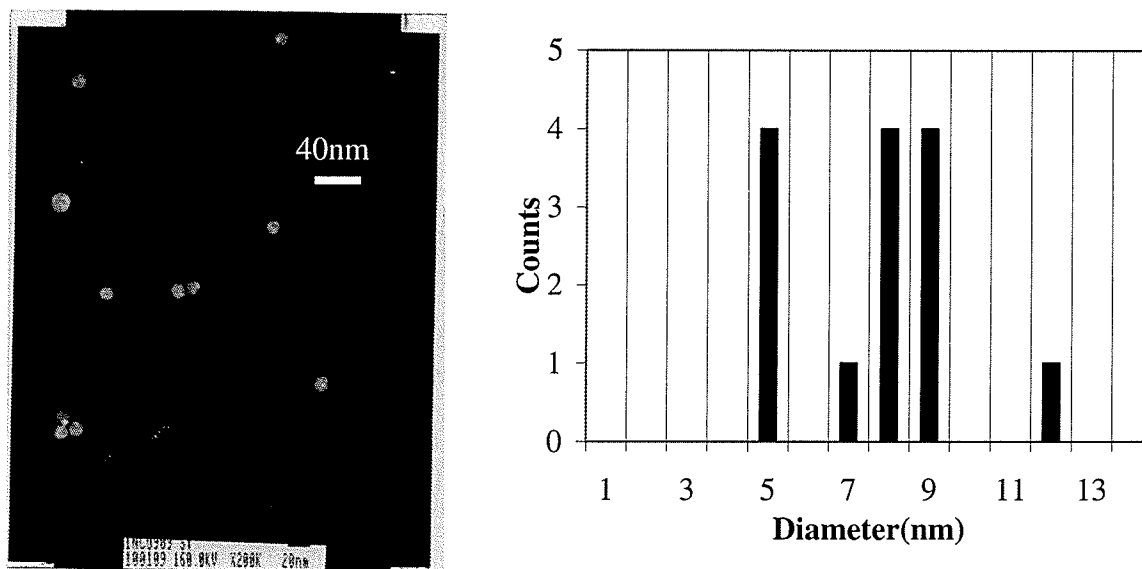


Figure 4.4 - Transmission electron microscope image of citrate-capped gold nanoparticles. The relatively small amount of gold particles is indicative of the low concentration obtained using this synthesis method.

Citrate-capped gold nanoparticles from the reduction of tetrachloroauric acid by sodium citrate (section 3.2) are illustrated in the TEM image of Figure 4.4. These gold nanoparticles were spherical in shape with an average size of 7 nm. In the Mie extinction theory analysis the size distribution was between 10 and 30 nm. This would indicate that Mie extinction theory does not give an accurate account to the size distribution.

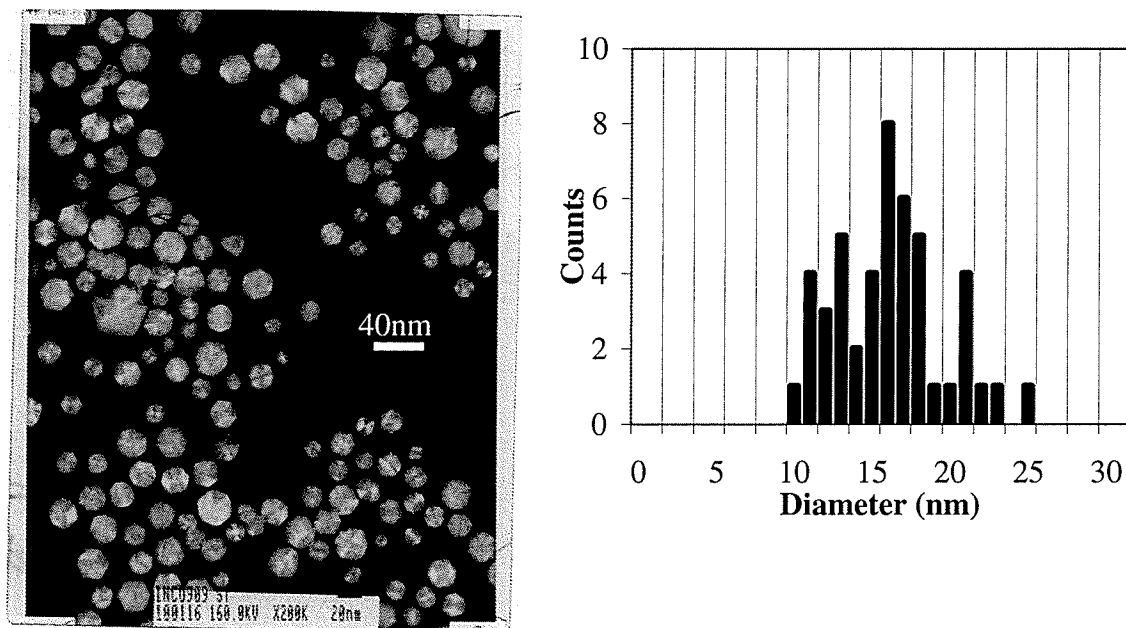


Figure 4.5 - Transmission electron microscope images of PVP-capped gold nanoparticle suspension. The average particle diameter is 17 nm.

Polyvinylpyrrolidone-capped gold nanoparticles, produced as described in section 2.6, are shown in Figure 4.5. These gold nanoparticles appear to be n-polyhedral objects in the image. An automated image analysis algorithm was used to extrapolate spherical objects from the image but, as illustrated, the particles are not perfectly spherical. Verification of the results was carried out by manually measuring the particles in a commercially available software package, Scion Image (Scion Corporation). In this package the area of each particle is measured and assuming a spherical particle, a diameter of the particle can be deduced from it. The two methods resulted in the same distribution illustrated in Figure 4.5 and therefore the image analysis algorithm was deemed successful. It should be noted that the Scion Image software can only process images under 800 x 600 pixels, thus the resolution of the image is limited. The automated image analysis was performed in MATLAB where the image size was not limited. Furthermore the manual method was tedious and consumed much time, depending upon

the amount of particles to analyse. The automated method did not require much intervention and therefore was a good choice for image analysis.

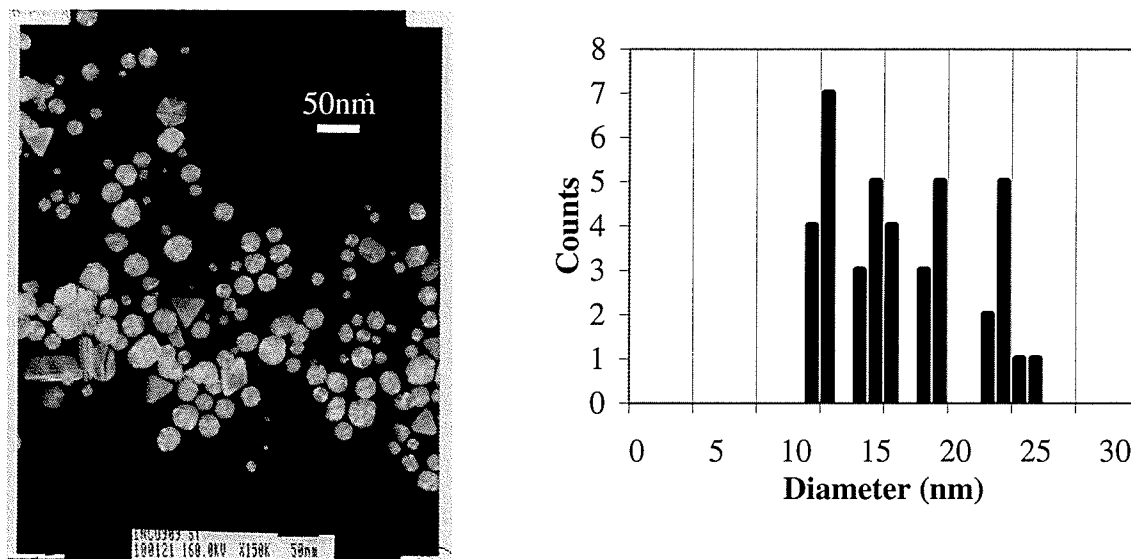


Figure 4.6 - Transmission electron microscope image of octadecanethiol gold nanoparticles produced by a ligand exchange reaction with PVP capped gold nanoparticles. The average particle diameter is 17 nm.

