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ELECTROCHEMICAL ETCHING GOLD TIPS

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Abstract. In this work, we propose a simple and easy method to produce sharp and smooth conical gold tips for atomic force microscope and scanning near-field optical microscopy. The method is electrochemically etching process, based on gold, Pt wire and HCl acid (37%) as a solution. Comparing to other methods, we use only HCl as electrolyte. A function generator was used to produce rectangular pulse wave with 3 kHz and 7 V to obtain smooth and very sharp conical tip with diameter less than 10 nm. By controlling etching parameters (pulse shape, frequency and voltage), the fabricated etching tip achieved about 80% yields. Moreover, the etching time is about 13 second, which is very fast etching process. This method provides a suited tip for tip-enhanced Raman scattering, adiabatic nanofocusing of aperturless-scanning near-field optical microscopy and field emission electron microscopy.

Keywords: Electrochemical etching method; AFM tips; Scanning electron microscope (SEM);

1. Introduction

The techniques of scanning tunnelling microscopy (STM)[1], atomic force microscopy (AFM) [2] and scanning near-field optical Microscopy (SNOM)[3] have established that, they are enormous tools in the investigation of properties of matter at the nanoscale. They are now daily used for different field of applications. These techniques have partnership to use of sharp tips to analyse properties at the atomic scale, with extremely depended on resolution and stability, as well as dependent on the tip's physical and chemical properties. According to these factors which should be in the mind, attempts and hard work to increase the excellence of the manufactured tips [4-6] and to improve tips created on new materials continued.[7-9]. The process of electrochemically etching tips has been interested by the need to increase development over earlier ways. The most effortless and cheapest strategy of making tips is by mechanical cutting, however this simple strategy owned poor reproducibility.[6]. The most standard and reliable strategy for making sharp tips is the "drop off" method which can be adjusted for utilize with diverse sorts of metallic tips, such as tungsten, silver and gold. In all cases, the desired etched wire should be served as positive pole and is located in the centre of a wire ring which have to be served as the negative pole. The electrolyte that is utilized in etching process changes depending on the type of material that to be etched.[10]. The sharpness of the tip is mainly affected by some factors such as applied voltage, potential time, type of electrolyte and even the wire length that is immersed within the electrolyte. The length of the wire under etching point can have effect to aspect ratio of tip (length to the diameter of wire) [11]. So, if more wire is immersed in the electrolyte, the extra weight of the wire can produce a tip with longer apex. Moreover, the extra weight from the longer immersed wire may causes the tip to be cut earlier. As a result, a big radius of curvature and long tip will produce which is

useless for many application [12]. In etching tip process, fabrication of sharp metal tip with respect to a little aspect ratio is the target. Another key parameter is cut off time that can enormously has effects on the quality of the tip when using electrochemical etching, where a faster cut off time produces sharper tip [13].

Silver tips can now be efficiently made by etching in a solution using a combination of concentrated $HClO_4$ and pure methanol (1:4) at an anodic voltage between1.6 V to 2.0 V [14] or by etching in a 10%-35% ammonia solution at 10 V [15]. To fabricate gold tips, a method by using $CaCl_2$ solution of 10%-50% saturation at 30 V, or in 3 M NaCl and KCl solution at 10 V was used [16, 17]. But this procedure produces tips with a big apex. A procedure used by Baykul, using a 0.8 M KCN with a 12 V etching voltage leads to a tip difference in radius between 200 nm and 500 nm which is too big for AFM [18]. A lower etching voltage between (1.5 to 2.0 V) have been used to fabricate gold tip,[19] however, the tips with very rough surface was produced by this method. A rough tip surface shows a great affinity for adsorbing carbon even from air.[19].

It is possible to use both alternating and direct current in etching method. Tips that has been fabricated by DC voltage has very rough surface compared to those whom with AC voltage [20]. The research group of Max Eiesele was used DC voltage with the etching time of 10 mine to fabricate the tips with a good smooth surface [21]. In this work, we focused on a method using AC voltage and only HCl as electrolyte to fabricate a smooth and very sharp gold tips. This method is easy and simple method that produce the desired tip regarding to the tip radius and smoothness. Furthermore, this method is very fast process (13 second) and reproducible method with 80% yield. The parameters that have been used are: 3 kHz frequency, an ac voltage of 7.5 V and square wave function and pure HCl as electrolyte.

2. Experiment

The experimental setup of etching gold tips is very simple. By using a beaker for containing HCl solution with volume 10 ml. Putting a platinum (Pt) ring of about 6 mm diameter which was made from 0.1 mm of platinum wire on the surface of the solution. About three-quarters height of the ring was flooded in the solution. The solution is hydrochloric acid (37%). A gold wire of 0.125 mm diameter (purity 99.99%, Advent research materials) by crocodile claps was immersed within the center of the ring. In order to see clearly the end of the tip in the bottom of Pt ring, the length of the wire that was immersed is about 2-3 mm as shown in Figure 1. A Fixing camera (CMOS Camera: USB 2.0) and 100 mm focal length lens were used to display in real time the etching process. A Pt ring was connected as the cathode, while Au wire as the anode and applying a 7.5 AC voltage by function generator with square wave function and frequency of 3 kHz. By these parameters, one can see a little vortex on the surface of the solution during camera monitor. Thus, etching process of gold wire will start and necking region will occur at the air/electrolyte interface. When the narrowest region can no longer hold the submerged part of wire, the wire breaks and two sharp tips forms at the surface of electrolyte. This process takes 13 seconds approximately for each tip. Usually, the bottom tips were neglected because it became too thin as it dissolved in the electrolyte. As mentioned in introduction, it is very crucial to open the circuit as soon as possible after seeing the bottom part of the wire was fallen. Because, even after fallen the bottom part of the wire, the current can still have the capability of flow through the tip in to the electrolyte due to the applied potential and leads to a bad tip apex. After etching, it is essential to clean the fabricated tips from the solution. For this purpose, acetone was used for cleaning directly after the etching tip.

