

# A NOVEL HIGH THROUGHPUT METHOD FOR NANOPARTICLE PRODUCTION BY ATOMIC VAPOUR DEPOSITION ON A LIQUID JET

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## *A NOVEL HIGH THROUGHPUT METHOD FOR NANOPARTICLE PRODUCTION BY ATOMIC VAPOUR DEPOSITION ON A LIQUID JET*

### ABSTRACT

INJECTING A LIQUID JET INTO VACUUM, AND CO-DEPOSITING THIS WITH ATOMIC VAPOUR, VARIOUS NANOMATERIALS WERE SYNTHESISED. NANOPARTICLES OF ZINC OXIDE, COPPER, SILVER AND SILICA WERE PRODUCED. THE SILVER VAPOUR / ETHANOL LIQUID JET SYSTEM WAS CHOSEN TO BENCHMARK THIS NEW SYNTHESIS METHOD.

PARTICLES OF SILVER IN ETHANOL HAD A LOG-NORMAL SIZE DISTRIBUTION, WITH A MEDIAN SIZE PROPORTIONAL TO THE LOGARITHM OF SILVER CONCENTRATION, OVER THREE ORDERS OF MAGNITUDE. PARTICLES SHOWED A PLASMON RESONANCE CHARACTERISTIC OF SILVER NANOPARTICLES. IT WAS SHOWN THAT THE PLASMON ABSORPTION PEAK SHAPE (HEIGHT TO WIDTH RATIO) WAS APPROXIMATELY CONSTANT FOR SILVER/ETHANOL SAMPLES, REGARDLESS OF CONCENTRATION OR AGEING. THE SOLVENT USED HAD A PROFOUND EFFECT ON BOTH THE PARTICLE SIZE, WHICH WAS MEASURED VARYING FROM 2 NM IN WATER TO 10 NM IN ISOPROPANOL, BUT ALSO ON THE PLASMON SHAPE. THIS RATIO CHANGED DEPENDENT ON THE SOLVENT CHEMISTRY, BUT WAS LARGELY INDEPENDENT TO OTHER PARAMETERS.

BY DISSOLVING COMMERCIALY AVAILABLE SPHERES OF SILICA IN METHANOL, JETTING, AND CODEPOSITION WITH SILVER, SILICA PARTICLES WERE DECORATED WITH SILVER. THESE PARTICLES WERE CATALYTICALLY ACTIVE, AND EVOLVED AWAY METHANOL AT A RATE OF  $1.65 \times 10^{-7} \text{ MOL G}^{-1}\text{S}^{-1}$ .

A PHASE OF ULTRA-SMALL CLUSTERS WAS IDENTIFIED IN BOTH SILICA AND SILVER SAMPLES BY MIRCOSCOPY AND SPECTROSCOPY. IN THE CASE OF SILVER, THESE WERE TENTATIVELY ASCRIBED TO CLUSTERS OF  $\text{Ag}_2 < N < 5$ . SILVER DEPOSITED WITH PURE WATER WAS HIGHLY SELECTIVE OF THESE PARTICLES. ATOMIC FORCE MICROSCOPY STUDIES OF ARRAYS OF THESE

PARTICLES ON SURFACES SHOWED EVIDENCE FOR THE CO-EXISTENCE OF THREE PHASES OF A CLUSTER FLUID. ORDER OF MAGNITUDE DIFFUSION RATES WERE ESTIMATED FROM EXPERIMENTAL DATA. LIQUID LIKE CLUSTER ARRAYS HAD DIFFUSION RATE ON THE ORDER OF  $10^{-2} \text{ nm}^2\text{s}^{-1}$  AND GAS PHASE CLUSTERS WERE ESTIMATED TO HAVE A DIFFUSION RATE ON THE ORDER OF  $1 \text{ nm}^2\text{s}^{-1}$ .

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# LIST OF COLLABORATORS

THE FOLLOWING COLLABORATORS CONTRIBUTED TO CHAPTER 3: HANIEH YAZDANFAR, MUMIN KOC, ANDREW WARD, OLIVER YOULE, OSARENKHOE UWUIGBE

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*Everything starts somewhere, although many physicists disagree.*

Terry Pratchett

# 1

## Introduction

METAL PARTICLES WITH dimensions less than one ten millionth of a metre are considered nanoparticles. Metal nanoparticles are now known for their many applications across all modern technologies including energy harvesting [1, 2], catalysis [3, 4] and medicine [2, 4, 5].

Synthesis of nanoscale systems is commonly divided into two main categories, top-down and bottom-up [6, 7]. In bottom up synthesis, particles are assembled from individual atoms or molecules. Chemical synthesis techniques generate individual metal atoms or ions well dispersed in a solvent by chemical reduction [2, 4, 5, 8-11], and are considered a bottom-up technique. Often organic molecules are added to stabilise the resulting particles, or to provide templates for particle growth [7, 10, 12-14]. Such techniques can produce a dizzying array of nanoparticles with differing morphologies and sto-

ichiometry [8, 9, 11, 15]. However, in practice individual synthesis protocols are unique and specific to a particular metal and shape; "the synthesis of metal nanoparticles remains more of an art than a science" [10].

Top-down processes break down a larger target into smaller pieces to produce nano-materials. Top down approaches in solution include melting and emulsifying metal droplets in hot solvent [6], arc-discharge at metal electrodes [16, 17] and laser ablation in solution (LASIS) [18, 19].

In this thesis, a new technique is introduced that straddles these two concepts. By injecting a liquid jet into vacuum, solvents such as water and ethanol, traditionally associated with bottom up syntheses, can be mixed with pure atomic vapours in vacuum.

## 1.1 BOTTOM UP: CHEMICAL SYNTHESIS

The starting material in most syntheses of metal nanoparticles is a metal salt in solution [7, 10]. Metal ions can exist in complexes with ligands, counterions and solvent molecules. Metal ion reduction is the next step towards growing larger metal particles. Ions can be reduced by addition of a chemical reducing agent [12, 13, 20-22], by irradiation [23, 24], photoreduction [25, 26], and thermal reduction [21, 27, 28]. Once reduced from solution, metal atoms aggregate and grow into clusters. Growth by this method can be described as a *coprecipitation* reaction [29, 30].

### 1.1.1 NUCLEATION AND GROWTH

The classical model of coprecipitation, by La Mer [31], considers a homogenous solution of metal ions, where the reduction reaction changes the system parameters such that it becomes supersaturated. A saturated solution is one where the concentration of dissolved material has reached a maximum, and no further material can be dissolved. If system parameters are changed, for example the solution is cooled, then the maximum possible concentration of dissolved material,  $C_{eq}$ , can change. The solution is said to be *supersaturated* if the actual concentration of dissolved material in the solution,  $C$ , is greater than  $C_{eq}$ . The supersaturation  $S$  is given by  $S = C/C_{eq}$  [29].

Now we consider the free energy of a particle  $\Delta G$ , which is formed from the precipitated material in the solution with supersaturation  $S$ . This has two contributions, from the free energy of the surface  $\gamma$  and the crystal free energy  $\Delta G_v$ . The free energy of the crystal is dependent on temperature  $T$  and its molar volume,  $v$ .

A spherical particle of radius  $r$  with surface energy  $\gamma$  has total free energy given by equation 1.1 [14].

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_v \quad (1.1)$$

Where we can calculate the crystal free energy by equation 1.2 [14, 29],

where  $k_B$  is Boltzmann's constant and  $S$  is the supersaturation of the solution.

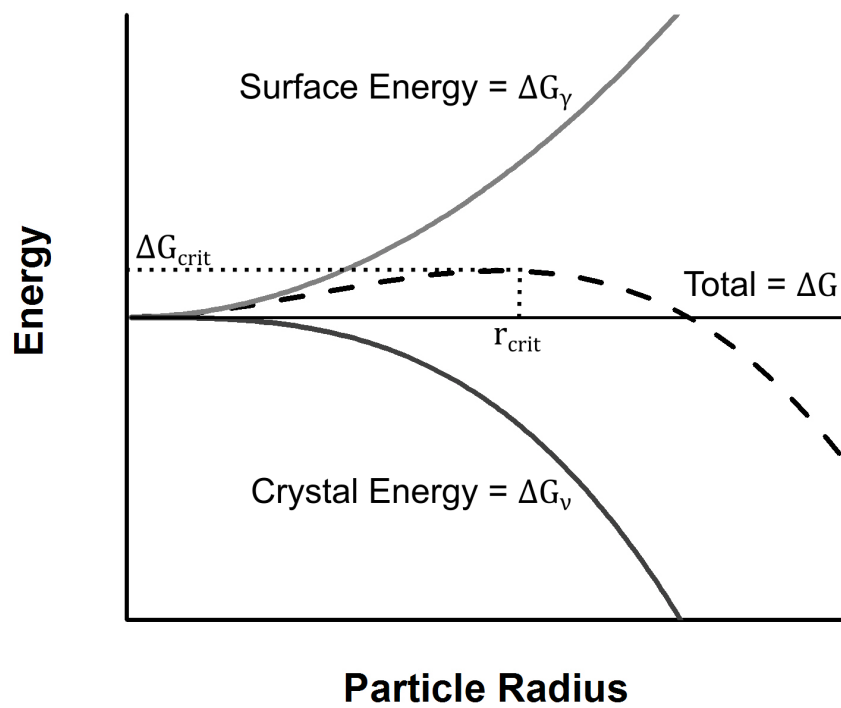
$$\Delta G_v = \frac{-k_B T \ln(S)}{v} \quad (1.2)$$

We can define a critical free energy  $G_{crit}$ , where the contributions of surface and volume free energies are balanced. This is schematically illustrated in figure 1.1.1 below [14]. By setting  $d\Delta G/dr = 0$ , we can find the critical free energy (equation 1.3 [14]) and the corresponding critical radius (equation 1.4 [14, 29]). Below this critical radius, particles are more likely to lose atoms to solution and dissolve. Above this radius, particles are more likely to accumulate more precipitating atoms and grow.

$$\Delta G_{crit} = \frac{4}{3} \pi \gamma r_{crit}^2 \quad (1.3)$$

$$r_{crit} = \frac{2\gamma v}{k_B T \ln S} \quad (1.4)$$

This first stage of particle growth is known as nucleation, where the first clusters which are thermodynamically stable against dissolution are formed. The rate of nucleation can be expressed as the Arrhenius type equation 1.5. The rate is dependent on the three parameters of temperature  $T$ , surface energy  $\gamma$  and saturation  $S$ . Crucially, the exponential shows that the rate of nucleation will be negligible until a critical exponent is reached, at which point



**Figure 1.1.1:** The relationship between the particle radius and total free energy,  $\Delta G$ . Contributions to total energy are from surface,  $\Delta G_\gamma$ , and crystal,  $\Delta G_v$ , terms. These cancel at  $\Delta G_{crit}$ , which is the maximum of  $\Delta G(r)$ . The corresponding radius is  $r_{crit}$ , the critical radius. Figure adapted from [7, 14, 29].

nucleation will become very rapid.

$$\frac{dN}{dt} = A \exp\left(\frac{-\Delta G_{crit}}{k_B T}\right) = A \exp\left(-\frac{16\pi\gamma^3 v^2}{3k_B^3 T^3 (\ln S)^2}\right) \quad (1.5)$$

Surface energy can be altered with the addition of surfactants to the solution. The adhesion energies of organic molecules to inorganic surfaces cannot be reliably measured [9], hence; modification of surface energy by addition of surfactants is not precise. It is known that trace impurities in a solvent can dramatically change the nucleation of nanoparticles [9, 10]. This suggests that even trace surfactants will unpredictably alter the surface energy term.

The temperature of the reaction is simple to control in principle. It follows that the nucleation rate could be well controlled with temperature. Empirically it is known that the pre-exponential factor  $A$  can change substantially with temperature [8]. This captures the changes in diffusion rate with temperature. For this reason, the temperature does not lead to a predictable change in nucleation rate.

The supersaturation,  $S$ , is then the key parameter in controlling the nucleation rate of particles. It follows that the nucleation rate is low, until the supersaturation of the solution reaches a critical level, at which point nucleation occurs rapidly. As particles nucleate, the supersaturation drops and the nucleation rate decreases. Particles then grow by steady addition of individual atoms. As illustrated in Figure 1.1.1; above the critical radius the activation energy cost for growth drops rapidly. This makes incremental growth energetically favourable even at lower supersaturation.

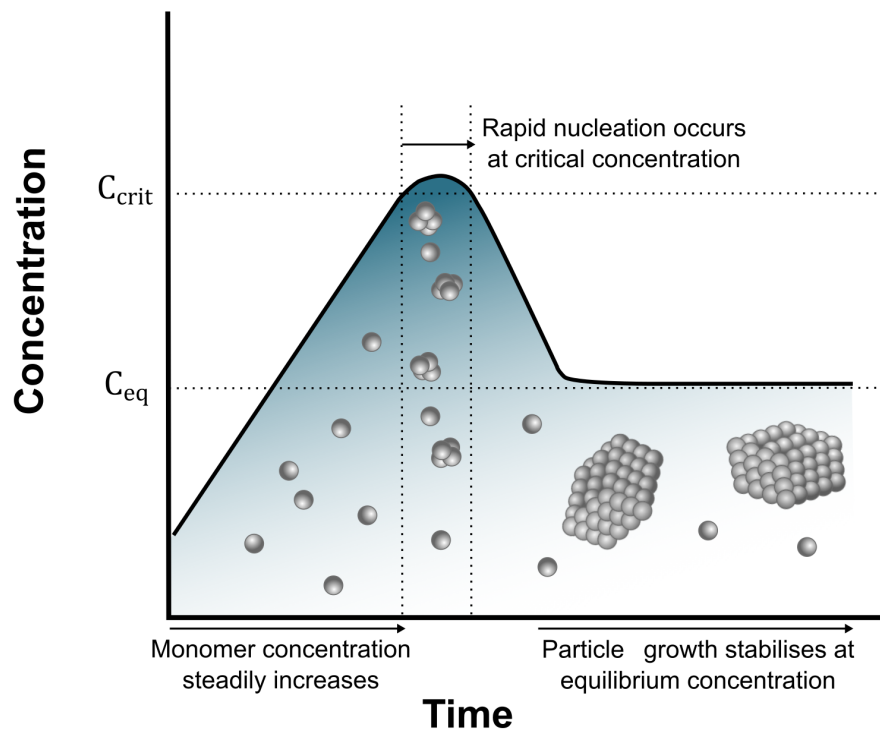
This classical model of particle nucleation and growth is schematically illustrated in figure 1.1.2. The concentration of monomer (metal atoms, ions) in solution is increased beyond supersaturation, until a critical concentration,  $C_{crit}$ , is reached. The nucleation rate increases dramatically, as expected from equation 1.5. For the purposes of this model, the nucleation rate is considered to be effectively infinite [8, 14, 29]. It is assumed that nuclei are formed continuously until the concentration drops below critical. At this point, the formation of new nuclei is essentially halted, and existing particles grow by addition of single monomers until the concentration reaches an equilibrium. In principle, the rate of cluster growth and dissolution is balanced at this point.

Chemical syntheses have limitations, particularly as regards waste and environmental impact [32]. Moreover there are many aspects of particle growth which are not captured by this model. For example, it is usually assumed that dissolved metal ions are monatomic. However; experiment has shown that solutions of  $\text{AgNO}_3$  contain up to 27 %  $\text{Ag}_3^+$  clusters [10], which leads to the formation of triangular nuclei and particles. Moreover, particles can aggregate, as opposed to growing by addition of single atoms, or can undergo further secondary processes such as Ostwald ripening (growth of large particles at the expense of smaller [29].)

## 1.2 TOP DOWN: PHYSICAL SYNTHESIS

Top down methods for nanoparticle synthesis in liquids are relatively new, Klabunde et. al. first reported the deposition of magnesium vapour into Hexane and THF to produce highly reactive magnesium slurries [33]. Since then a





**Figure 1.1.2:** Particle concentration over time in a classic nucleation model. The monomer concentration is raised above until reaching a critical level,  $C_{crit}$ . Here, the supersaturation,  $S = \frac{C_{crit}}{C_{eq}}$ , is high enough to initiate extremely rapid nucleation. Condensation of monomer onto the nuclei then rapidly lowers the concentration until it stabilises around the equilibrium value  $C_{eq}$ . Figure adapted from [7, 8].

few widely used techniques have been developed: laser ablation synthesis in solution (LASIS) [19, 34, 35], solvated metal atom dispersion (SMAD) [36-38] and sputtering onto liquids [39-43]. These physical methods for nanoparticle production disperse metal atoms in solution without the use of chemical precursors and reducing agents. They can achieve greater purity [19] and reactivity [33] than traditional chemical synthesis.

#### 1.2.1 SPUTTERING ONTO LIQUIDS

Atomic metal vapour can be produced by sputtering and thermal evaporation, and then be directly deposited into liquids with sufficiently low vapour pressures [39-42]. Silver nanoparticles with diameter  $3.7 \pm 1.3$  nm can be produced by sputter deposition into canola oil [41], and sputter deposition of gold into the ionic liquid N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)imide produced particles with diameter  $1.9 \pm 0.5$  nm [42].

In principle, this is very similar to our experiment: atomic vapours are mixed with solvents. However, these techniques as applied are limited to low vapour pressure liquids, such as ionic liquids or vegetable oils [43]. The particles produced are related to both the deposition parameters and the liquid used [39-41]. Based on a substantial review of experimental work, Wender [43] has concluded that sputtering onto liquid is a robust technique for producing a range of nanomaterials that are often challenging to produce with other methods. The optimal organic solvent, most compatible with typical inorganic chemistry, remains a vegetable oil [43].

### 1.2.2 LASER ABLATION SYNTHESIS IN SOLUTION

Laser ablation of metal targets immersed in solvent produces metal atoms in a small plasma plume ablated from the target [19, 34, 35], which can undergo reactions with the solvent and with each other to form nanoparticles. Typically, these particles have long-term colloidal stability and often have unmodified surfaces [35], making them highly suitable for easy functionalisation. This can produce similarly small particles: laser ablation of gold in toluene yielded particles with a diameter of  $1.8 \pm 1.0$  nm [34].

Laser ablation can cause the breakdown of dissolved material or even the solvent itself [34, 35]. This limits the options for solvents which can be used, as well as constraining which materials can be dissolved in the solution. Also, the generation of metal atoms in an energetic plasma plume introduces many additional reaction pathways and mechanisms by which nanoparticles can form.

### 1.2.3 SOLVATED METAL ATOM DEPOSITION

Metal vapours can be thoroughly mixed by co-deposition with solvent vapour in a vessel with liquid nitrogen cooled walls [36–38]. The atomic vapour and solvent vapour co-condense and freeze. When this ice melts, nanoparticles form in solution. The limitations to reaction possibilities in this system are related to the need to vaporise both the solvent and the metal. This method is only compatible with thermal evaporation, which is limited to a subset of metals, and is very challenging for semi-metals and compounds. Other

methods of metal evaporation would induce strong interactions with vapour present in the chamber.

Similarly, the necessary evaporation of the solvent means that it is challenging to produce samples in mixed solvents with arbitrary ratios, due to differential evaporation. It is also impossible to introduce certain dissolved materials, again for the simple reason that these cannot be reliably evaporated with a solvent in arbitrary concentrations.

One unique aspect of solvated metal atom dispersion which (to the author's knowledge) has not been reported for other methods is the high reactivity of particles after production and their propensity for digestive ripening. Silver colloids had very broad size distributions as produced, however digestive ripening for several hours in the presence of stabiliser molecules and heating produced particles with narrow size distributions [38]

### 1.3 OPEN RESEARCH QUESTIONS

The object of this thesis is to characterise the use of a liquid jet as a vehicle to mix metal atoms and solvents. Do typical growth processes apply? Does the co-precipitation model hold? What are the properties of the produced nanoparticles?

The first results chapter, Atoms and Nanoparticles, covers the basic properties of synthesised nanoparticles of single materials in single solvents. This focuses mainly on silver as a benchmark material.

The second chapter discusses the properties of nanoparticle produced in some mixed solvents, and when nanoparticles are dissolved in the jet prior to

deposition of silver.

The final results chapter demonstrates the novel behaviour of nanoparticles on surfaces. Small nanoparticles can align on surfaces, and these arrays show new dynamics.

*"As the man said, for every complex problem  
there's a simple solution, and it's wrong."*

Umberto Eco

## 2

# Methodology

A BROAD RANGE of experimental procedures and analysis tools have been brought together in this work to effectively provide a general characterisation of nano-materials. This chapter serves as an overview of techniques used and summarises those aspects most relevant to this investigation.

### 2.1 VACUUM LIQUID MICROJETS

There is a limited set of materials which can exist in liquid phase in a vacuum, typically those with very low stagnation vapour pressures. Some examples are vegetable oils and other dense organic solvents. Ionic liquids have an effectively zero stagnation vapour pressure, as they do not exist as a gases and so do not evaporate at any pressure. Most common laboratory solvents (water, alcohols) cannot exist in vacuum without immediately evaporating un-

til the chamber has reached equilibrium with the stagnation vapour pressure of the liquid. Static liquid surfaces can only exist where the external pressure is at least equal to the stagnation vapour pressure of the liquid. At room temperature, most common laboratory solvents have stagnation vapour pressures of thousands of Pascals. For example, at 20 °C, water has a stagnation vapour pressure of 2.3 kPa and ethanol has a stagnation vapour pressure of 5.3 kPa. If the pressure around the liquid drops below the vapour pressure, the liquid will begin to boil. In the case of water, the energy lost in latent heat of vaporisation is sufficient to freeze the remainder. Despite these difficulties, there is substantial interest in introducing liquids to vacuum in a controlled and stable manner, without spoiling the vacuum. Techniques such as X-ray scattering and photoelectron spectroscopy usually require vacuum. To deploy these techniques to analytes in solution, a new method was devised. Liquid micro-jets are continuous filaments of fluid of diameter below 100 µm. Their low surface area allows high vacuum to be maintained despite evaporation from the liquid surface. Such small diameter jets were originally developed to measure the photoelectron spectra of liquid water and other high vapour pressure liquids in vacuum [44]. Forcing a liquid under high pressure through an aperture with diameter on the order of few to hundreds of microns forms a liquid micro jet. This travels at high speed, and lands in a cryogenic or differentially pumped trap. With sufficient pumping speed, even a high vapour pressure liquid can be formed into a stable liquid surface in vacuum. Microjets represent a universal liquid template in vacuum.

## 2.2 DEPOSITION OF METALS INTO LIQUIDS

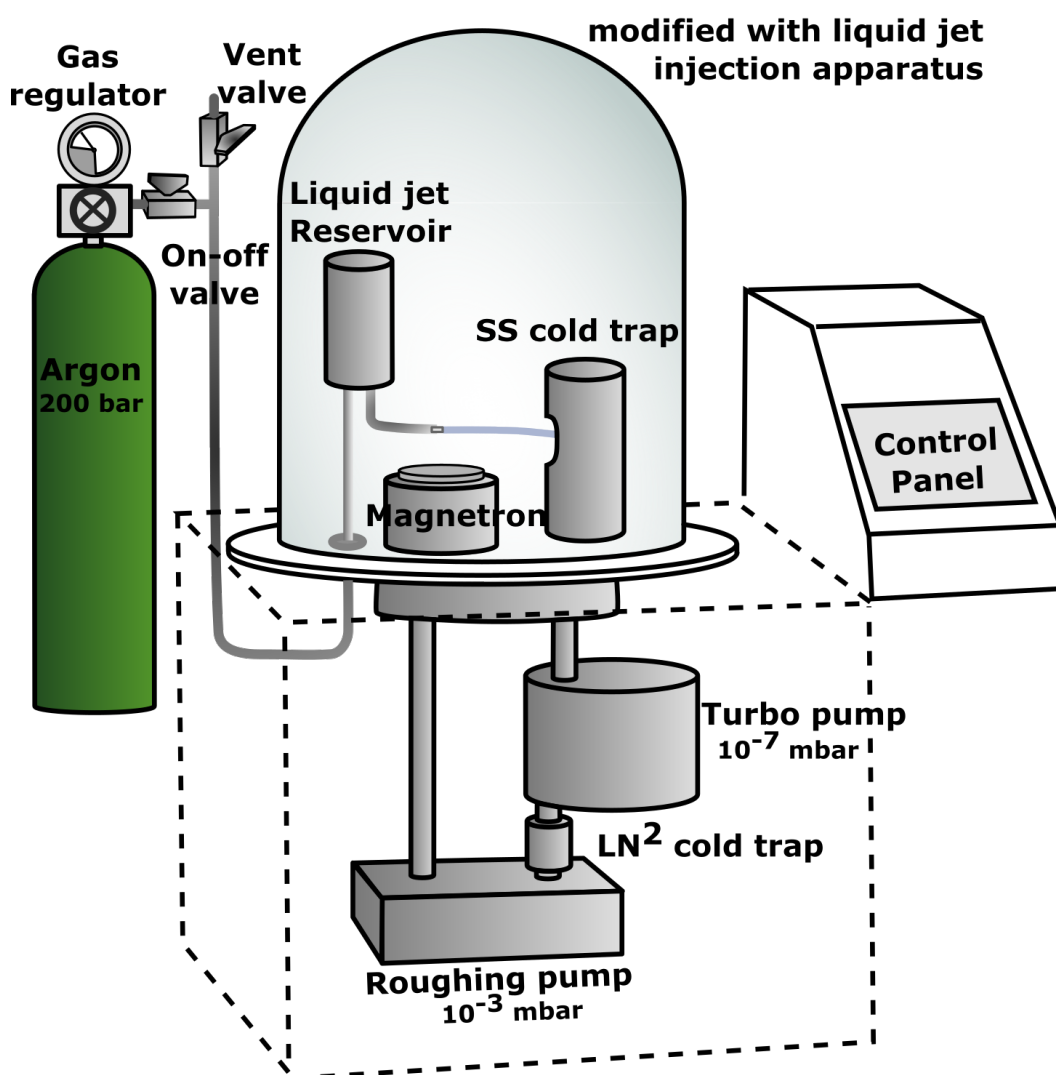
Samples of metal deposited into liquids, or co-deposited with liquids, were produced in a modified Edwards Auto 306 thin film coater, illustrated in figure 2.2.1. Before sputtering, the chamber was pumped to a pressure below  $10^{-6}$  mbar. The coater was then switched to process, where the vacuum system feedback maintains an approximately constant pumping speed. Once this had stabilised, a needle valve gas inlet was opened slowly to allow a flow of argon (BOC high purity 0 grade argon.) The valve was opened until the pressure had stabilised at  $5 \times 10^{-3}$  mbar. The ratio of high purity argon to remaining atmosphere was therefore 5000 to 1. Atomic metal vapour was produced by argon ion sputtering in an atmosphere of roughly  $10^{-3}$  mbar argon.

### 2.2.1 LIQUID JET OPERATION

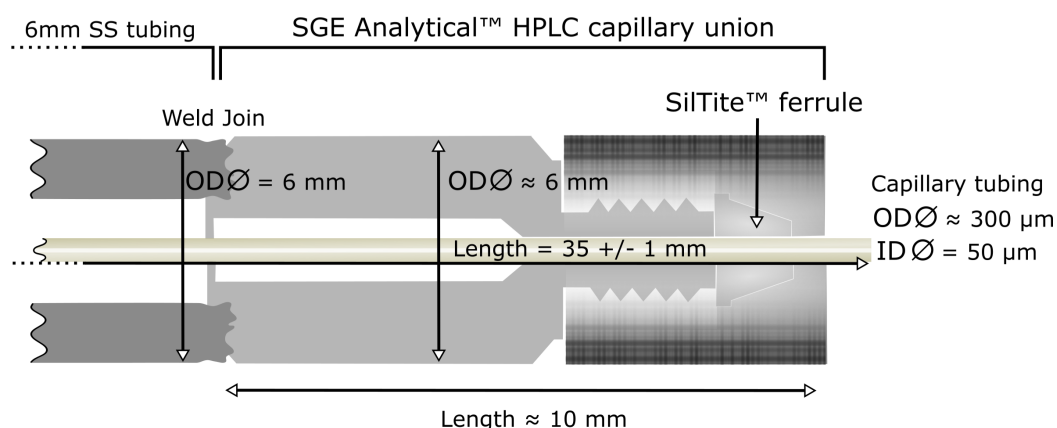
For the aperture of our liquid micro-jet we used silica micro-capillary tubing of inner diameter 50 microns. The tubing was cut to a length of  $35 \pm 1$  mm each time it was changed. After cutting, both ends of the capillary were inspected under an optical microscope for any damage to the inner walls. When cut correctly the face of the capillary is perfectly smooth. An imperfect cut showing damage to the inner capillary walls is unsuitable and a new capillary was cut. The capillary tube was fitted into an HPLC union (SGE Analytical) and sealed with a soft composite (Siltite<sup>TM</sup>) ferrule. This setup is illustrated in Figure 2.2.3.



## Edwards Auto 306 thin film coater



**Figure 2.2.1:** Diagram of the Edwards Auto 306 Coater, with added liquid jet system. This illustrates the pumping system below the cold trap; the highest achievable vacuum at each pumping stage; the liquid jet and gas pressure system; and the approximate layout of DC magnetron sputter head, liquid jet and cold trap.



**Figure 2.2.2:** Schematic of the SGE Analytical capillary fitting. Fused silica capillary tube (yellow) is fed through the union fitting. When the union is tightened, the Siltite ferrule forms a leak-tight seal around the capillary.

