1 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, 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 $10\,\mathrm{min}$ 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–$100\,\mathrm{ms}$ 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 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 over-potential is different. The previously valid voltages of -6 to $-8\,\mathrm{V}$ 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 $-3\,\mathrm{V}$. This is more comparable to reported nucleation over-potentials, as measured relative to a standard hydrogen electrode (SHE), more negative than $-1\,\mathrm{V}$ []. Similar exposure times are still used.

Linear voltage sweep measurements of both Au and Pt tips (Figure 2) show that the onset of growth is earlier
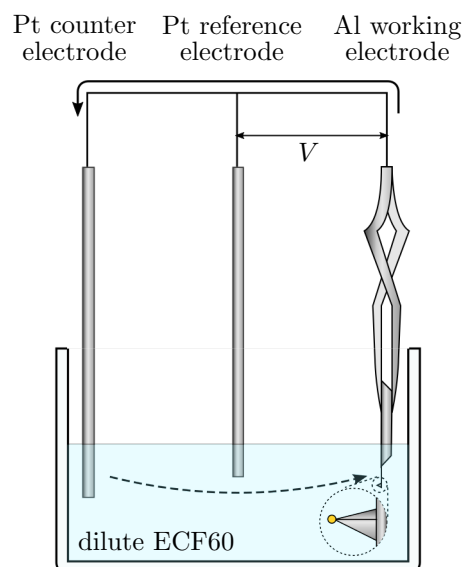

Figure 1: Diagram of the modified electrochemical cell for electrochemical AuNP tip fabrication. The ITO glass active electrode used for simultaneous fabrications is removed and replaced with an aluminium clamp fitting a single tip along with the addition of a Pt reference electrode. Over potentials are now measured relative to the reference electrode.
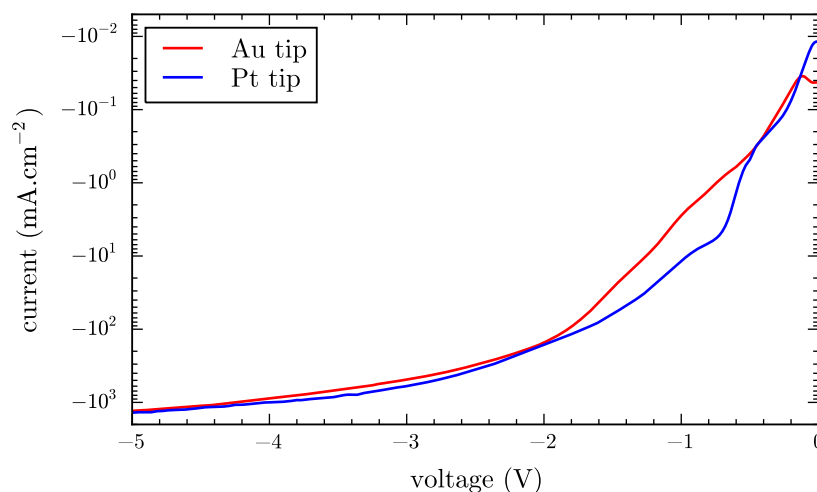
Figure 2: Linear sweep measurements

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

The more negative the potential the more localised growth is to the apex (Figure 3b). However with large overpotentials comes a large current and therefore a need to decrease exposure. For every $-1\,\text{V}$ added to the potential the current approximately increases by a factor of 10 (Figure 3a). To control deposition more effectively the current is reduced by diluting the ECF60/electrolyte. This allows nucleation to occur during electromigration-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 $-4\,\text{V}$ becomes more controllable using exposure times previously used at $-3\,\text{V}$.

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 H_2SO_4:H_2O_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.[1] The activity of piranha solution degrades over time and the solution is only effective for $\sim$15 min. During its initial stages, the piranha reaction is extremely exothermic with temperatures reaching up to $120\,^\circ\text{C}$. 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 $120\,^\circ\text{C}$. 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

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[1]Piranha 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.
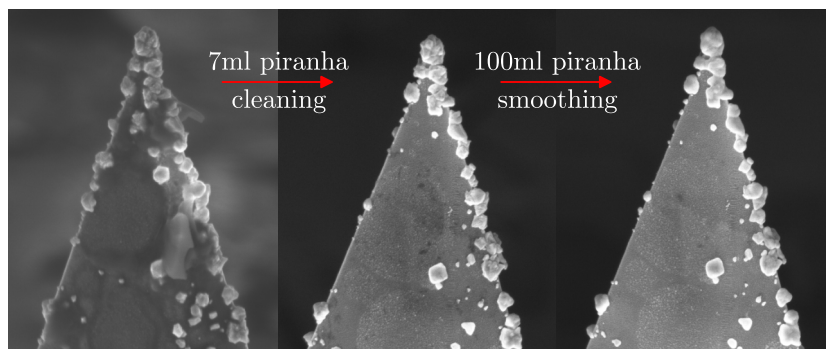
Figure 4: Post-processing effects of piranha solution. Low volume and temperature piranha solution removes organics from the Au surface while large volumes at 120 °C smooth the surface.

(Figure 4).