An image of ODT-capped gold nanoparticles synthesized by a ligand exchange reaction with PVP-capped gold nanoparticles, as outlined in section 3.2, are presented in Figure 4.6. The images of the nanoparticles show a variety of polyhedral nanoparticles. The peculiar particle geometry is a by-product of the high PVP concentration and the weak reducing agent during the synthesis steps. This observation was noted in another study [77] and was concluded the PVP adsorbed onto facets faster than a spherical particles, leading to the preferential construction of faceted particles. The PVP-capped gold nanoparticles presented in Figure 4.5 were used for the ligand exchange reaction to produce the ODT-capped gold nanoparticles presented in Figure 4.6. The average diameter of the particles did not change between the two images and therefore the ODT ligand-exchange reaction did not initiate further aggregation of the nanoparticles. Tan *et*

al. [77] have also illustrated the ligand-exchange reaction does not initiate further particle aggregation. This synthesis method required several days and as such the additional effort did not seem merited and this synthesis pathway was not used.

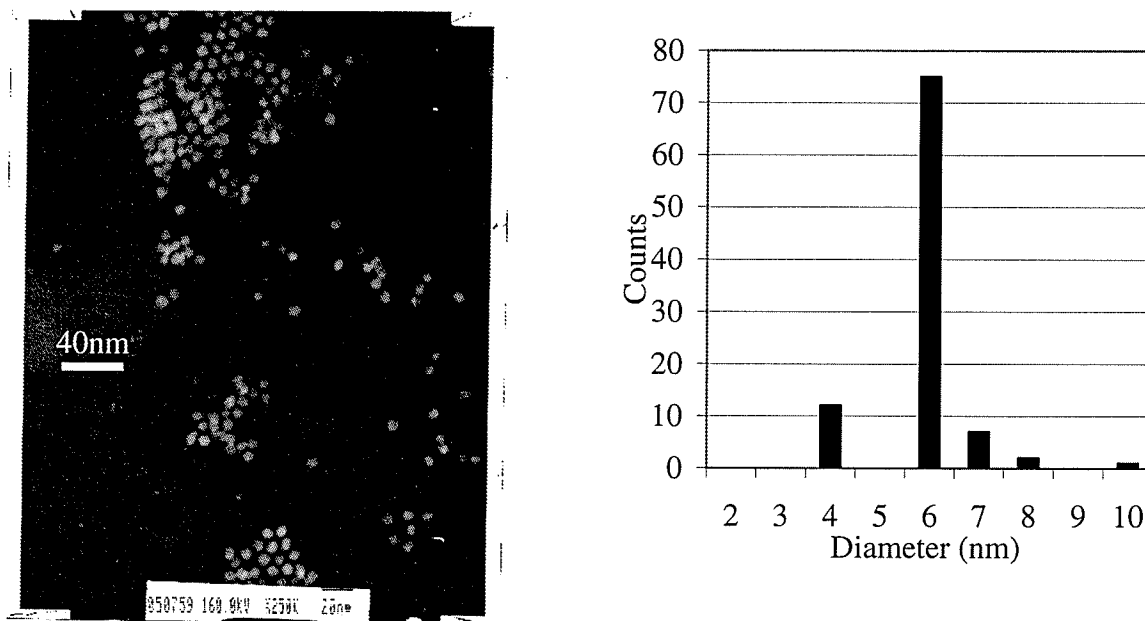


Figure 4.7 - Transmission electron micrograph of PVP capped gold nanoparticles that were reduced by sodium bitartrate. The average particle diameter is 5 nm.

Gold nanoparticles were synthesized through the reduction of tetrachloroauric acid by sodium bitartrate and subsequently capped in the presence of PVP. As illustrated in Figure 4.7, the particles are spherical with an average particle size of 5 nm with a relatively small size distribution. This synthesis method is simple, reproducible and can produce nanoparticles that are capped with several different capping agents, for example, citrate and PVP.

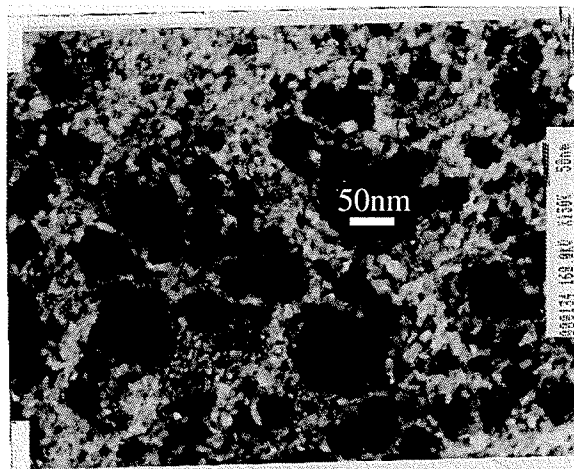


Figure 4.8 - Transmission electron micrograph of citrate capped gold nanoparticles that were reduced by sodium borohydride. The synthesis of spherical gold nanoparticles was performed at a higher temperature than desired, hence the extra aggregation.

As shown in Figure 4.7, sodium bitartrate produced gold nanoparticles with a size on the order of 5 nm. The main drawback of this method is the relative difficulty in reproducing the relatively small gold nanoparticles. As illustrated in Figure 4.8, the aggregation of all particles may occur as a result of the synthesis proceeding at a temperature higher than close to that of an ice-bath.

4.2 *Mechanical Break Junction Experiments*

Mechanical break junction experiments were performed to provide a basis for comparison with the dielectrophoretic wire growth experiments. Mechanical break junctions were performed by slowly bringing two gold bond wires (0.25 mm in diameter) into contact and subsequently separating them using a micrometer drive, as illustrated in Figure 3.5. Throughout the experiment a voltage of $V_{\text{app}} = 0.1 + 0.05 \cos(10\pi t)$ was applied across the junction in order to measure the conductance. Mechanical break

junctions were performed in air, deionized water, dodecane, and solutions of the capping agents.

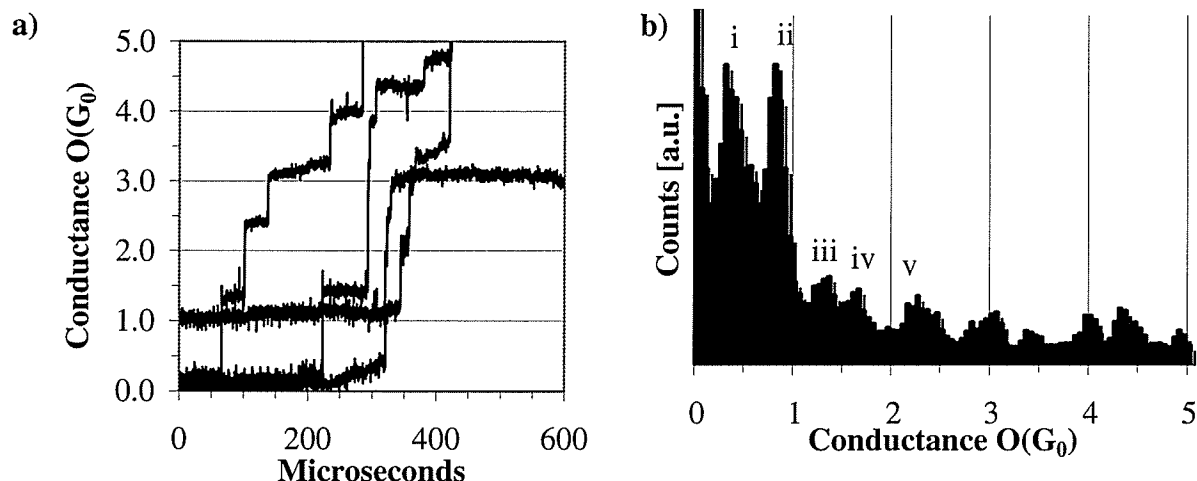


Figure 4.9 - Conductance of mechanical break junctions performed in air at room temperature. a) 30 conductance traces were used to compile the histogram illustrated in b)

Conductance plateaus and conductance peaks are clearly visible in the conductance traces and conductance histograms for mechanical break junction performed in air, as illustrated in Figure 4.9. The conductance obtained from the experiments performed in air show conductance peaks near integer multiples of G_0 , indicating metallic low-dimensional conductance. The occurrence of the conductance peaks away from $1 G_0$ and $2 G_0$ (depicted in Figure 4.9 as ii and v respectively) may be due to contact resistance rather than the low-dimensional conductor. The difference in the conductance peaks occurring at ii, iv may be due to a contact resistance rather than the low-dimensional conductor [88]. Additional conductance peaks close to $0.5 G_0$ and $1.5 G_0$, depicted in Figure 4.9 as (i), (iii) and (iv), may be the result of several factors including impurities in the gold bond wires used [89].