The backing pressure was supplied by bottled argon (BOC, zero grade, 99.999 % pure) with a bottle pressure of 200 Bar. This was regulated down to a maximum working pressure of 70 Bar. The regulator, gas line, reservoir, and capillary assembly were all connected by Swagelok<sup>TM</sup> stainless steel fittings. A drilled blanking plug provided a gas line feed-through into the coater. For pressure and leak testing, the capillary assembly was removed and sealed with a Swagelok<sup>TM</sup> blanking plug. The system was then gradually pressurised to 100 bar, to give a 40 % safety margin over maximum working pressure. If there is any audible leaking or any visible deformation then the gas bottle is immediately sealed, the system is vented and then inspected. Any damaged or deformed components cannot be used. Once the system was pressurised to 100 Bar, the gas bottle was sealed. The regulator gauge was then inspected for any pressure decrease. If no pressure loss was visible, the coater was evacuated to below  $5 \times 10^{-5}$  mbar and the system was left for 10 minutes. If no further pressure loss was visible, then the pressure and leak test was successful. The Swagelok blanking plug can be replaced with the capillary assembly and the system is ready to use.

### 2.2.2 LIQUID JET CAPTURE

An externally cooled stainless steel cold trap was cooled by immersion in liquid nitrogen before insertion into the vacuum system. All cold traps and glassware were cleaned before use, first with Teepol detergent, then rinsed with distilled water and finally rinsed with isopropanol. The stainless steel cold trap was a cylinder of diameter of 50 mm, with an aperture of 38 x

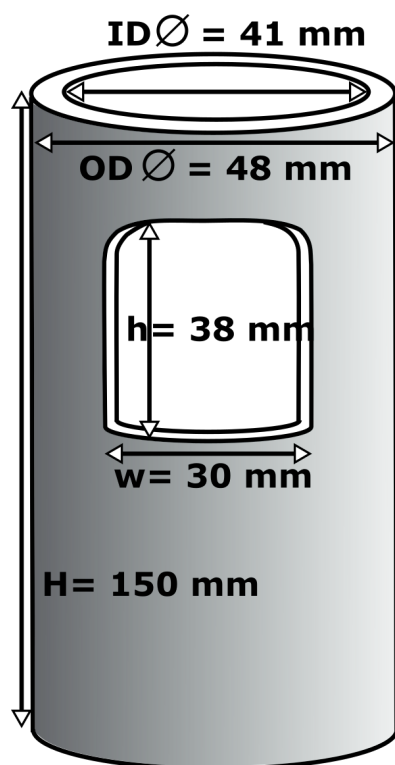


Figure 2.2.3: Schematic of the stainless steel cold trap with dimensions. Image is not to scale.

30 mm bored in one side to allow the liquid jet and atomic vapour to enter (Figure 2.2.3). Before cooling, the steel cold trap was typically placed in a small glass petri dish for sample collection, then both were wrapped in foil. The foil prevented any deposition on the outside of the cold trap from entering the sample dish. The foil wrapped trap was then immersed in liquid nitrogen until the boiling from the metal surface had ceased, at which point the cold trap was at the same temperature as the liquid nitrogen. The cold trap was then placed into the coater, and the coater was pumped down to vacuum.

### 2.2.3 FLOW RATE

The liquid jet flow rate was calibrated by measuring the mass of liquid exhausted over a fixed time. A metal vessel was sealed with a clear adhesive “cling-film.” The vessel was then weighed on a digital scale with minimum scale division of 0.1 milligram. This was then positioned so that the capillary nozzle pierced the film seal. The film seal minimised liquid evaporation during the experiment. The backing gas pressure was set at the bottle regulator before opening the gas line stop valve. Although the experiment was conducted in air rather than in vacuum, this only introduced a 1 Bar difference in exhaust pressure. The systematic error due to atmosphere was smaller than the measurement error in reading the regulator pressure gauge, which was  $\pm 2.5$  bar, half of the minimum scale division. After running the liquid jet for 5 minutes, the mass of the container was measured.

Measurements were taken at a range of pressures. Pressures were chosen based on the liquid properties and how jetting could be established. At low pressures, it was often difficult to establish jetting. At higher pressures, the jet could break up into a spray.

It was important not only to measure the flux of liquid, but to determine an appropriate predictive model for liquid jet flux. Some solvents would be unsafe to measure in this way (e.g. methanol and chloroform are both highly volatile and toxic.) The proposed model was the Hagen-Poiseuille law relating the pressure drop ( $\Delta P$ ) in a cylindrical tube (of length  $L$  and radius  $R$ ) to the flux of liquid (flux =  $\Phi$ ) through the tube. The Hagen-Poiseuille equation is

given by equation 2.1

$$\Phi = \frac{dV}{dt} = \frac{\pi R^4}{8\nu} \cdot \frac{\Delta P}{L} \quad (2.1)$$

Results are shown in figure 2.2.4. Empty points represent measurement data and straight lines are the predicted flux from the Hagen-Poiseuille equation. Values were calculated using liquid properties and experimental geometry. An excellent match can be observed for water and isopropanol. Ethanol shows the expected linear trend, however the gradient is less than expected. This could be due to evaporation over the course of experiment. Only small volumes were exhausted during the experiment, and if we assume that volume is proportional to area (as the liquid spread out entirely) then the evaporation would have been proportional to volume exhausted. This would have led to the observed decrease the gradient of the  $\frac{P}{V}$  graph. There are also other possible sources of error, including "spraying" of the jet contributing to evaporative losses, measurement error in the capillary length.

The flow through the liquid jet generally obeyed the Hagen-Poiseuille law. When necessary, volumes of solvents and flow rates have been calculated from these results, favouring experimental data over theoretical. The plot for methanol only shows theoretical results, as it would not be safe to exhaust a methanol jet into the lab atmosphere.

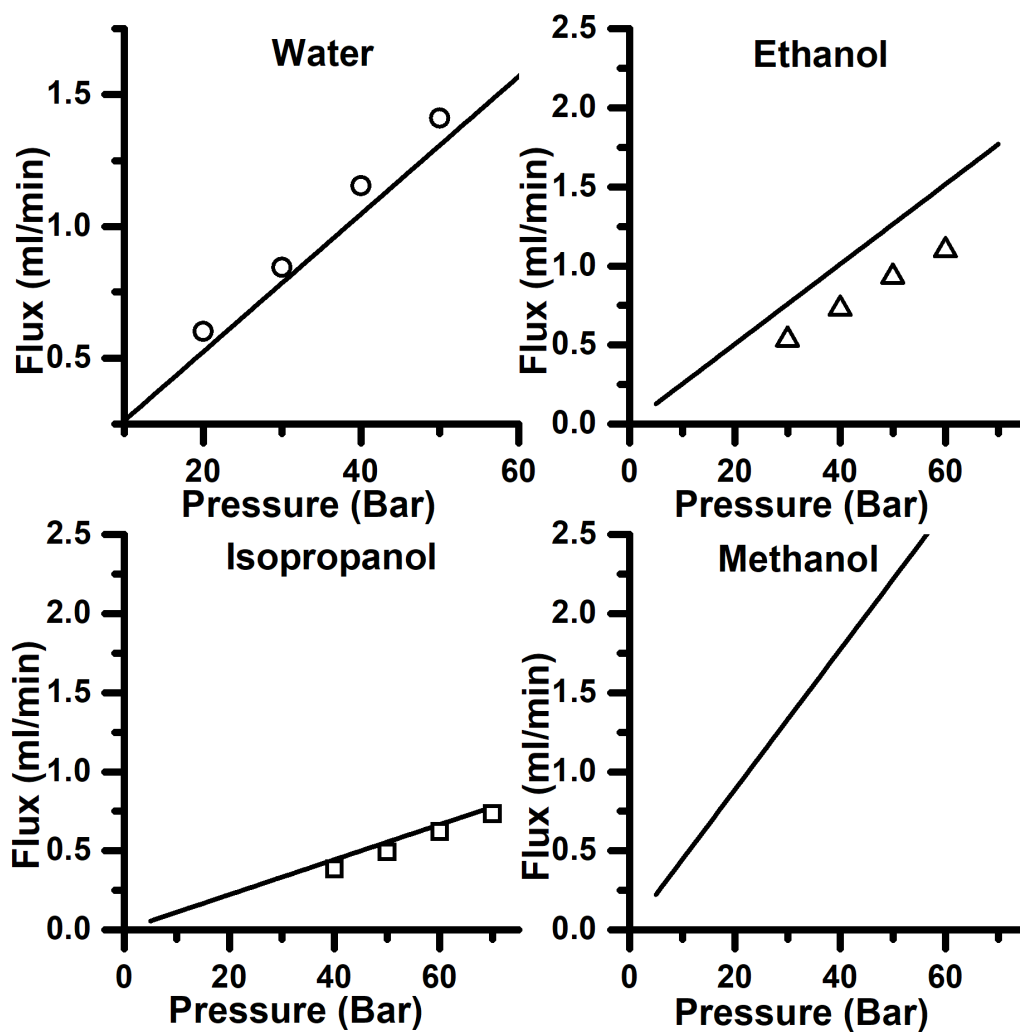


Figure 2.2.4: Mean measured flow rate, (shapes), and, (lines), flow rate calculated from Hagen-Poiseuille law 2.1. The standard deviation around the mean was smaller than the shapes on the graph, so error bars were not plotted. Methanol is illustrated as a theoretical line only, as it would not be safe to exhaust methanol into the lab.

## 2.3 VAPOUR DEPOSITION

Metal atomic vapour was generated by argon ion sputtering. In this process, argon atoms are ionised in a continuous discharge and then accelerated into a metal target. The argon ions impacting a metal surface with sufficient energy will eject metal atoms from the surface. Neutral metal atoms can escape the argon plasma and travel outwards. If the pressure is sufficiently low then the trajectories can be considered nearly ballistic (mean free path is roughly equal to chamber dimension.)

### 2.3.1 SPUTTERING PARAMETERS

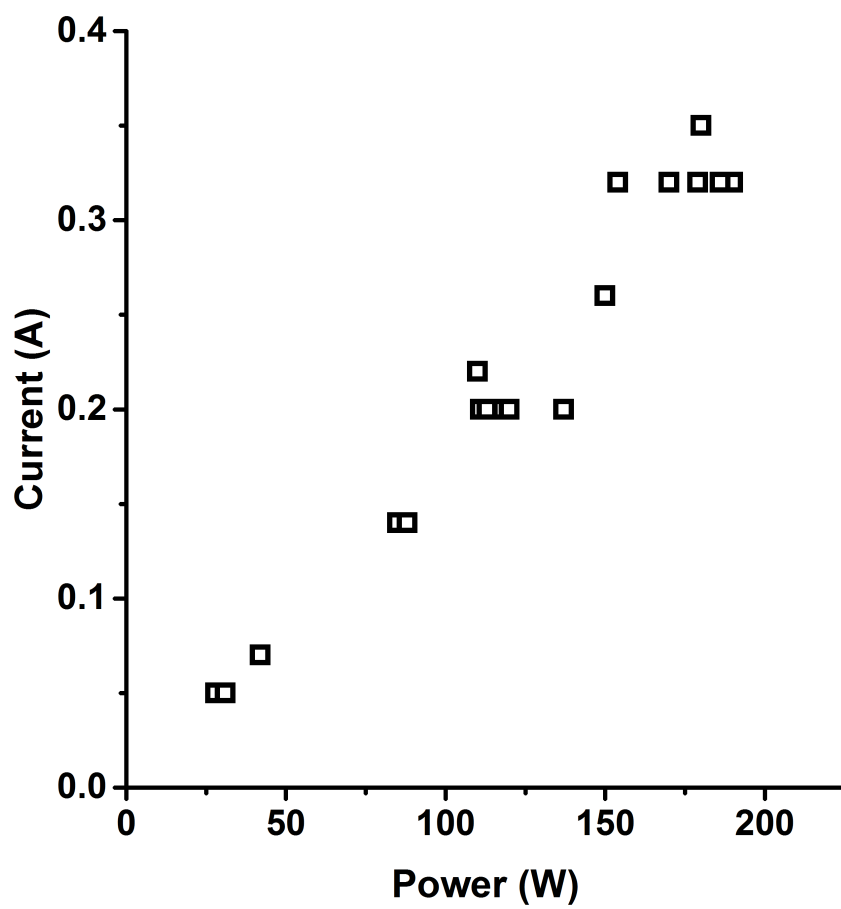
The sputtering process has several key parameters. These are the accelerating voltage, the sputtering current and the pressure of sputtering gases. These parameters are linked, and it is non-trivial to disentangle them. However; general relationships are known from the literature.

#### ACCELERATING VOLTAGE

The energy of the impacting ions is proportional to the accelerating voltage. The ions generated will be singly ionised. This means that for a given voltage, the kinetic energy of each particle will be equivalent to the accelerating voltage multiplied by the electronic charge. The energy of the impact then determines the magnitude of the following collision chain and the energy of ejected particles.

As the energy increases the probability of ejection of multiple atoms, or





**Figure 2.3.1:** Sputter power supply power and current output. The linear trend indicates that the accelerating voltage is approximately constant at 600 V, and hence that the ion energy is approximately constant at 600 eV.

even small clusters also increases. At energies of 600 eV (of the range measured in our experiment, Figure 2.3.1) it has been observed that for metals (specifically Cu and Ni) roughly 10% of the material emitted would be as dimers, and roughly 1% as trimers [45]. Wucher *et. al.* measured a smaller value of dimer and trimer yield for silver [46] at a 4.5 keV ion energy, although there is substantial uncertainties in making a direct comparison, as many larger clusters are emitted in the higher energy collisions. Maximum cluster yields in our experiment are estimated at 10 % Ag<sub>2</sub> and 1 % Ag<sub>3</sub>.

#### ION YIELD

Many metal particles ejected will be ionised in the ejection process. However, these particles will also be accelerated back towards the metal target along with the argon ions. Yields of ejected metal ions have been measured for silver foils sputtered by 10µs pulses of 15keV [47]. The measured fraction of singly charged silver ions to neutral atoms was  $10^{-4}$ . Given the much lower energies in our experiment (roughly 0.5 keV,) we would expect lower yields by several orders of magnitude. Nevertheless, this is of considerable consequence for further reactions when arriving in the jet. Metal ions may act as charge stabilisers, or to initiate chemical reactions with solvent molecules. However; we are unable to measure the ion yields in our experiments. We assume that the ion yield should be similar in experiments for a given sputtering voltage, current and total pressure. Any effect will be consistent across all samples.

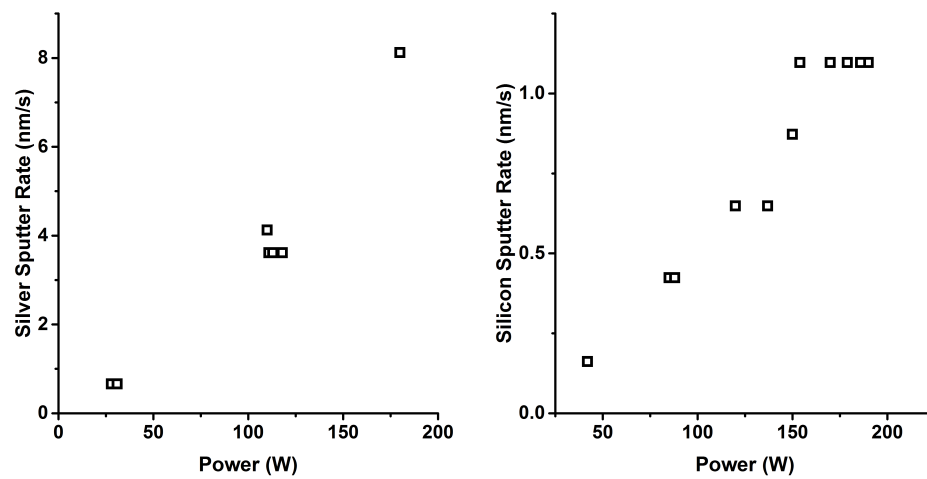
## SPUTTERING CURRENT

The sputtering current maintains the flow of positively charged ions into the metal target, and of free electrons into the magnetron cathode. Hence, it determines the total number of ion impacts and therefore the overall rate at which material is sputtered from the target. The magnetron power supply delivers an approximately constant voltage (Figure 2.3.1). The current is therefore proportional to the power applied. The sputter rates for silver and silicon measured with a crystal thickness monitor at a distance of 0.25 m from the sputter head are shown in Figure 2.3.2. Sputter rates are linear with applied power, as expected.

## GAS PRESSURE

The pressure of the sputtering gas determines the necessary discharge voltage to ignite a plasma. The pressure also has a non-linear effect on sputtering rate. The optimal pressure differs by material. Literature typically discusses sputter pressure in one of two contexts: optimising for sputter rate or deposited film quality, or cluster generation. At higher pressures, three body collisions allow metal atoms to grow into clusters, and their size is determined by the pressure of neutral gas and metal atoms.

The partial pressure of other gases is also very important in the sputtering process. The presence of other gases in the chamber can alter the chemistry of sputtered material, as well as redepositing material back onto the sputter target. Elemental or diatomic gases readily react with sputtered atoms. More



**Figure 2.3.2:** Measured sputter rates at 0.25 m of silver and silicon (nm/s) plotted against magnetron sputtering power (W)

complex molecules such as organics can be cracked in the plasma. Both the original molecules and breakdown products may then react with sputtered metal atoms. These reactions can take place in the gas phase, in the plasma, and on the surface of the sputter target. Reactions on the surface of the sputter target can rapidly build up a layer of non-conducting material which then slows the sputtering process. Obviously, the reactions can also produce compounds of the metal and any elements present in the gas.

When producing samples, we maintained all parameters constant as a default. For a limited set of experiments we varied the sputtering current to determine if there was a correlation with the rate at which material was deposited.

## 2.4 ANALYTICAL METHODS

### 2.4.1 SPECTROSCOPY

The optical properties of materials are determined by their physical and electronic structure. For this reason the interaction of light with matter provides a useful tool to probe the internal structure of materials.

The wavelength of light correspond to energies and hence to the physical processes characteristic of these energy ranges.

Spectroscopic characterisation of materials was carried out using UV-visible, fourier transform infra-red (FTIR) and X-ray photoelectron spectroscopy.

## 2.4.2 ULTRAVIOLET-VISIBLE SPECTROSCOPY

Ultraviolet-Visible (UV-VIS) spectroscopy covers the range 1 eV to 6 eV. This range covers the near infrared, visible light and UV. This energy scale covers the typical electronic densities of states, electronic band structures and plasmon resonances in materials.

The spectrum of light from a mercury-halogen lamp is split with a diffraction grating and a monochromated beam is selected. This is then split and passed to a sample and reference detector. The signal output is Absorbance  $A = \log_{10} \frac{I_{\text{sample}}}{I_{\text{reference}}}$ . The operation of the spectrometer is schematically illustrated in figure 2.4.1.

Spectra were recorded with a Thermo-Fisher Evolution<sup>TM</sup> 220 spectrometer. Spectra were recorded at steps of 1 nm, with a spectral bandwidth of 1 nm. Samples were analysed in Suprasil<sup>TM</sup> quartz cuvettes from Hellma.

Spectra were fit and quantified using the fityk [48] software package. To ensure consistency in measurement of peak heights and widths, the simplest possible fitting protocol was used. A flat baseline was subtracted from the data. A single Gaussian peak was then fit to the data in the relevant range. For the silver plasmon resonance this was consistently in the range 300 - 600 nm. Physically unrealistic fits (e.g. Gaussian mean with negative values) were rare, and were immediately discarded from data. Peak parameters were then extracted and used for analysis. Systematic errors with this technique were limited to slight under-estimates of the plasmon band width for very intense samples.

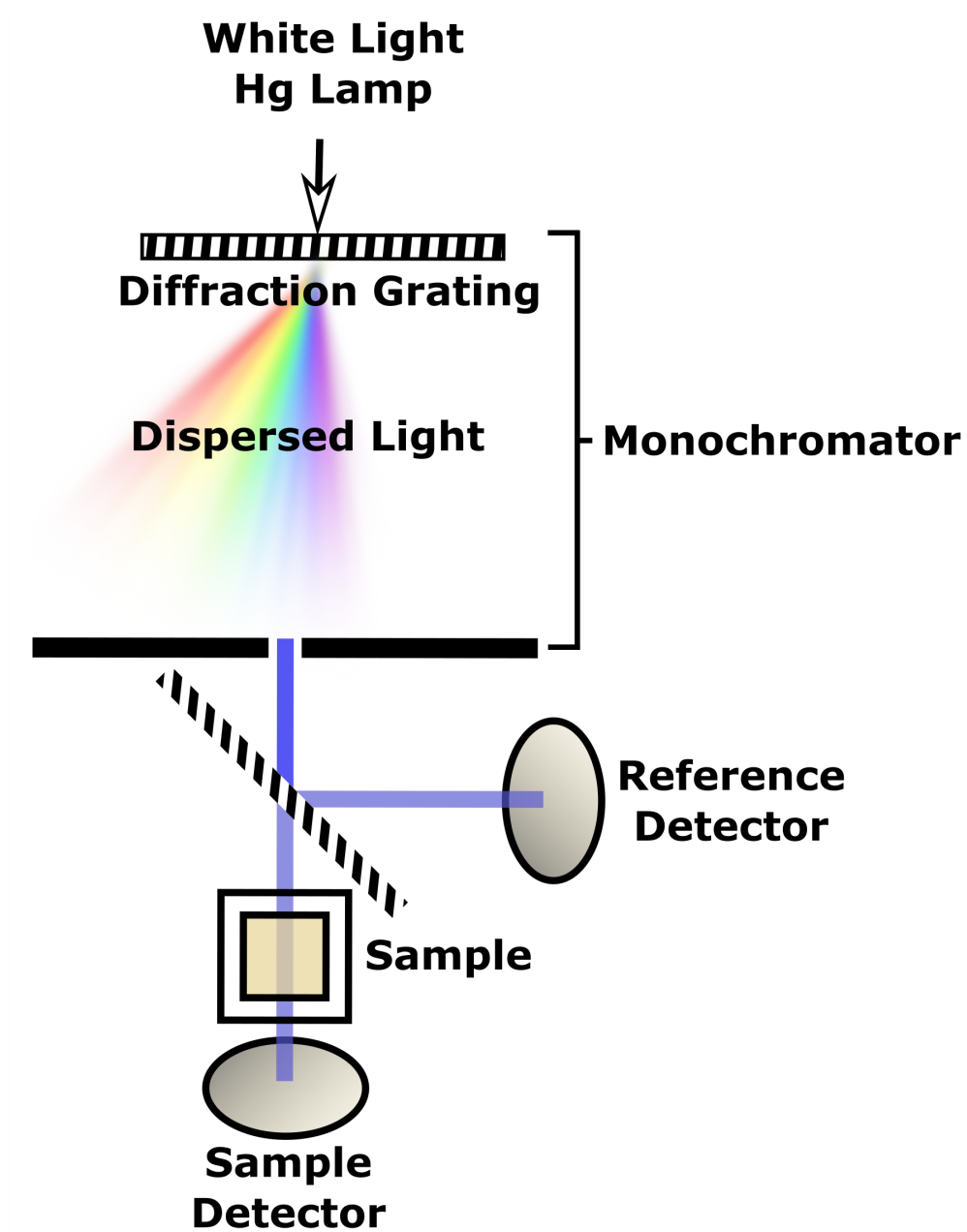


Figure 2.4.1: Schematic of the operation of a UV visible spectrometer.

Absorbance spectra of zinc oxide particles were analysed using the following relationships, valid for direct and indirect interband optical transmissions [49]:

$$\alpha h\nu = A(h\nu - E_g)^m \quad \text{for } h\nu > E_g$$

and

$$\alpha h\nu = 0 \quad \text{for } h\nu < E_g$$

where  $A$  is a constant depending on details of the band structure,  $h\nu$  is the photon energy,  $E_g$  is the energy gap, and  $\alpha$  is the measured optical absorbance. For an allowed indirect transition  $m = 2$  and for an allowed direct transmission  $m = 0.5$ . Plotting  $(\alpha h\nu)^{1/2}$  as a function of photon energy and extrapolating linear regions to the abscissa will yield the band gap  $E_g$  [49].

#### 2.4.3 INFRARED SPECTROSCOPY

FTIR covers the range from 50 meV to 0.5 eV. This energy range covers the vibrational energies of many molecular bonds. Molecular vibrations refer to the oscillations of atoms within molecules. Infrared energy in this range is absorbed by molecular bonds at characteristic frequencies. It is possible to determine which molecular bonds are present in a sample and their approximate proportions. Slight shifts in bond positions and intensities can indicate change in chemical or physical environment. For example, molecules could be physisorbed or chemically bonded on a surface. These attachments then damp the oscillations and shift the measured wavenumber.

In an FTIR spectrometer, the beam is not monochromated. To disperse infrared light would require an impractically large optical arrangement. FTIR



dispenses with this requirement by recording data as an interference pattern. An imaging detector records the interference pattern between the sample and the reference beam. The path length is changed while the images are processed in instrument software. After several passes a spectra is recorded.

FTIR spectra were recorded using a Thermo-Fisher Nicolet is5 FTIR spectrometer. Spectra were acquired in attenuated total reflectance mode using a Diamond ATR crystal.

#### 2.4.4 X-RAY PHOTOELECTRON SPECTROSCOPY

Photoelectron spectroscopy refers to the measurement of the energies of electrons ejected from a sample by photoelectric processes. Free motion of the electrons to the detector requires vacuum. Electrons are excited from the sample using ultraviolet or X-rays.

The X-ray source used in this work is a magnesium anode source. Electrons are accelerated into the magnesium anode by an acceleration voltage of 15-20 kV. These electrons have sufficient energy to eject the core level electrons (1s) from the atom. This vacancy is then filled by the transition of a higher shell electron to the 1s level. In this process a photon is emitted. By far the most probable transition in this system is 2p to 1s, which produces the K-alpha spectral line. The magnesium K-alpha line has a peak energy of 1253.4 eV [50].

The X-rays pass through a very thin aluminium shield between the source and the sample. This blocks most lower energy radiation. The X-rays also excite electrons from the metal shield, which provides a flood of electrons

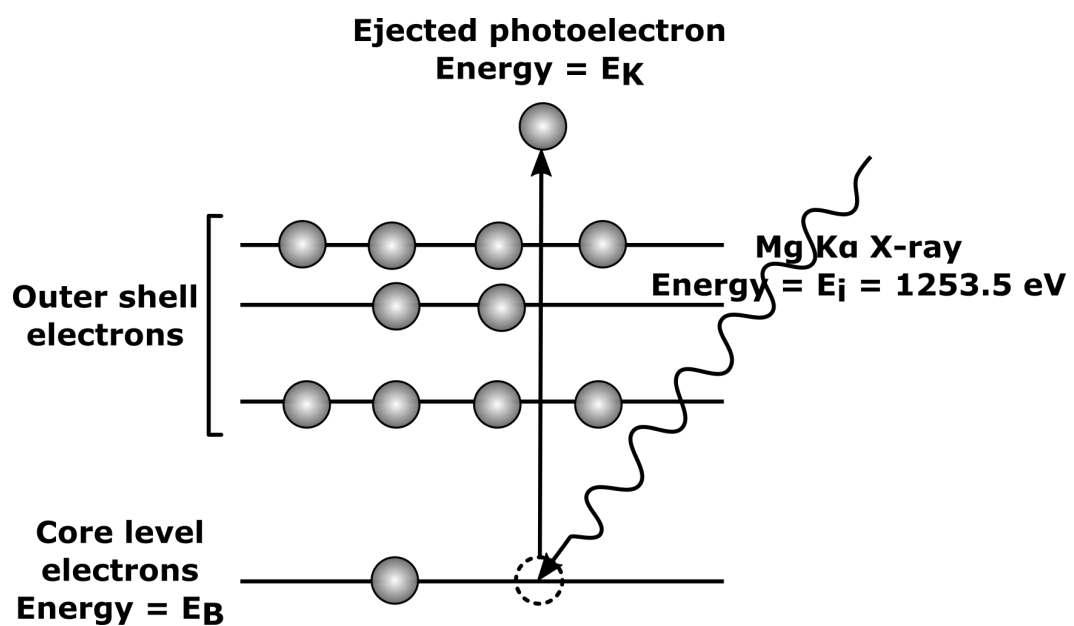


Figure 2.4.2: Schematic energy diagram of X-ray photoelectron spectroscopy. Incident photoelectrons with energy  $E_i = 1253.5$  eV [50] arrive at the sample and excite electrons from the sample. A core level electron is ejected with kinetic energy  $E_K = E_i - E_B$ . Here,  $E_B$  is defined as the energy required to promote an electron from a bound state in an atom to the vacuum level.

which help with charge neutralisation on the sample.

The X-ray beam easily penetrates the sample to a depth of microns. Electrons are excited from core levels of atoms in the material and are ejected. Electrons are much more likely than X-rays to undergo scattering, so have a much shorter path length. For the purposes of understanding the signal in an XPS measurement, the inelastic mean free path (IMFP) is a key parameter. This is typically between 1-20 crystal lattice planes in the energy range 10-2500 eV [51]. Calculated values are based on estimated complex dielectric constants from optical data and elastic-peak photoelectron spectroscopy [51]. Figure 2.4.3 shows a 'universal curve' illustrating the relationship between electron energy and path length in materials. For the relevant energies in this investigation, 100 to 1000 eV, electrons have a path length between 1 and 10 nanometres. The electrons escaping the sample and reaching the detector must be from this surface layer.

The kinetic energy distribution of electrons ejected from each level has a sharp peak, corresponding to the core binding energy. There is then a continuum of lower kinetic energy electrons which have lost energy through interactions [52]. Example interactions are with electronic states within the atom (initial and final state effects,) collective effects in the material (plasmon or phonon interaction,) and scattering from atomic lattices.

