

Chapter 1

Electrochemical Fabrication of Spherical AuNP-Tipped AFM Probes

As discussed in the previous chapter, nanostructuring a tip can create the necessary geometry and electromagnetic interfaces (**increased electromagnetic density of states**) to support far-field antenna modes. This enables the coupling far-field light into plasmons and can improve the plasmonic performance of such tips. Consequently, this means that excited plasmons scatter into the far-field and are therefore observable. This is an important property when using tips to measure fundamental plasmonics. To this extent, one of the major aims of this project is to produce robust nanostructured, plasmonic tips. The spherical geometry is targeted for its simplicity.

Fabrication of spherical tips for plasmonics has been achieved by mounting single nanoparticles onto the apex of a tip. This concept has been reported numerous times over the last decade [**gan2007**], beginning with the use of fibres as mounting structures [**kalkbrenner2001**, **barsegova2002**, **sqalli2002**, **kawata2003**] and progressing onto the use of scanning probe microscopy (SPM) tips [**umakoshi2012**, **hayazawa2012**, **park2012**, **okamoto2001**, **vakarelski2006**]. Whilst mounting nanoparticles onto SPM tips is more difficult than with fibres the additional capabilities of the SPM tip have made such tips desirable. However, these tips typically require complicated assembly processes to precisely secure a single nanoparticle at the apex of the tip, greatly increasing their fabrication time and costs. More recent methods have attempted to address the complexity issue by directly depositing nanoparticles onto the apex by exploiting localised chemical reactions. However, these techniques have still been limited by cost or required specialist equipment [**sqalli2002**, **okamoto2001**], incompatible with SPM probes [**kharintsev2013**, **barsegova2002**] or subject to limitations in nanoparticle growth, either in size [**cheng2013**] or material [**umakoshi2012**]. To date it is still a challenge to simply and efficiently produce spherically nanostructured tips. This chapter describes a simple method developed to produce spherical nanoparticle tips using apex-selected electrochemical growth. The process of electrochemistry is first described followed by discussion of the original method

of tip production and its limitations. A second method is then discussed, addressing the issues with the original method and showing how they can be circumvented but at the cost of production rate.

1.1 Electrochemical Growth - The Theoretical Background

Electrodeposition is a method of electrochemistry, the study and application of chemical reactions occurring on the surface of an electrode that are either caused by or generate an electrical current. In general, this requires two electrically connected electrodes, submerged in an ionic solution (a.k.a. electrolyte), with a potential difference. Depending on the electrode potential, and how it compares with the energy required to activate a specific chemical reaction between ionic species, ions are either used or created at the electrode-electrolyte interface through the addition or removal of electrons, respectively. Connecting electrodes enables the transfer of excess electrons donated at one electrode to fill the electron deficit at the other electrode. An electrochemical cell reaction is therefore split into two half reactions to necessitate electron capture and generation processes, with one occurring at each electrode. These processes are known as *oxidation* and *reduction* reactions, which combine to form an overall *redox* reaction. Oxidation occurs at the anode whereby a half reaction is achieved by donating electrons to the electrode. Electrons are then removed from the cathode as positive ions undergo reduction. The rate of both half reactions dictates the rate of electron capture and generation therefore the current flow between electrodes is a measurable representation of the underlying reaction. For this reason electrochemistry is a powerful technique, containing a direct method of directly monitoring the state of a chemical process.

Each oxidation and reduction reaction has an associated standard potential, E^0 , characterising the potential required to add or remove an electron from the chemical species. Chemical species with highly negative standard potentials can readily donate electrons and are known as reducing agents. Chemical species with highly positive standard potentials are more likely to be reduced and are therefore known as oxidising agents. In general, having $E^0 < 0$ means the chemical species is highly likely to dissociate into an ionic while $E^0 > 0$ means a chemical species is more likely to be found in a charge neutral or lesser charged state.

Depending on cell conditions, electrochemistry works in many different ways. In a solution supporting ionic transport with two different material electrodes there is an inbuilt voltage generated by the difference in standard potentials. Electrons move to equilibrate the potential and the resulting current can be used to power an external load. This is the battery effect.¹

¹Consider the example of a battery constructed of a Zn cathode and Cu anode in a $\text{Cu}_2\text{O}/\text{Zn}_2\text{O}$ electrolyte connected via a salt bridge. The half reactions are $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ ($E^0 = 0.339\text{ V}$) and $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ ($E^0 = -0.76\text{ V}$) with an overall reaction $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Cu} + \text{Zn}^{2+}$. The potential of this

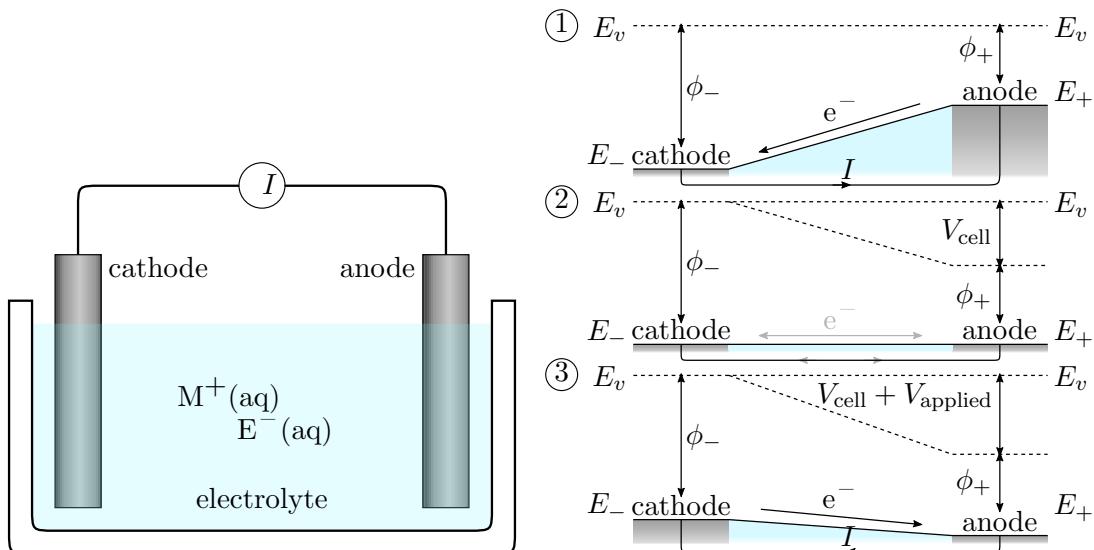
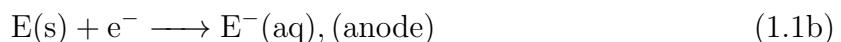
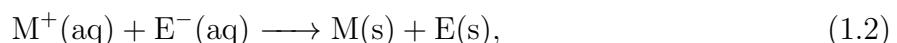