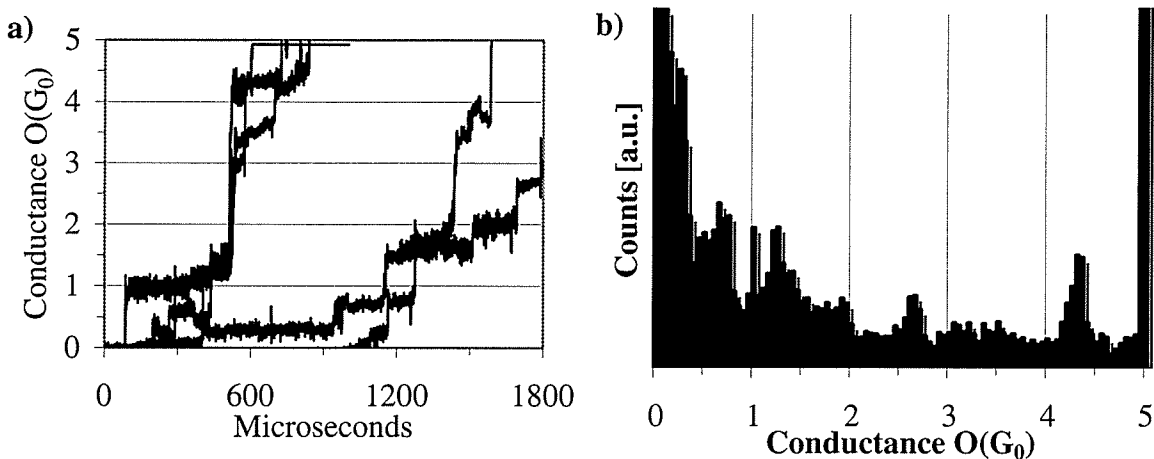


Figure 4.10 - Conductance of mechanical break junctions performed in deionized water. A total of 30 conductance traces (a) were used to compile the histogram illustrated in (b).

Mechanical break junction experiments performed in deionized water show conductance plateaus and conductance steps at, or near, integer multiples of G_0 (as illustrated in Figure 4.10). The conductance histogram obtained from mechanical break junction experiments performed in air (Figure 4.10) does not change significantly when these experiments are performed in the presence of deionized water (Figure 4.9). The system may be thought of as two electrical resistors in parallel where the low-dimensional system is one resistor and the aqueous solution is the other resistor. The resistance through the solution is relatively high (on the order of $20 \text{ k}\Omega$) and constant but the resistance through the low-dimensional conductor is continuously changing as illustrated in Figure 4.10. When the resistance of the low-dimensional conductor is approximately the same as through the solution, then changes in the conductance of the metallic conductor are not well defined and therefore the conductance peaks below $0.5 G_0$ ($< \sim 20 \text{ k}\Omega$) are smeared out.

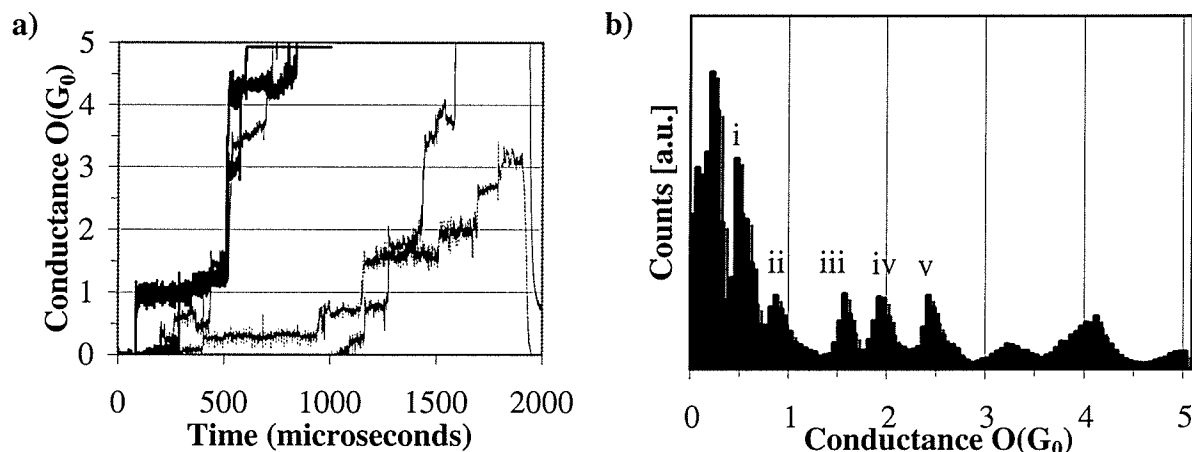


Figure 4.11 - Conductance of mechanical break junctions in the presence of sodium citrate solution. A total of 30 conductance traces (a) were used to compile the histogram illustrated in (b)

Conductance of the mechanical break junctions performed in the presence of sodium citrate show conductance plateaus at, or near, integer multiples of G_0 (Figure 4.11) It should be noted that conductance peaks at 1.5, 2 and 2.5 G_0 were not clearly observed in the conductance plots for air (Figure 4.9) or deionized water (Figure 4.10) and therefore this may suggest the conduction pathway is not through a single low-dimensional structure. A low-dimensional metallic conduction pathway is indicative of conductance peaks at integer multiples of G_0 and not at non-integer multiples. The contribution that the citrate gives to the conductance is unclear. Conductance peaks lower than integer multiples of G_0 (ii, iv) may be due to ionic mobility or contact resistance as it introduces a constant resistance in parallel or series with the low-dimensional metallic conductor [90]. The conductance peaks at fractional integers of G_0 (i, iii, v) may be due to the metallic conductor as illustrated by another study [38].

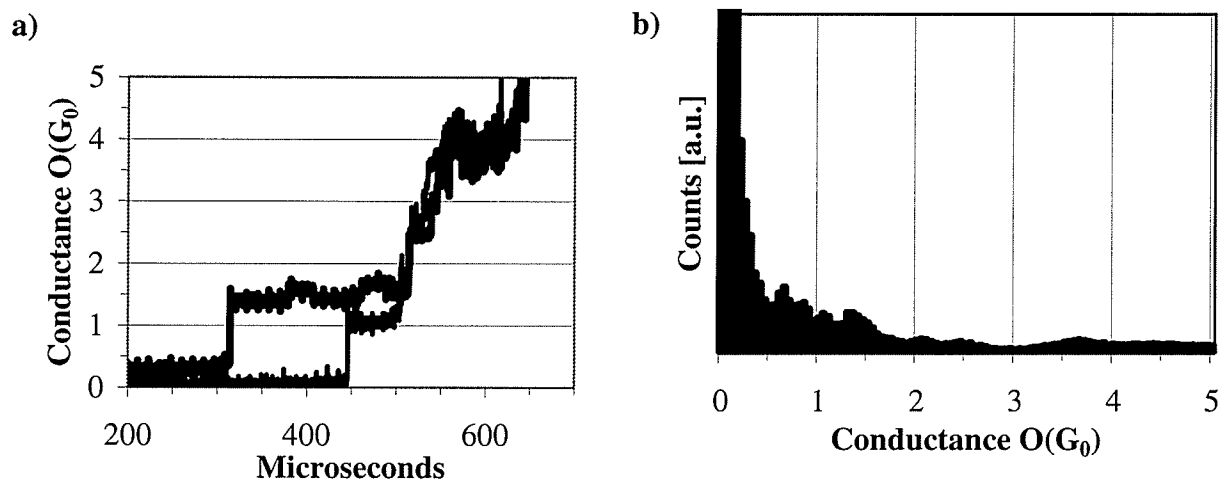


Figure 4.12 - Conductance of mechanical break junctions performed in the presence of an aqueous solution of PVP. A total of 30 conductance traces (a) were used to compile the histogram illustrated in (b).

Mechanical break junction experiments performed in the presence of aqueous PVP solution are illustrated in Figure 4.12. Some conductance traces showed conductance steps at $1G_0$ but no other non-linear conductance steps were observed. The conductance histograms did not illustrate the presence of these conductance steps, as the histogram resembled an exponential decay. The presence of an exponential decay in the histogram suggests the conductance is through a tunnelling process through the PVP ligands. [41] Conductance peaks are observed for mechanical break junctions performed in deionized water (Figure 4.10) and therefore it is clear, PVP contributes to the conductance.