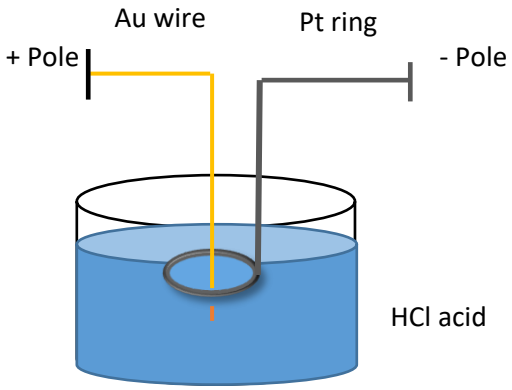

Figure 1. The schematic diagram of the setup for etching gold tip.

3. Results and discussion

To achieve electrochemical etching, the most importance in this method is the quality of fabricated tips. So any changes in parameters within the process may have effects on results. Therefore, not all the fabricated tips by this method have a particular shape. The reasons that causes to the sharpness of the tips, smooth surface and also long tip apex depends on different parameters. We found that cut off time has the most importance role in the tip sharpness. A faster cut off time produces a sharper tip. During etching process and after falling down the bottom part of the wire, it is necessary to cut off the applied potential from the circuit immediately. Otherwise and as mentioned before, the current can flow through the electrolyte to the tip. Any extra potential in the setup can have bad effects on the tip and may blunt the tip apex. Rough tip surface is another unwanted problem in this method that faced us. Contamination of electrolyte, dirtiness of the usage beaker for electrolyte are the reasons behind this problem. For this trouble, we used pure HCl 37% as an electrolyte and using ultrasonic device with nitrogen gas to clean the usage beaker. People used ethanol with HCl with a volume proportion 1:1, however, during the etching process the ethanol would evaporate and consequently the volume proportion which have been changed and this results to a different tip quality[22]. In other hand, the produced tip should be cleaned by putting in Acetone for 3-4 sec to avoid form being rough. According to what we observed in this work, sometimes the produced tips has a long tip apex. Due to its long-small angle of apex, tips can easily be damaged or bent during the scan in atomic force microscopy, since any mechanical vibration or tips hard contact to the sample is enough to reduce the performance resolution of the tip. The length of wire immersed in the electrolyte under the etching point is responsible for long tip apex. If the wire that was immersed in the electrolyte is more than needs, the result will be a long and small angle tip apex due to the extra weight of tip below the etching point, because the extra weight of the submerged wire will lead to cut the tip prematurely when less of the wire is submerged. In general, under the best conditions, a tip of radius less than 10 nm with smooth surface and short tip apex is achieved by this work as shown in Fig 2 which is an ideal tip for AFM and SNOM.

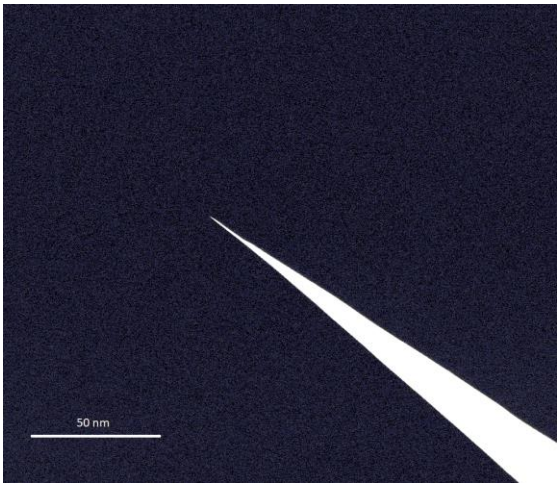

Figure 2. SEM image of produced tip

The produced tip was used in a homemade AFM to scan a carbon nano-particles. As a results, we saw that the tip was works properly and it seems that our methodology to fabricate gold tips was successful for AFM. Fig.3 shows the results of fabricated tips used in AFM with less than 20 nm. Moreover, the yield of the present process that produce smooth and sharp tip is about 80% and very fast (13 second). From our knowledge, the yield and etching time are remarkable comparing to other works.

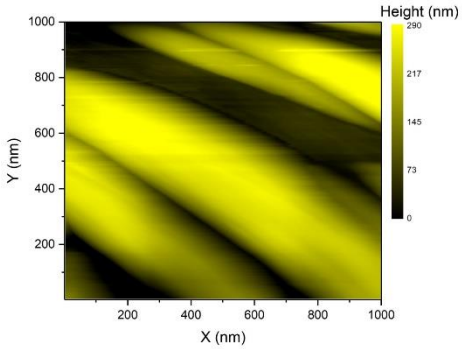

Figure 3. AFM picture of produced tip

4. Conclusion

In conclusion, we developed a simple, fast and easy electrochemical etching method based on ac voltage and using only hydrochloric acid. By controlling ac voltage parameters, one can yields 80% of sharp-smooth gold tips with diameter less than 10 nm. The optimal applied voltage was found to be 7.5 volt with rectangle function. The method is inexpensive, easy and reproducible. Tips that have been fabricated by this method found to be appropriate for scanning near-field optical microscopy and can produce image with high resolution.

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