Electron energies are measured using a hemispherical electron analyser. Electrons are focused and slowed by an electrostatic lens. The electrons entering the analyser are slowed to a constant acceptance energy, usually of tens of eV, in order that they can be curved around an analyser of diame-

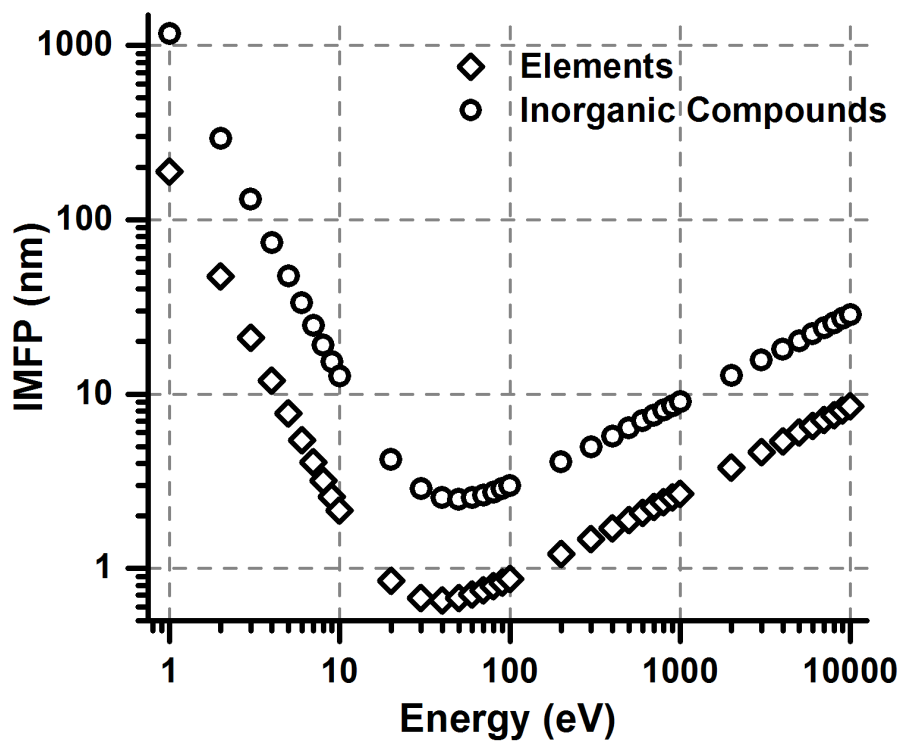


Figure 2.4.3: Inelastic mean free path of electrons in material against electron energy. The universal curves plotted here are  $IMFP = 538E^{-2} + 0.41(\frac{E}{2})^{\frac{1}{2}}$  for elements and  $IMFP = 2170E^{-2} + 0.72(\frac{E}{2})^{\frac{1}{2}}$ , based on Seah and Dench [53] using a monolayer thickness of  $\lambda = 0.5 \text{ nm}$

ter roughly 0.5 m. The analyser consists of two parallel hemispheres with a potential difference between them. The electrons follow a curved path and land on a strip of 7 silicon CCDs able to count single electrons. For a given potential difference, there will be a focus energy. Electrons having this energy will land on the central CCD, whilst those slightly above and below will land on the neighbours. By scanning through the pass energies, a complete spectrum is recorded.

Substrates for XPS were mounted on a molybdenum sample tray for loading into vacuum. The typical substrate used was HOPG, 9x3x3 mm wafer, high purity 0.8 degree spread (Pi-Kem). The HOPG was pressed into a piece of tape, and a layer of graphite was cleaved from the top when the tape was peeled away. The now cleaved wafer was then fitted into the sample holder and placed into vacuum as soon as the sample was prepared on the wafer.

The energies measured by the analyser are the kinetic energies ( $E_K$ ) of ejected electrons. These can be related to the binding energies of electrons in the atoms ( $E_B$ ) by  $E_B = E_i(E_K + \phi)$ , where  $E_i$  is the initial photon energy (1253.4 eV [50]) and  $\phi$  is the detector work function, calibrated as 4.51 eV. The peak binding energies measured correspond to the core energy levels of atoms, which are unique to each element. XPS is therefore diagnostic of the elemental composition of the surface. However, features observable due to various energy loss mechanisms can also provide information about the chemical and structural environment.

The most substantial shifts observable in XPS spectra are charging shifts. Charging of a non-conductive surface can induce shifts up to hundreds of

eV in measured binding energies. Charging can be observed by a change in measured binding energies as the sample spends more time under X-ray excitation.

Similarly, for small particles, there is an energy associated with particle charging [54]. This can be estimated from the energy of charging a spherical capacitor, and is plotted in figure 2.4.4. However, in practice, the energy shift measured in nanoparticles is smaller than this, and cannot be reliably used to deduce nanoparticle size [54].

The chemical environment of an atom can also have a strong effect on measured binding energies [54]. As electrons are ejected from an atom, they can interact with electrons in outer shells - those which are involved in chemical bonding. As the electron density around the atom is drawn outwards in chemical bonds the effective screening of the nucleus is reduced and so core level electrons are more tightly bound. Typically, the strength of the bond determines the chemical shift.

XPS spectra were fitted using fityk [48]. Gaussian peak shapes were used to avoid over-fitting errors with excessive parameters. XPS peaks are typically fit using a convolution of a gaussian and lorentzian peaks known as a voigt peak. The gaussian represents the instrumental broadening, whilst the lorentzian represents the lifetime broadening of the peak. In this work only gaussian fits were used. The low signal measured from very thin and dispersed nanoparticle films was such that the instrument could not be tuned to give a peak narrow enough to show a significant lifetime component to their width. Shirley background was subtracted from spectra in R statistics

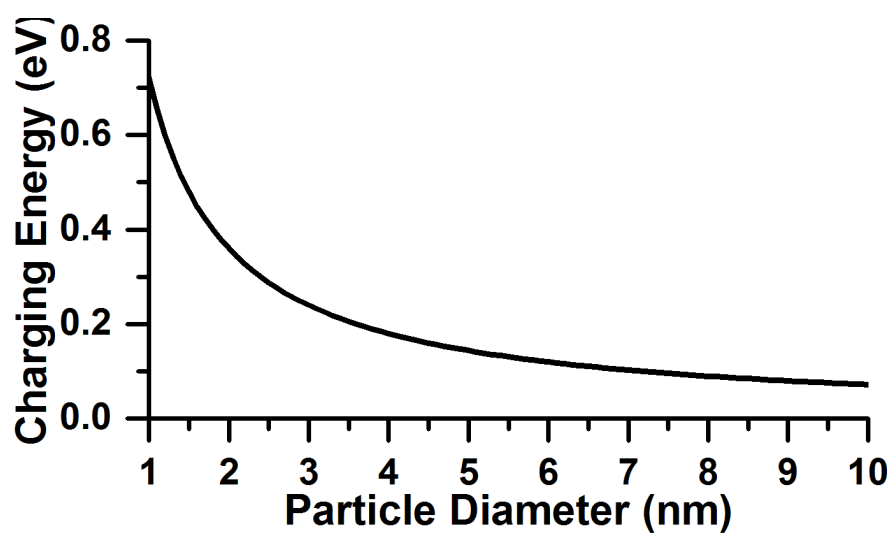


Figure 2.4.4: Energy in (eV) to single charge a conducting sphere, against the sphere diameter (nm).

software using code in Appendix B.

XPS core level shifts in silicon 2p lines were fit using a method based on that of Yang et. al. [50]. Peak energies listed in Appendix A (6.1) were used to infer a shift of  $1 \pm 0.05$  eV per increase in oxidation state. A custom script in fityk was used to link 5 peaks together to represent Si<sup>0</sup>, Si<sup>1</sup>, Si<sup>2</sup>, Si<sup>3</sup>, Si<sup>4</sup>, with energies separated by 1 eV, and linked widths.

## 2.5 MICROSCOPY

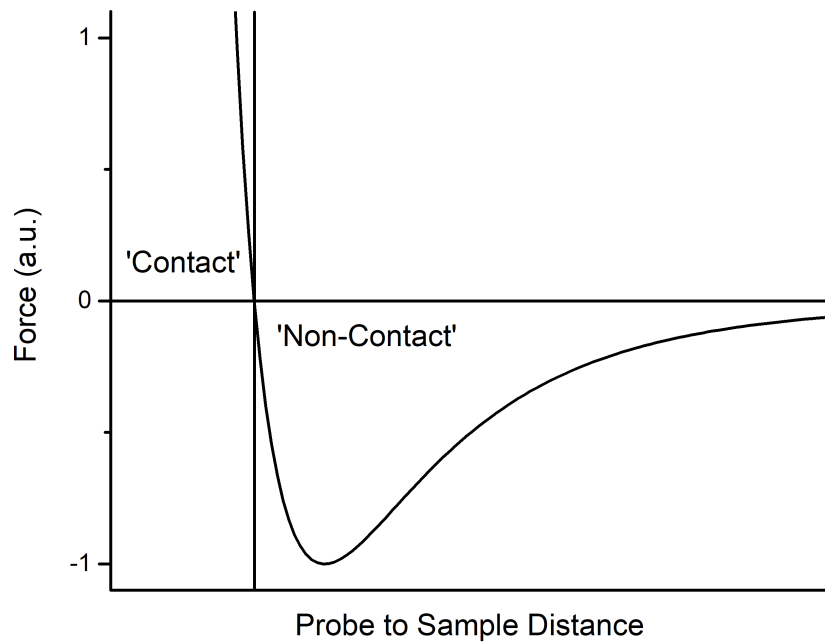
### 2.5.1 TRANSMISSION ELECTRON MICROSCOPY

Images were acquired in a JEOL 2100 microscope operated at 200kV, under a range of magnifications. Samples were prepared for TEM analysis by drop casting 2  $\mu$ l of the nanoparticle solution onto a carbon film substrate (Agar scientific, S160).

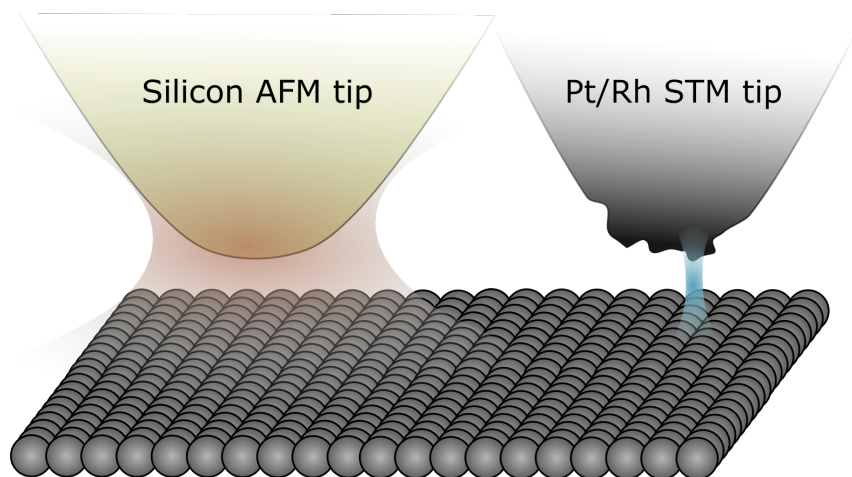
### 2.5.2 SCANNING PROBE MICROSCOPY

All image series were recorded at ambient temperature, without heating. Images were recorded using a variable temperature AFM from Omicron Nanotechnology. This was operated in non-contact, constant force mode, all measurements were taken at room temperature. A 20 nm radius SiN tip was used (Mikromasch) with a resonance frequency of 307 kHz and a nominal stiffness of 40 Nm<sup>-1</sup>. The vertical axis was calibrated on single and double step edges of the graphite, of 3.5 Å and 7 Å height respectively.





**Figure 2.5.1:** Lennard-Jones potential between two molecules or surfaces. This force arises from the interactions between induced or permanent dipoles.



**Figure 2.5.2:** Scanning probe techniques can acquire images from nanometer to atomic resolution. Atomic roughness of the tips is corrected for by the scanning mechanisms. In an AFM experiment, (**left**), the measured forces act between the entire tip and an area of the surface. The force can be modelled as a Lennard-Jones potential, (**figure ??**), where the interaction region (tip-surface distance) is of the same order as the tip radius of curvature. The force measured by the probe therefore comes from a large region of the surface. STM measures the tunnelling current between the tip and a conducting sample. This drops off exponentially with distance, meaning that the tunnelling current is between a single atom at the tip of the probe.

### 2.5.3 IMAGE ANALYSIS

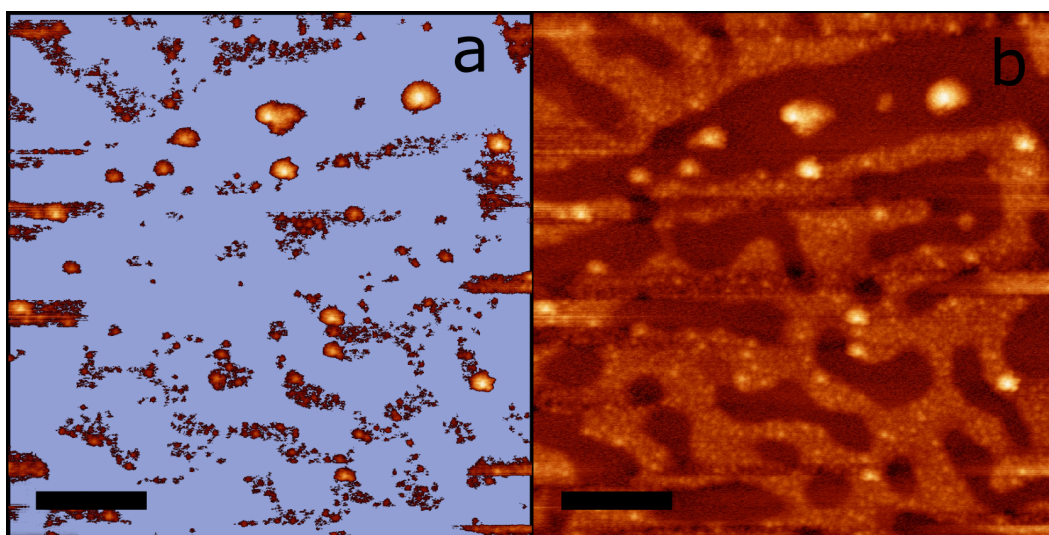
AFm images were analysed using software packages WSXM [55] and Gwyddion [56]. TEM images were analysed using Gatan Digitalmicrograph software and ImageJ [57].

To measure size distributions from force microscopy measurements, images had a threshold applied to find islands. An example image is shown in figure 2.5.3. Software then retrieved the highest point in every island. By processing multiple images, a size distribution was built up.

Measured size distributions were fitted to a log normal distribution function (LNDF, equation 2.2) with mean  $\bar{x}$  and multiplicative standard deviation  $\sigma$ . Errors quoted were the average differences between the 68 % confidence intervals and the median, given by equation 2.3. Log normal distributions were fit using fityk.

$$LNDF(\bar{x}, \sigma, A) = \frac{A}{\sqrt{2\pi \ln \sigma}} e^{\frac{(\ln x - \ln \bar{x})^2}{2 \ln^2 \sigma}} \quad (2.2)$$

$$\delta LNDF(\bar{x}, \sigma) = \frac{\bar{x}}{2} \left[ \sigma - \frac{1}{\sigma} \right] \quad (2.3)$$



**Figure 2.5.3:** Flood filling of AFM images. **(left)**, flood filled image, light blue represents the threshold (in this case, roughly 5 Å). **(right)**, original image of silver nanoparticles deposited on HOPG. The scale bars are 50 nm.

*"If speaking is silver, then listening is gold."*

Turkish Proverb

# 3

## Metal Atoms and Nanoparticles

METAL ATOMS AND SOLVENTS are easily mixed using many techniques. By depositing atoms directly onto a liquid jet, the reaction is greatly simplified compared to other methods. There are minimal impurities, there are no reagent by-products and the atoms are well dispersed. The atoms will be highly mobile within the solution. This system has been used to explore metal-solvent reactions and nanoparticle growth. In this chapter benchmarks will be established for some basic metal-solvent systems. Some general principles for understanding reactions in a broader sense will also be established.

The predominant metal studied in this chapter is silver. Silver is a noble metal, and its low reactivity ensures that it is likely to form metallic particles in most solvents. Sputtering of silver is well documented for film growth [58-60] and cluster formation [46]. It is a malleable metal, which greatly sim-

plified cleaning of equipment and hence experimental turnaround time. Silver nanoparticles have a distinctive absorption peak in the visible spectrum, which is easily measured and also allows visual inspection of samples when produced. This absorption is due to the plasmon resonance of silver, which can be related to particle size [61-66], shape [64, 67, 68] and chemical environment [62, 67, 69-72]. A broad literature covers silver nanoparticle synthesis [8, 66, 73-77] for application as antimicrobials [74, 75, 78, 79], catalysts [66, 80, 81], and in sensors [82-85]. Finally, silver nanoparticles have been synthesised by physical methods: LASIS [19, 35, 86-88], SMAD [89], sputtering onto ionic liquids [79, 90] and dense organic oils [79]. Silver represents a model system for this investigation.

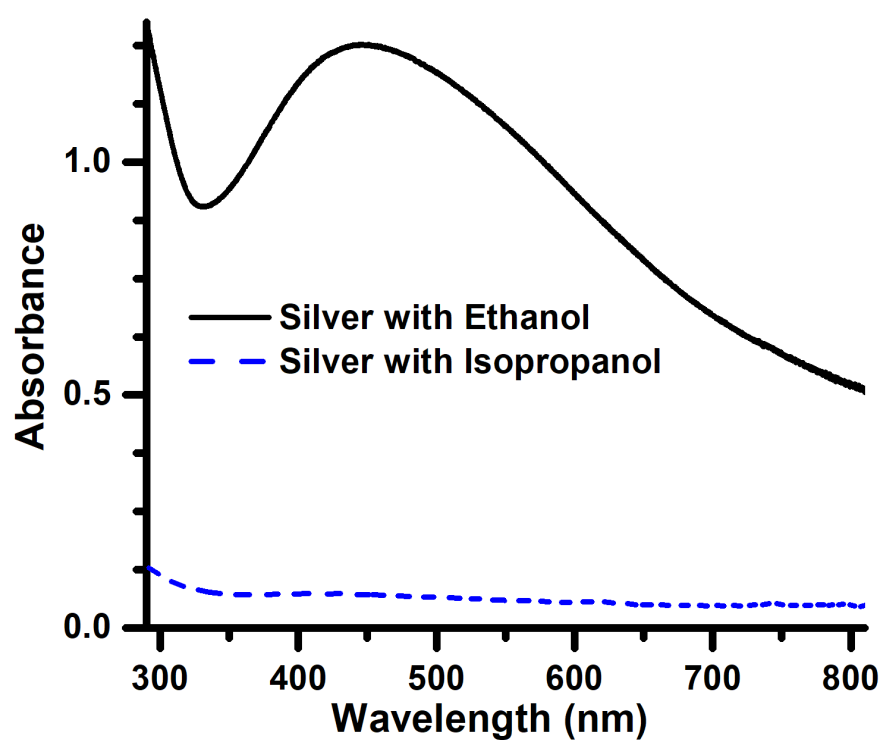
### 3.1 INITIAL BENCHMARKING OF SILVER

The first samples of silver were produced allowing deposition of silver onto the cold trap exterior, interior and along the liquid jet. Liquid jets of ethanol and isopropanol were used. These alcohols were chosen for their low cost and for the ease of generating and sustaining the liquid jet. The liquid jet was captured inside the cold trap, and substantial solvent vapour also condensed on the exterior of the cold trap. When the sample was melted and collected, material from all cold trap surfaces was collected. The total mass deposition rate calculated for all silver impinging on or in the cold trap was  $1.7 \pm 0.9 \mu\text{g}/\text{min}$ . Taking into account liquid jet flow rates calculated from equation 2.1, the concentration of silver was estimated as  $2.6 \pm 1.1 \text{ mg}/\text{ml}$  in ethanol, and  $4.6 \pm 1.9 \text{ mg}/\text{ml}$  in isopropanol. These samples represent the highest con-

centration of silver produced using the liquid jet method.

Both samples had visible, macroscopic precipitates. Flakes and powder agglomerates were visible. The ethanol sample was a dark red, almost black. The isopropanol sample was transparent with a slight yellow tinge. UV spectra of the liquid phases were recorded within 5 minutes of sample production and are shown in figure 3.1.1 below. There is a dramatic difference in the measured absorbance between the isopropanol and ethanol sample. Repeat sample productions showed that silver rapidly formed large agglomerates in isopropanol and precipitated out of solution. Samples in ethanol showed much less agglomeration and a larger absorption peak was consistently recorded. With a good ability to stabilise silver particles, ethanol was chosen as a primary solvent for production of silver nanoparticles.

The plasmon resonance of silver in ethanol has a broad peak at 432 nm. This is consistent with silver nanoparticles with sizes of the order of 100 nm [66]. The peak asymmetry at higher wavelength indicates that there may be contributions to the plasmon resonance from the quadropole resonance of larger particles [66]. The baseline shows the presence of opaque material, such as silver particles with diameters greater than 300 nm. Particles with dimensions approaching the wavelength of the absorbed light are not expected to show plasmon resonance [68]. This confirmed that the metal atoms deposited into solvent could aggregate into nanoparticles. This also confirmed that with the correct conditions particles could be stabilised in solution.



**Figure 3.1.1:** UV-visible spectra recorded within 5 minutes of production. Spectra show silver sputtered into ethanol (**squares**), and isopropanol (**circles**). Samples were produced at the highest possible concentrations. Significant material precipitated from the isopropanol sample prior to measurement.

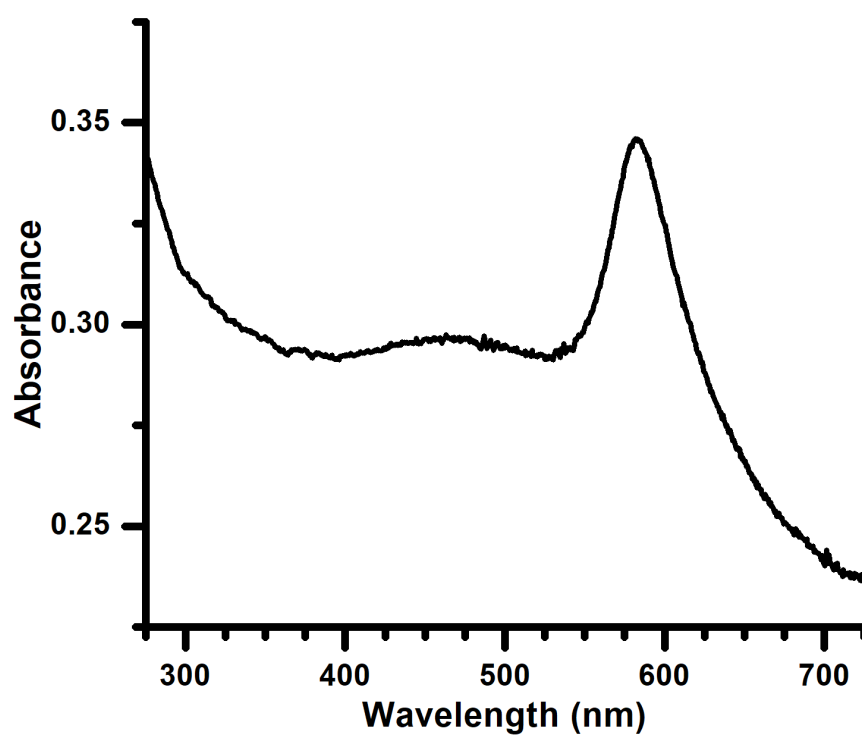
## 3.2 FURTHER BENCHMARKING: COPPER, ZINC AND SILICON

Samples were also produced in limited numbers for a small range of other metals and solvents. This allowed simple comparison of the behaviours of different materials. Silicon has been subject to previous investigations using related techniques [91-96]. Deposition of silicon into liquid or frozen water produces small [95, 96] silicon containing nanoparticles which exhibit blue fluorescence under UV light [94]. Investigation of silicon in this thesis is limited to a small run of nanoparticle solutions. These were produced and characterised for further investigation under AFM and STM. Two additional metals, copper and zinc, were also tested in a small run of samples. Copper is a noble metal with applications in catalysis [97] and solar cells [98]. Zinc is a moderately reactive metal which readily forms an oxide layer. Zinc oxide has been extensively studied and is well characterised [99]. This survey covers two noble metals, a transition metal and a semi-metal.

### 3.2.1 COPPER

Deposition of copper into water resulted in large ice crystals tinted with a pinkish deposit. This melted into a pink liquid. A UV-Visible absorption spectrum was recorded within 30 minutes of sample production. Figure 3.2.1 shows a plasmon resonance absorption peak characteristic of metallic copper nanoparticles at 590 nm. The flat absorption at lower wavelength is due to inter-band transitions [97]. The colouration present in the ice indicates that nanoparticles formed before the sample melted. This sample was produced





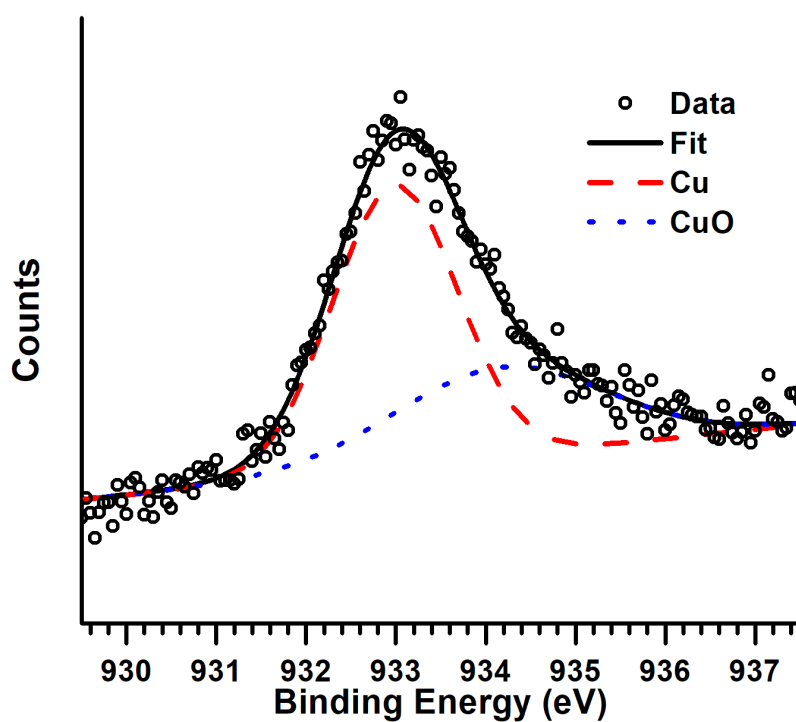
**Figure 3.2.1:** UV-visible spectrum of copper sputtered into water, recorded within 30 minutes of production.

using a separate, custom apparatus, which limited the copper generation to a cluster source. For the same reason, it was not possible to measure the deposition rate. Clusters were probably produced before capture in the jet. The resulting solution began precipitating a black soot almost immediately. This material then strongly adhered to any surfaces, including the sample vials. As this included the cuvettes used for optical spectroscopy, no further spectra were recorded over time.

Figure 3.2.2 shows photoelectron spectra of copper nanoparticles. Films were drop-cast from solution onto freshly cleaved HOPG within 2 days of sample production. Photoelectrons were excited with Mg K $\alpha$  photons with energy of 1253.4 eV. The spectrum is fitted with the reference values for the Cu(2p<sub>3/2</sub>) peak in bulk copper and in copper oxide [98]. The instrument linewidth was calculated as roughly 0.6 eV from the operating manual.

### 3.2.2 ZINC

Zinc was sputtered from a high purity target (Lesker, EJTZNXX453A4, 99.995 %) inside the Auto 306 coater chamber. Zinc was co-deposited with a jet of ethanol, chosen as a test solvent for ease of sample production. Timed UV spectra are shown in Figure 3.2.3. A pronounced shoulder at the absorption onset is observable in all 3 samples, red shifting from 310 nm to 330 nm after 3 days aging, and eventually to 340 nm after 6 months. The typical, bulk, value of the zinc oxide band gap is 3.4 eV [99, 100], corresponding to optical absorption around 360 nm [99]. The measured absorption spectra are consistent with zinc being present in the form of zinc (II) oxide, ZnO. The



**Figure 3.2.2:** Cu(2p<sub>3/2</sub>) x-ray photoelectron peak of copper sputtered into water, recorded within 2 days of production. Incident photons are Mg K $\alpha$ , E = 1253.4 eV. Fit lines are the Cu(2p<sub>3/2</sub>) (red line) and O-Cu(2p<sub>3/2</sub>) (blue line).

blue-shift of the absorption spectra may be due to the known quantum size effect in ZnO nanoparticles [100, 101]. After sample production, and a repeat experiment, no further zinc samples were produced. Once a zinc sample had been produced, the coater dome was coated in a tough layer of zinc which resisted washing and required intense mechanical abrasion to remove. The difficulty of cleaning the glass dome and coater internal equipment led to the decision to cease production of zinc samples.

Tauc plots [49] of the zinc absorption spectra show that the optical band gap of the zinc/ethanol sample decreases with time. At  $t = 0$  hrs, the band gap is  $3.60 \pm 0.05$  eV. By comparison with the measured band gaps in size controlled ZnO by Lin *et. al.* [100], particles as produced are smaller than 3.5 nm. The reduction of this band gap with time is a strong indication that the particles grow over time. By  $t = 70$  hs, the bandgap has reduced to  $3.45 \pm 0.05$  eV, which would correspond to a particle size between 5-8 nm. Two weeks post production, fluorescence emission and excitation spectra were recorded. In figure 3.2.5, the fluorescence intensities are plotted against wavelength and energy.