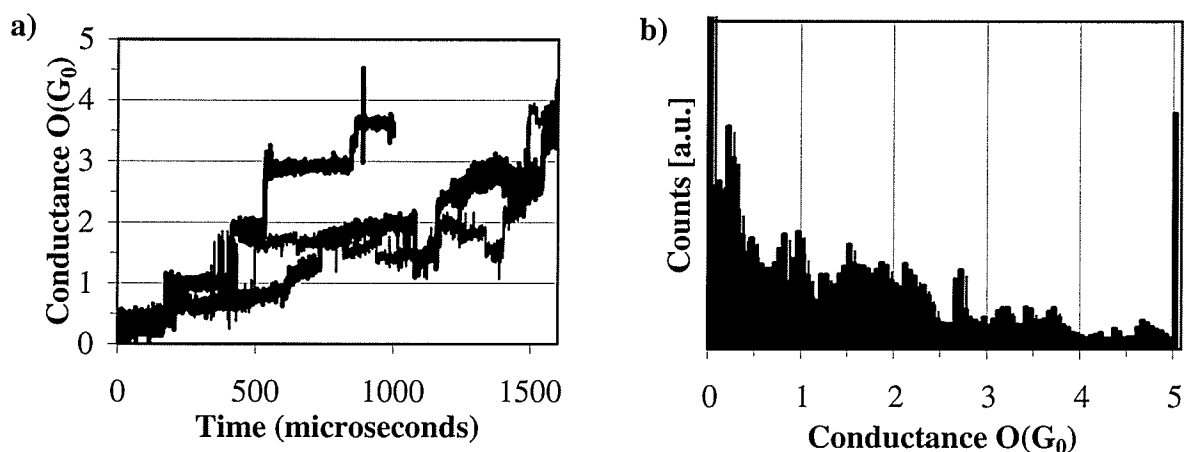


Figure 4.13 - Conductance of mechanical break junctions in the presence of dodecane. A total of 30 conductance traces (a) were used to compile the histogram illustrated in (b).

Mechanical break junction experiments performed in the presence of a non-polar solvent (dodecane) are presented in Figure 4.13. Non-linear conductance steps are observed in the conductance traces however, compilation of the 30 conductance traces into a histogram does not reveal clear conductance peaks. The conductance traces of the mechanical break junctions performed in dodecane (Figure 4.13) appear to have much more noise compared to that obtained in air (Figure 4.9). The compilation of the conductance traces for dodecane into the histogram analysis resulted in conductance peaks that are not well defined. The absence of well defined conductance peaks excludes any conclusions that the conductance may be due to a metallic low-dimensional conductor.

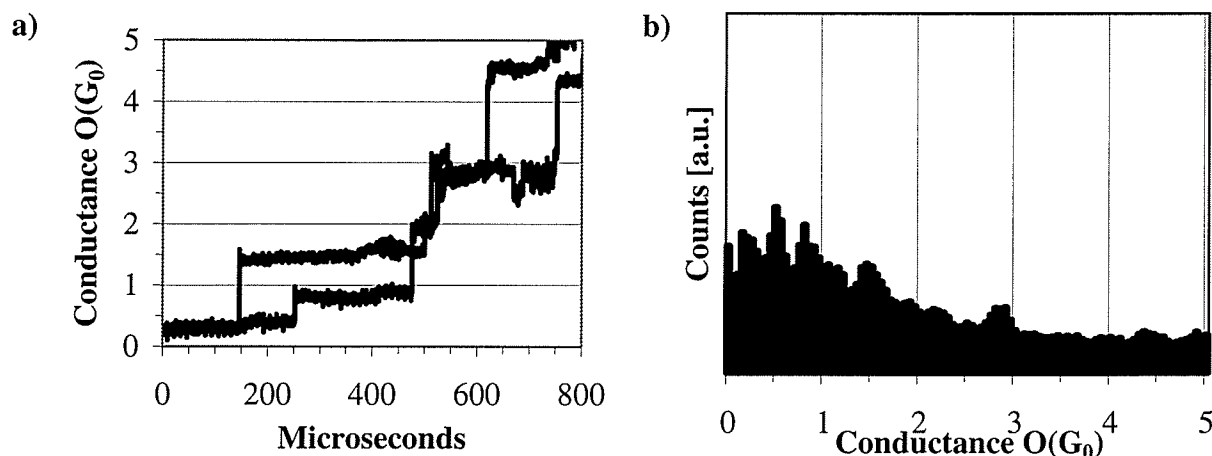


Figure 4.14 - Conductance of mechanical break junctions performed in the presence of a solution of ODT dispersed in dodecane. A total of 30 conductance traces (a) were used to compile the histogram illustrated in (b).

Mechanical break junction experiments were performed in the presence of a solution of ODT dispersed in dodecane and a histogram generated from 30 conductance traces. (Figure 4.14). A few conductance plateaus and conductance steps are clearly visible at integer multiples of G_0 in the conductance traces. Although the conductance plateaus were stable over a longer period of time in comparison to those obtained in dodecane alone (Figure 4.13), the histogram compiled from the conductance traces of the ODT capped gold nanoparticles (Figure 4.14) does not show clear conductance peaks. A more detailed study is required to fully understand the contribution ODT gives to the low-dimensional conductance character.

4.3 Conductance through dielectrophoretically grown gold wires

The purpose of this investigation was to investigate the conductance through dielectrophoretically grown wires from a colloidal suspension of gold nanoparticles. In

this section the conductance data obtained from the dielectrophoretically grown wires are presented and important aspects are discussed.

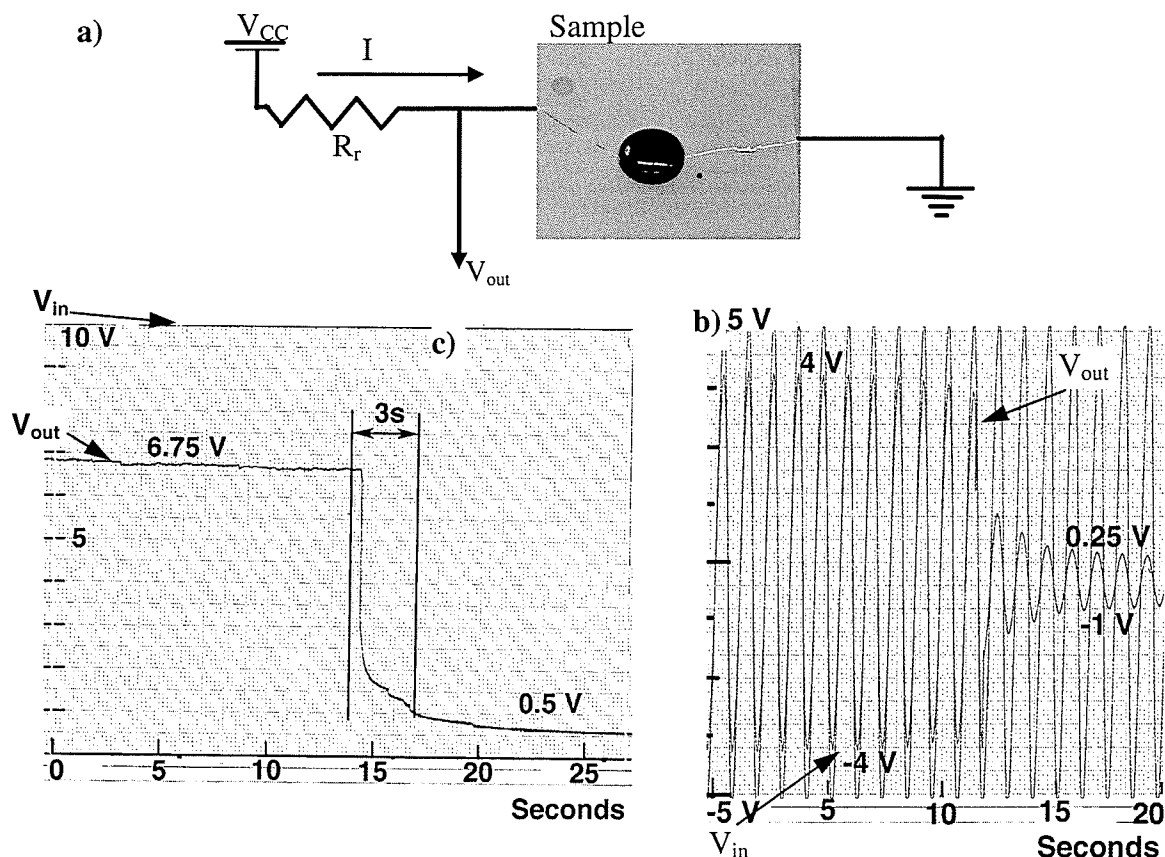


Figure 4.15 - Plots of output voltage for dielectrophoretic grown wires from PVP-capped gold nanoparticles. Wire formation was completed in approximately 30 minutes.