Figure 1.1: Schematic and energy level diagrams of an electrochemical cell. (a) Diagram of an electrochemical cell, showing two electrodes are submerged in an ionic solution. Depending on the potential, ions can either be oxidised or reduction at each electrode-electrolyte interface, generating a current between electrodes. (b) Energy level diagram of the electrochemical process (right). An initial difference in the Fermi levels of the cell, caused by a difference in the work functions of each electrode, means charge flows to equilibrate the Fermi levels (1 → 2). This is the battery effect. The cell can be biased with an applied voltage to initiate electrochemical reactions (2 → 3).

Electrodeposition is an opposite effect caused by applying a voltage across a cell. If both cell half potentials are overcome a redox reaction is activated. Ions from the solution are reduced onto the cathode surface as a complementary oxidation occurs at the anode. This is the basis of electroplating. Equations representing each half reaction are given by,



where M represents a metal and E an electrolyte. Metallic ions are reduced on the surface of the cathode whilst the complementary oxidation donates electrons at the anode. The overall reaction can be considered to be,



where the electrodes mediate the reaction. The electrochemical cell voltage of this overall reaction is given by the difference of the half reaction standard potentials,

$$E_{\text{cell}}^0 = E_{\text{ox}}^0 - E_{\text{red}}^0. \quad (1.3)$$

reaction is $\phi_{Cu} - \phi_{Zn} = 0.339 - -0.76 = 1.099 \text{ V}$.

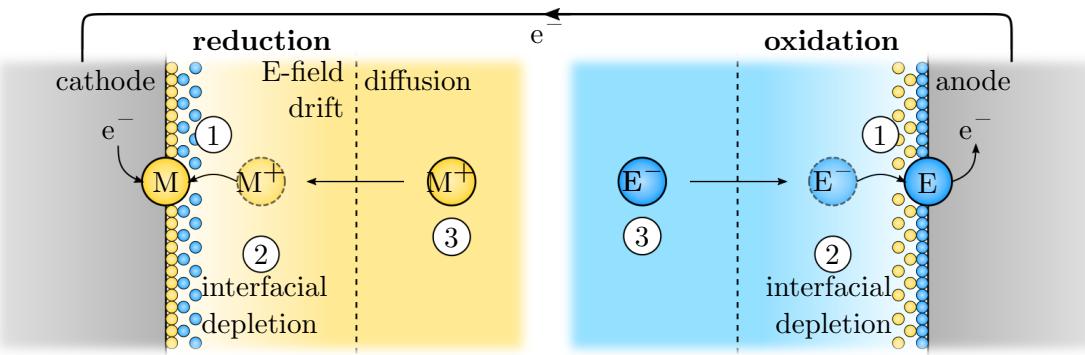


Figure 1.2: Diagram of the electrodeposition process over time. Metallic ions initially at the interface are completely reduced at short time scales (1). Nearby ions drift to the surface following the field lines. Accumulation of the surface charge at the electrode leads to attraction of a diffuse layer of the oppositely charged ion, partially screening the local field. Depletion of ions in the vicinity of the surface (2) creates a concentration gradient. Further growth is limited by diffusion (3). The balance between drift-limited and diffusion-limited growth is determined by the concentration of the solution.

The rate at which each half reaction occurs depends on the work functions of the two electrodes and the electric field between them. Work functions dictate which reactions are possible. A potential needs to be applied to correctly bias the electrode to overcome the activation energy and allow a reaction. This allows metallic ions situated at or near the cathode interface to be reduced whilst electrolyte ions on the anode surface oxidise. The accumulated surface charge at the electrode surface (unreacted ions) attracts a more diffuse layer of oppositely charged ions. This is known as the *electrical double layer* and partially screens the local field. After these initial reactions the reaction rate is set by the rate at which either ions or electrons arrive at each interface. The electronic rate depends on the current limit whilst the rate of ion movement is dictated by the electric field and the ion concentration. Nearby ions follow the field lines to the electrode surface where they can react. Depletion of ions used in reactions also leads to the formation of a concentration gradient towards the electrode. Ions then diffuse to these regions. The reaction rate then depends on if the reaction is *diffusion-limited* or *drift-limited*. Each case is determined based on the current ionic velocity components. In analogy with semiconductor physics the current density is given by,

$$\mathbf{J} = q(n\mu_i \mathbf{E} + D\nabla n), \quad (1.4)$$

where q is the ion charge, n is the number density of charges, μ_i is the charge mobility and D is the coefficient of diffusion, therefore $v_{\text{drift}} = n\mu_i \mathbf{E}$ and $v_{\text{diffusion}} = D\nabla n$. Drift depends on the charge carrier concentration and the electric field whereas diffusion depends only on the concentration gradient. Each component can therefore be controlled using the field strength and solution concentration. If the drift velocity is small compared to the diffusion velocity

then the reaction is diffusion-limited and can be controlled by varying the concentration of the cell solution. Alternatively, if the diffusion velocity is small compared with the drift velocity, for example in the presence of a large field, then the reaction is field- or drift-limited. Due to charge conservation the rate of reaction depends on the minimum rate of either the oxidation or reduction reactions. For deposition the minimum rate is ideally set by the rate of reduction.