The fluorescence emission peaks at 3.6 eV, which matches the initially measured optical band-gap from the Tauc plots. However, the emission from ZnO nanoparticles typically has an energy 0.1-0.2 eV lower than measured from the absorption onset edge [99, 100]. Similarly the excitation peak onset is 4 eV, higher than expected [100]. The simplest explanation for this is that the bulk of optical absorption is due to larger particles, larger than 5 nm. Meanwhile, fluorescence is from smaller particles, with sizes below 3.5 nm. Zinc oxide

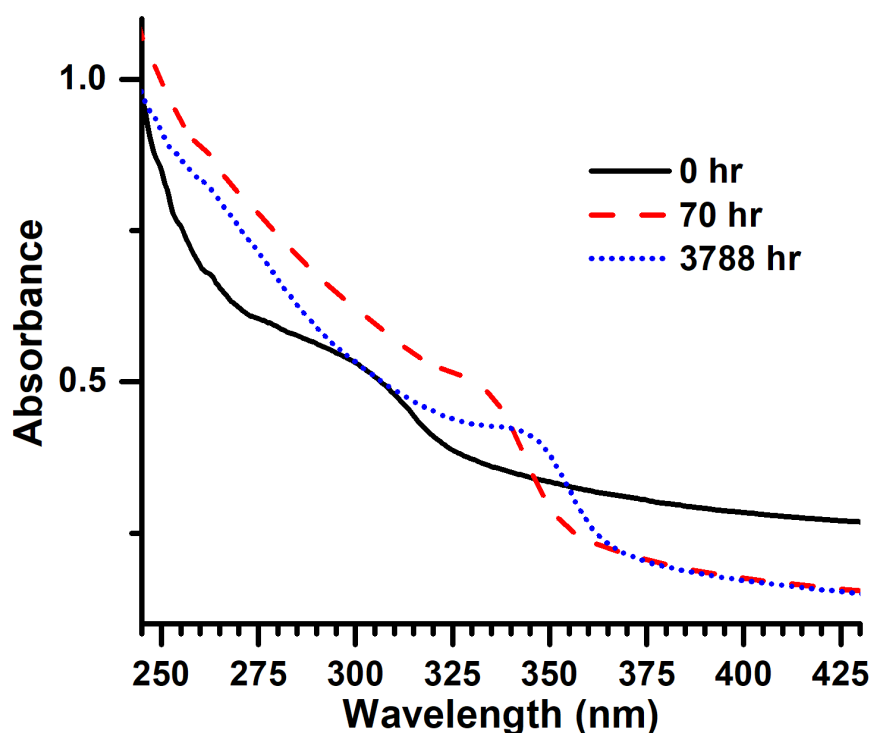


Figure 3.2.3: UV-Visible absorption spectra of zinc sputtered into ethanol. The sample has been aged over months and spectra recorded at intervals.

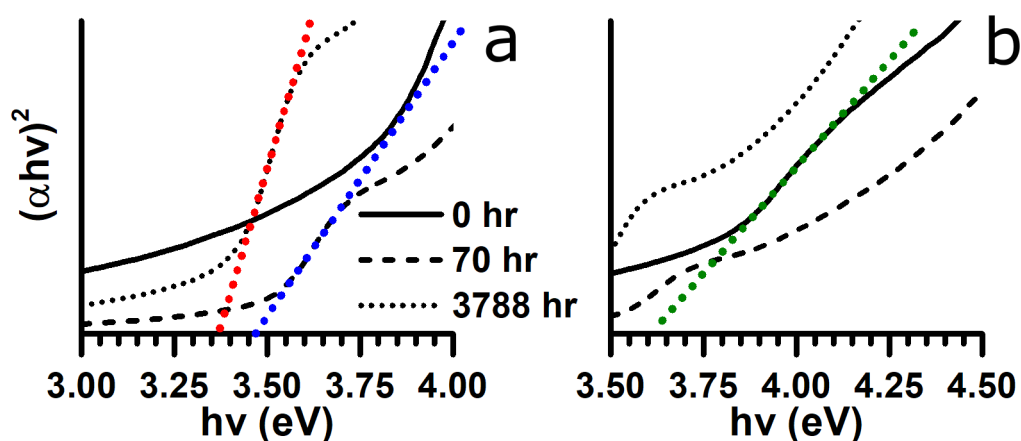


Figure 3.2.4: Tauc plot [49] for direct band-gap of spectra shown in figure 3.2.3. Fits to linear regions are shown as dotted lines. Both plots show the same data but scaled to different regions to facilitate fitting. (right) Linear fit (green) to 0 hour spectrum intercepting at  $3.60 \pm 0.05$  eV, (left) Linear fit (blue) to 70 hour spectrum intercepting at  $3.45 \pm 0.05$  eV and (red), 3788 hours at  $3.35 \pm 0.05$  eV.

nanoparticles are formed with a broad size distribution which changes over time, with the smallest particles showing deep blue fluorescence.

### 3.2.3 SILICON

The inspiration for the liquid jet concept was born out of the work of Brewer et. al. [94], who co-deposited sputtered silicon with water vapour. This produced a cluster solution showing deep blue fluorescence. The first liquid jet experiments were developed to further test the mixing of silicon atoms and water. Silicon-liquid interactions have been extensively investigated by Yazdandar [91]. For this work, a limited number of samples were produced, sputtering silicon into a water jet. Characterisation provided an example of semi-metal interactions in the liquid jet as a counterpoint to the metals. Furthermore, this thesis also covers the dynamics of silicon nanoparticles deposited on HOPG surfaces, produced by the same methods.

Silicon was sputtered from a p-doped silicon target (Lesker, EJTPSIX503A2, 99.999% pure) and deposited into the cold trap with a jet of liquid water (AnalaR NormaPur, max 1 ppm dry residue).

### UV -VISIBLE ABSORPTION OF SILICA NANOPARTICLE SOLUTIONS

Comparison of the UV-vis spectra of the silica nanoparticle solutions produced by both production methods shows comparable results. Neither show strong absorption until an edge at 250 nm. The sample produced by co-deposition shows a slightly stronger onset at 300 nm. However, this spectrum is not an ideal comparison, as the co-deposition sample was produced four years

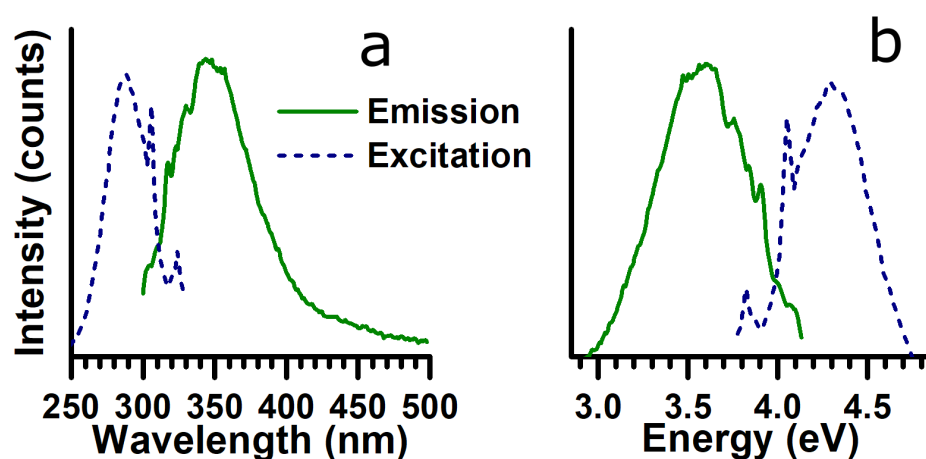


Figure 3.2.5: Fluorescence emission and excitation spectra of zinc co-deposited in ethanol, recorded one week after sample production. Count rates are plotted against wavelength, (left) and energy, (right). Sharp peaks in the excitation spectrum correspond to the Raman shifts of ethanol.

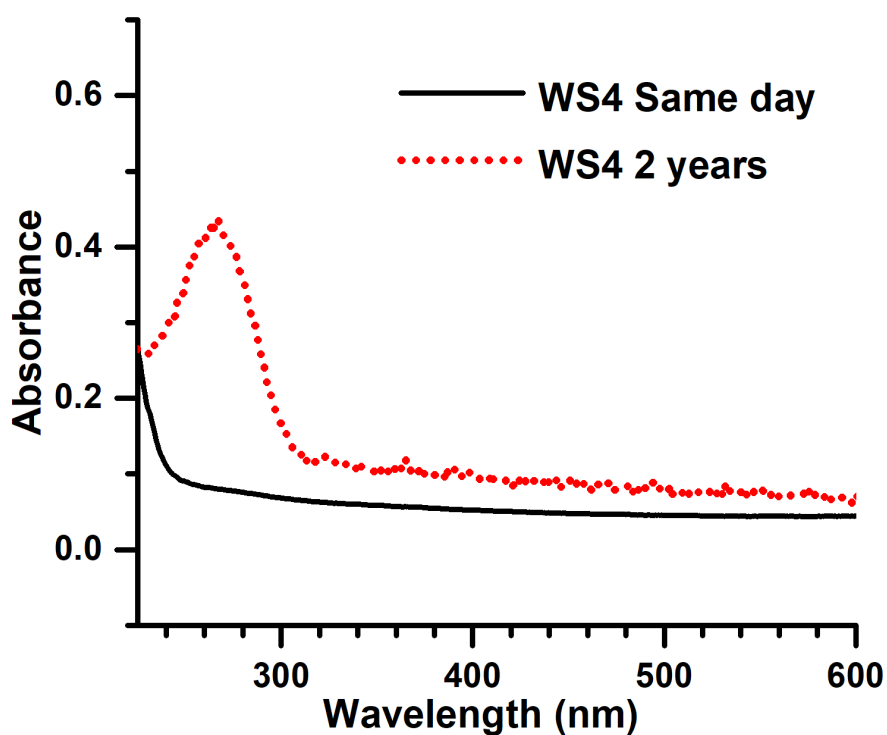


Figure 3.2.6: Comparison of UV-vis spectra of silicon sputtered into a water jet, as produced and after two years aged. The spectra corresponds to sample WS4 in Figure 3.2.8

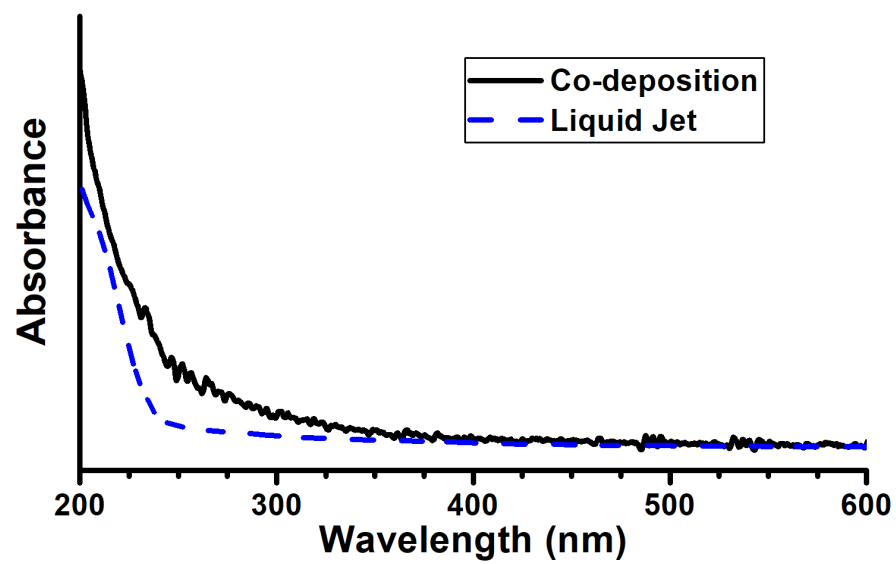


Figure 3.2.7: UV-visible spectra of silicon mixed with water by two different methods: (black squares), produced by Brewer et. al. [94] co-depositing silicon and water vapour, (blue circles), produced by deposition of silicon with a liquid jet.



earlier than the liquid jet sample. A comparison between the jet sample as made, and two years on is shown in figure 3.2.6, where it is clear that an intense peak at 265 nm has evolved. This feature is present all four separate samples produced by the same method. Figure 3.2.8 shows water-silicon samples (WS) 1 to 4 measured after two years. The same peak has developed in all samples, with differing intensities. The 'shoulder' at this position in sample WS2 suggests that the onset edge at 300 nm in figure 3.2.6 is the same absorption band.

#### INFRA-RED ABSORPTION OF SILICA NANOPARTICLE SOLUTIONS

The Infra-Red absorption spectra of these same samples, after aging, is shown in figure 3.2.9. Peaks common to both samples are associated with OH bonds,  $3100\text{--}2600\text{ cm}^{-1}$  [102], the band from  $1050\text{--}1150\text{ cm}^{-1}$  is the O-Si-O anti-symmetrical stretch [103], from  $1150\text{--}1300\text{ cm}^{-1}$  is O-Si-O symmetrical stretch [103] and the band from  $800\text{--}900\text{ cm}^{-1}$  with Si-H and Si-OH bonds [103, 104]. The bands at  $1350\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$  are tentatively ascribed to oxygen rich states in silica. These peaks have been identified by Tremblay et. al. in the spectrum of  $\text{SiO}_3$  produced by matrix isolation FTIR studies of  $\text{SiO}_2$  and Si reactions with  $\text{O}_2$  molecules [105]. These peaks are not present in water dried on the spectrometer crystal. The most likely alternative for these peaks is that they represent some form of hydrocarbon contamination, as these bands are common for various  $\text{Si}-\text{C}_x\text{H}_y-(\text{OH})_z$  species [104]. However, these peaks do not appear in the spectrum of silicon sputtered into alcohols [91].

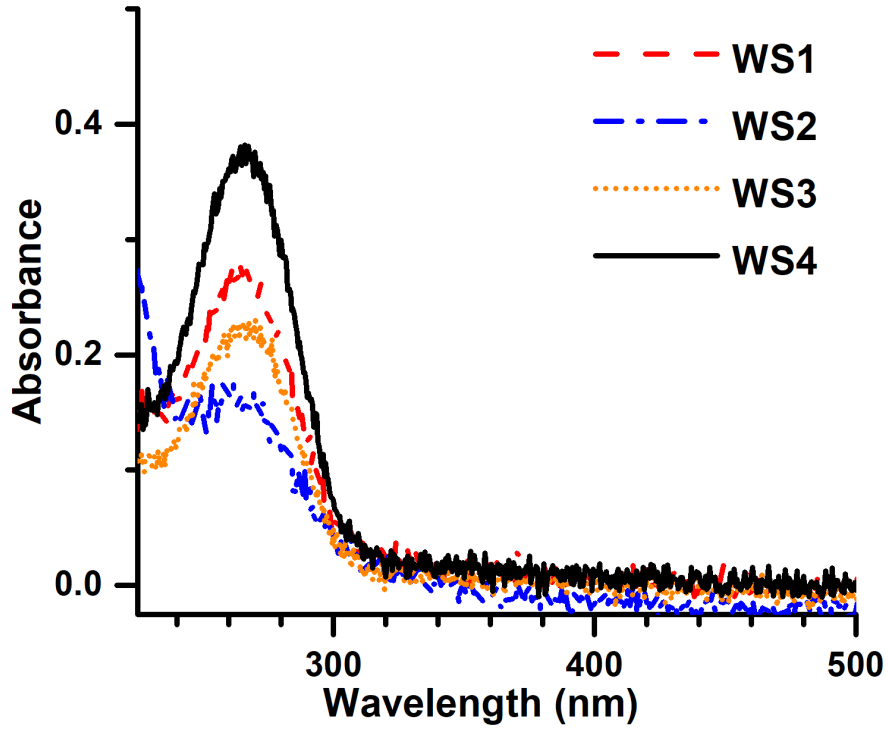


Figure 3.2.8: All aged spectra from a series of silica nanoparticle solutions, WS1-4. All four samples were produced by deposition of silicon into a liquid jet of water. All samples were produced with identical conditions other apart from silicon sputter rate.

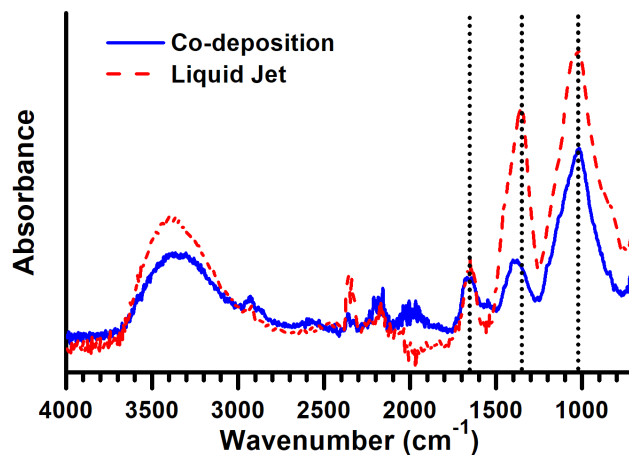


Figure 3.2.9: Infra-Red of silicon mixed with water by two different methods: (black squares), produced by Brewer et. al. [94] co-depositing silicon and water vapour, (blue circles), produced by deposition of silicon with a liquid jet. The dotted black lines show the major peaks common to both samples, at  $1000\text{ cm}^{-1}$ ,  $1350\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$ . The broad peak at  $3100 - 3600\text{ cm}^{-1}$  is known to be from hydroxyl (OH) groups [102], whilst the peak at  $1000\text{ cm}^{-1}$  is from silicon dioxide [104].

## XPS

The oxidation state of the silicon can be further established by photoelectron spectroscopy. Shifts in core levels indicate the different coordination of silicon atoms [50, 106]. Silicon peak energies and widths are linked in the fitting process. Both fits are consistent with  $\text{SiO}_x$  particles, with a further shift of approximately +1.5 eV from literature values [50, 106, 107]. The good agreement in positions of  $\text{Si}^n$  peaks between the samples indicates that this fitting method is robust, and that the binding energy shifts are consistent between particles. The presence of elemental silicon can be ruled out, that is, there is no evidence for Si fully bonded with other Si atoms. The liquid jet sample shows higher  $\text{Si}^3$  and  $\text{Si}^4$  peaks. Highly oxidised silicon nanoparticles, for example,  $\text{SiO}_x$  where  $x > 2$ , would be consistent with these results and the peak at  $1650\text{ cm}^{-1}$ , which is also higher for the liquid jet sample in figure 3.2.9.

## AFM

AFM measurements were taken of one hundred times dilution of a silicon in water sample. Using flood filling to find islands over a threshold height, size distributions were built up from the peak height of these islands. Figure 3.2.13 shows that the silica particles have a size distribution peaking at a height of  $0.9 \pm 0.1\text{ nm}$ . We take this measurement to be a good approximation of the nanoparticle diameters.

The co-deposition of silicon with a liquid jet of water has produced small silica nanoparticles, of size  $0.9 \pm 0.1\text{ nm}$ . These particles have a probable

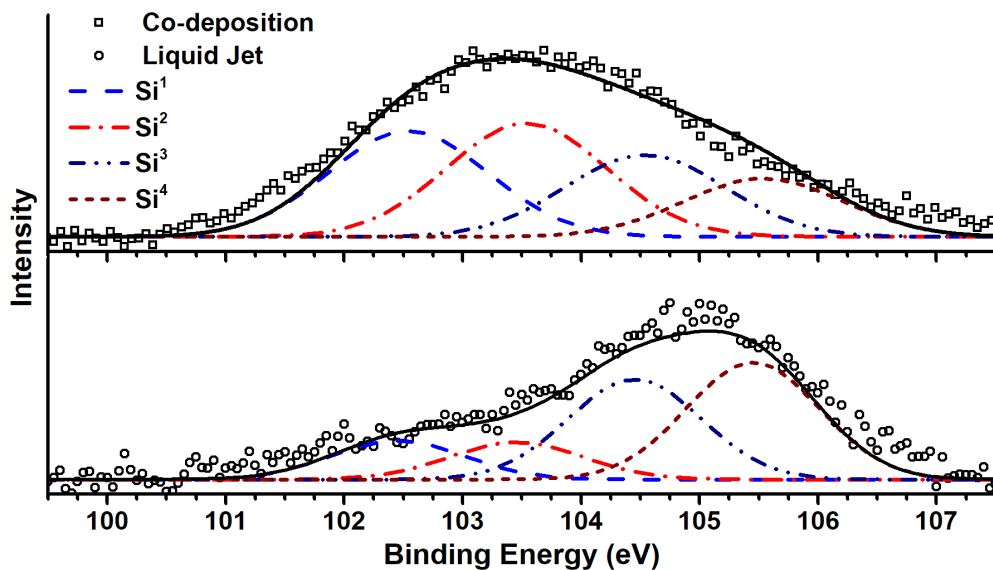


Figure 3.2.10: Comparison of XPS spectra and Gaussian fits to components of different silicon oxidation states. (**black squares**), produced by Brewer *et. al.* [94] co-depositing silicon and water vapour, (**black circles**), produced by deposition of silicon with a liquid jet. The solid black lines are the summed fit. Silicon oxidation states are fit using the protocol described in the methodology chapter. The liquid jet sample shows a higher proportion of higher oxidation states of silicon.

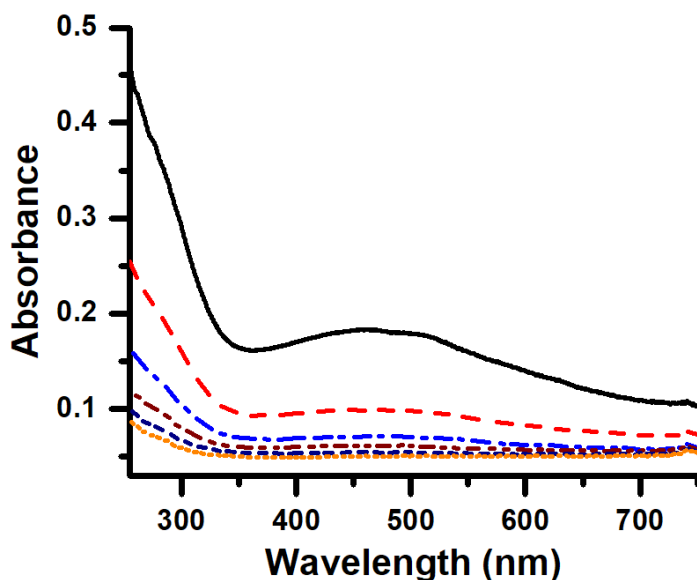


Figure 3.2.11: Dilution series measurements of silver co-deposited with an ethanol liquid jet. Sample was diluted with the same pure ethanol as used in production. The absence of major changes in peak shape and the linear decay in absorbance shows that particle-particle interactions are minimal in the sample.

stoichiometry of  $\text{SiO}_x$ , where  $x > 2$ . Co-deposition with a liquid jet likely leads to higher oxidation of clusters than co-deposition with water vapour.

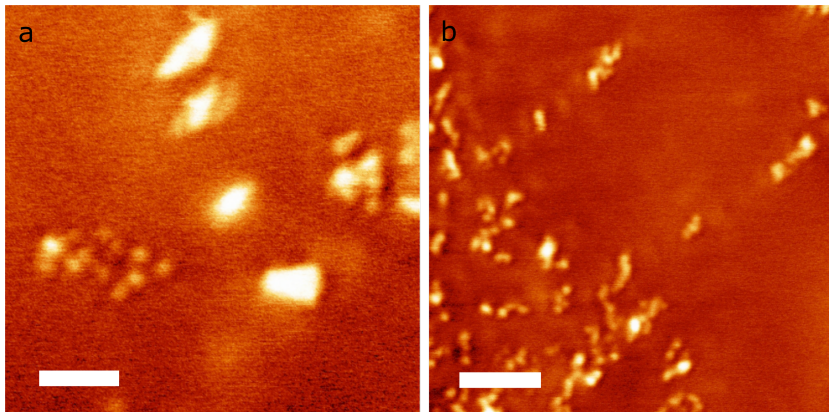
### 3.3 CHARACTERISATION OF SILVER NANOPARTICLES

The bulk of the effort of this thesis was directed towards the investigation of silver as a model system to characterise the liquid jet in more general terms. The plasmon resonance of silver was the initial focus of this investigation. Dilution series measurements of the plasmon resonance as exemplified in Figure 3.2.11 showed that the peak position and shape was consistent with dilution. This effectively ruled out particle - particle interactions, such as red shifting of the plasmon resonance for small separations (typically less than 10 nm for Au nanoparticles [68, 108]).

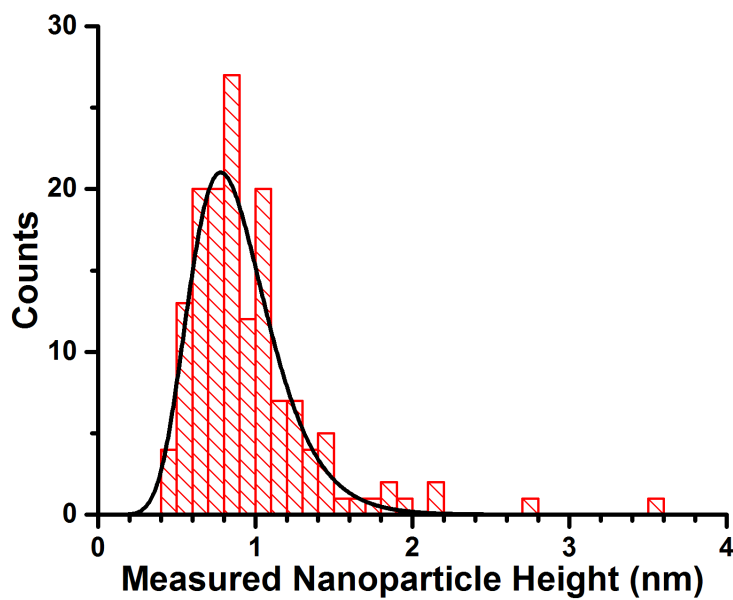
Detail of the 'shoulder' region is shown in Figure 3.3.1. Three distinct peaks are noticeable here. The absorption 'shoulder' at wavelengths less than 350 nm scales with the concentration. This scaling indicates that this is a feature of the sample rather than a systematic artefact in the spectra. To elucidate the nature of this 'shoulder', spectra of silver co-deposited with other solvents were examined.

#### 3.3.1 SILVER IN WATER

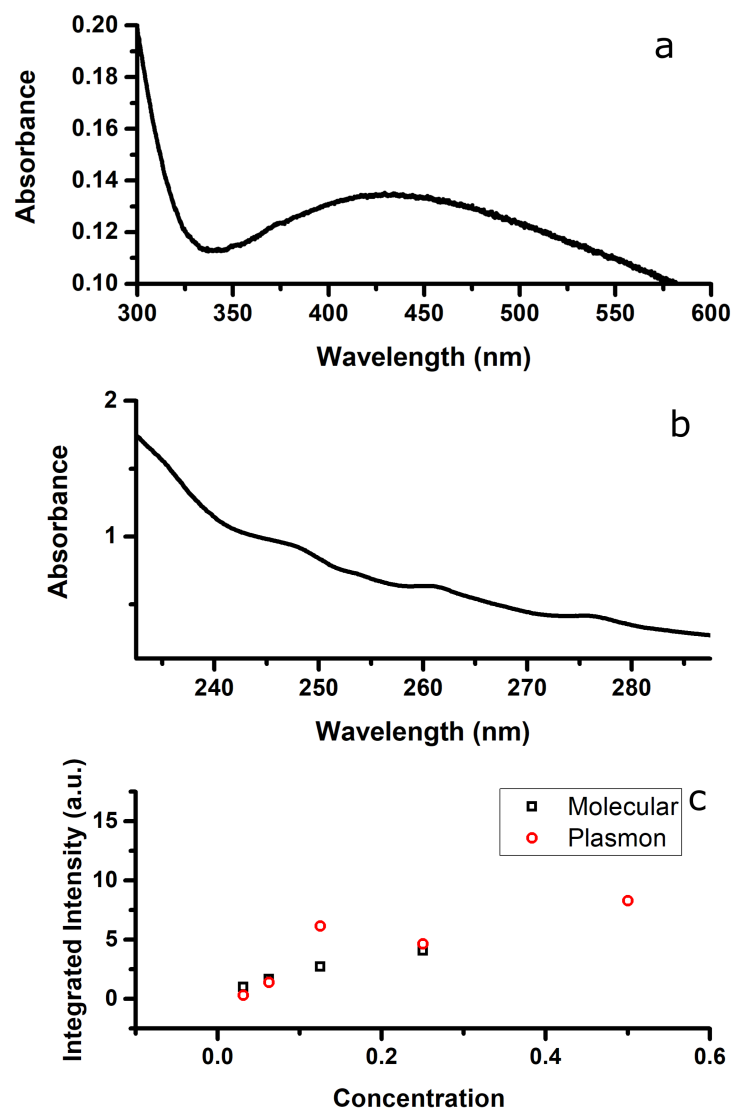
Silver co-deposited with a water jet did not show a plasmon resonance. However, rather than an absorption shoulder at low wavelengths, figure 3.3.2 shows three intense peaks at 235 nm, 275 nm and 306 nm. These peaks can be tentatively identified with the UV-visible absorption peaks for the



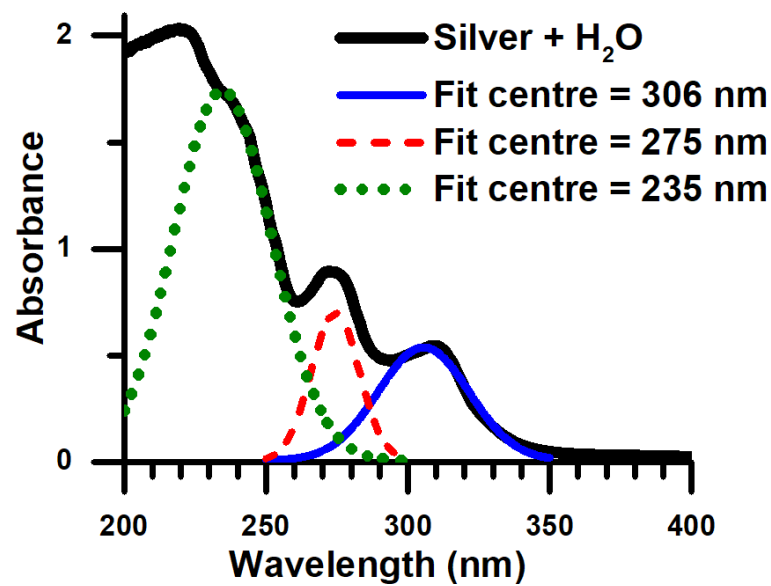
**Figure 3.2.12:** Non-contact atomic force microscopy. **(a)** detail of small nanoparticle clusters. Scale bar is 50 nm. **(b)** broad area scan. Scale bar is 100 nm.