Dielectrophoretically-grown wires were synthesized using the simple manual control system described in Figure 3.4. The electrodes were setup as illustrated in Figure 4.15 a) and voltage measurements were taken and plotted in Figure 4.15 b) and c). First a dc signal of 10 V was applied to the electrodes to initiate wire growth and growth was completed within 30 minutes. All the while during the wire growth experiment the voltage slowly dropped – an indication of wire growth. Upon completion of wire growth

it was noted that the output voltage dropped further, an indication of further aggregation of gold particles onto the grown wire.

Secondly an ac voltage of 10 V_{p-p} at 1Hz was applied to the apparatus to dielectrophoretically grow wires between the two manually placed electrodes. Wire formation between the gold electrodes required ~30 minutes to complete and the input and output voltage is plotted in Figure 4.15 c). Once again, the output voltage progressively dropped as the experiment progressed indicating a decrease in resistance from the separated electrodes. The resistance between the separated electrodes depends upon the separation distance and therefore an observed decrease in resistance suggested wire growth. Upon completion of wire formation, the voltage once again dropped for a further 3 minutes, suggesting further aggregation of gold particles.

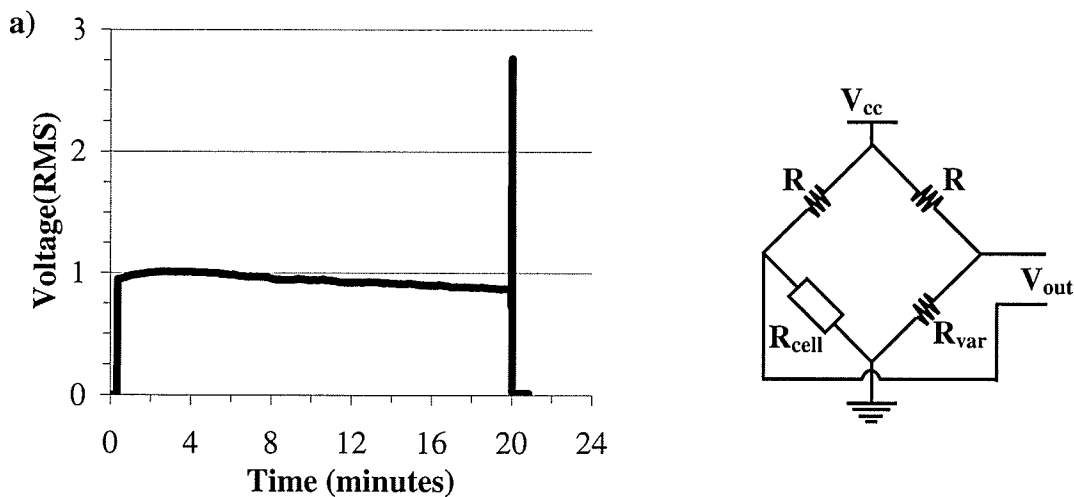


Figure 4.16 - Measurements of dielectrophoretically grown wires from a colloidal suspension taken across a Wheatstone bridge. Wire formation was completed in approximately 20 minutes.

In order to increase the sensitivity of the measured resistance during wire formation a Wheatstone bridge was used as illustrated in Figure 4.16. Measurements were acquired using the manual control system setup, illustrated in Figure 3.4. Microwire

formation in this fashion proceeded in the same manner as previously observed. The voltage continually dropped over a period of 20 minutes until the wire growth was completed.

Dielectrophoretic wire growth experiments were also accomplished using the automated control system illustrated in Figure 3.5. Two freshly-cut gold wires were manually brought into contact and separated to a distance of 1-10 μm using the micrometer drive. An applied voltage of $V_d = 0.2 + 0.5 \cos(10\pi t)$ was used to initiate the dielectrophoretic aggregation and upon completion of wire growth a voltage of $V_d - V_H = 0.02 + 0.05 \cos(10\pi t)$ was used to study the conductance of the newly-formed wire. The resulting conductance data are summarized and plotted in Figures 4.17-4.19.

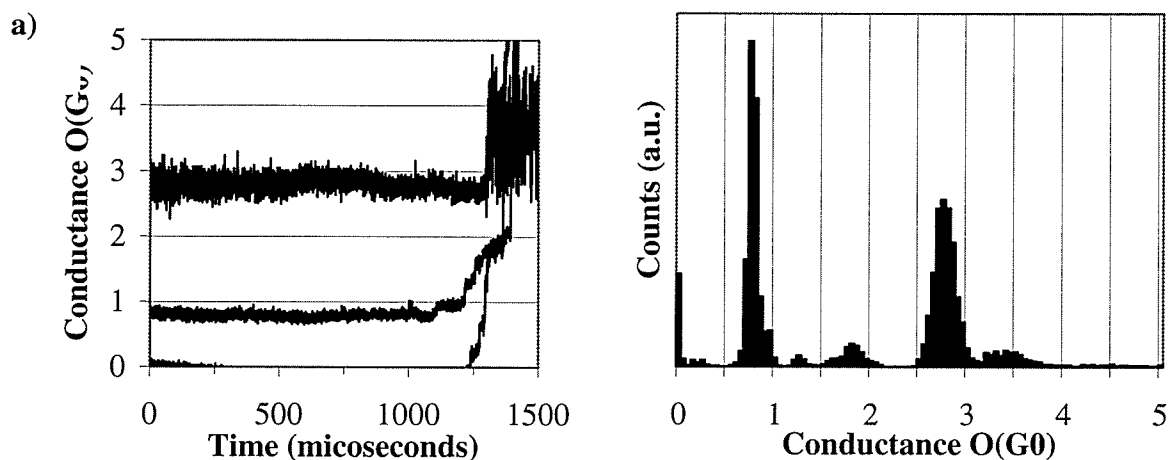


Figure 4.17 - Conductance data through dielectrophoretic grown wires from citrate capped gold nanoparticles. A total of 5 conductance traces such as those in (a) were used to compile the histogram (b).

Conductance through dielectrophoretically grown wires from a solution of citrate capped gold nanoparticles (Figure 4.17) showed conductance plateaus at integer multiples of G_0 but no definitive non-linear conductance steps were observed. The histogram presented in Figure 4.17b illustrates conductance peaks at integer multiples of

G_0 but due to the limited conductance traces (5 traces) used and the fact no conductance steps were observed in the conductance traces Figure 4.17a, and therefore no conclusions can be made.

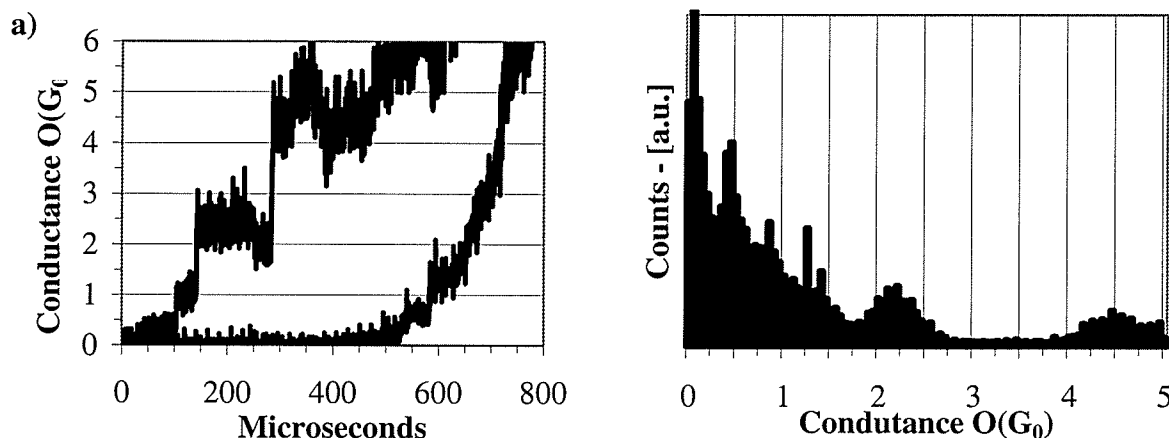


Figure 4.18 - Conductance data through dielectrophoretic grown wires from PVP capped nanoparticles. A total of 15 conductance traces (a) were used to compile the histogram illustrated in (b).