1.1.1 Experimental Electrodeposition of Au

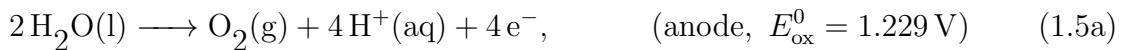
Electrodeposition is the process used to fabrication AuNP AFM tips. The metallic ions undergo reduction and solidifies while the electrolyte oxidises on the counter-electrode, thus depositing a metallic growth. The dynamics of deposition depend heavily on the potential (electric field), the exposure time and the electrode/cell geometry. Much care has gone into optimising this process to controllably coat an object used as an active electrode in a layer of metal. In this case the technique is typically renamed 'electroplating'.

In experimental electrochemistry a potentiostat is used to apply or measure a potential between two electrodes whilst also measuring the current through the cell. A reference electrode, with a well-known potential, is used to determine the individual potential of the working (active) electrode relative to the solution. The simplest reference electrode is the standard hydrogen electrode (SHE), however many other options exist, including the saturated calomel electrode and the Ag/AgCl electrode. The dissociation of hydrogen into an electron and a proton is set at 0 V therefore most electrochemistry methods reference their potentials relative to a SHE, even when using a different reference electrode. A disadvantage to using solution based reference electrodes is their large impedance, which significantly reduces their response time and therefore the temporal bandwidth of potentiostatic measurements. When high bandwidth measurements (high temporal resolution) are required it is necessary to use a Pt reference electrode [sawyer1995electrochemistry]. The large conductivity of the noble metal means the bandwidth is large and Pt is inert to most reactions making it acceptable as a reference point.

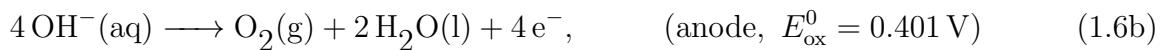
There are many available precursor solutions for depositing Au. A simple precursor is AuCl_3 but is not particularly widely used. Many of the available solutions, however, are cyanide based (e.g. AuCN), which pose significant health risks. Sulphite-based solutions ($\text{Au}(\text{SO}_3)_2^{3-}$) on the other hand are less hazardous at the cost of deposition quality. One of the most widely used Au precursor electrolytes is the commercial ECF60 solution from Metalor, a safe-use sulphite-based solution. A smooth quality of the deposition morphology is typically achieved by depositing in a low-potential (diffusion-limited) regime and using additives, known as brightener, to achieve smoother coatings. However, when depositing nanostructures, additives are not necessary since the amount of Au deposited is typically very small. Additionally, ECF60 contains water therefore dilution is simple, giving control of the

concentration of Au ions. Its water content also means that a water splitting half reaction occurs at a Pt counter electrode at low potentials to donate electrons to the circuit.

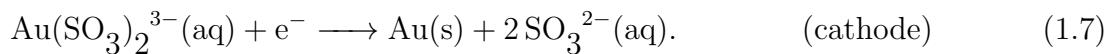
Assuming a typical metallic reduction reaction (since the actual composition of ECF60 is proprietary), two sets of possible half cell reactions are [haynes2013crc],



and,



which both result in a redox reaction of $2 \text{H}_2\text{O(l)} \longrightarrow 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g})$. The standard potential of (1.5a) is $E_{\text{ox}}^0 = -1.23 \text{ V}$ ($E_{\text{red}}^0 = 1.23 \text{ V}$ for (1.6a)). In general, both these reactions occur simultaneously with a build up of H^+ at the anode and a build up of OH^- at the cathode. Electrons produced in this reaction in ECF60 solution also have a chance to reduce Au ions in the solution via (assuming sulphite ions),



The standard potential for this reaction is $E_{\text{red}}^0 = 0.111\text{--}0.116 \text{ V}$ [green2007gold]. Since this occurs purely at the cathode it competes with the reduction of water. The oxidation of water is then the dominant method of electrolysis leading to a buildup of H^+ in the solution. Growth should then occur on application of a potential -1.341 V , or higher with increased temperature.

Electrochemical deposition is highly suited to the tip geometry because of the large field enhancement localised at the sharp point. Due to the significantly reduced radius of curvature at the tip apex, the equipotential surface resulting from an applied voltage leads to compression of field lines in the region. This strongly increases the field amplitude at the tip apex and is known as the lightning rod effect. Under such conditions the rate of electrochemical reactions is significantly increased around the vicinity of the tip apex. By exploiting this localised field enhancement it is possible to grow a spherical nanoparticle directly onto the tip apex. Whilst use of the lightning rod effect for electrochemical growth has been used to grow dense forests of nanoparticles [tian2006, yang2011] it has yet to be applied to the fabrication of single nanoparticles at the tips apex. A disadvantage of electrochemical deposition is that it is difficult to selectively grow nanoparticles on the tips. Here by using single-pulse high-field electrochemical growth, we selectively grow nanoparticles on the tip apex. Using

this approach we demonstrate an efficient, high-throughput technique for reliably producing metallic spherical nanoparticle tips using only a simple electrochemical cell.

When aiming to grow a nanoparticle at the apex of an AFM tip the objective is not to obtain an even coating, hence well-documented techniques such as electroplating are not of use. Growth must be initially completely field dependent, taking advantage of the tip's lightning rod effect, but not over sufficient time that the smoothing of the apex curvature reduces the field and diverts growth around the resultant neck.