**Figure 3.2.13:** Size distribution of silica nanoparticles from heights measured in AFM imagery. Data was generated by flood filling AFM images to threshold height, then recording the maximum height of each island.



**Figure 3.3.1:** Illustration of the distinct peaks in the UV 'shoulder' of the silver nanoparticle in ethanol solution. (a), Plasmon resonance peak. (b), Shoulder region. Three peaks are fit by 245 nm (5.0 eV), 261 nm (4.74 eV) and 276 nm (4.48 eV). (c), Integrated absorption peaks of plasmon and shoulder region recorded from dilution series silver in ethanol sample. Both the plasmon and the shoulder region scale with concentration.



**Figure 3.3.2:** UV-Vis spectrum of silver samples produced by co-deposition of silver with a liquid jet of deionised water.



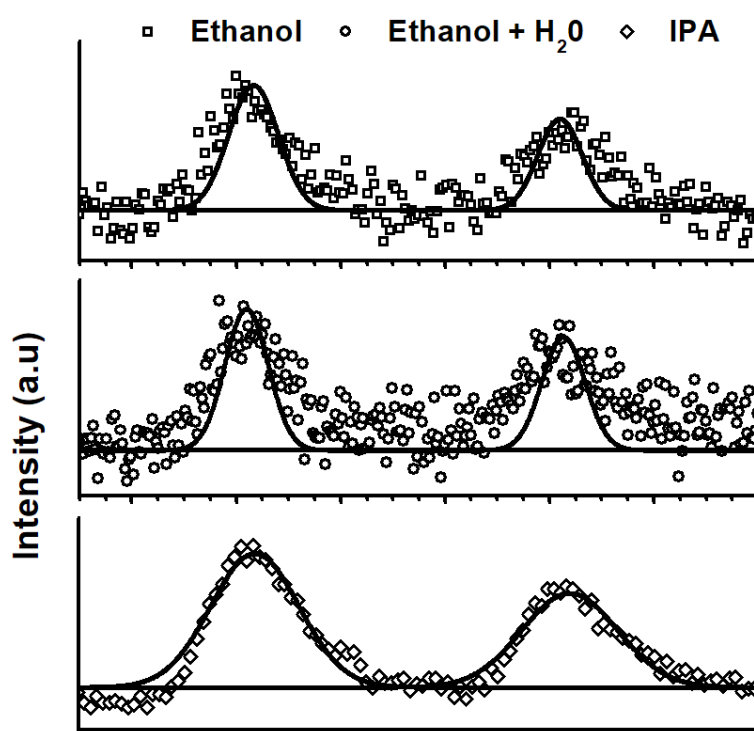
small silver clusters  $\text{Ag}_1$ ,  $\text{Ag}_2$ ,  $\text{Ag}_3$ ,  $\text{Ag}_4$  and  $\text{Ag}_5$  [109, 110], which have been identified in matrix isolation studies of silver clusters in neon, in the ice of co-deposited of silver vapour and water vapour [111], in aqueous ionic solutions of silver [23, 112], in cryophotoclustering of Ag/Ar matrices [110] and by polyacrylamide gel electrophoretic separation of phases in nanoparticle solutions produced by reduction of silver thiolates [113]. The assignment must remain tentative as energies will be shifted in liquid water relative to those spectra measured in the cited experiments. Moreover, absorption lines due to neutral clusters can overlap those due to ionised clusters [24, 109, 110, 112]. It is likely that these clusters exist as ions, as this would stabilise them. This spectrum is stable over a timeframe of months.

### 3.3.2 XPS

Photoelectron spectra of silver containing samples are shown in figure 3.3.3. Obviously the signal from silver in water is negligible and is at the limit of detection. However, this is consistent with silver present in small ( $n = 1-5$ ) clusters, which would be very thinly and widely dispersed. Spectra of silver in alcohol containing samples show peaks corresponding to metallic silver. The sample of silver in isopropanol had an intensity three times greater than in ethanol and over thirty times that of silver in water.

### 3.3.3 SIZE OF SILVER PARTICLES

The sizes of silver nanoparticles were measured by both AFM and TEM. Data for particles produced in different solvents are summarised in figure 3.3.5.



**Figure 3.3.3:** 3d peaks in XPS spectra of silver samples drop cast on HOPG. Spectra were recorded from samples produced with isopropanol, ethanol, water and an ethanol-water mix. The noticeable variation in noise between samples is due to strong variation in signal between samples. Solid lines are Gaussian fits to data. Due to the very low signal, the fit to silver in water was only possible for  $\text{Ag}3d_{5/2}$ , the more intense of the 3d states. Alcohol containing samples match canonical values for  $\text{Ag}3d_{5/2} = 368 \text{ eV}$  and  $\text{Ag}3d_{3/2} = 374 \text{ eV}$  [63].

These size distributions exclude particles with diameter on the order of ten standard deviations larger than the median. Very large particles will disturb the tip during the imaging process. Despite this, the large areas scanned in AFM measurements (typically around  $1 \times 1 \mu\text{m}$ ) mean that measured size distributions are representative of the whole sample.

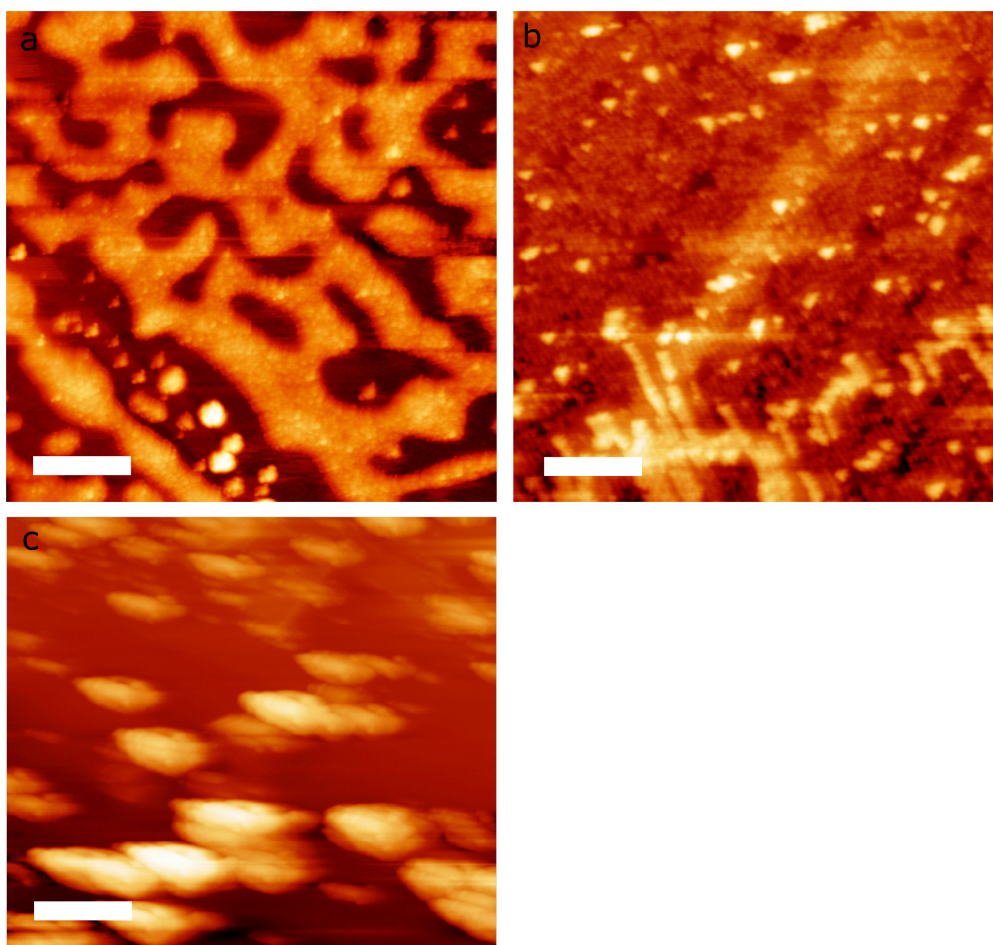
Comparing samples produced in ethanol with isopropanol, there is a four-fold increase in median particle size. This provides evidence of the solvent dependency on particle sizes. From figure 1.1.1, lowering the surface energy of a particle will lower the critical nucleation radius, ultimately lowering the median size of particles produced<sup>1</sup>. Solvents can be ranked isopropanol « ethanol < ethanol + water + citrate < water in terms of the inverse particle size, and hence lowering of the silver-solvent interface energy.

In the silver-in-water sample, there is a bimodal size distribution. The distribution with the smaller peak size could represent the  $\text{Ag}_n$  clusters, whilst the larger sizes are a phase of larger nanoparticles. Importantly, such a phase can be present in the silver/ethanol samples, but simply be impractical to analyse due to the prevalence of larger particles.

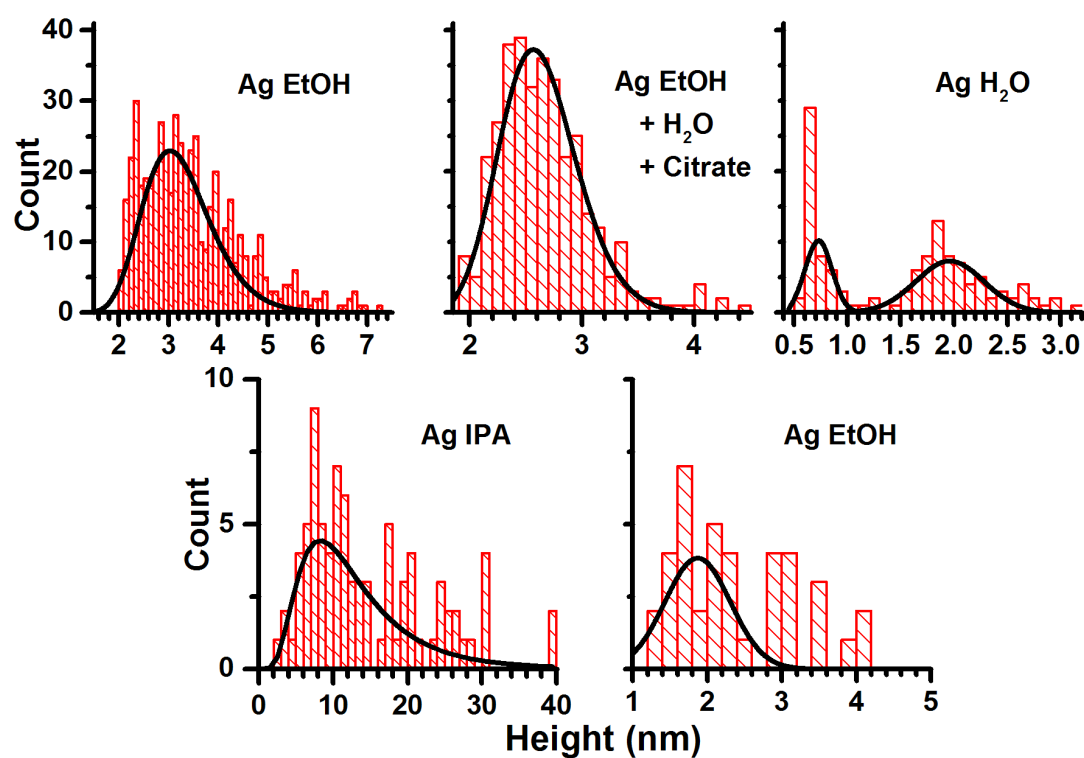
Transmission electron microscope images were recorded of silver samples drop cast onto ultra-thin carbon grids. Size distributions were calculated from semi-automatic thresholding of TEM images. Sizes as measured by TEM are in good agreement with those measured in AFM, as evidenced by the top left frame in both figures 3.3.5 & 3.3.7. All TEM images are samples produced

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<sup>1</sup>intuitively, lowering the critical energy and radius will lead to a larger number of particle nuclei, and hence spread the total material between a larger number of particles, which will grow to a smaller size.



**Figure 3.3.4:** Non-contact AFM images of: **(a)**, silver nanoparticles produced in ethanol. Scale bar is 400 nm. **(b)**, produced in water. Scale bar is 400 nm. **(c)**, produced in isopropanol. Scale bar is 200 nm.



**Figure 3.3.5:** Size distributions of silver particles generated by semi-automatic analysis of AFM imagery. Distributions are fit with a log-normal function (equation. 2.2). Count rates are included for indication of signal to noise ratio of fit results.

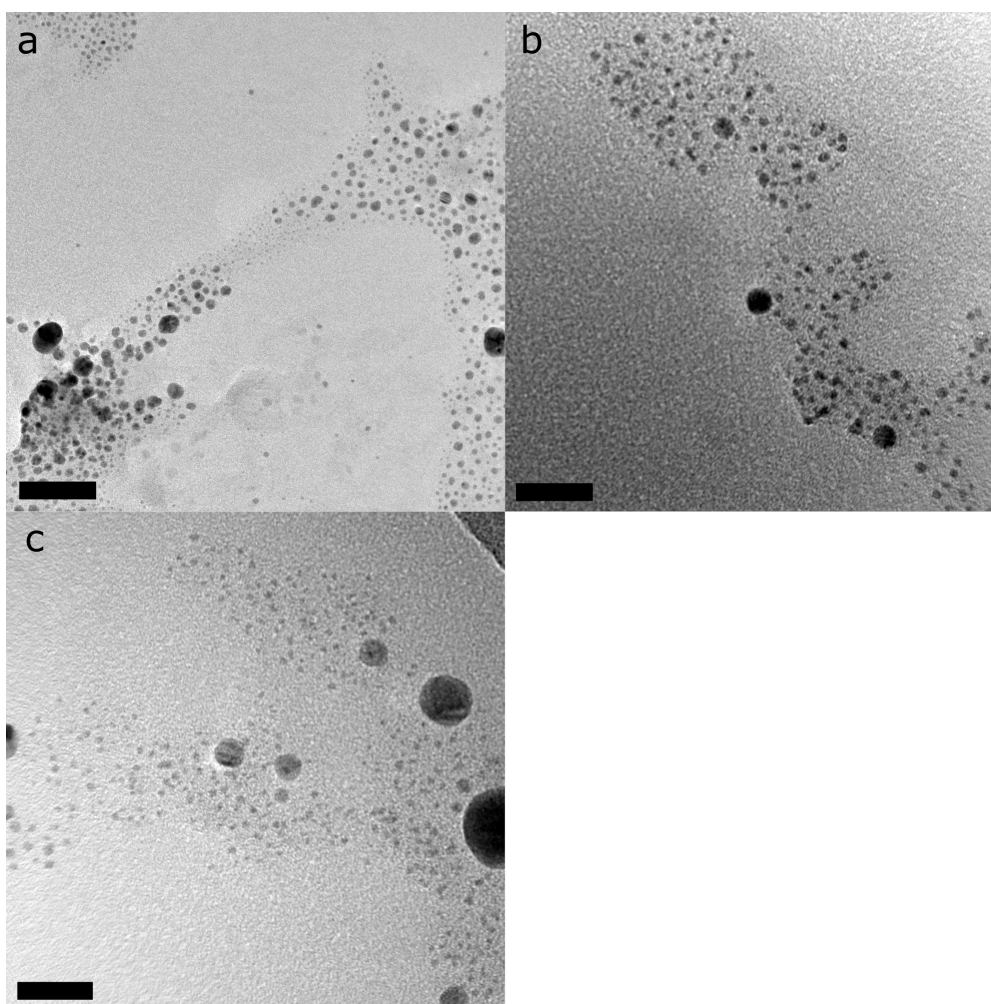
with ethanol as the solvent. Samples are produced both by deposition only onto the liquid jet, as well as co-deposition. Silver concentration was varied over 3 orders of magnitude by varying the sputter rate and the area available for deposition<sup>2</sup>. The peak nanoparticle sizes in each distribution are plotted against the estimated concentration, showing a logarithmic trend. This is largely expected from the log-normal distribution. The total volume of the log-normal distribution  $LNDF(x)$  is proportional to  $\ln(x)$ . Therefore, an exponential increase in volume will only lead to a linear increase in particle radius. This shows that the mass of silver sputtered into the sample is linearly related to the mass of nanoparticles represented in these distributions.

### 3.3.4 THE SILVER PLASMON RESONANCE

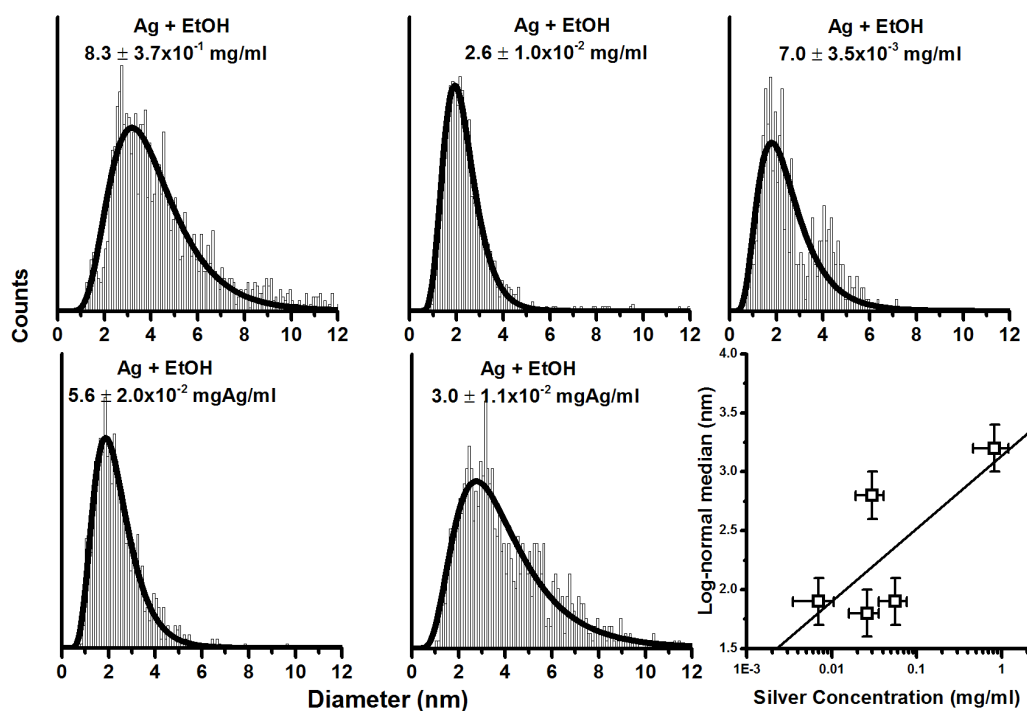
Timed measurements of samples were limited to UV-Vis spectra due to the experimental limitations inherent in microscopy and analysis in vacuum, with high turnaround time and analysis required to extract useful information. However, timed UV measurements, as shown in figure 3.3.8, raised more questions than answers. Peak intensity decreases with time, however, there is insufficient evidence for a trend. A further question is raised by comparison of shaken and unshaken samples. The increase of plasmon intensity above the initial value in some shaken samples shows that precipitated material can de-aggregate and re-disperse. It also shows that both precipitation and aggregation must be factors in the decrease of the plasmon intensity, but these cannot be easily deconvoluted.

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<sup>2</sup>Area was varied by changing between deposition onto the jet only and deposition into the cold trap.

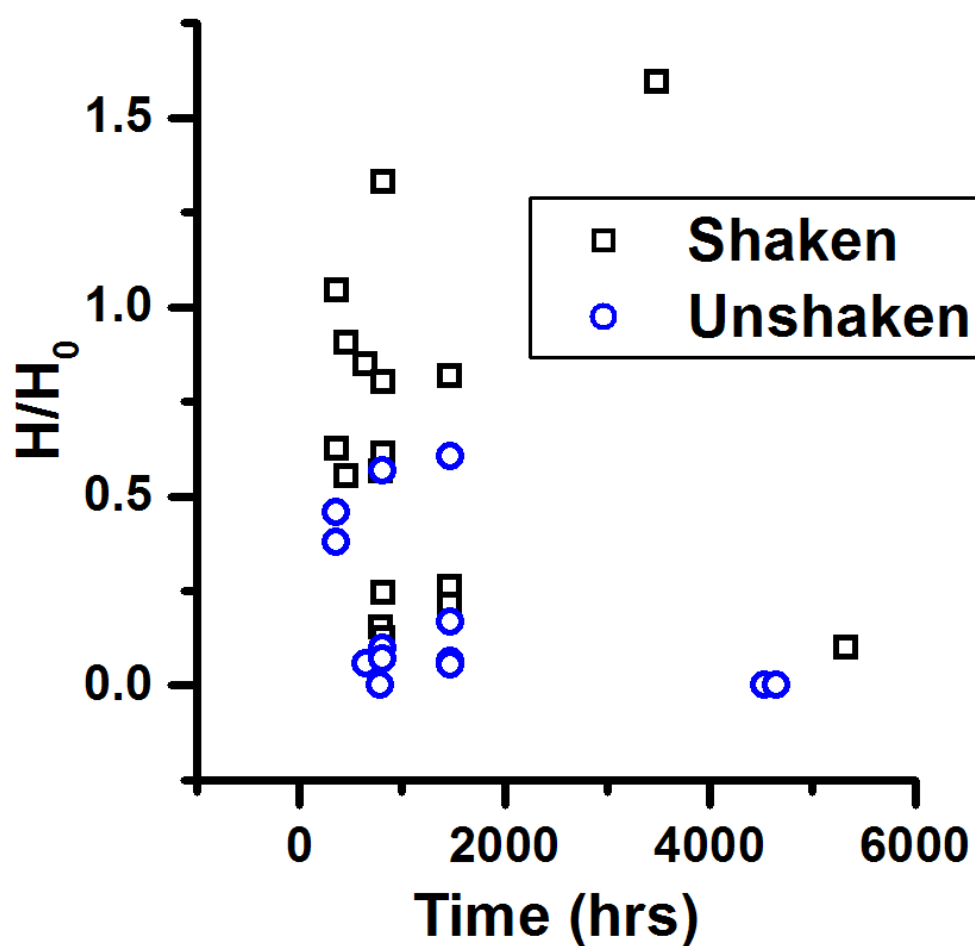


**Figure 3.3.6:** Transmission electron microscopy of silver nanoparticles produced in ethanol. **(a)** scale bar is 50 nm. **(b&c)** scale bar is 20 nm.



**Figure 3.3.7:** Size distributions of silver particles generated by semi-automatic analysis of TEM imagery. **(top left)**, size distribution from the same sample as **(top left)** in figure 3.3.5. **(bottom right)**, median size of log-normal distribution plotted against  $\log_{10}(\text{silver concentration in mg/ml})$ . Straight line is log fit to data (weighted by fractional error) with equation  $3.14 + 0.62 \log_{10}(\text{Concentration})$ .





**Figure 3.3.8:** Plasmon peak relative intensity  $H(t)/H(t_0)$  plotted against time at which spectra were recorded. These values are derived from 30 spectra of 6 samples of silver in ethanol. Outliers where  $H(t)/H(t_0) > 1$  are shaken samples where macroscopic precipitates have re-dispersed / re-dissolved. All spectra have had a linear baseline subtracted (removing absorbance of 'black' macroscopic particles which do not contribute towards the plasmon resonance).

The peak position and width were similarly poorly correlated with time, and it was not possible to draw useful conclusions from these measurements. However, it was possible to produce a measure of peak shape. Plotting the peak height against the half-width showed that these lay along a straight line, figure 3.3.9 which represents a constant plasmon peak shape. Data from ten silver in ethanol only samples were plotted, spanning three orders of magnitude in concentration and three orders of magnitude in time. This provides strong evidence that the plasmon resonance peak of silver-ethanol samples is independent of sample concentration and aging. If this evidence is valid, then the silver in ethanol system represents a stable and reproducible system. However, fitting the same data but without subtraction of a flat baseline is shown in Figure 3.3.10. This does not show a trend, and suggests that the observed linear trend may only be an artifact of fitting.

### 3.4 SUMMARY AND PROSPECTS

Vapour deposition with liquid jets has been demonstrated to be a synthetic route towards nanoparticles of metals and metal oxides. Nanoparticles produced by this method have a log-normal size distribution.

The production of silver nanoparticles has been demonstrated in several solvents, and it has been shown that the solvent choice strongly influences the size of stable nanoparticles. Sizes produced range from nanoparticles of median diameter 10 nm, to small silver molecules of as few as two atoms. Measurement of particle sizes by atomic force microscopy and transmission electron microscopy has shown good agreement between these methods. It

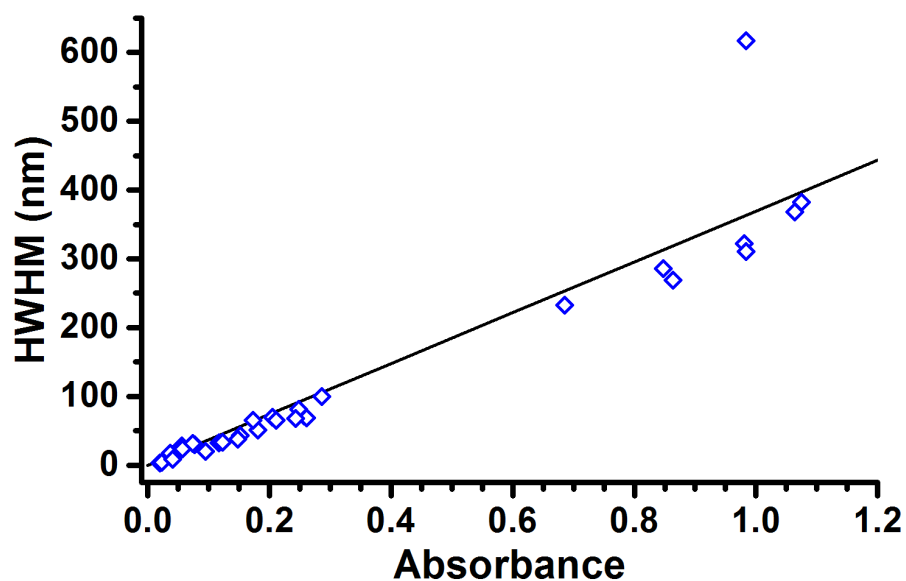


Figure 3.3.9: Plotting the plasmon resonance peak heights against half-width (blue diamonds), for 32 spectra recorded from 10 samples of silver in ethanol. The range of concentrations of silver spans three orders of magnitude. Spectra are included from co-deposition with a jet and from deposition only onto the jet. Spectra are included from immediately after production up to years post production. The solid line is a linear fit to the data (including outlier) and constrained to the origin.

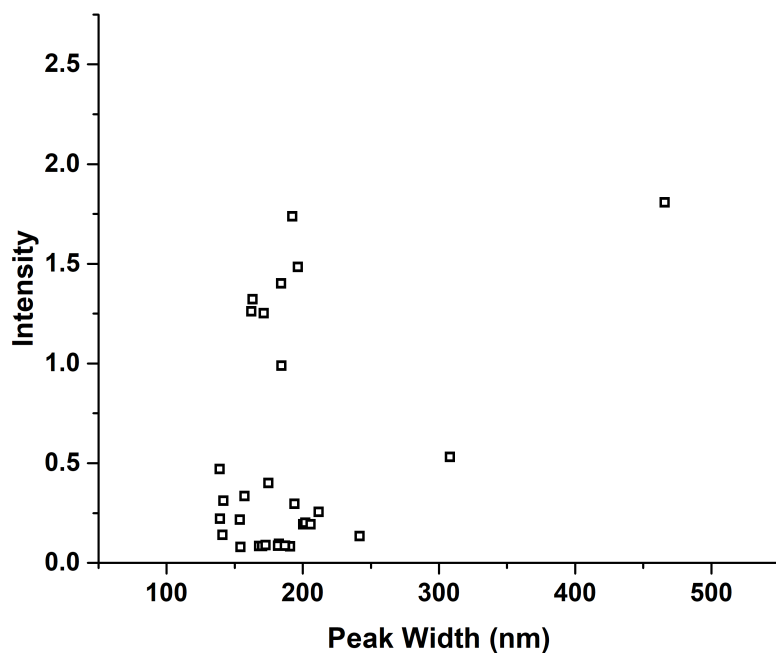


Figure 3.3.10: Plotting the plasmon resonance peak heights against half-width, without any baseline subtraction. Original spectra are those from Figure 3.3.9, but without baseline subtraction prior to gaussian fit.

has been shown that, for ethanol, the median particle size is proportional to the logarithm of the silver concentration.