Conductance measurements through dielectrophoretically-grown wires fabricated from PVP-capped gold nanoparticles showed conductance steps at or near integer multiples of G_0 . The conductance histogram (Figure 4.18) showed an exponential shape suggesting other transport process such as tunnelling (see section 2.3) [41]. Against this large ‘background’ some histogram peaks at or near integer multiples of G_0 are observed – suggesting low-dimensional metallic conduction. A comparison with the conductance data obtained through the mechanical break junction experiments (Figure 4.12) in the presence of PVP did not show conductance peaks in the histogram. The presence of conductance peaks in the histogram for dielectrophoretic wire growth experiments suggest the presence of a metallic low-dimensional conductor.

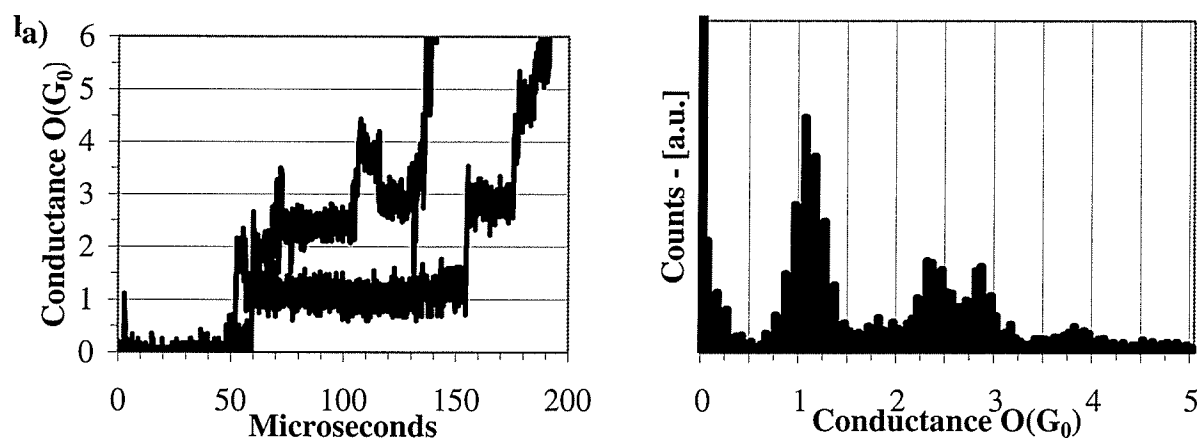


Figure 4.19 - Conductance data of dielectrophoretically grown wires from ODT capped gold nanoparticles. A total of 15 conductance traces (a) were used to compile the histogram illustrated in (b).

Conductance measurements through dielectrophoretically-grown wires fabricated from ODT capped gold nanoparticles dispersed in dodecane show conductance peaks at, or near, integer multiples of G_0 . A comparison to the mechanical break junctions performed in the presence of dodecane (the solvent used in the dispersal of the ODT-capped nanoparticles) of Figure 4.14 b) illustrates that low-dimensional metallic conductance is indeed observed through the dielectrophoretic growth of the ODT-capped particles. It should also be noted the low-dimensional conductance of the wires formed from ODT capped gold nanoparticles was stable for several minutes, indicating very slow aggregation of gold nanoparticles on the gold wire.

5. Discussion

Size distribution analysis of the gold nanoparticles was first performed by a comparison of the measured to the calculated extinction spectra. In the calculation of the extinction spectra it was assumed the index of refraction was that of bulk gold. This is a significant assumption as the index of refraction of bulk gold depends upon many parameters, including the impurity density of the gold. Furthermore, a solution of nanoparticles was studied. It was found the presence of the stabilizing ligand would further affect the index of refraction. In order to calculate the extinction peak exactly, a modified set of values for the effective index of refraction is required. It was assumed the stabilizing ligand did not contribute appreciably to the extinction spectra.

As discussed in section 2.6, citrate and PVP will preferentially adsorb onto the surface of the gold nanoparticles to produce a thin dielectric layer on the surface of the nanoparticle. The thickness of the layer determines the size of the contribution. Thus, it was reasonable to neglect the contribution of the citrate layer (monolayer coverage) but the PVP layer (10-15 nm thick) probably contributed to the extinction spectra. A more rigorous study of the extinction contribution given by PVP but would only be useful if the index of refraction of the nanoparticulate gold was known.

Also, as discussed in section 2.6, ODT will preferentially adsorb onto the surface of gold in monolayer coverage with the thiol group (SH) oriented towards the surface of the gold film. The extinction spectra of ODT capped gold nanoparticles (Figure 4.3) did not exhibit an extinction peak at or near 520 nm – as predicted by Mie theory. A primary assumption into the absence of this peak was that the nanoparticles were very small (<10nm) and therefore produced a peak that was below the noise floor of the data

obtained. Other authors have reported [87] that the thiol group in the ODT induces localized holes from the Au-S bond, quenching the surface plasmon absorption responsible for much of the extinction.

Dielectrophoretic wire growth experiments were successfully accomplished using several apparatus illustrated in section 3.3, while using nanoparticles capped with citrate, PVP, or ODT. The reproducibility of the wire growth experiments was a concern as only ~50% of the experiments performed produced a wire. The absence of wire formation was not clearly explained, as many variables including electrode geometry and separation were not fully controlled.

In the analysis of the conductance through the gold wires it was assumed that any low-dimensional conductance in the junction was dominated by low-dimensional metallic conductance, as described by the Sharvin or Landauer conductance models. Mechanical break junction experiments were performed preceding the dielectrophoretic wire growth experiments for use as a basis of comparison of conductance through nanowires. Conductance histograms of mechanical break junction experiments performed in the presence of a PVP solution resemble an inverse exponential relationship to increasing conductance – a characteristic of electron tunnelling through a dielectric (section 2.2) [41]. This may be attributed to the presence of PVP as the mechanical break junctions performed in an aqueous environment (Figure 4.10) did show conductance steps and peaks. The absence of conductance steps in the presence of PVP may be due to the relatively large layer (10-15 nm) PVP forms on a gold surface [60].

However, the dielectrophoretic wires grown from PVP-capped gold nanoparticles show conductance peaks at integer multiples of G_0 , an indication of low-dimensional

metallic conduction. The evolution of conductance peaks in the dielectrophoretic wire growth experiments from the mechanical break junction experiments support the assumption the conductance is the result of low-dimensional metallic conduction. It is recognized that this evidence is not conclusive and further experiments must be performed to provide a statistically meaningful data set.

Mechanical break junction experiments performed in the presence of ODT appear to strengthen the histogram peaks at G_0 and $2 G_0$, as illustrated in the difference in conductance data of dodecane and ODT solutions. While conductance peaks usually preclude metallic conductance, the absence of conductance peaks at other integer multiples of G_0 and a peak close to zero indicate otherwise.

The conductance data obtained from the dielectrophoretically grown wires from a solution of ODT-capped gold nanoparticles show a much better result. The conductance traces of the ODT-capped gold nanoparticle wire illustrate many conductance steps at integer multiples of G_0 and the conductance peaks show peaks at integer values of G_0 . The conductance differences between the mechanical break junction experiments and the dielectrophoretically grown wires suggest the conductance mechanism is through a low-dimensional metallic system. The perturbation to the density of states as the result of thiol group in the ODT chain remains relatively unexplored and as a result its effects on the conductance is not known. In one observation the thiol tends to allow the stable formation of an atomic arrangement with relatively large interatomic spacing that in turn alters the conductance to allow the stable formation of conductance plateaus at odd integers of G_0 [27]. A further observation of trapped charge induced on a nanoparticle surface by an alkanethiol suggests the altering of the density of states. Obviously, a much

larger data set must be found to make conclusive observations the conductance is due to metallic conduction rather than a more 'exotic' process.

6. Conclusion and Future Work

Gold nanoparticles were synthesized, and characterized for their size distribution using Mie extinction theory and analysis of images obtained through a transmission electron microscope (TEM). It was found the Mie extinction theory gave a rough estimate of the size distribution as the index of refraction of the nanoparticles was not exactly known. Size distributions were successfully obtained from TEM images of dried samples.

Gold nanoparticles were constructed into wires through the action of a non-uniform electric field (dielectrophoresis). Conductance measurements taken at the conclusion of wire growth suggest there exists a low-dimensional conductance pathway as that predicted by the Landauer and Sharvin conductance theory. Histogram analysis seems to support the conclusion of the low-dimensional conductance through wires formed from ODT-capped gold nanoparticles, while the PVP in the PVP capped gold nanoparticles seem to contribute to the conductance. The influence of the capping agents cannot be totally ignored even though the wires formed from the ODT suggest little, or no, contributions to the conductance.