1.2 Initial Fabrication of Spherical AuNP-Tipped AFM Probes

A simple initial method is used to successfully demonstrate that a spherical AuNP can be electrochemically grown at the apex of a metallic AFM probe tip. Fabrication of spherical AuNP tips onto commercial AFM probes (BudgetSensors GB/E series) is achieved using single-pulse high-field electrochemical growth. Conductive coatings are required for the electrochemical reaction, therefore Au- and Pt-coated AFM tips are used. The adhesion of molecular layers can prevent deposition of Au therefore tips must be cleaned thoroughly prior to deposition. Tips are pre-treated with 20 min oxygen plasma to remove organic contaminants from the surface prior to growth. A simplified two-electrode system (AutoLab PGSTAT 302N potentiostat) is employed for growth since both the cell geometry and electrodeposition solution are kept the same between fabrications. AFM probes are attached to fluorine-doped tin oxide (FTO) conductive glass, used as a working electrode, opposite a Pt wire counter-electrode, spaced 10 mm

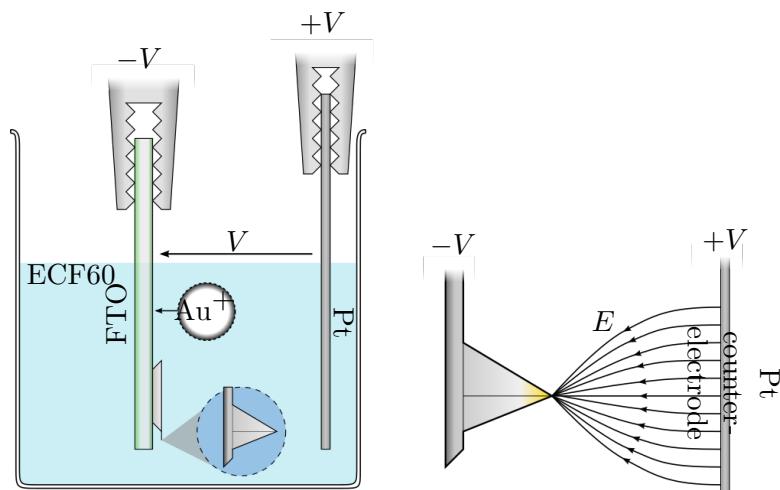


Figure 1.3: Experiment geometry for pulsed electrochemical deposition of Au onto an AFM tip. Electrochemical cell for growth of Au onto the apex of an AFM tip. Termination of field lines at tip apex due to the lightning rod effect enhances localised electrochemical growth for single NP growth.

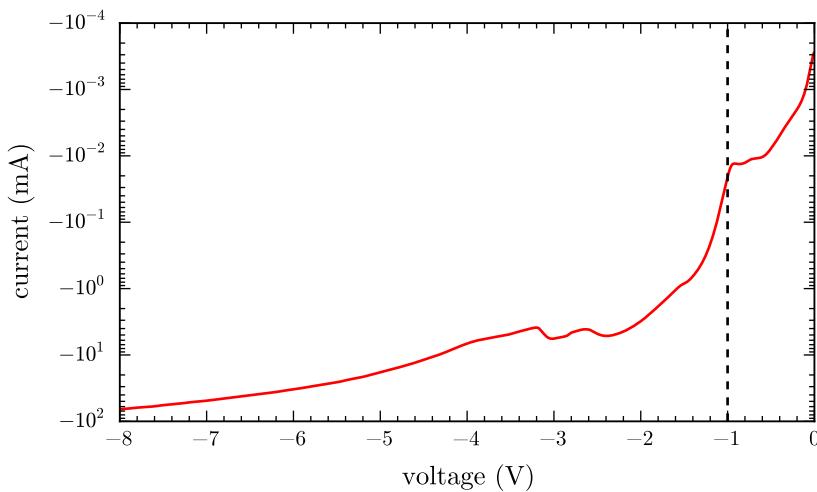


Figure 1.4: Linear sweep voltammetry of a single AFM cantilever in ECF60. The AFM probe is held by an Al clamp cathode out of solution, replacing the standard FTO electrode to show growth characteristics of only the tip. The remaining geometry is the same as in Figure 1.3.

apart (Figure 1.3). FTO glass is cleaned through sonication in 10 min steps using de-ionised water, ethanol and finally acetone. Metalor ECF60 is used as the electroplating solution with no additives. Simultaneous fabrication of both Au and Pt tips is carried out by contacting multiple tips, closely spaced side-by-side on the same FTO surface.

Linear sweep voltammetry of a single AFM tip in ECF60 (Figure 1.4) shows that Au growth starts at -1.1 V . This is similar to the predicted reaction potential for the reduction of Au and the oxidation of water. The increased potential is expected due to working at room temperature.

A single high-voltage pulse is applied to nucleate and grow a single AuNP at the tip apex. Due to the large field amplitude at the tip apex, field lines from across the cell terminate at the apex inducing ions to drift towards the tip (Figure ??b). Multiple combinations of applied voltage and pulse time were investigated to optimise growth parameters. The growth of Au onto the AFM tip is confirmed by current dynamics, revealing a 2–3 ms initiation followed by relaxation to continuous diffusion-limited growth within a few 10s of milliseconds. SEM imaging, carried out on a LEO GEMINI 1530VP FEG-SEM Scanning Electron Microscope, is used to characterise the resulting growth morphology.