Major themes will be continued throughout the following chapters of this thesis. Figure ?? includes additional data for samples produced in ethanol-water mixed solvents. The exploration of mixed solvents and mixed particles will make up the next results chapter.

| Sample                              | AFM Median (nm) | AFM S.Dev. (nm) | TEM Median (nm) | TEM S.Dev. (nm) |
|-------------------------------------|-----------------|-----------------|-----------------|-----------------|
| Silver Ethanol (i) (co-deposition)  | 3.03            | 0.68            | 3.30            | 1.52            |
| Silver Ethanol (ii) (co-deposition) | 2.56            | 0.68            | –               | –               |
| Silver Ethanol (i) (jet only)       | –               | –               | 1.93            | 0.70            |
| Silver Ethanol (ii) (jet only)      | –               | –               | 1.80            | 1.00            |
| Silver Ethanol (iii) (jet only)     | –               | –               | 1.88            | 0.81            |
| Silver Ethanol (iv) (jet only)      | –               | –               | 2.76            | 1.66            |
| Silver Ethanol (citrate added)      | 2.56            | 0.33            | –               | –               |
| Silver Water (small particles)      | 0.69            | 0.09            | –               | –               |
| Silver Water (large particles)      | 1.92            | 0.31            | –               | –               |
| Silver Isopropanol                  | 8.27            | 5.71            | –               | –               |

*"The salt of any interesting civilization is mixture."*

Antonio Tabucchi

## 4

# Colloidal Particles and Interactions

COLLOIDAL SOLUTIONS of silver nanoparticles in ethanol have been characterised in the previous chapter. The silver-ethanol system is robust against changes in silver concentration, showing only a linear change in median particle size with order of magnitude increases in concentration. The plasmon peak shape, as measured by the ratio of peak height to width, remains approximately constant with changing concentration and sample ageing. The dramatic changes in observed absorption spectra and particle sizes with different solvents suggests that the chemical environment has the most substantial effect on the formation of particles.

To understand how the chemical environment influenced the particles, particles were produced in mixed solvents, such as those in ethanol - water mixes. Figure ?? provided some tentative evidence for a different peak shape in these

samples. To test the idea that the chemical environment is critical to particle properties, experiments were conducted mixing samples of silver in ethanol with varying concentrations of citric acid. Concentrations of citric acid ranged from 5 mM to 1 M, UV-Vis spectra were recorded at intervals from immediately after mixing to several days later, and samples of different molarities and ages were heated to determine reaction dynamics. Much like the early work with silver and ethanol, no consistent trends were identifiable relating molarity, aging or heating to any trends. Again, plotting the peak height against half-width proved more informative. This is summarised in figure 4.0.1, showing that peak shape is changed compared to silver in ethanol. The reduced gradient indicates that the plasmon peak is narrower in this system.

#### 4.1 SYNTHESIS OF COMPOSITE PARTICLES

Colloidal silica nanospheres of diameter 20 nm (LUDOX HS-30) were chosen as a material for combined deposition in the liquid jet. There are many grades of colloidal silica available, but this sample was chosen as it could be easily dispersed in methanol, which is an easy solvent for use in the liquid jet. The colloidal silica as supplied is in a solution of 30% SiO<sub>2</sub> by weight. The silica particles have a negative surface charge, and are stabilised with sodium counter ions. The maximum concentration possible for LUDOX in methanol is 5% silica by weight. Higher concentrations than this gel the mixture.

Before production of solutions with silica present, silver was co-deposited with a pure methanol jet. This produced a suspension of dark red coloured macroscopic aggregates. These could be dispersed by agitation, however

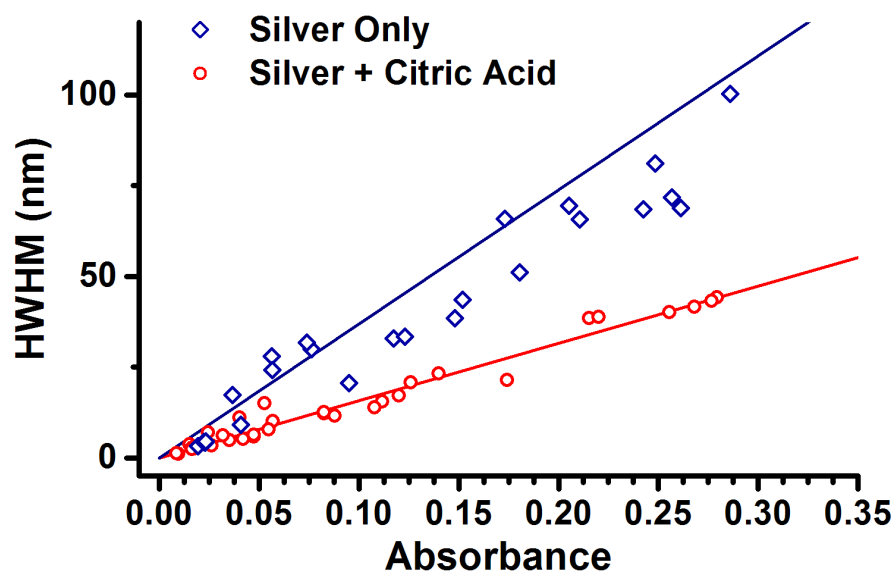


Figure 4.0.1: Comparison of ethanol only data with data for silver samples in ethanol with added citric acid. Data is from 33 spectra recorded of 12 samples at 10 different concentrations of citric acid in ethanol. The concentration of silver in each sample was maintained constant.

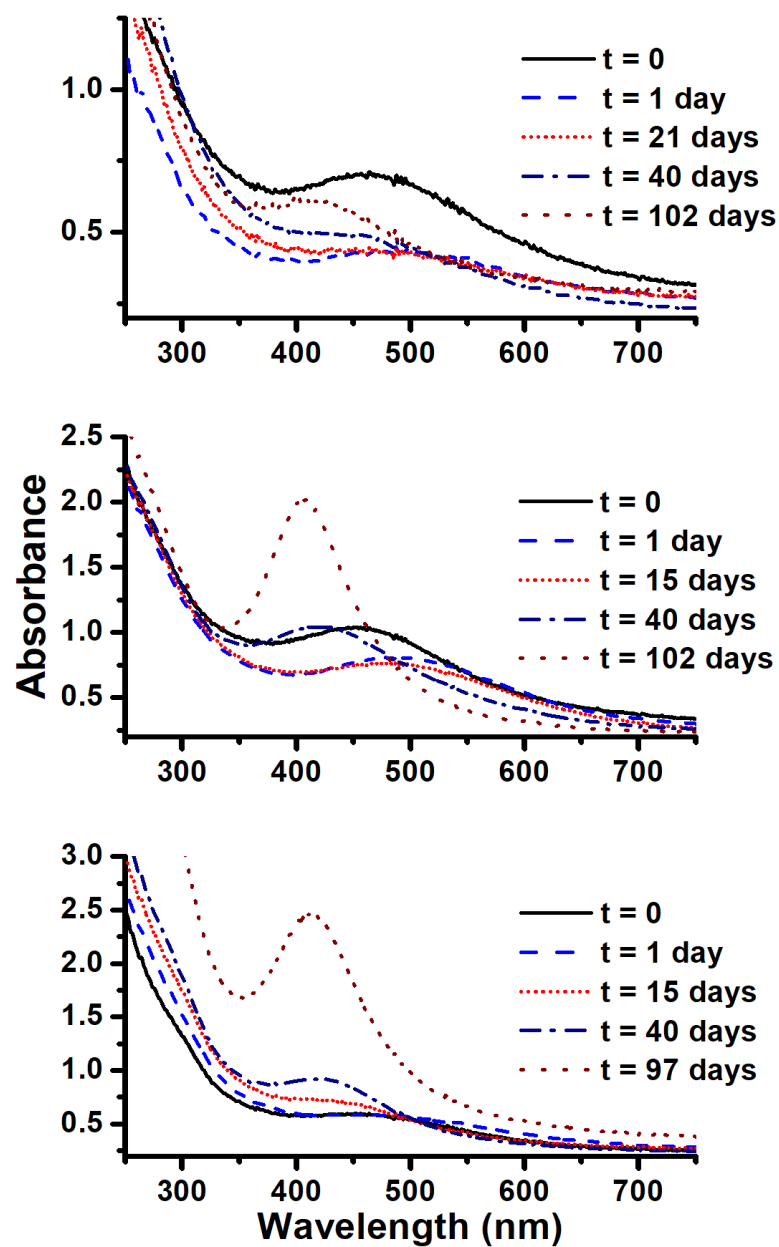


they would immediately aggregate again. Adding a small amount of LUDOX (0.1%) to this solution stabilised the silver particles, and after sonication the solution had a spectrum very close to that of silver in ethanol, with a broad peak at 450 nm. A fraction of the un-stabilised silver in methanol was left for 22 hours. At this point it could not be re-dispersed by agitation. However, adding 0.1% LUDOX followed by sonication regenerated a plasmon resonance at 440 nm.

Solutions were produced of LUDOX in methanol at 1%, 0.1% and 0.01%  $\text{SiO}_2$  concentrations for loading into the liquid jet. Experiments were carried out with the lowest concentration of silica first to avoid cross contamination of solvents in the reservoir. Before and after the experiment the liquid jet apparatus was flushed with water and methanol, and the resulting wash solution was examined using FTIR spectroscopy in order to confirm that minimal silica was present.

#### 4.1.1 UV-VIS CHARACTERISATION

These samples had a unique evolution over time. Of all samples as yet produced, there had been no systematic evolution over time. However, samples with added silica showed a distinct change. Immediately after production, the solutions had a colouration similar to silver - ethanol samples. This is illustrated in the  $t = 0$  lines in figure 4.1.1. The plasmon resonance began to change immediately, and visibly to the naked eye. For 0.01 % and 0.1 % silica, material began to precipitate within 1 day. The  $t = 1$  day line confirms this. Sample intensities decreased by half and one third for 0.01 % and 0.1 % sam-



**Figure 4.1.1:** Absorption spectra of 20 nm colloidal silica (LUDOX HS-30) dispersed in methanol and co-deposited with silver. From top to bottom: 0.01 % SiO/wt, 0.1 % SiO/wt, 1 % SiO/wt. Spectra were recorded at intervals over several months.

ples respectively. The spectrum then began to narrow and blue-shift until reaching a peak position of 410 nm.

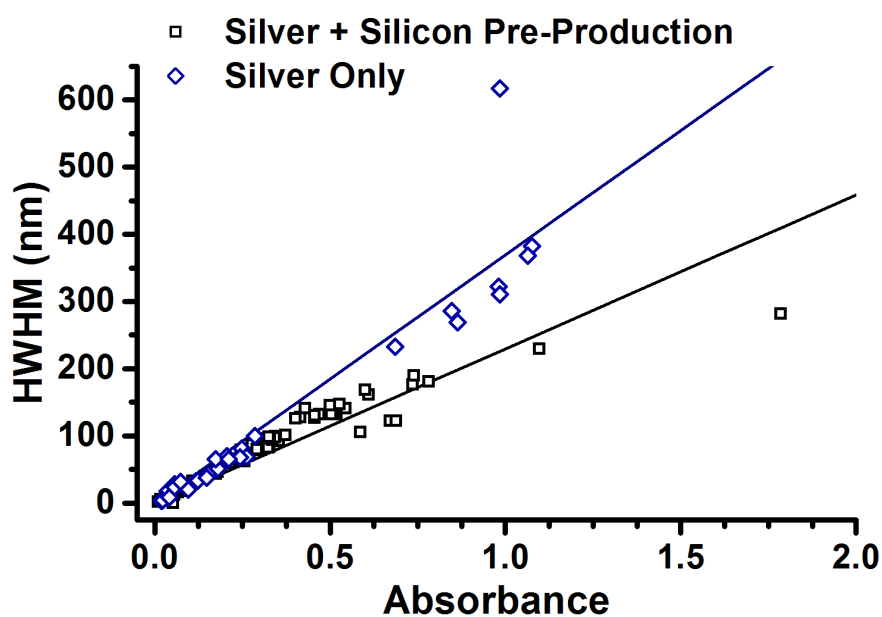
The final peaks of all samples are more intense than the starting peaks. This is consistent with narrowing of the peak shape in the sample with 0.01 % silica. However, the intensities of absorption peaks in the more silica rich samples cannot be explained only by peak narrowing. In these samples, a substantial amount of liquid had been lost from the sealed sample container.

The UV-Vis spectra measured of all samples where colloidal silica was present in solution are plotted in figure 4.1.2. This includes data from all three concentrations of silica. All three samples were produced with the same sputtering conditions, so should have approximately the same silver content. Immediately after production dilutions of 50 % and 10 % in pure methanol were produced. Absorption peaks for these spectra are included in the plot. All timed measurements are included. These points lie on a separate line than the silver in ethanol samples, but there is substantial overlap.

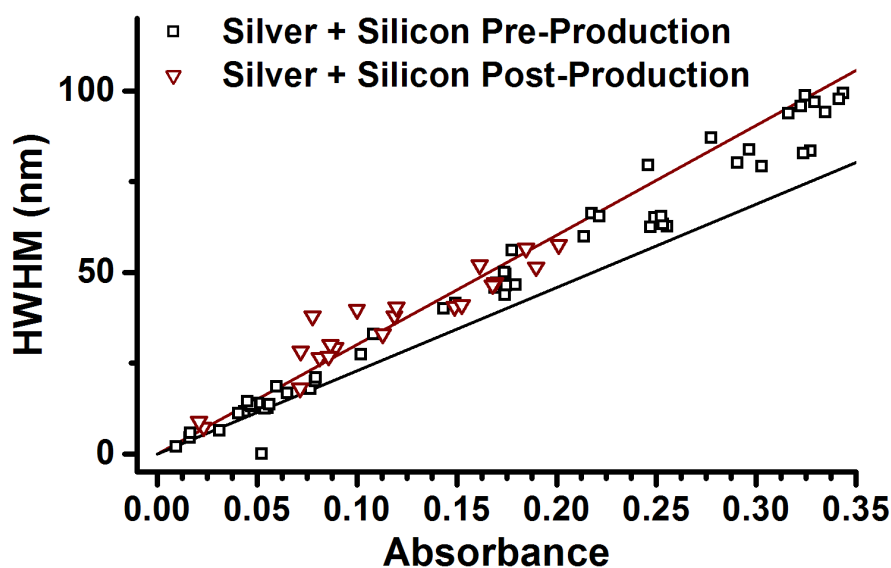
#### 4.1.2 CATALYTIC PROPERTIES

To determine the cause of liquid loss in samples, some were transferred to different vials, and a set of control vials were set up containing only methanol. Over several weeks these confirmed that no mass was being lost due to evaporation. Eventually, despite being re-diluted with methanol, the sample with the greatest amount of silica dried out to form a hard crust.

To determine the mass loss in these samples, they were weighed several times over a period of days. The crusted sample was crushed into pow-



**Figure 4.1.2:** Comparison of ethanol only plasmon shape line with shape of spectra of silica silver hybrid particles. Data plotted are taken from 82 spectra of 3 different solutions, covering 3 orders of magnitude of silica content, all having (approximately) the same silver content. 3 different dilutions of each sample are included, as are timed measurements up to 100 days after production.



**Figure 4.1.3:** Plot of the plasmon shape of samples where colloidal silica has been added to methanol before, (black squares), and after, (maroon triangles), co-deposition with silver. Straight lines represent linear fits to the data. Graph shows a small section of data, hence the apparent discrepancy between pre-production linear fit and displayed data.

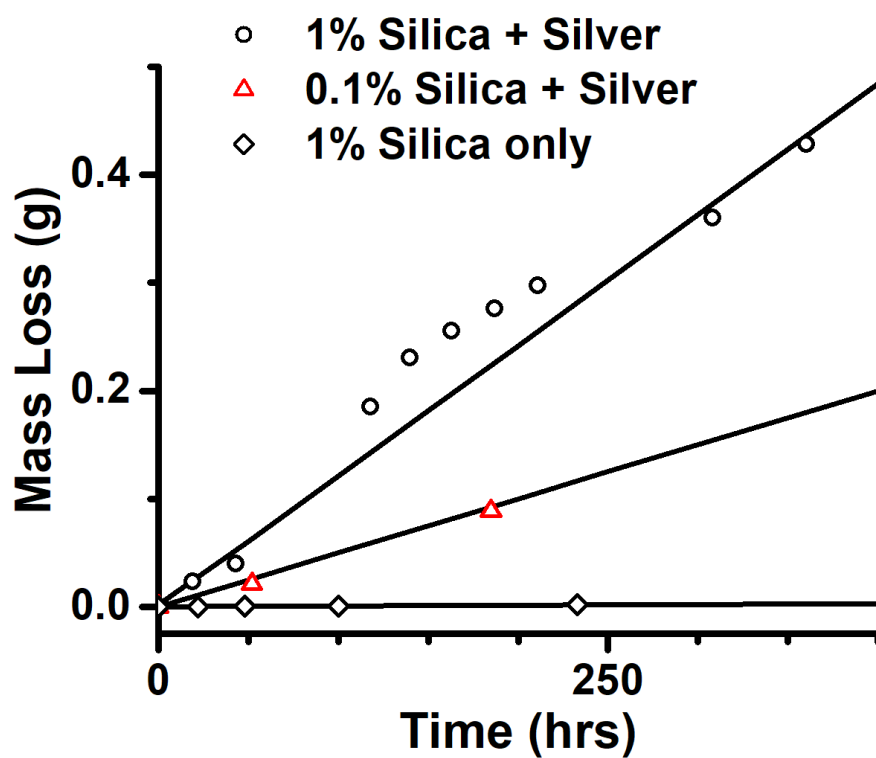


Figure 4.1.4: Plot of the loss in mass of methanol evolved from samples of silica particles decorated with silver nanoparticles. Data for sample with 0.01 % silica is not plotted as the rate was too small to be visible on this scale. The mass loss of 1 % silica only in methanol was comparable to the scale precision.

der, 50mg of this was placed in a fresh vial and topped up with 5 mg of methanol. Because it had dried and could be weighed apart from solvent, and lost methanol at the highest rate, this provide the most accurate values of mass lost over time and was more thoroughly investigated. The weight of the empty vial, vial with powdered material and vial topped up with methanol were measured using a scale with precision  $\pm 0.1$  mg. The mass loss over time is plotted in figure 4.1.4 below. LUDOX colloidal silica in methanol was used as a control measurement.

The mass loss varied as with the mass of silica in the samples. In figure 4.1.6, the mass loss is plotted as a fraction of the mass of silica present in the sample. In the crushed sample, this could be known to within 5 % (the approximate fraction of mass which was silver.) In other samples the error was much higher, as it compounded the errors in silica dilution, injected liquid flow rate and evaporation rate in vacuum. The measured rates of mass loss show reasonable agreement for the three concentrations of silica and provide strong evidence of a reaction caused by silver modification of the silica spheres. The most likely reaction is a catalytic reaction with the methanol. Silver is an important catalyst for partial oxidation of methanol to formaldehyde [80, 81] and Ag -  $\text{TiO}_2$  catalysts have been used for photocatalytic evolution of hydrogen from methanol and water. The linear fit to data in figure 4.1.6 corresponds to a reaction rate of  $1.65 \times 10^{-7} \text{ mol g}^{-1} \text{ s}^{-1}$  of methanol. If this is converted to a turnover fraction, representing the number of reactions per active catalytic site per second. The precise reaction or reactions are unknown, oxidation of methanol leads to the formation of gases (either formaldehyde

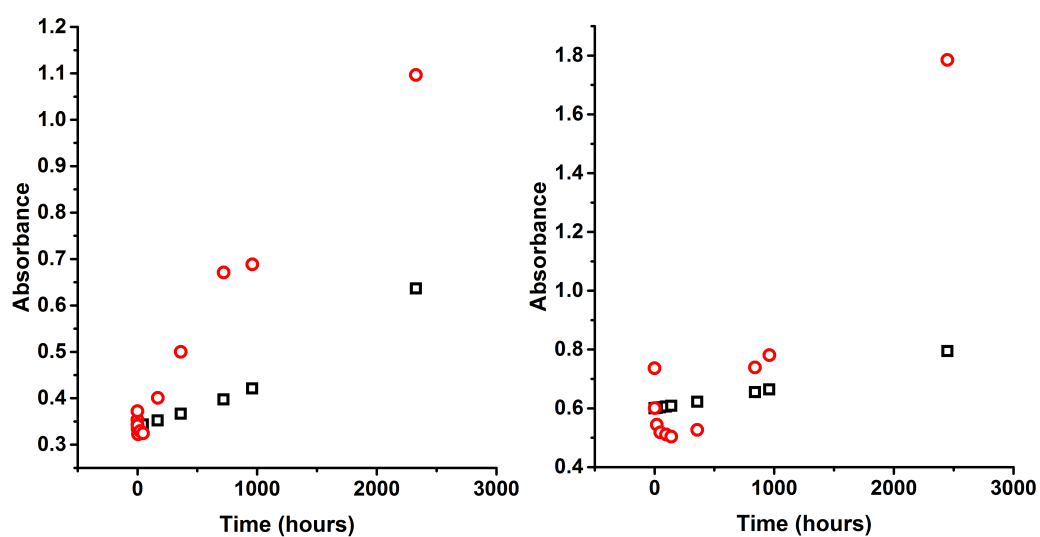


Figure 4.1.5: Peak plasmon resonance maximum (red circles) and predicted resonance, compensating for the increased concentration as methanol is lost (black squares). The correction is a linear scaling to the expected intensity had no liquid been lost from the sample. (left), 0.1 % silica. (right), 1.0 % silica. The increase in plasmon peak absorbance can be accounted for by narrowing of the peak.

or carbon dioxide, hydrogen and water vapour) and so could lead to all the material evaporating.

#### 4.1.3 MICROSCOPY

Transmission electron microscope images were acquired of silver-silica samples with concentrations of 0.01 % silica and 1 % silica. In all images examined, more than 99.6 % of silver particles were on top of or adjacent to a silica sphere. Whilst these are dried films, and the binding of silver and silica in the liquid phase cannot be certain, the difference in plasmon resonance peak position, shape and the catalytic properties of the solutions strongly suggest that the silver is bonded to the silica. Moreover, the similar reaction rates for both colloidal particles and the dried silver / silica powder also provides strong evidence that composite particles are formed in solution.

Size distributions of silver particles attached to silica spheres were acquired semi-automatically in software. However, at least half of the contribution to particle measurement was manual, as it was difficult to appropriately discriminate between silver particles and silica overlaps using image thresholds or local thresholding algorithms. Manual measurement was made by measuring an ellipse around the particle and taking the average of the axes as the particle diameter. Figure 4.1.8 shows all available TEM size distributions, including data from figure 3.3.7.

The size distributions of silver nanoparticles attached to LUDOX in methanol is of the same order of magnitude as silver particles in ethanol. The median diameters and silver concentrations in these samples follow a diameter to



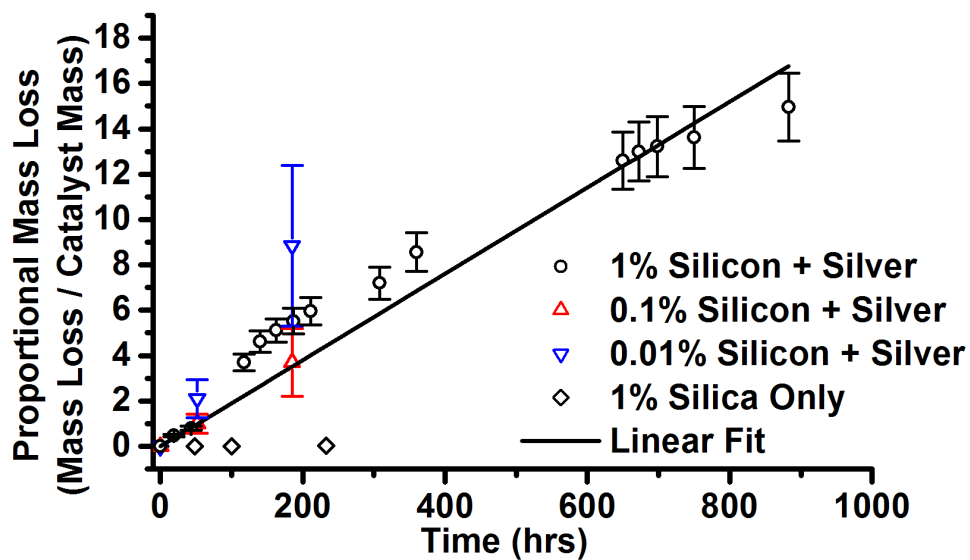


Figure 4.1.6: Plot of the loss in mass of methanol relative to the total mass of catalyst in solution for all three concentrations of silica pre-production. A line is fit to all three sets of data for 1%, 0.1% and 0.01% silica content.

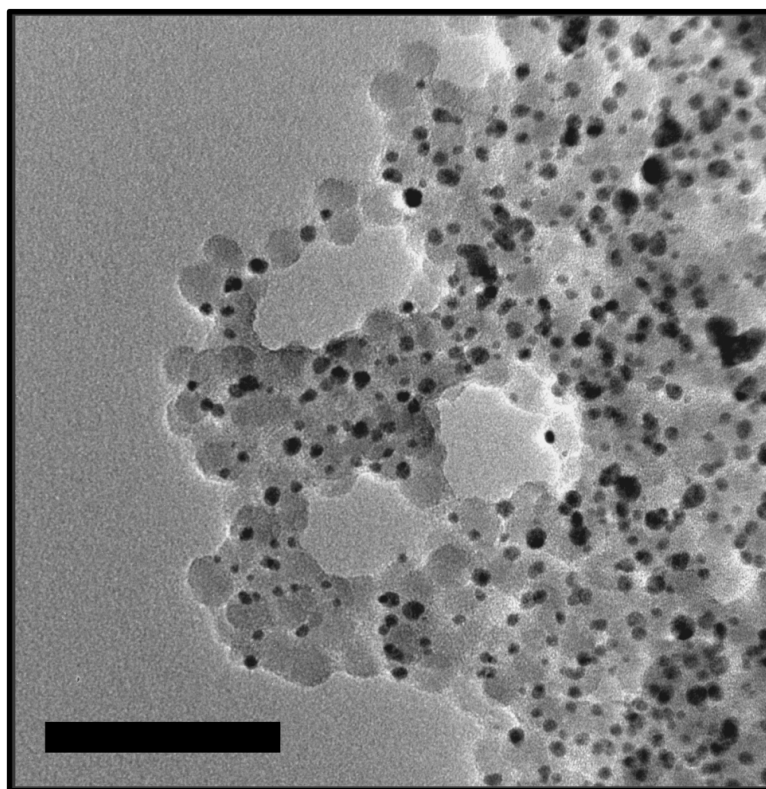


Figure 4.1.7: TEM image of silver decorated silica nanoparticles. Scale bar is 100 nm.

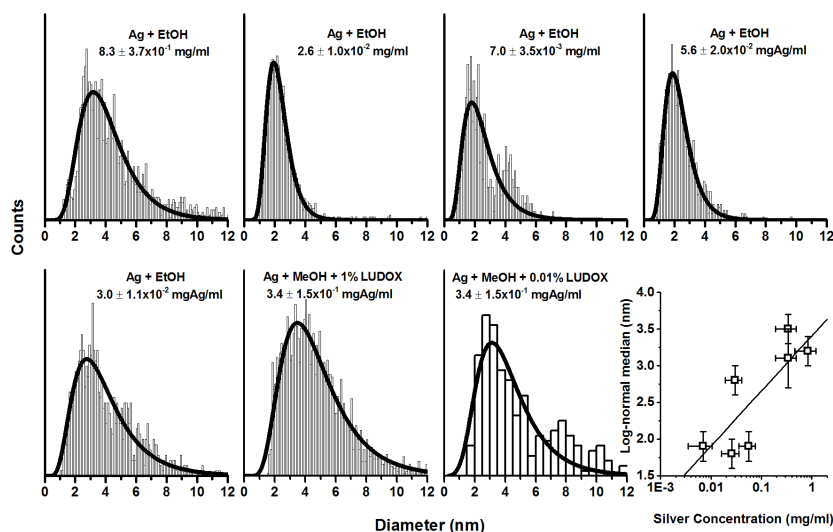
log(concentration) dependence. It is uncertain whether this is simply a coincidence, given the dramatic effects that solvent seemed to play in particle sizes seen in figure 3.3.5.

It is also worth noting that the change in the plasmon resonance in silver / silica samples could well be explained by narrowing of the size distribution. The silica spheres provide a template on which silver atoms and clusters can nucleate and ripen.

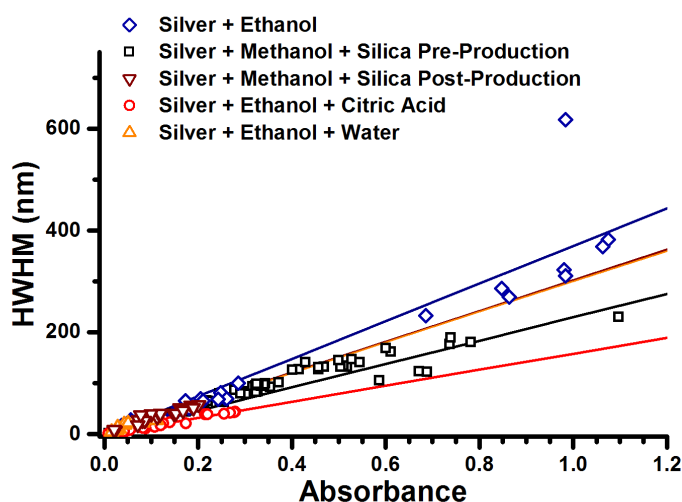
## 4.2 EVALUATION AND REFLECTIONS

This chapter has demonstrated the general principle that the shape of the plasmon resonance of silver nanoparticles produced by mixing silver atoms and alcohols is primarily governed by the solvent chemistry. The size distributions of silver nanoparticles on the surfaces of silica nanospheres also seems to have confirmed the proportionality between the median particle size and log concentration.