The objective of this dissertation was to study the conductance through dielectrophoretically grown wires from a colloidal suspension and possibly allude to a fabrication method for constructing contacts in a molecular electronic device. Although this study has produced evidence for low-dimensional conductance, the viability for producing electrodes used in constructing a molecular electronic device remains relatively unexplored. Further studies are required to study the viability of using

dielectrophoresis as a construction technique for fabricating a contact in a molecular electronic device.

Wire growth experiments were performed on an optical table with some isolation from electronic and acoustic noise. If the experimental apparatus had been completely isolated from these noise sources, the conductance traces and histograms may have contained better defined conductance plateaus and histogram peaks. An STM-based system would offer further isolation from acoustic and electronic noise as well as providing a better-defined electrode geometry and separation.

It has been illustrated the conductance pathway may have been through a low-dimensional metallic conductor (mechanical break junctions and dielectrophoretic wire growth). In the analysis of the conductance traces it was primarily presumed the main source of noise was due to the driving electronics. A series of experiments performed at temperatures ranging from 0°C up to 75 °C might lead to an understanding of the temperature dependence of the noise spectrum. The results of such a study would greatly assist the understanding of the transport character illustrated in the histograms presented in this dissertation. This would be a suitable starting point for future work in this area.

7. References

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Appendix A Mie scattering theory code

File: Absorbance.m

```
%the absorbance of the colloidal system
clear all
close all

%initialize the variables
Qtotloop=[];
Nsum=5;
Qt=load('Qt.txt');

%Wavelength to compute extinction at
%corresponds to the measured extinction points
N1=316;
wavelength=linspace(190e-9,820e-9,N1);

%index of refraction of the particle
N2=500;
m=index(wavelength);

%Compute the extinction peak assuming a normal distribution
%meanloop is the average particle radius
%stdfactor is the standard deviation of the distribution

meanloop=linspace(1e-9,399e-9,400);
stdfactor=linspace(0.01,0.10,10);

%Compute through all possible distributions
%including the average particle diameter (O) and standard deviation (P)

for P=1:length(stdfactor)
    for O=1:length(meanloop)

        Qtot=zeros(N1,1);
        mean=meanloop(O);
        std=stdfactor(P)*mean;
        diameter=linspace(1e-9,500e-9,N2);
        fd=(1/(sqrt(2*pi)*std))*exp(-(0.5)*((diameter-mean)./std).^2);
        %Simpson Rule for numerical integration employed
        %From Single Variable Calculus D.W.Trim

        for M=1:N1
            Q=fd(1)*Qt(1,M);
```

```

        Qtot(M)=Q+Qtot(M);
    for N=2:N2-1 %diameter
        Q=fd(N)*Qt(N,M);
        if mod(N,2)==1
            Qtot(M)=2*Q+Qtot(M);
        else
            Qtot(M)=4*Q+Qtot(M);
        end
    end
    Q=fd(N2)*Qt(N2,M);
    Qtot(M)=Q+Qtot(M);
end
O*P
Qtotloop=[Qtotloop Qtot];
end
P
end

%save the results as a text file for later compilation
save 'theoretical.txt' Qtotloop -ascii

```

File: table.m

%Calculate a table of extinction values for Qext
 %For a given wavelength and a given diameter of particle

```

N1=316;
N2=500;

wavelength=linspace(190e-9,820e-9,N1);
diameter=linspace(1e-9,500e-9,N2);
Nsum=5;
m=index(wavelength);

for M=1:N1
    for N=1:N2
        Q(N,M)=sumQext(m(M),wavelength(M),diameter(N),Nsum);
    end
    M
end

save 'Qt.txt' Q -ascii

```

File: SumQext.m

%Summation of all the Q values required.
 %the function Qext calls this in order to compile the table used in the main program

```

function sumQextres = sumQext(m,wavelength,diameter,Nsum)
%result of Qext for all N specified
%is of the form sumQextres = sumQext(m,wavelength,diameter,Nsum)

sumQextres=0;
for I=1:Nsum
    %Qext(d,y)
    [an,bn] = Qext (m,wavelength,diameter,I);
    sumQextres=sumQextres+(2*I+1)*real(an+bn);
end

sumQextres=sumQextres*(2*pi*diameter/wavelength);

```

File: Qext.m

% Calculation of extinction parameters an, bn
% for a given wavelength, diameter and order

function [an, bn] = Qext (m1, lamda, d, N)

% Calculation of the Mie Scattering Coefficient
% Qext

% m is refractive index of bulk gold
% 1.33 is the assumed index of refraction

m = m1/1.33;

a = pi*d/lamda;
B = m*a;

% numerator and denominator calculations of the extinction parameter an
annum = a*sbesselj(N, a)*dersbesselj(N, B) - B*sbesselj(N, B)*dersbesselj(N, a);
anden = a*dersbesselj(N, B)*shankel(N, a) - B*dershankel(N, a)*sbesselj(N, B);

an = annum/anden;

% numerator and denominator calculations of the extinction parameter bn
bnnum = B*sbesselj(N, a)*dersbesselj(N, B) - a*sbesselj(N, B)*dersbesselj(N, a);
bnden = B*dersbesselj(N, B)*shankel(N, a) - a*dershankel(N, a)*sbesselj(N, B);

bn = bnnum/bnden;

Appendix B Image analysis code

```
function out=picto(im,radius,conf)
%Function to extract circular objects from an image
%Uses the circular hough transform to accomplish this

ime=edge(im,'sobel');
out=[];
[x_size,y_size] = size(im);

for r=radius(1):radius(2):radius(3)
    r
    Imh = hough3c(ime,r);
    points = center(Imh,r,conf);

    %remove the circle from the original image
    for p=1:size(points,1);

        for x_off = -r:r
            for y_off = -r:r
                x_point=points(p,1);
                y_point=points(p,2);
                %skip if out of range of original picture
                if ((x_off+x_point)<1) | ((x_off+x_point)>x_size) | ((y_off+y_point)<1) |
                    ((y_off+y_point)>y_size)
                    %ignore
                else
                    %determine if on the circle of transformed image
                    %add a point if true
                    if (round(sqrt(x_off.^2+y_off.^2))<r+1)
                        ime(x_point+x_off,y_point+y_off)=0;
                    end
                end
            end
        end
    end
    %imshow(ime)
    out=[out;points];
end
```

```

function points = center(Im,radius,conf)
%Extract only the center point for the circular object

[x_size,y_size]=size(Im);

%threshold the image
Imt=(Im>(conf*2*pi*radius));

%find x,y point of all of these values that are true
points=[];
for x_point =1:x_size
    for y_point=1:y_size
        if Imt(x_point,y_point)==1
            points=[points; x_point, y_point, radius];

            %take out all points within the radius
            for x_off = -radius:radius
                for y_off = -radius:radius
                    Imt(x_point+x_off,y_point+y_off)=0;
                end
            end
        end
    end
end
end
end