SEM images of four tip samples fabricated at -8 V are shown in Figure 1.5, three of which were fabricated simultaneously on one FTO glass slide, to show the effects of tip pre-treatment and exposure time in the applied field. These images demonstrate that spherical AuNP tips can be reliably fabricated using the proposed electrodeposition procedure. Spherical AuNP growth diameters between 150–450 nm are achieved using 100–200 ms pulses across the electrochemical cell on both Pt and Au tips. Evidence of growth localisation to the high field regions is clearly exhibited by the formation of spherical AuNPs at the tip apex. The morphologies obtained

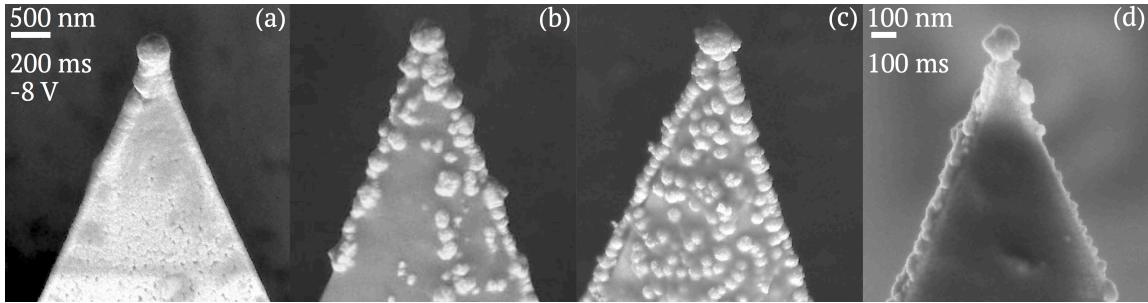


Figure 1.5: Comparison of AuNP-tipped AFM probes, fabricated on various base structures using -8 V pulses of different lengths. The first three tips were produced simultaneously using a 200 ms pulse on (a) a commercial Pt tip with no pre-treatment, (b) a plasma-treated Pt tip, (c) a plasma-treated Au tip. (d) Duplicate spherical tip produced separately on a plasma treated Pt tip using a 100 ms pulse.

differ with and without plasma pre-treatment. Using tips as supplied leads to a smooth sphere at the tip apex resulting from the lightning rod effect, followed by a broad neck and semi-uniform Au coating across the exposed surfaces of the tip (Figure 1.5a). Plasma treatment removes organic contamination and can also oxidise the surface [li2003, fuchs2009]. Removal of contaminants prevents growth at defect sites. The formation of an insulating metal oxide layer prevents growth on surfaces, limiting growth only to sharp regions with a small radius of curvature (Figure 1.5b–d). These regions remain conductive and the electric field is large and highly localised. Because Au is more difficult to oxidise than Pt, the shielding effect is different for plasma-treated Au-coated AFM probes, which exhibit significant localised nanoparticle growth on all exposed surfaces (Figure 1.5c). A longer pulse time can result in a bigger diameter of spherical AuNP, as shown in Figure 1.5b and Figure 1.5d. A 200 ms pulse growth leads to a spherical AuNP on the Pt tip with a diameter of $\sim 450\text{ nm}$ (Figure 1.5b), while the diameter of the AuNP is 150 nm with a 100 ms pulse (Figure 1.5d).

To investigate the dependence of fabricated tip morphology on the pulsed voltage across the electrochemical cell, the growth of AuNP on Pt tips at different applied voltages is further studied. SEM images of such fabrications along with corresponding current transients are shown in Figure 1.6. Images show that apex-selected growth occurs only once the voltage is more negative than -3 V . This voltage dependence is attributed to changes in deposition mechanism with field strength. At low voltages ($\geq -2\text{ V}$), electrodeposition forms smooth film coatings (Figure 1.6b) similar to direct-current electrodeposition. Under these conditions growth is dominant over nucleation and the field profile caused by the lightning rod effect is eventually evened out, yielding smooth rounded tips. Even with 500 ms exposure time no apex-selective growth is observed despite the charge transfer being equivalent to AuNP tip growths at more negative potentials.

The electrodeposition morphologies on tips fabricated at potentials more negative than -2 V can be understood to a certain degree by considering the most common nucleation