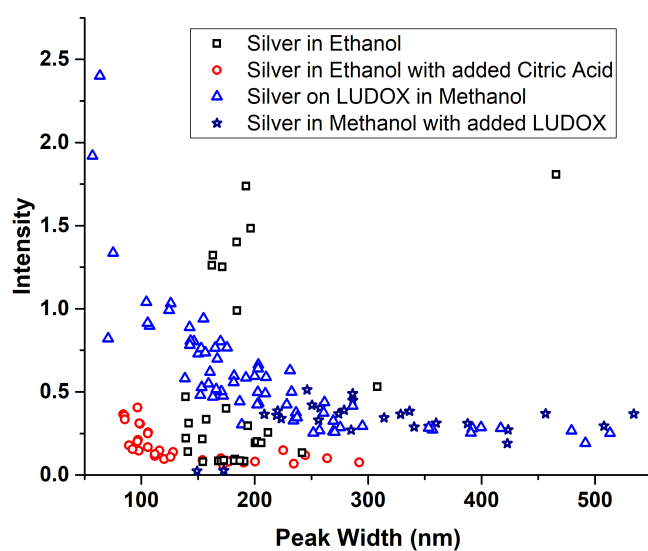
There is an apparent contradiction between the small changes in median size between nanoparticles, and the fairly large changes in plasmon resonance shape between different sample types. For example, the median size of nanoparticles on silica is approximately equal to the median size of particles in ethanol with a similar total concentration of silver. This implies that the correlation between median particle size and plasmon resonance is weak. The plasmon resonance intensity is primarily proportional to the mass of the nanoparticle. In a log-normal size distribution, the mass distribution peaks at a higher value than the diameter, and is also broader. This will have a multi-



**Figure 4.1.8:** Size distributions of silver particles produced in ethanol compared with distributions of silver particles attached to silica spheres in methanol. Straight line fit, (bottom right), is  $3.44 + 0.78\log_{10}(\text{concentration})$ . Samples suspended in methanol were separately diluted (1 % SiO/wt  $\times 10000$ , 0.01 % SiO/wt  $\times 100$ ) to reach an ultimate concentration of 0.0001 % SiO/wt. Low resolution scanning electron microscopy had determined that this was the appropriate concentration to achieve less than one monolayer coverage of silica. The diluted samples were then drop-cast onto ultra-thin carbon TEM grids.



**Figure 4.2.1:** Plot of the plasmon shape of samples produced by deposition into or along with a liquid jet. All sample types with sufficient spectra showing a plasmon resonance are included. Every series includes data from at least two unique samples (produced separately in different experimental production runs) and measured at different ages, concentrations, dilutions and chemistries as applicable.



**Figure 4.2.2:** Plot of data originally plotted in Figure 4.2.2, but without flat baseline subtraction. This shows almost the opposite trend to Figure 4.2.2. However, different production chemistries plot in distinct regions.

plying effect on the broadening of the plasmon resonance. A small change in median diameter can have a large effect on the mass distributions.

Ultimately the direct interpretation of plasmon peak position and shape is complicated. Increase in homogeneous linewidth [61, 114] and red shifting [69] of the silver plasmon peak with decreasing size have been reported for nanoparticles smaller than 10 nm, which would correlate well with the plasmon resonances and particle sizes we observe.

The liquid jet system represents a platform for introduction of metals to pure solvents which is largely independent of the physical parameters of the system such as sputter rate, liquid jet flow rate and exactly where and how the atoms are mixed with liquids. The chemistry of the solvent is the key parameter to understanding the product. Intriguingly, the method of generating silver atoms is itself largely independent of the solvent chemistry. This separation of atom generation from solvent chemistry represents an interesting experimental platform, which has been shown to produce particles stable in solution ranging from large nanoparticles to few atom clusters. Evidence for these clusters will be the focus of the next chapter.

"We adore chaos because we love to produce order."

M.C. Escher

## 5

# Nanoparticle Arrays on Graphite

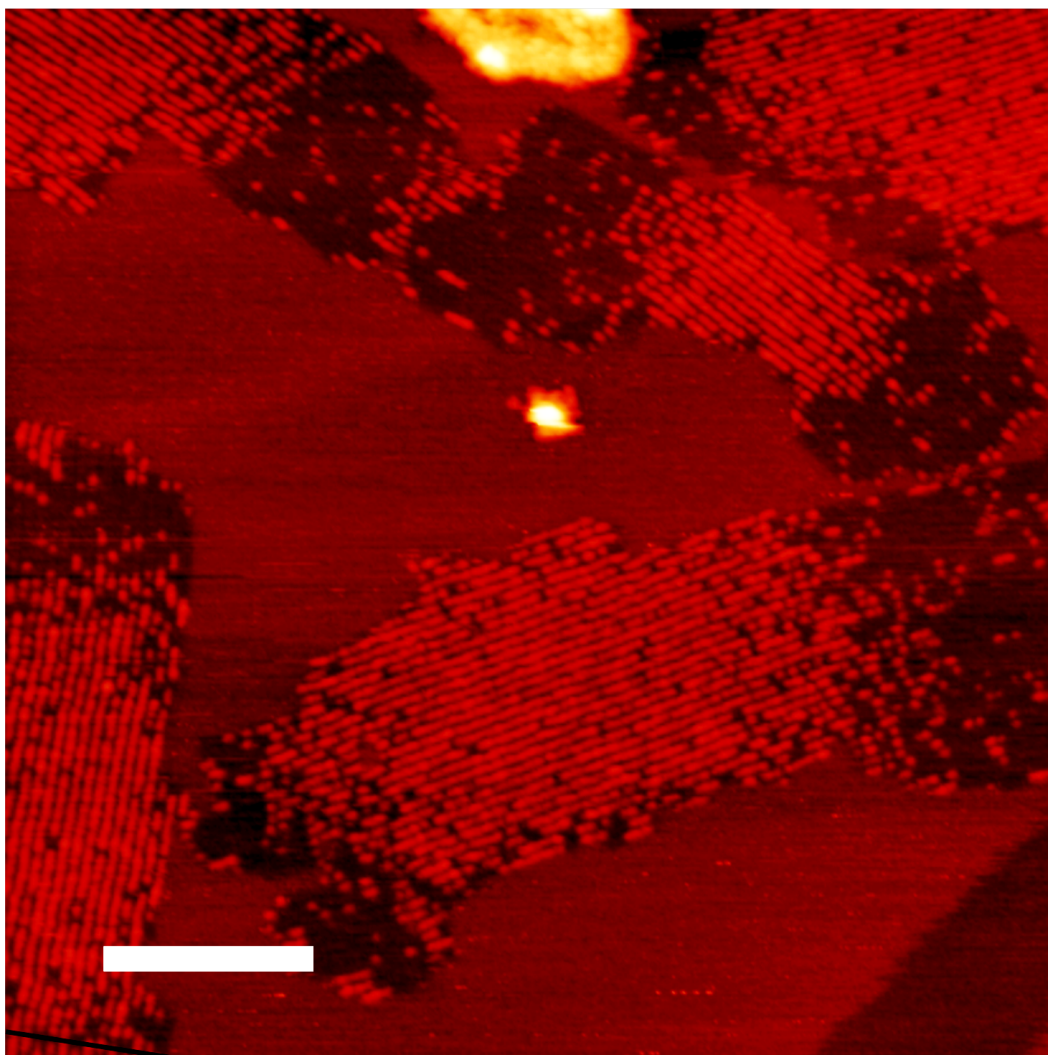
Drop casting of nanoparticle solutions on highly oriented pyrolytic graphite surfaces has been the standard preparation for analysis by atomic force microscopy throughout this thesis. To measure particle sizes, solutions had to be diluted until dried films were less than one monolayer. Then roughness information from the sample could be related to particle height. During the course of routine experimental work it was observed that samples in water did not dry evenly on the graphite surface. This was likely due to the high surface tension of water causing the water to gather in droplets and create high local concentrations of nanomaterials in the dried droplet location or in 'coffee cup' rings [115].

To avoid this behaviour, nanoparticles suspended in water were diluted with isopropanol. Dilution factors greater than 10:1 showed excellent wetting of the graphite surface. However, when analysing samples produced in water

and diluted in isopropanol, novel surface structures were observed. Large areas of aligned stripes were formed on the HOPG surface. An example is shown in figure 5.0.1. These arrays could be well ordered over sizes greater than 1 micron, were of row heights of 0.5-0.7 nm, with line separations normally a uniform value of a few nanometres.

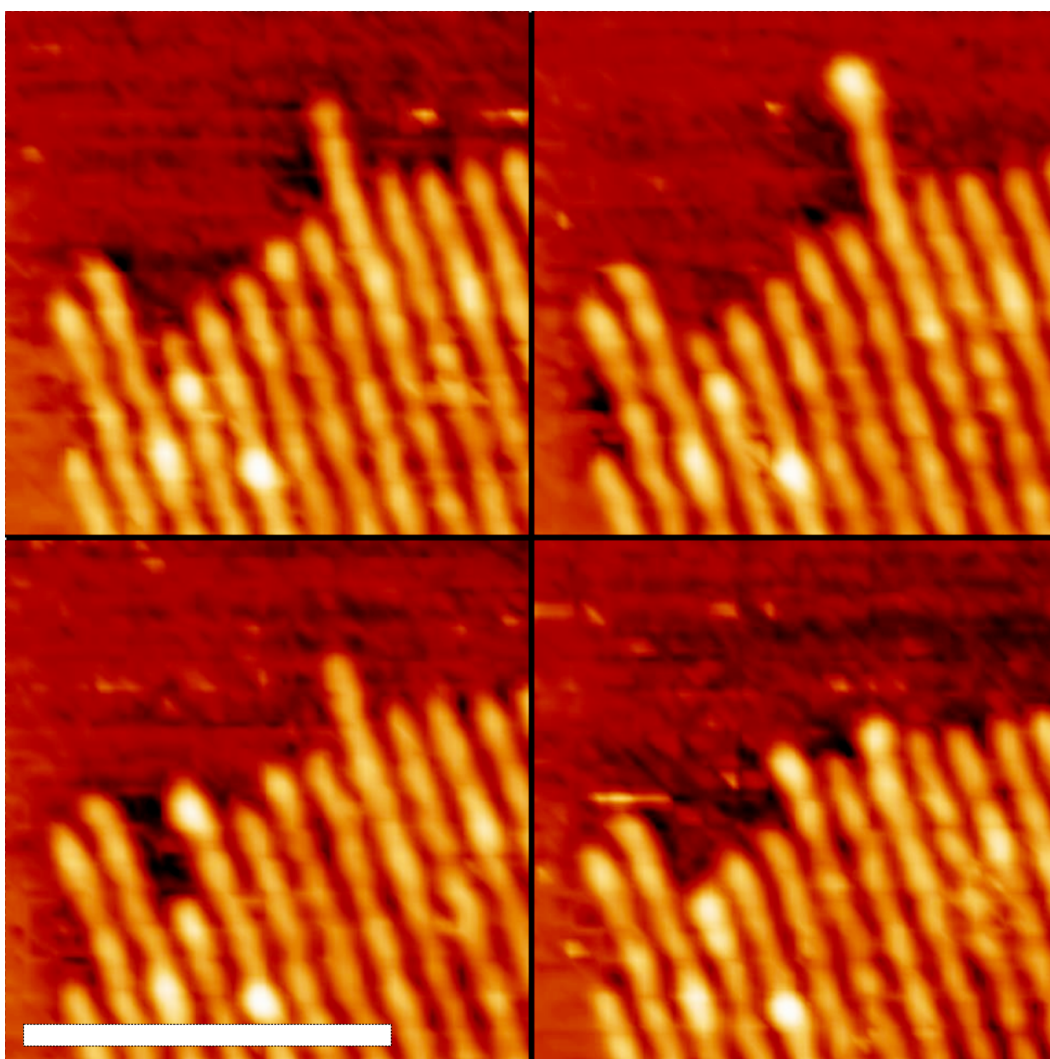
Analysis carried out during this investigation showed that well ordered linear arrays could be reliably carried out by drop casting solutions of silica nanoparticles, isopropanol and water onto HOPG. Previously published work by the author has established that alignment of the striped areas reflected the threefold symmetry of the graphite surface [116]. This work showed how stripe arrays could be templated on superlattices [116] generated by underlying Moiré patterns commonly observed in HOPG [117, 118]. Superlattice templated growth or adsorption has been observed in metal nanoparticles [119-125] and  $C_{60}$  [126]. The linear organisation of metal nanoparticles matching the substrate crystallinity has also been observed for gold nanoparticles on the H-passivated Si(111) surface [127]. In this investigation, substantial differences were observed between the behaviour of arrays aligned along different axes of the moiré pattern [116]. Arrays aligned along the zig-zag direction were highly stable, and were observed growing in discrete steps, illustrated in figure 5.0.2, where individual particles attach and detach from the array line tips. Conversely, samples which had grown along the armchair direction in the Moiré pattern were observed growing in intensity homogeneously along the length, and disappearing very rapidly as shown in Figure 5.1.1.

Silicon in water samples produced using the liquid jet were diluted with



**Figure 5.0.1:** Arrays of silica clusters, produced by co-deposition of silicon with water vapour [94]. The original sample has been diluted 15 times with isopropanol. Arrays are approximately 0.5 nm high base to peak, with line spacing of 5.5 nm. Line spacing is related to the angle between arrays. The angular deviations from  $60^\circ$  between arrays  $\psi$  is related to line spacing  $D$  by  $D = \frac{\alpha}{2\sin(\frac{\psi}{2})}$ . Typically two angles are measured  $\theta \pm \psi$ . In this array averaged value of  $\psi$  over multiple measurements was  $2.6^\circ$ , corresponding to a line separation of 5.4 nm. The scale bar is 100 nm.





**Figure 5.0.2:** Step-wise growth of linear cluster arrays. Scale bar is 50 nm. Figure is adapted from [116]. Sample is the same as that used for Figure 5.0.1.

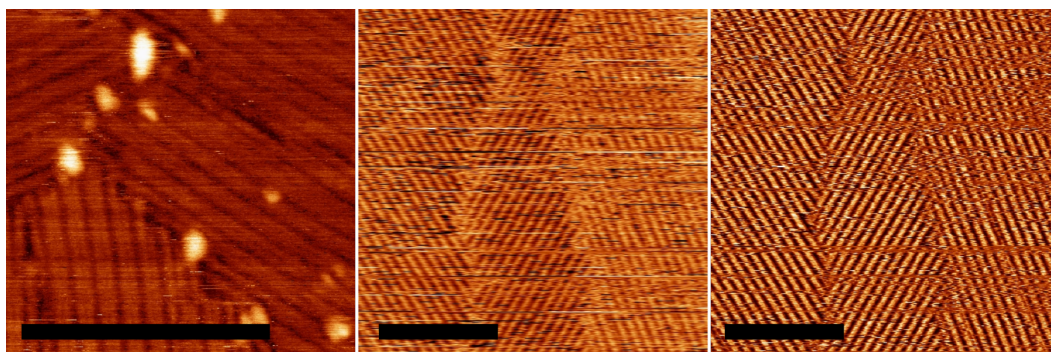
isopropanol and drop cast onto freshly cleaved HOPG, before imaging with both AFM and STM. Stripe arrays were visible in both imaging modes 5.0.3, confirming both that stripe arrays are present in liquid jet samples as well as in samples produced by the method of Brewer *et. al.*. The reproduction in STM of images seen in AFM is an excellent confirmation of the presence and morphology of these structures. Higher resolution images and image series were acquired in both imaging modes, however, data analysis of these new images was not possible in a reasonable timeframe.

## 5.1 MEASUREMENT OF NANOPARTICLE ARRAY DYNAMICS

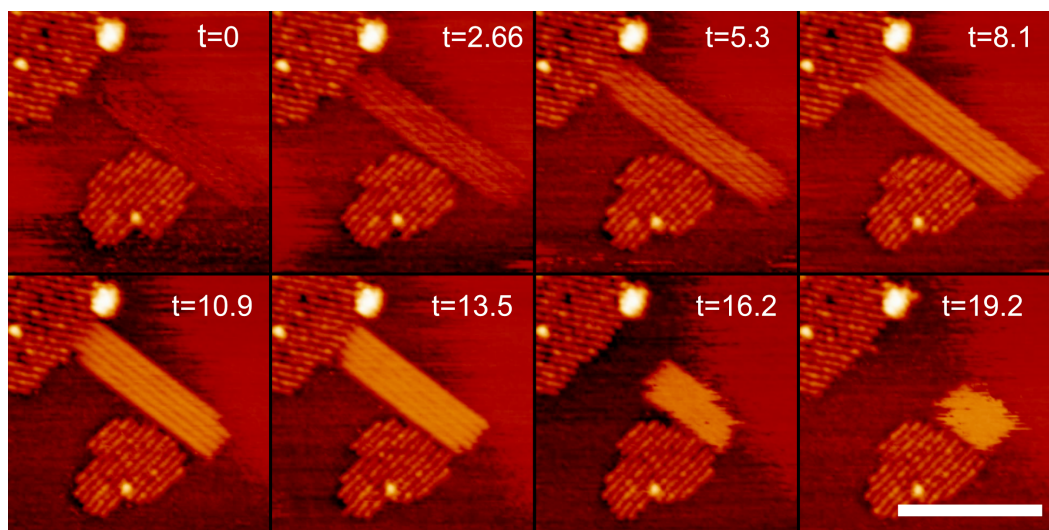
These prior results implied that phase changes were taking place, analogous with crystallisation, melting and evaporation. These phenomena were studied further by analysis of image series showing changes in array sizes and structure. All images analysed for growth and dynamics of arrays were produced by the method developed by Brewer *et. al.* [94]. Samples were analysed at a constant temperature. However, the bulk temperature of the substrate does not necessarily correspond to the temperature of the surface under analysis as the interaction of the scanning probe tip with the surface transfers energy to the sample.

### 5.1.1 LINEAR GROWTH

Growth along lines was observed in many samples such as that shown in Figure 5.1.2. This figure is part of a series of 32 images. The length of the lines was measured in each image, and the results are summarised in figure 5.1.3.



**Figure 5.0.3:** Sample of silicon deposited with a liquid water jet. **(left)** AFM image of stripe pattern formed from silica diluted 15 times in isopropanol. **(center)**, STM height map of different region on the same sample, **(right)**, the same image but measuring current rather than z-height. Scale bars are 100 nm. Note the good match of line spacings in both AFM and STM images.



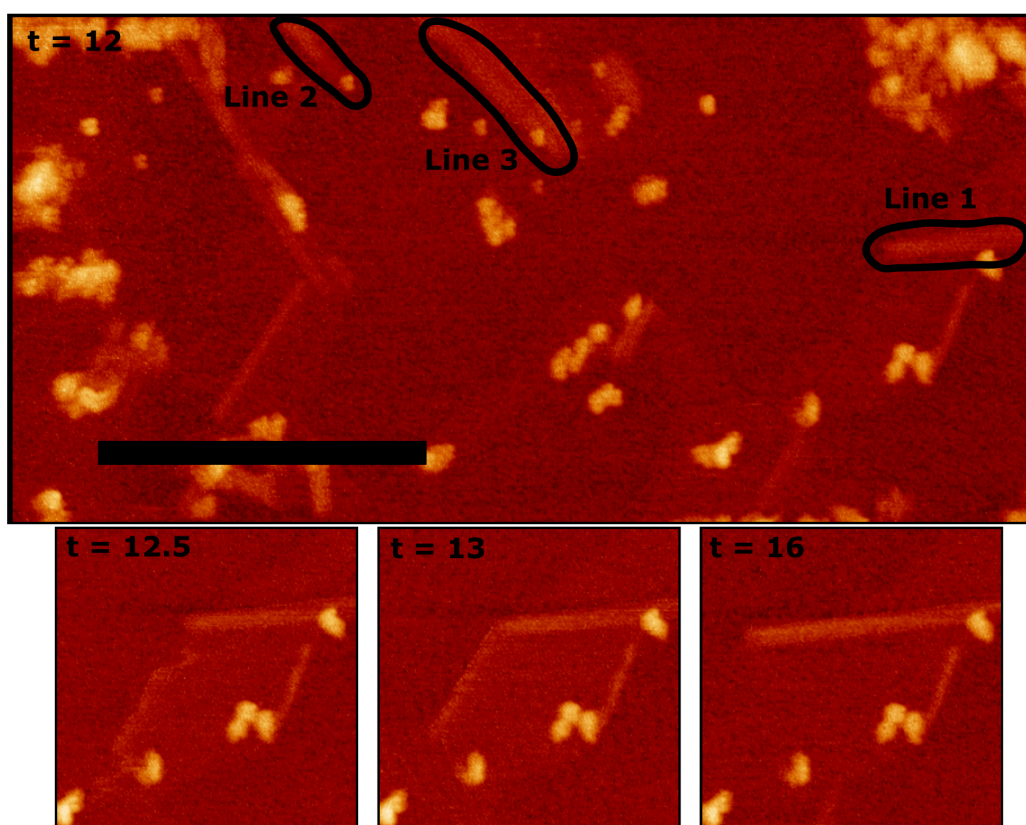
**Figure 5.1.1:** Fluid-like growth of linear cluster arrays. Scale bar is 100 nm. Figure is adapted from [116]. Sample is the same as used in figure 5.0.1.

For all three lines, the rate of growth is very nearly linear, except for line one at  $t > 20$  hours. In figure 5.1.3 right, we see that both Line 2 and Line 3 have a constant growth rate with line length. However, Line 1 shows an increasing growth rate with length, after 20 hours had passed.

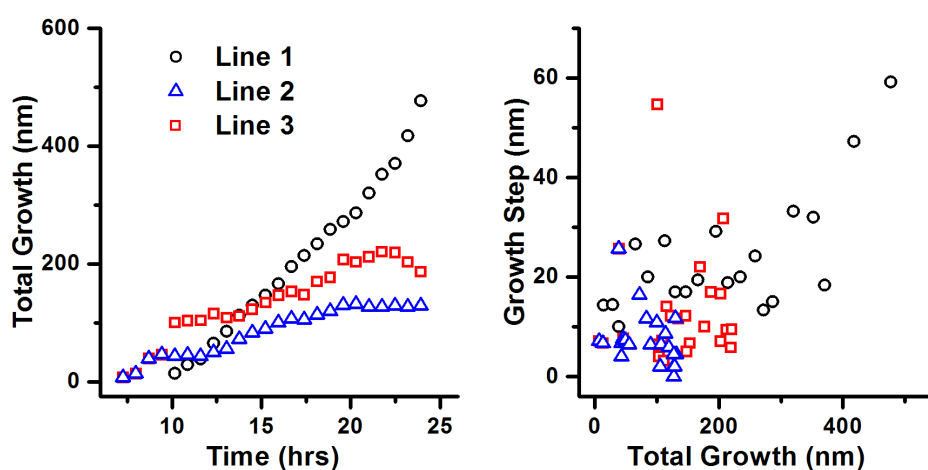
In the case of linear growth, we can assume that growth is taking place by addition of material only at the ends of the line, otherwise the rate would increase with the line length. Also, lines 1 & 2 are 'pushing' a larger particle at the end of the arrays. There will be a greater barrier to growth represented by the energy to push the larger particle another step forward. The larger particle may block material from adding at the tip of the line. Line one shows a higher growth rate, consistent with the idea that the particles at the tips of lines 1 & 2 are slowing growth. In Figure 5.1.3 (bottom) new material can be seen actively joining line 1 at the tip. In this image series there is no clear indication of why the line growth sped up. However, growth proportional to the line length shows that new material is arriving on the whole line length. As no increase in width is obvious in the images, this material may have very high mobility on the line surface, transporting it rapidly to the tip. Alternatively, the line may be undergoing collective growth: that is, each segment of the line is both expanding and being displaced by the expansion of neighbouring segments.

### 5.1.2 AREA DISSOLUTION

Large arrays were observed in many samples, with differing degrees of stability. Arrays typically appeared and disappeared on timescales of hours. A



**Figure 5.1.2:** AFM microscope image from a series showing growth along the length of arrays. Scale bar is 500 nm. Time  $t$  is in hours. **(bottom)** series of images illustrating growth of line 1; joining of dispersed material travel along an aligned trajectory. Sample was produced with the same method as used in figure 5.0.1 [94].



**Figure 5.1.3:** Growth of linear structures, either single lines or arrays. **(left)**, total length growth over scanning for hours. At  $t=0$ , scanning began on this region, whilst growing lines are plotted from when they appear in the scan region. **(right)**, Individual growth step over 0.725 hours plotted against the total line length grown.

representative set of arrays was chosen for analysis, primarily as it had the longest unbroken set of stable images. These arrays are illustrated in figure 5.1.4. At the start of imaging, all four arrays are shrinking. Array areas were measured by flood filling where possible, and by manual outlining when thresholding was not possible.

The measured areas of arrays are plotted against time in figure 5.1.5. All four arrays are steadily decreasing in area at a constant rate. Array 3 shows a 'kink' where the rate temporarily increases. The images corresponding to these times are shown in figure 5.1.4, (bottom row). A small hole-like defect emerges from the array. This is visible in the original array, and remains in the HOPG surface after the array withdraws from around it. Material around this defect is lost very rapidly, almost in one step at  $t = 3$ , and for the following steps the area drops at a higher rate. It is likely that this defect temporarily increases the rate of material loss from the array.

The linear rate of material loss from these clusters shows that the rate is not dependent on the array size. Only as array 4 is almost completely gone does the rate of material loss increase substantially. If the rate is not dependent on the size (either area or perimeter) then we can conclude that material leaving the arrays is diffusing away at a constant rate. The rate at which material leaves the array can then be identified as a limiting diffusion rate. Material must diffuse away from the array at a minimum rate in order to be consistent with the measure loss of array area. This diffusion rate can be measured in  $\text{nm}^2\text{s}^{-1}$ . Array 2 shows almost double the loss rate than other arrays. This could be due to the larger particle in the centre of the array. The



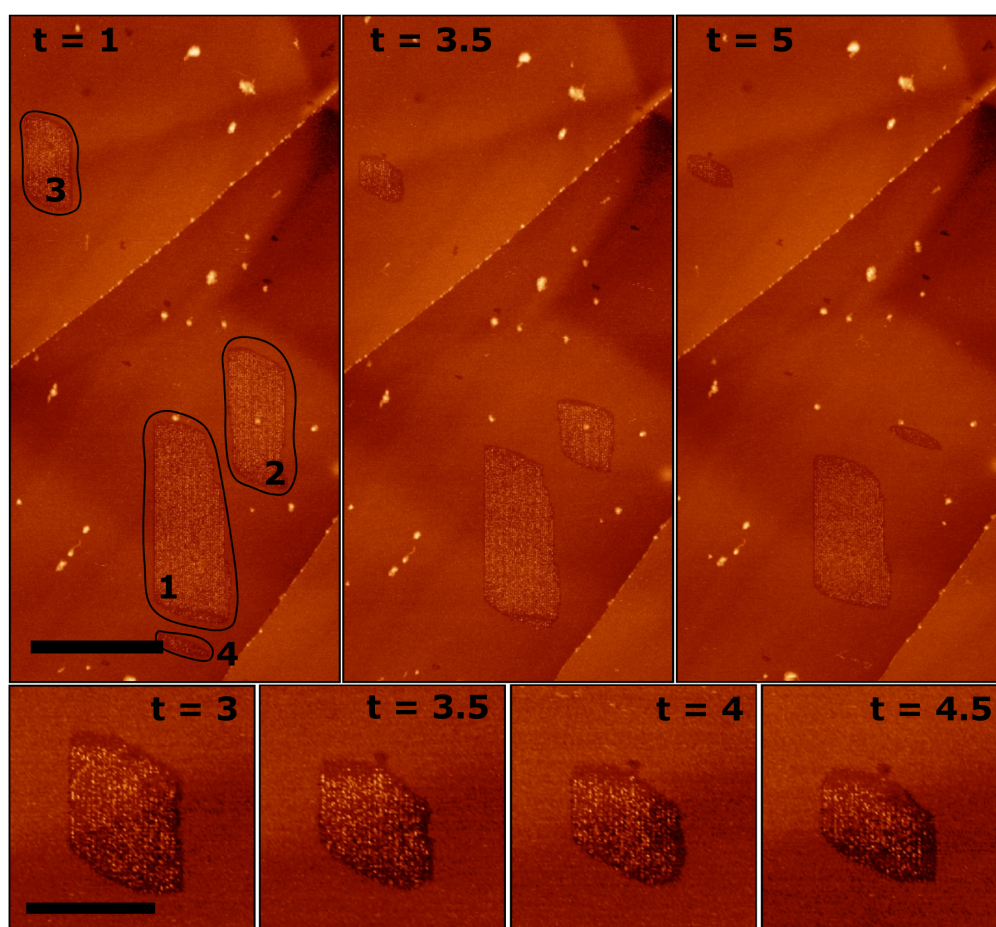


Figure 5.1.4: Arrays of nanoparticles dissipate over time whilst scanning continues. Circled Time  $t$  is in hours. Upper scale bar is 500 nm. Lower scale bar is 250 nm.

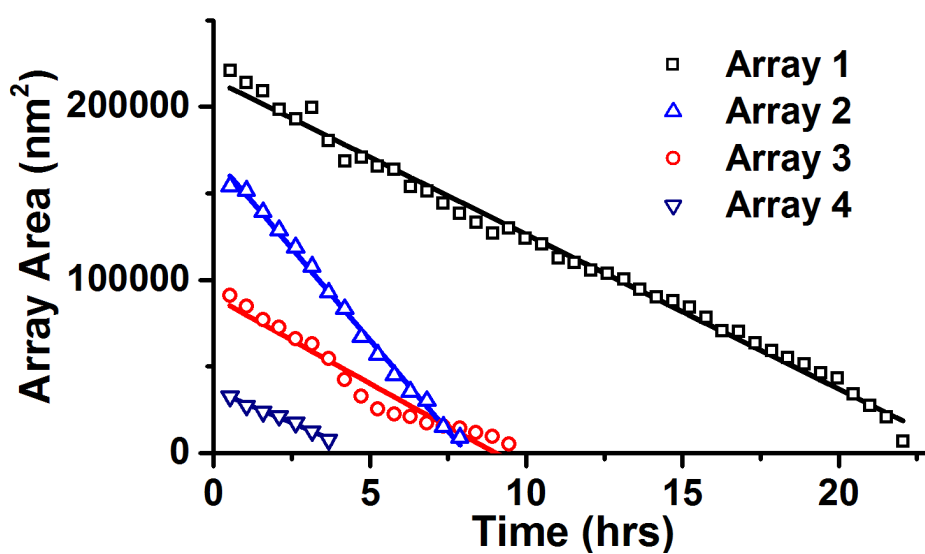


Figure 5.1.5: Area of stripe arrays over time in hours.

larger particle has a stronger interaction with the AFM tip than the particles in the array (hence the greater height.) This would transfer energy to the array, effectively heating it.