```

```

function Imhough = hough3c(Im,radius)
%circular Hough transform
%Original image must be binary edges
%Inputs to this transform are the original binary image
%plus the radius of the circular hough transform

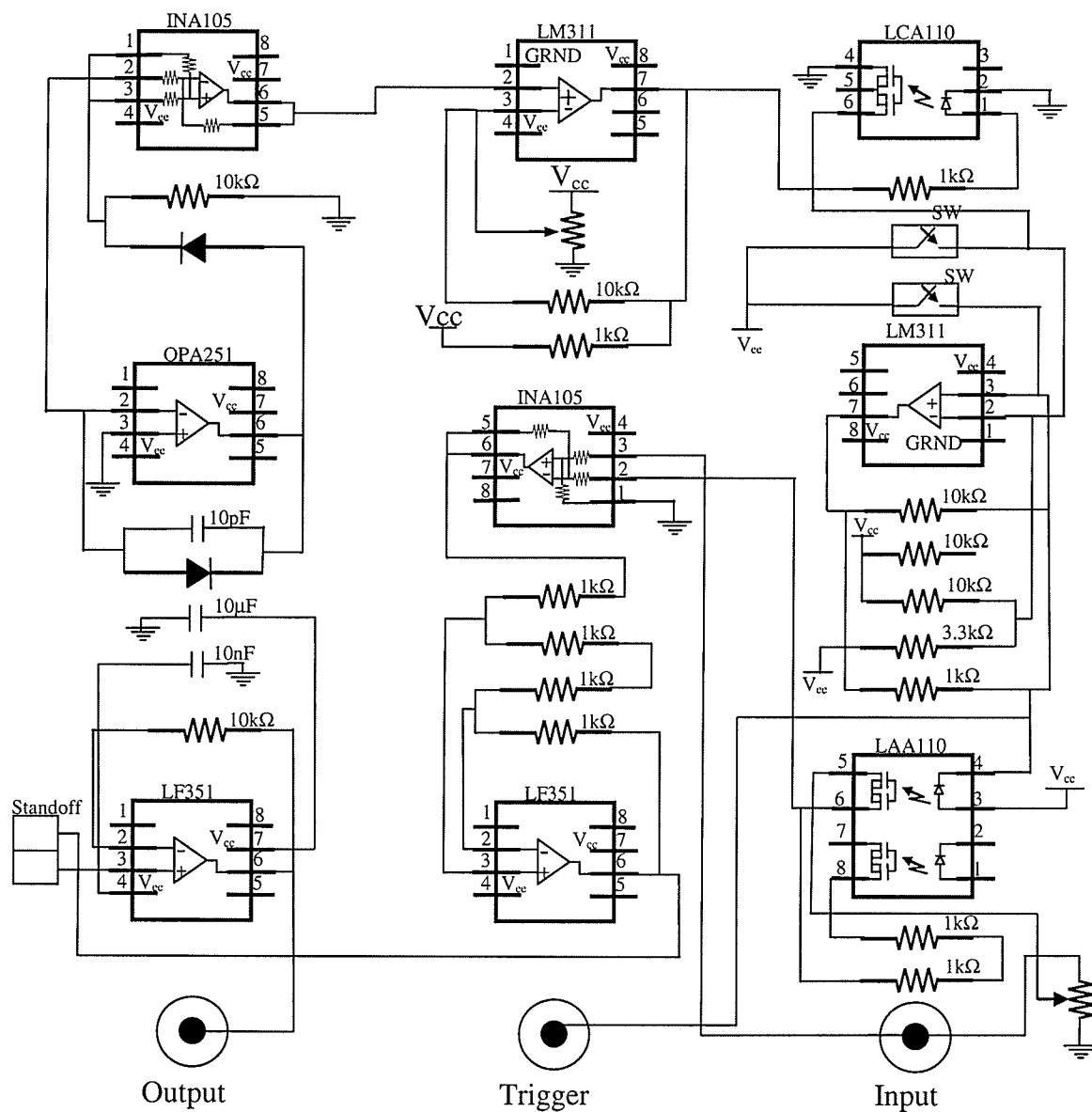
%Determine the dimensions of the picture
[x_size,y_size] = size(Im);

%Initialize the hough transform picture
Imhough=zeros(x_size,y_size);

%Scan through the picture and determine if there is a point
%on original image
for x_point=1:x_size
    for y_point=1:y_size
        if(Im(x_point,y_point)==1)
            for x_off = -radius:radius
                for y_off = -radius:radius
                    %skip if out of range of original picture
                    if ((x_off+x_point)<1) | ((x_off+x_point)>x_size) | ((y_off+y_point)<1) |
((y_off+y_point)>y_size)
                        %ignore
                    else
                        %determine if on the circle of transformed image
                        %add a point if true
                        if (round(sqrt(x_off.^2+y_off.^2))==radius)
Imhough(x_point+x_off,y_point+y_off)=Imhough(x_point+x_off,y_point+y_off)+1;
                        end
                    end
                end
            end
        end
    end
end
end
end
end
end

```

Appendix C Electronic Circuit Schematic



Appendix D Alternative Electrode Design

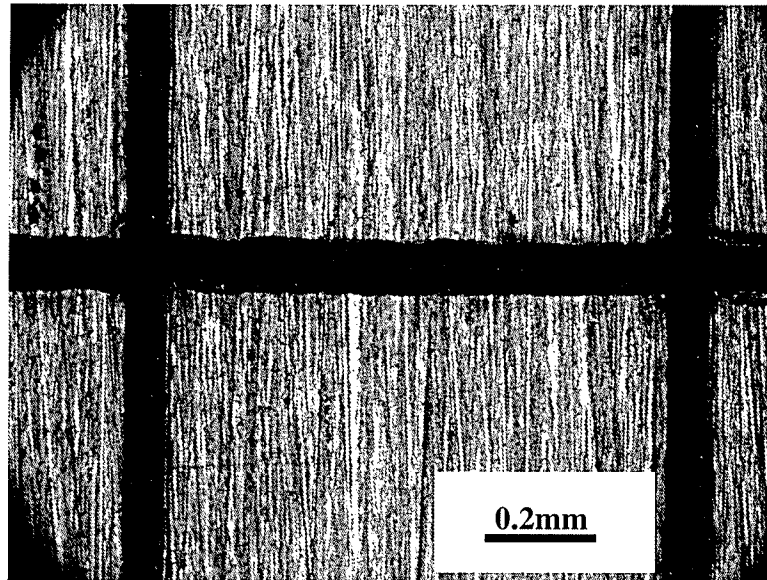


Figure D.1 - A typical electrode for a CNC fabricated from a printed circuit board (PCB)

Electrodes were also fabricated from copper-clad dielectric (normally used for printed-circuit boards). The electrode array shown in Figure D.1 was milled from a blank board using a computer-numerical-controlled (CNC) milling machine.

The final electrode design studied involved deposition of a thin film (120nm) of gold on a silicon wafer. No special precautions were taken to eliminate a native oxide layer preceding the deposition of the film and therefore an unknown thickness of silicon dioxide lay beneath the gold film. Subsequently the gold film was patterned into several bowtie structures, a process described in [91].

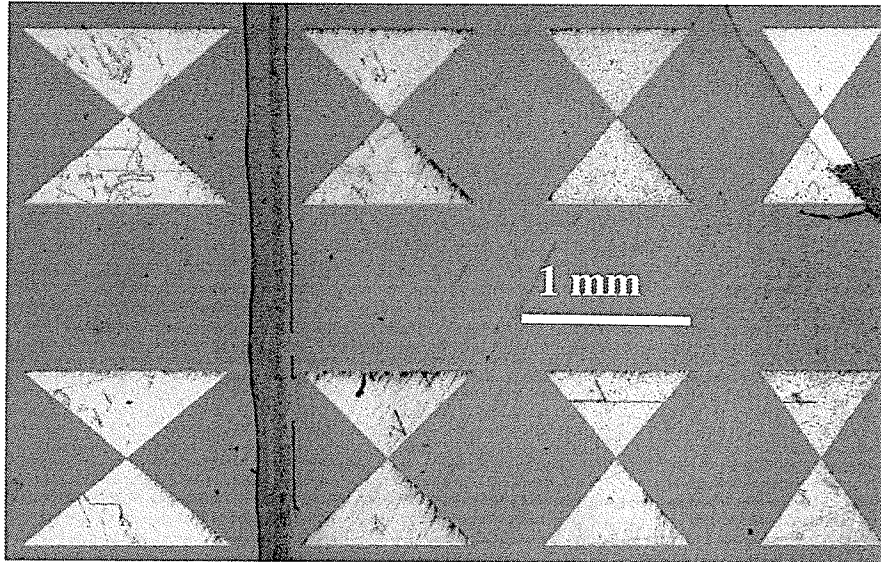


Figure D.2 - Optical image of the bowtie structures that were used to construct electrodes by electromigration.

Following fabrication, electromigration of the thin film was performed to produce the required electrode gaps.

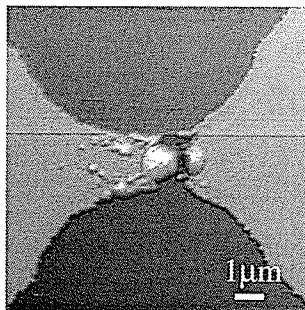


Figure D.3 - Atomic force microscope picture of an electrode pair following electromigration of a thin gold film deposited on silicon.

Electromigration of the thin-gold film was performed using a dc voltage source and a multimeter that were both controlled through a LABVIEW interface. There were two methodologies that were used to create the desired electrodes. First, a dc voltage was increased by a 0.01V increment every second until the film ruptured. This was

determined by monitoring the current through the structure and calculating the resistance through the film. Once the resistance exceeded $1\text{M}\Omega$, the film was considered to have ruptures and the applied voltage was removed. Once all the electrodes had been formed, the electrode spacing was measured from images obtained using a Digital Instruments/Veeco Dimension 3100 operating in contact AFM mode.

A second method was utilized to create larger electrode spacing ($\sim 20\mu\text{m}$). This involved the application of 3 volts to the film until the formation of the electrodes. Only three electrodes were fabricated in this method and therefore an estimate to the reproducibility of this method to create the large electrodes could not be made.

[91] Rohde, C., "Fabrication and Characterization of nano-antennas", M.Sc. thesis, University of Manitoba (2006) [*At time of writing this thesis was still in preparation*].