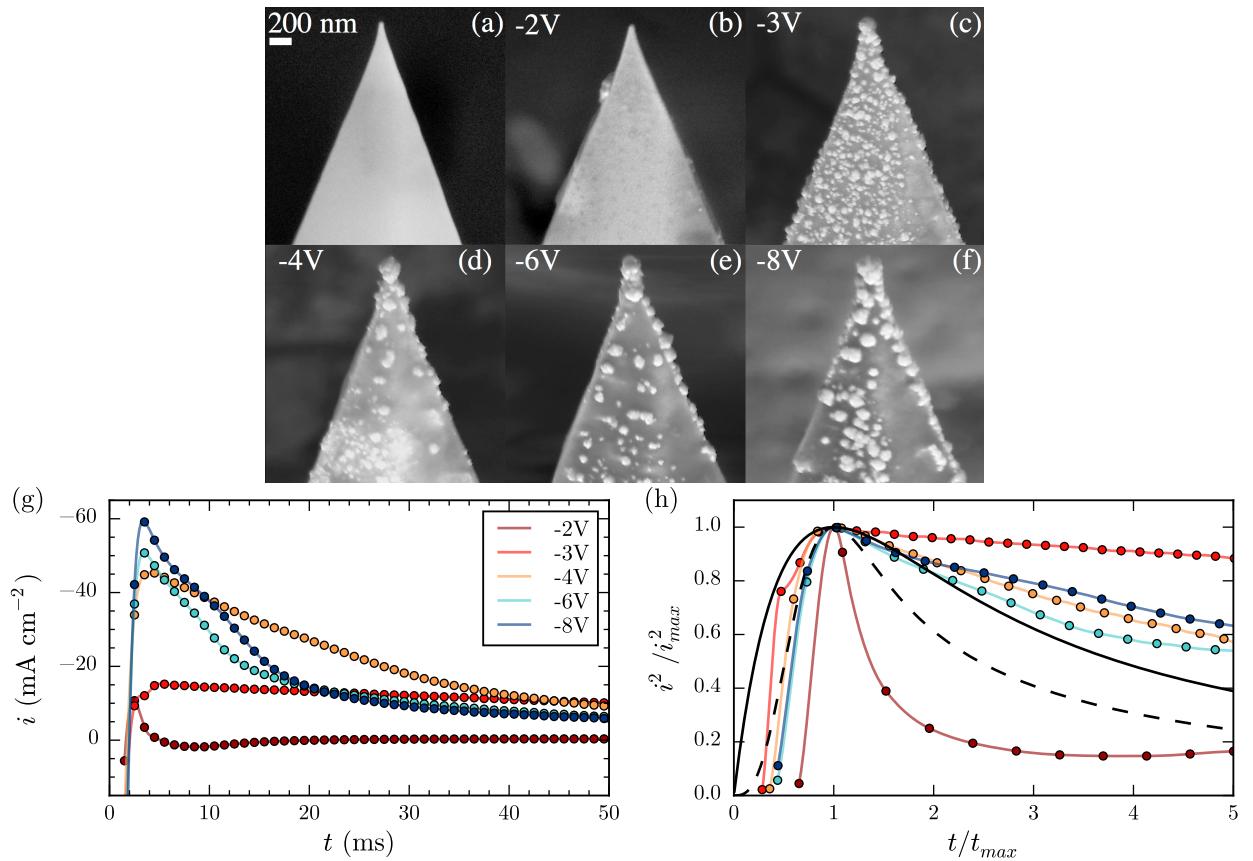


Figure 1.6: Voltage dependence of pulsed electrodeposition onto Pt tips. Comparison between a standard Pt AFM tip (a) and AuNP growth on plasma-treated Pt tips (b-f) using 150 ms pulses for voltages between -8 and -3 V and a 500 ms pulse at -2 V. This shows the change in deposition mechanism as the magnitude of applied field strength is increased, with no spherical growths above -3 V irrespective of exposure time. (g) Current transients from current traces measured during fabrication of tips shown in (b-f), offset by the saturation current density (-10 , -31 , -34 , -78 , -142 mA/cm 2 , respectively). (h) Variable-independent reduced current transients (coloured lines) measured at various applied voltages during fabrication compared with theoretical curves for progressive (dashed) and instantaneous (solid) nucleation current transients [scharifker1983].

mechanisms known from AuNP growth on planar electrodes [scharifker1983]. These are progressive and instantaneous nucleation. During progressive nucleation, nuclei form at a time t then grow, increasing the size of the diffusion zone around them, thereby preventing further nucleation within that zone. At the end of progressive nucleation there are many nuclei of different sizes due to the different times at which they originally nucleated. During instantaneous nucleation all nuclei are nucleated at $t = t_0$ and then grow at the same rate until their diffusion zones overlap. The overlap of diffusion zones stunts growth as the finite ion flow is split between the two nuclei. For a sparse distribution of nuclei the end result is ideally a set of equally sized particles. The current transients for progressive and instantaneous nucleation

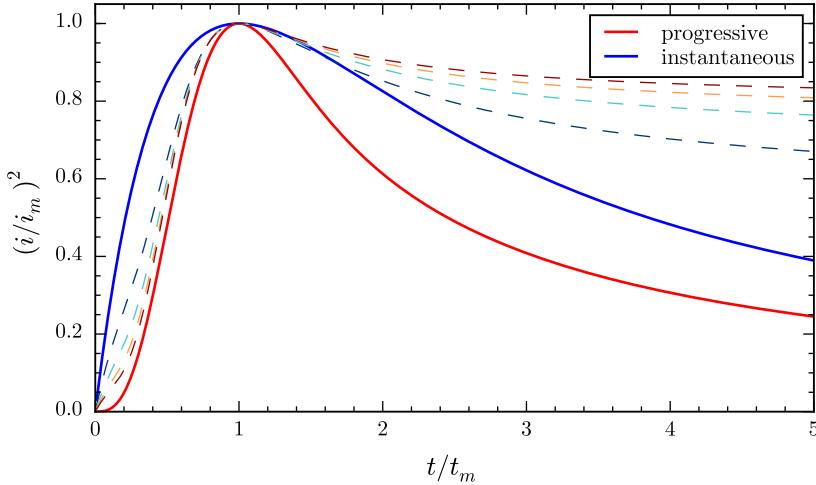


Figure 1.7: Reduced current transients for the two extremes of nucleation [sharifker1983]. The normalised current, $(i/i_m)^2$, is plotted as a function of time normalised to the maximum, t/t_m . Dashed lines show reduced transients from linear transitions between instantaneous nucleation, assuming instantaneous nucleation occurs first then decreases.

are given in the Scharifker and Hills model by,

$$\left(\frac{i}{i_{\max}}\right)^2 = \frac{1.2254}{t/t_{\max}} \left[1 - e^{-2.3367(t/t_{\max})^2}\right]^2, \quad (1.8)$$

and.

$$\left(\frac{i}{i_{\max}}\right)^2 = \frac{1.9542}{t/t_{\max}} \left[1 - e^{-1.2564(t/t_{\max})}\right]^2, \quad (1.9)$$

respectively, where t_{\max} is the time at which the current density maximises at i_{\max} .

Increased nucleation is observed at -3 V where spherical tip growth is initiated under a progressive nucleation mechanism with some preferential growth at the tip apex, as evidenced by the large number of nucleated particles and variation in particle size (Figure 1.6c). For more negative voltages (≤ -4 V) nucleation becomes more selective, leading to clean surfaces and improved apex-selected growth (Figure 1.6d-f). This is due to a transition to instantaneous nucleation, in which a fixed number of particles nucleate at selected active sites on application of a field [hyde2003]. This occurs preferentially at sharp edges where the field is highest. Further selection may occur through depletion of ions in the vicinity of the growing tip, preventing additional growth sites. This helps to produce an isolated AuNP at the tip apex. Increasing the magnitude of the voltage increases the number of active sites available for nucleation and more of the tip surface surpasses the field threshold for instantaneous nucleation. Hence, using less negative voltages within the instantaneous nucleation regime reduces the number of active nucleation sites leading to cleaner spherical growth at the tip apex.

This changeover in nucleation mechanisms is also observed in current transients (Fig-

ure 1.6g)² as the shape distinctly changes when decreasing the voltage below -2 V . The largest change in transient shape occurs at -3 V , indicating the onset of short time-scale nucleation. Elongation of the transient time is likely caused by contribution to the current from progressive particle nucleation throughout the exposure. The large short-time-scale transients observed for potentials more negative than -4 V support the hypothesis of an instantaneous nucleation mechanism as the fast current decay indicates the saturation of all active sites leaving only diffusion-limited growth.