### 5.1.3 LARGE NANOPARTICLE VOLUME LOSS

The total volume of larger clusters (heights > 1.25 nm) was measured by flood filling. Any material lost from the arrays could have re-deposited on larger clusters. If that was the case, then the above theory about cluster heating would be invalid (as clusters would have to be higher temperature than the surrounding area.) It would also provide evidence for where material was transferred. The total volume of clusters is plotted against time in figure 5.1.6. Both number and volume show a very slight decrease, albeit with substantial error.

### 5.1.4 ARRAY INFILL

Finally, the filling of holes in the centre of an array was analysed. The chosen region for analysis is shown in figure 5.1.7. A large hole in the array, between two nanoparticles is filled in with new material that organises to extend the array. As the array grows, segments of the hole are cut off and separated. Hole areas were measured by flood filling below the height of the surrounding arrays. The measurements are summarised in figure 5.1.8.

This figure illustrates three major aspects of the infilling of holes within this array. The first is that, in line with measurements of other systems, the filling is linear with a constant rate. However, there is a discontinuity at



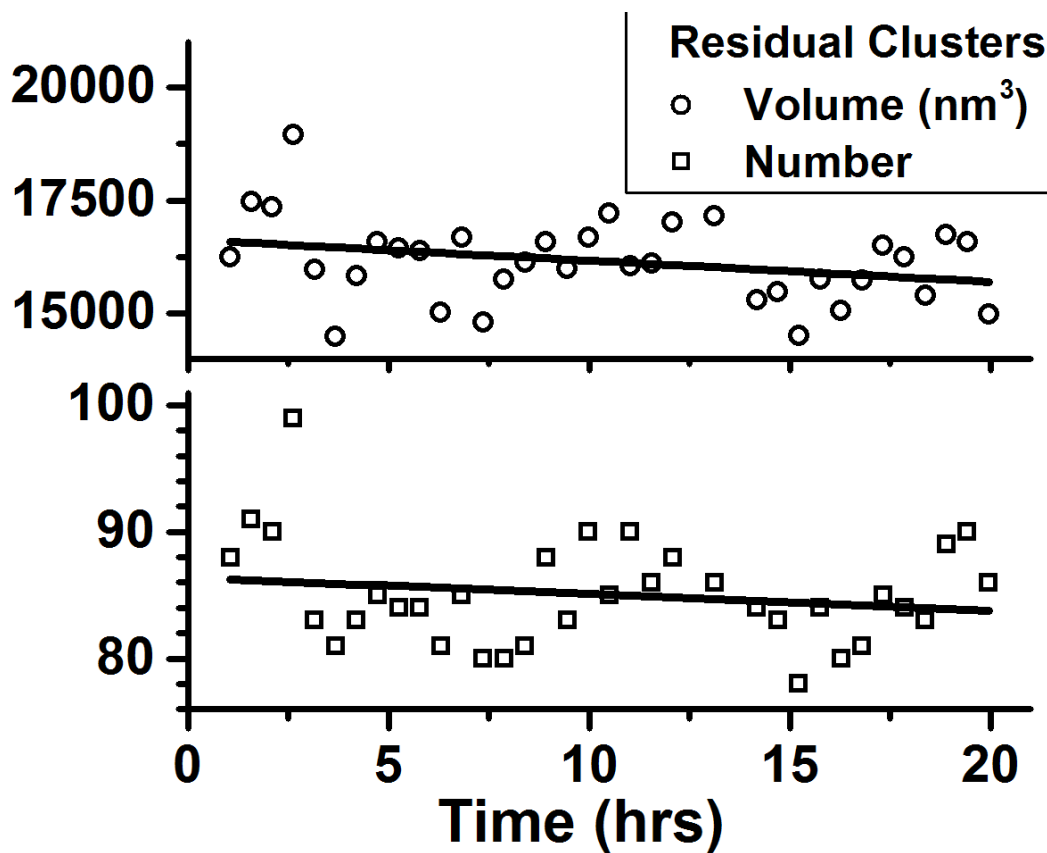


Figure 5.1.6: Total volume of large clusters and islands over time. Linear fits show a slight decrease in total volume (error in gradient =  $\pm 100\%$ ), and no increase.

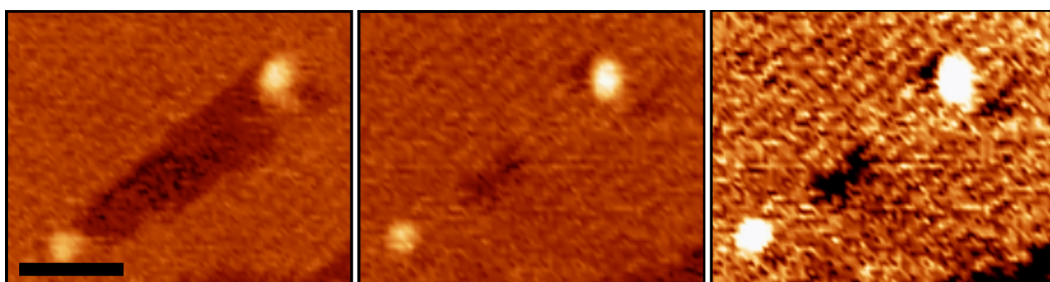


Figure 5.1.7: A large hole defect in an array is bounded by two larger nanoparticles (**left**), this defect is filled in with material which builds up and extends the array, holes are left around the upper nanoparticle (**middle**). A thresholded image, showing the hole between the particles and those around the upper nanoparticle (**right**). Note that the holes are at the same level as the substrate in the bottom right corner of all three images. Scale bar is 50 nm.

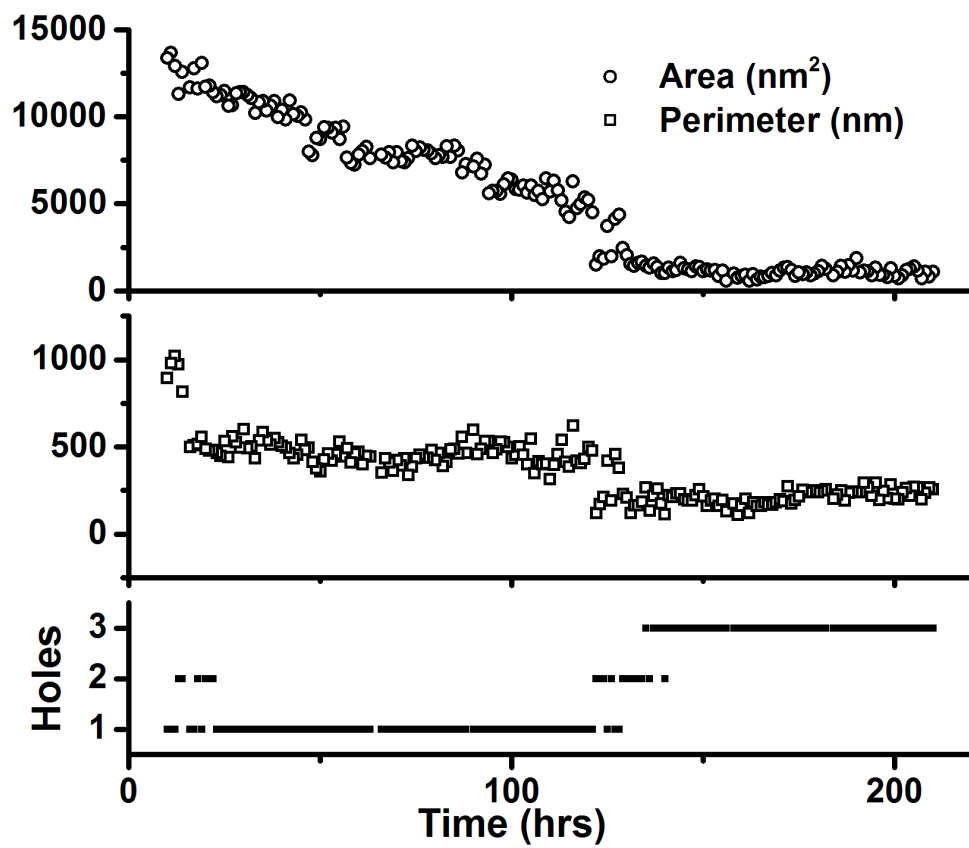


Figure 5.1.8: Area (top), perimeter (middle) and (bottom), number of separate holes evolving over time in a hole defect in a cluster array.

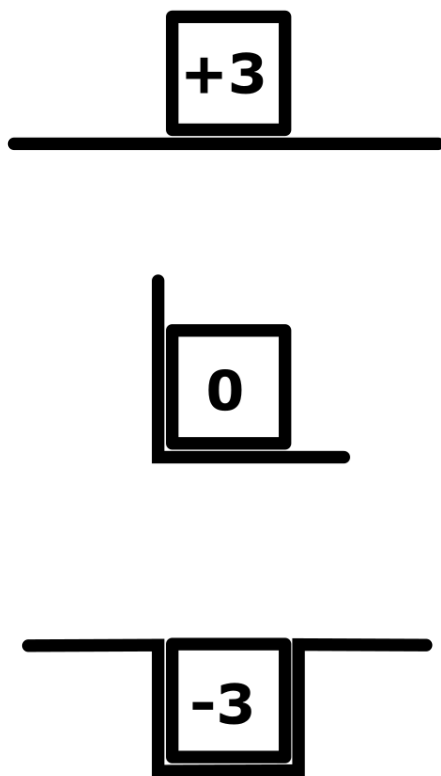
around 120 hours, where the area drops substantially, before the hole area stabilises and no further infilling takes place. Secondly, the perimeter of the holes changes via rapid discontinuities and otherwise remains approximately constant. Thirdly, the discontinuities in the perimeter occur at the same time as the number of holes changes.

The linear rate of filling indicates that this process is predominantly diffusion led - although this is less certain than the results for array dissipation, as the perimeter remains constant for most of the process. The constant perimeter can be understood by considering piecewise filling of the hole by small clusters. A small added particle will cause a linear change in area, but the net change in perimeter will depend on the position of added particles (figure 5.1.9). This will hold as long as new particles preferentially grow in array positions.

The increase in the number of holes as the holes stabilise also suggests that the holes contain defects. A mismatch defect between two arrays end to end would prevent particles from filling in the holes.

#### 5.1.5 COMPARISON OF DIFFUSION RATES

Diffusion rates from line growth, array dissolution, hole filling inside arrays and from large cluster volume loss were recorded. The diffusion rate in array and hole area changes is simply the rate of change of area. In the case of the clusters, an area was calculated by dividing the volume by the perimeter. Line growth was calculated by multiplying the line growth rate by the width of the line. For each set of measurements, this area was summed, and the gradient



**Figure 5.1.9:** The change in perimeter with addition of a single particle depends on the particle location. A particle attaching to a wall will result in a net increase in perimeter. A particle attaching in a corner results in no net change to perimeter. A particle filling a vacancy will result in a net loss in perimeter. For discrete attachment and detachment events in a linear array the approximation of a square is appropriate.

of a linear fit to data was taken as the rate of change of area.

The data is summarised in table 5.1.1. Errors quoted are calculated from the linear fit to the data, however the rates quoted are only estimates of the true diffusion rates. They obviously represent limiting values. Material must be able to diffuse at these rates, else the array dissolution or hole filling would slow down.

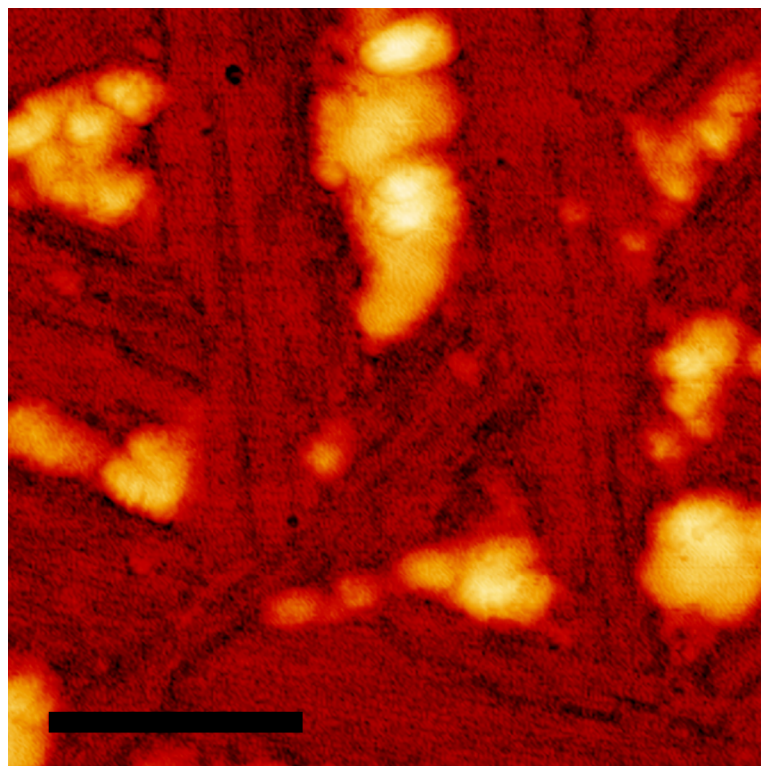
Diffusion rates of nanoparticles in this system have been measured by Koç [128], and are in good agreement with the order of magnitude of measured diffusion rates in this work. A qualitative assessment of the hole filling arrays in the same work described the linear cluster arrays as having liquid like properties, and measurements of the random walk of nanoparticles on the HOPG surface provided strong evidence for a two dimensional cluster gas constrained on the surface [128].

The data summarised in table show three distinct order of magnitudes for three different phenomena - mass lost from large nanoparticles and islands has a diffusion rate of order  $10^{-4} \text{ nm}^2\text{s}^{-1}$ . Hole filling, and hence self diffusion within arrays is of order  $10^{-2} \text{ nm}^2\text{s}^{-1}$ . This corresponds well with a model of line growth by self diffusion of material along and inside the linear structures in figure 5.1.3. Finally, the rate of dissolution of arrays has a rate of order  $1 \text{ nm}^2\text{s}^{-1}$ . This suggests the intriguing possibility that we observe three separate phases, analogous to solid, liquid and gas, in the silica cluster / HOPG surface system.

Finally, we show some new evidence that suggests that ultra-small clusters may be commonly produced with the liquid jet synthesis technique. Samples of silver co-deposited with an ethanol liquid jet, estimated concentration  $8.3 \pm 3.7 \times 10^{-1} \text{ mg/ml}$ , were diluted 5 times in ultra-pure ethanol and drop cast onto HOPG. Spaced between islands of large nanoparticles, figure 5.1.10 shows arrays of ultra-small particles filling the available HOPG surface. These

| Sample         | Rate $\text{nm}^2\text{s}^{-1}$ | Statistical Error $\text{nm}^2\text{s}^{-1}$ |
|----------------|---------------------------------|----------------------------------------------|
| Large clusters | $4.7 \times 10^{-4}$            | $3.6 \times 10^{-4}$                         |
| Hole filling   | $2.1 \times 10^{-2}$            | $4.7 \times 10^{-4}$                         |
| Line 1         | $1.7 \times 10^{-1}$            | $4.3 \times 10^{-2}$                         |
| Line 2         | $4.5 \times 10^{-2}$            | $1.1 \times 10^{-2}$                         |
| Line 3         | $6.6 \times 10^{-2}$            | $1.7 \times 10^{-2}$                         |
| Array 1        | 2.5                             | $3.5 \times 10^{-2}$                         |
| Array 2        | 2.8                             | $1.7 \times 10^{-1}$                         |
| Array 3        | 5.9                             | $1.1 \times 10^{-1}$                         |
| Array 4        | 1.6                             | $9.7 \times 10^{-2}$                         |

**Table 5.1.1:** Table of diffusion rates measured from AFM measurements of silica clusters on HOPG surfaces



**Figure 5.1.10:** Stripe arrays observed in a silver ethanol sample drop cast onto HOPG. Large silver nanoparticles are present on the surface in agglomerates. Thin, aligned layers of ultra-small particles are spread between the larger islands. Scale bar is 200 nm

particles may possibly be identifiable with the  $\text{Ag}_n$  clusters shown in chapter

3.



*"The more fondly we imagine something will last forever, the more ephemeral it often proves to be."*

Iain M. Banks, *Excession*

## 6

# Discussion and Conclusions

THIS THESIS BEGAN WITH A QUESTION, what happens when atoms of material directly mix with a liquid? I have attempted to answer this by studying the end products of the reaction, nanoparticles of silver and silicon. I have also studied the dynamics of some of these particles on surfaces, providing further evidence for the fundamental processes at work.

The growth of nanoparticles in solution is a complex and diverse field. Moreover, the stable particles formed are not truly fixed states. Instead, they are commonly in a metastable equilibrium, with exact size, structure and properties in constant flux. This equilibrium is dependent on almost every parameter of the system studied. Temperature, concentration, solvent, dissolved material, pH, the nanoparticle material and surface structure, exposure to light, all can profoundly affect the state of particles in solution.

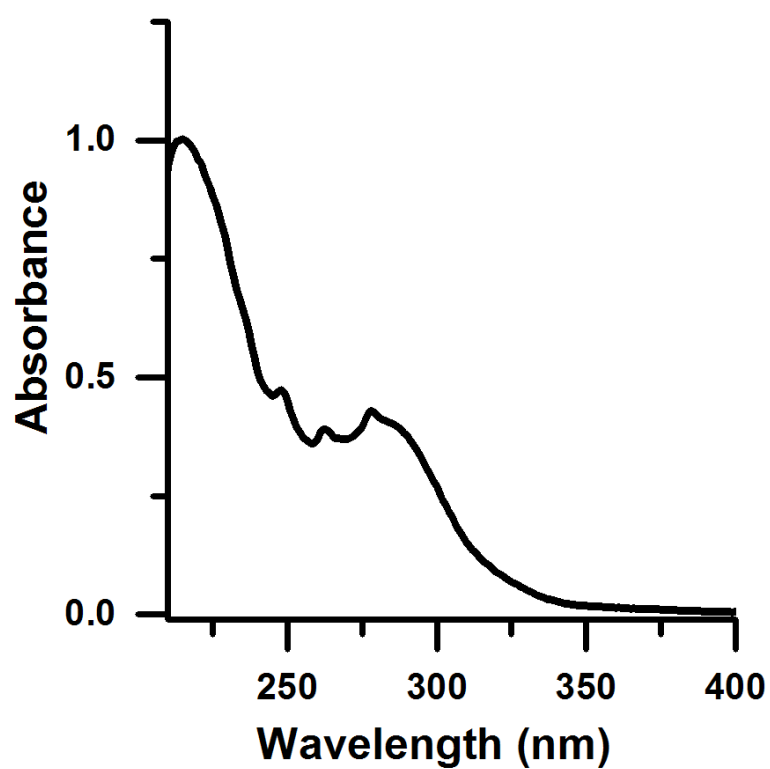
This thesis has shown that the atomic vapour co-deposition with a liquid jet is a robust method for generation of nanoparticles of metals and metal oxides. With no ingredients other than metals and solvents, fluorescent zinc-oxide, metallic silver, metallic copper, highly oxidised silica clusters and small silver clusters  $\text{Ag}_2 < n < 5$  have been produced.

The relationship between loading of material into the jet and the nanoparticle size has been explored. Sizes of metallic silver nanoparticles have a log-normal distribution. The median size of silver nanoparticles deposited in ethanol increases linearly with the logarithm of the concentration of silver mixed in the jet. This relationship apparently holds over three orders of magnitude. However, most important factor in the size of silver particles produced is the solvent used for production. Solutions in water, ethanol and isopropanol had median sizes of roughly 2, 3 and 10 nm respectively.

The size distributions and stabilisation do not appear to follow classic models for nucleation, growth and ripening. It is possible that the origins of the size distribution lie in the distribution of sputtered neutral clusters and ions.

Solvent choice may also determine what gas phase reactions are possible. However, investigating this is beyond the scope of this thesis.

The relationship between the plasmon resonance in metallic silver nanoparticles and the particle size and age is not clear. However, the ratio of plasmon peak height to width is approximately constant for a specific solvent or solution chemistry over three order of magnitude changes in silver concentration and time since sample production. Remarkably, it is possible to dramatically change the optical properties of these solutions a long time after production,



**Figure 6.0.1:** Recent experimental data provides evidence for a spectrum of stable small silicon / silica clusters generated by deposition of silicon into an ultra-pure ethanol jet. This could be a phase of clusters analogous to those present in silver samples.

as shown by samples of silver in ethanol with added citric acid.

The most important factor in determining the properties of particles of produced in a liquid jet synthesis reaction is the chemistry of the solvent or solution used. In fact, the product seems remarkably insensitive to the physical parameters of the synthesis. This shows a profound advantage of this method, it can take advantage of the enormous control and flexibility offered by chemical syntheses, but with the purity offered by vacuum technology, and free from limitations such as solubility of precursors and impurities in reagents. A direct application has been demonstrated: the formation of silver-silica heterogenous catalysts.

Studying these particles on surfaces has provided evidence for a phase of ultra-small particles, for which liquid jet synthesis may be ideal. There is evidence for an ultra-small phase in both silver and silica, from both microscopic and spectroscopic data and evidence for metal-solvent combinations which can improve selectivity for these phases.

Finally the study of silica nanoparticles on surfaces provided some evidence to support the hypothesis of a cluster fluid existing on these surfaces, with three phases analogous to solid, liquid and gas, and diffusion rates separated by 2 orders of magnitude for each phase.

Sputtering onto liquids has already been established as an effective and simple route towards metal nanoparticles. Bimetallic particles and exotic hybrids can be easily achieved [43]. To date, these techniques have been limited to dense oils, ionic liquids and other low vapour pressure liquids. Our work shows that liquid micro-jets can enable deposition into high vapour pressure

solvents such as alcohols. This represents a qualitative step forward in physical nanoparticle synthesis. With the full range of solvents, metals and semiconductors being available, synthesis options are vast. Moreover, solvents can be chosen to enable any desired material to be dissolved. We anticipate the liquid jet technique inspiring new possibilities in synthesis and leading towards the development of entirely new materials.

Some systems, such as supported catalysts [97] and fluorescent labels [129], gain functionality by addition of a small number of metal atoms. The liquid jet is ideal for enabling these syntheses, allowing material to be dissolved and atomic materials to be deposited without additional chemicals such as reducing agents or stabilising ligands complicating the synthesis.

Using only metal atoms and solvent molecules must be the simplest starting point for a synthesis of metal particles in liquids. By providing an experimental platform to realise this concept, we open the door to systematic exploration of the fundamentals of colloidal synthesis and enable future applications. Vapours of metals, alloys, ceramics and semiconductors can be readily produced in vacuum. The deposition of these into a wide range of liquids will result in the development of new nanomaterials.

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## 6.1 APPENDIX A: SILICA 2P BINDING ENERGIES

| Formula             | Si-O Energy (eV) | Si-1 Energy (eV) | Si-2 Energy (eV) | Si-3 Energy (eV) | Si-4 Energy (eV) | Article |
|---------------------|------------------|------------------|------------------|------------------|------------------|---------|
| SiO                 |                  |                  | 101.7            |                  |                  | [130]   |
| SiO <sub>0.4</sub>  |                  | 99.8             |                  |                  |                  | [131]   |
| SiO <sub>0.93</sub> |                  |                  | 101.9            |                  |                  | [132]   |
| SiO                 |                  |                  | 102              |                  |                  | [133]   |
| SiO <sub>1.02</sub> |                  |                  | 102.2            |                  |                  | [134]   |
| SiO <sub>1.05</sub> |                  |                  | 102.2            |                  |                  | [132]   |
| SiO <sub>1.19</sub> |                  |                  | 102.4            |                  |                  | [134]   |
| SiO <sub>1.24</sub> |                  |                  | 102.4            |                  |                  | [132]   |
| SiO <sub>1.35</sub> |                  |                  |                  | 102.7            |                  | [132]   |
| SiO <sub>1.52</sub> |                  |                  |                  | 102.8            |                  | [134]   |
| SiO <sub>1.49</sub> |                  |                  |                  | 102.8            |                  | [132]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103              | [135]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103              | [136]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103              | [137]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.04           | [138]   |
| SiO <sub>1.78</sub> |                  |                  |                  |                  | 103.1            | [132]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.1            | [139]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.1            | [140]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.2            | [141]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.2            | [142]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.2            | [143]   |
| SiO <sub>1.8</sub>  |                  |                  |                  |                  | 103.2            | [138]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.3            | [144]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.3            | [145]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.4            | [146]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.5            | [147]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.5            | [148]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.6            | [146]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.6            | [149]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 103.6            | [150]   |
| SiO <sub>2</sub>    |                  |                  |                  |                  | 104              | [151]   |
| Si                  | 99.6             |                  |                  |                  |                  | [152]   |
| Si                  | 99               |                  |                  |                  |                  | [152]   |
| Si                  | 99.6             |                  |                  |                  |                  | [153]   |
| Si                  | 99.6             |                  |                  |                  |                  | [154]   |
| Si                  | 98.9             |                  |                  |                  |                  | [155]   |
| Si                  | 99.22            |                  |                  |                  |                  | [156]   |
| Si                  | 99.1             |                  |                  |                  |                  | [157]   |
| Si                  | 99.3             |                  |                  |                  |                  | [158]   |
| Si                  | 99.2             |                  |                  |                  |                  | [136]   |
| Si                  | 99.59            |                  |                  |                  |                  | [159]   |
| Si                  | 99.61            |                  |                  |                  |                  | [159]   |

## 6.2 APPENDIX B: CODE FOR SHIRLEY BACKGROUND SUBTRACTION

```
#####
# Shirley Baseline for XPS #
# Mike McNally #
# Based on iterative fitting #
#####

#Define Functions
#Returns the first iteration of a Shirley background vector
#of length npt from data vector IData with Energy spacing EInterval
# p[1] = low energy point
# p[2] = constant

ShirleyA <- function(p) {
  Base <- vector()
  Base <- p[1] + cumsum((p[2]*((EInterval/2)
* (IData[-npt] + (diff(IData)/2) - p[1]))))
  Base <- append(Base,Base[npt-1])
  return(Base)
}

#Returns the nth iteration of Shirley background where
#IData is the data vector and vector BaseA is iteration n-1
ShirleyN <- function(p) {
  Base <- vector()
  Base <- BaseA[-npt] + cumsum(p[1]*((EInterval/2)
* (IData[-npt] + (diff(IData)/2) - tail(BaseA,length(BaseA)-1))))
  Base <- append(Base,Base[npt-1])
  return(Base)
}

#Returns the mean square deviation of data vector BaseB
#from Shirley background with params p for first and last "range" pts
ShirleyfitA <- function(p) {
  Endvars <- 0.5 * (mean((IData[1:range] - ShirleyA(p)[1:range])^2)
+ mean((IData[(npt-range):npt] - ShirleyA(p)[(npt-range):npt])^2))
  return(Endvars)
}

#Because R isn't C++ and I'm too lazy to look up how
#I might make function classes / objects or whatever
ShirleyfitN <- function(p) {
  Endvars <- 0.5 * (mean((IData[1:range] - ShirleyN(p)[1:range])^2)
+ mean((IData[(npt-range):npt] - ShirleyN(p)[(npt-range):npt])^2))
  return(Endvars)
}
```

```

}

#read data
Data <- read.table("./Table.dat", header=FALSE, as.is=TRUE, sep=",")

#set up data

E <- Data$V1
I <- Data$V2

E <- rev(E)
I <- rev(I)

IData <- I

#set up initial parameters

range <- 200

npt <- length(E)

EInterval <- E[1]-E[2]

IEndA <- mean(I[1:500])

ConstA <- 0.1

A.0 <- c(IEndA, ConstA)

NLM <- nlm(ShirleyfitA, A.0)

A.1 <- NLM$estimate

B.0 <- 0.05

nloop <- 1

BaseA <- ShirleyA(A.1)

while(nloop > 0) {

nloop <- nloop + 1

NLM <- nlm(ShirleyfitN,B.0)

```

```

B.O <- NLM$estimate

BaseA <- ShirleyN(B.O)

if (nloop > 10) {break}

}

plot(E,I)

lines(E,ShirleyN(B.O))

IData <- I - ShirleyN(B.O)

plot(E,IData)


pak <- matrix(nrow=length(E),ncol=2)

pak[,1] <- E

pak[,2] <- IData

write.table(pak, file = "Output.dat", append = FALSE, quote = FALSE, sep = " ",
            eol = "\n", na = " ", dec = ".", row.names = FALSE,
            col.names = FALSE, qmethod = c("escape", "double"),
            fileEncoding = "")

```

# Colophon

**T**HIS THESIS WAS TYPESET using  $\LaTeX$ , originally developed by Leslie Lamport and based on Donald Knuth's  $\TeX$ . The body text is set in 12 point Tide Sans, a humanist sans font designed by Kyle Wayne Benson. This template, which can be used to format a PhD thesis with this look and feel, is based on the Harvard thesis class, released under the permissive MIT (x11) license, and can be found online at [github.com/suchow/](https://github.com/suchow/) or from the author at [suchow@post.harvard.edu](mailto:suchow@post.harvard.edu).