The influence of instantaneous nucleation for isolated AuNP tip growth is further evident in comparisons to theoretical reduced current transients for diffusion-limited progressive and instantaneous nucleation (Figure 1.6h) developed by Scharifker and Hills (SH model)[**scharifker1983**]. Reduced current transients are normalised to $(i/i_{\max})^2$ and plotted against t/t_{\max} to remove variable dependencies, where i_{\max} and t_{\max} represent the peak current and corresponding time. In general, for less negative deposition potentials (-2 V), nucleation resembles more closely progressive nucleation and growth, while at more negative potentials ($< -4\text{ V}$) it resembles more closely instantaneous nucleation. This correlates well with the SEM images shown in Figure 1.6d-f. Variations from theory occur due to the variable field profile present across the tip leading to localised instances of both progressive and instantaneous nucleation contributing to the overall current. The SH model is built upon assumptions such as random nucleation and provides valid results only for the limiting cases of only progressive or instantaneous nucleation for which the validity fails in such a selectively grown system[**dudin2010**].

A simple model can be developed using the SEMs and current transients. Whilst the large surface area of the FTO glass likely dominates the behaviour of the current density, SEM images do show localised changes in the morphology of the tip. Identification of the nucleation mechanism through the reduced current transients is likely only applicable to the FTO surface but does give some information regarding the apex behaviour. When the apex of the tip has a field profile above the threshold for instantaneous nucleation, caused by the increase in field due to the lightning rod effect, a single particle may nucleate at the apex and quickly grow. As it nucleates quicker than the rest of the tip its diffusion zone increases to prevent particles nucleating and growing nearby. This leads to a clean single AuNP growth at the tip apex. If the threshold for instantaneous nucleation is not met then many smaller particles form around the apex (Figure 1.6c). On the other hand if too much of the tip can nucleate instantaneously then the chance for a clean growth is again reduced (Figure 1.6f) since many particles nucleate around the apex. Through this reasoning it is apparent that the choice of voltage is imperative to enable selective growth of a single AuNP at the apex.

²Current measurements are interpolated to create a smooth line through data points. Transients are analysed by first making a quadratic interpolation of experimental data points before data reduction to extract the reduced current transients. This approach is used due to the limited number of points available in the peak region.

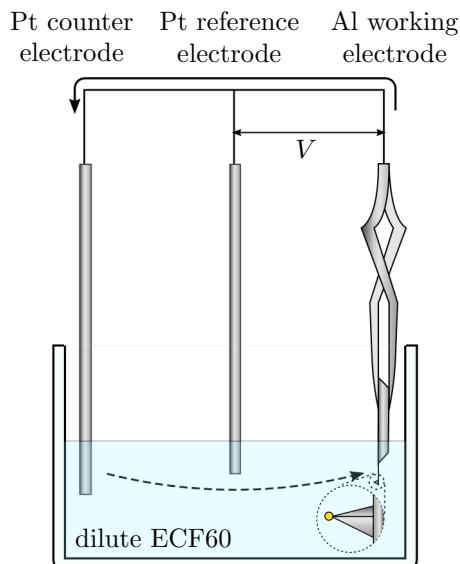


Figure 1.8: Diagram of the modified electrochemical cell for electrochemical AuNP tip fabrication. The ITO glass active electrode used for simultaneous fabrications is removed and replaced with an aluminium clamp fitting a single tip along with the addition of a Pt reference electrode. Over potentials are now measured relative to the reference electrode.

1.3 Modified Method for Controllable Fabrication of Spherical AuNP Tips

The previous method of fabrication provided a means of demonstrating that electrodeposition can be used to produce spherical tip apices but failed to give sufficient reliability or understanding of growth due to the variability in the FTO working electrode contact resistance and scale with respect to the attached tips. A modified cell geometry for pulsed electrodeposition on a single tip improves upon the fabrication process. The setup, shown in Figure 1.8, does not have the capability of simultaneously depositing on multiple tips but provides more control and monitoring of the growth of a single tip.

To retain good plasmonic confinement to the spherical AuNP apex, Pt-coated AFM tips are used as a base structure to maintain an electromagnetic boundary between the AuNP and the tip. A 10 min O_2 plasma pretreatment is still used to clean tips before electrodeposition. A compact potentiostat (Ivium CompactStat) replaces the larger potentiostat and a 3d printed electrode support frame is used for stability. Controllability is improved by measuring the current during electrodeposition more carefully and referencing the potential using a Pt wire electrode. As stated previously, Pt wire is chosen as a reference electrode as its high conductivity maintains a high measurement bandwidth during 10–100 ms time scale pulsed deposition [sawyer1995electrochemistry]. The quality of the tip contact with the working electrode is a large factor limiting the reproducibility between repeated experiments in the initial method. Unreliable contacting of the tips to the FTO glass is likely to be the dominant

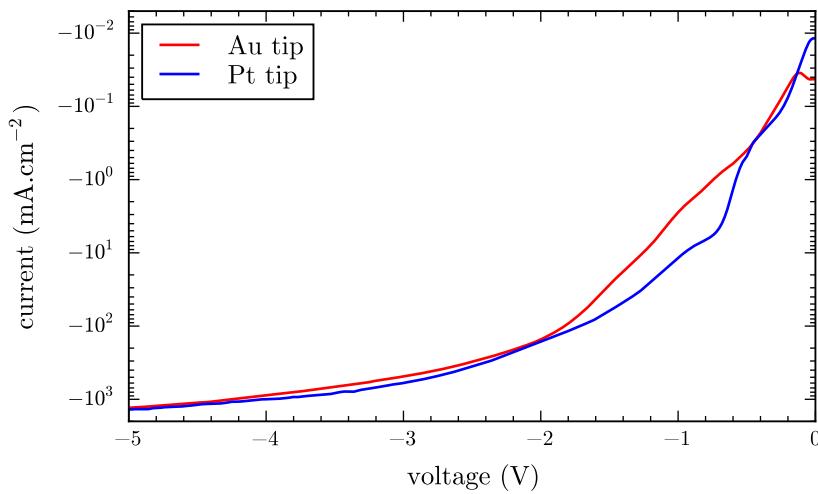


Figure 1.9: Linear sweep measurements

cause. This is improved in the new method by replacing the FTO glass with an aluminium clamp capable of holding a single tip. Though it prevents simultaneous fabrication of multiple tips, the clamp provides a reliable, highly conductive contact. The potential at the apex is therefore held stably at the applied potential.

The major consequence of the changes made to the setup is that the required applied overpotential is different. The previously valid voltages of -6 to -8 V no longer produce successful growths and the system requires optimising with new parameters. Since the working electrode potential is now relative to the solution, rather than the counter electrode, the magnitude of the overpotential decreases. The result of this is that successful fabrications occur mostly around -3 V. This is more comparable to reported nucleation over-potentials, as measured relative to a SHE, more negative than -1 V [6]. Similar exposure times are still used.

Linear voltage sweep measurements of both Au and Pt tips (Figure 1.9) show that the onset of growth is earlier for Pt. Pt's use as a catalyst may be the cause of this reduction in reaction energy.

(a) Diffusion-limited currents during electrodeposition for different potentials.

(b) Comparison of growth localisation at different potentials. The more negative the potential the more localised growth is to the apex.

Figure 1.10: Both growth localisation and current increase with more negative potentials.

The more negative the potential the more localised growth is to the apex (Figure 1.10b). However with large overpotentials comes a large current and therefore a need to decrease exposure. For every -1 V added to the potential the current approximately increases by a factor of 10 (Figure 1.10a). To control deposition more effectively the current is reduced by diluting the **ECF60/electrolyte**. This allows nucleation to occur during electromigration-

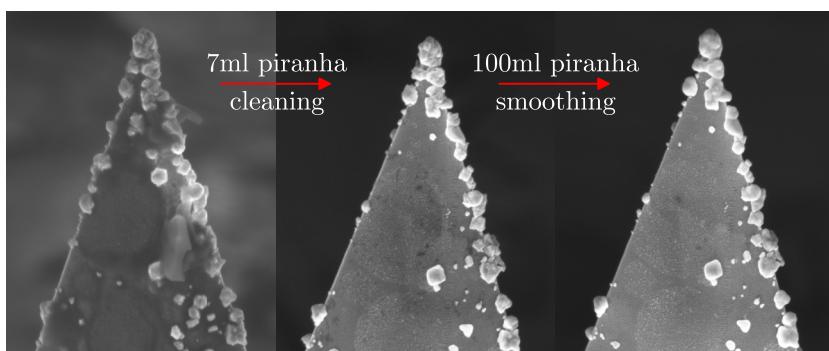


Figure 1.11: Post-processing effects of piranha solution. Low volume and temperature piranha solution removes organics from the Au surface while large volumes at 120 °C smooth the surface.

limited growth on short time-scales before the restricted diffusion flow cuts it off causing only growth to pre-existing nuclei. Diluting by 50% reduces the current by approximately a factor of 10, hence more localised growth at -4 V becomes more controllable using exposure times previously used at -3 V .

Imaging tips using SEM after electrodeposition is necessary to determine the apex morphology but leads to contamination issues. Exposure to the electron beam is known to deposit layers of carbon onto samples. Despite washing tips in DI water and ethanol after deposition to remove thin films, the surface of the tip inevitably has carbon contamination after imaging. To ensure good electrical contact, AuNP-on-Pt tips must be cleaned before use. Although plasma cleaning is used to remove organics from the surface before fabrication it can oxidise the surface. Submerging tips in piranha solution ($3:1\text{ H}_2\text{SO}_4:\text{H}_2\text{O}_2$) proves to be an effective method for removing organics from the surface of the Au. Though it can still oxidise (or hydroxylate) surfaces it is to a lesser extent compared to plasma treatment since it is much less extreme.³ The activity of piranha solution degrades over time and the solution is only effective for $\sim 15\text{ min}$. During its initial stages, the piranha reaction is extremely exothermic with temperatures reaching up to $120\text{ }^\circ\text{C}$. The amount of heat generated is limited by the volume of solution used.

Tips treated with piranha solution contacted significantly more often than tips left untreated after SEM imaging. The morphology of tips can be somewhat adjusted by varying the temperature and exposure to the piranha solution. Piranha treatment is a heavily exothermic reaction with temperatures reaching up to $120\text{ }^\circ\text{C}$. The temperature depends on the volume of solution. Tips cleaned in small (5 ml) volumes show no changes in morphology whereas those treated in a large (100 ml) volumes are found to have their surfaces smoothed (Figure 1.11).

³Piranha solution is a strong oxidising agent and works via H_2SO_4 quickly dehydrating the surface. The reaction between H_2SO_4 and H_2O_2 creates oxygen radicals which oxidise the remaining carbon molecules into elemental carbon. The overall result is the decomposition of organic matter into carbon, carbon dioxide and water.

1.4 Conclusions

By using electrochemical deposition, the simple fabrication of spherical metallic tips has been successfully demonstrated. Tips can be fabricated within a short period of time and with high throughput using pulsed electrochemical deposition and exploiting the sharp tip geometry to nucleate and grow a single nanoparticle at the apex. Though simple and cheap compared with many other techniques, control of growth morphology quality still presents issues. Morphology control presents problems due to the many number of variables in the system, many of which were investigated to optimise and understand the deposition process. Despite significant efforts, the deposition process remains unreliable, though repeatable. It has, however, succeeded in its original purpose of providing spherical Au tips for application to plasmonics.