A double-electrolyte etching method of high-quality tungsten probe for undergraduate scanning tunneling microscopy and atomic force microscopy experiments

Article *in* European Journal of Physics · December 2018

DOI: 10.1088/1361-6404/aaf5e4

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IOP Publishing European Journal of Physics

Eur. J. Phys. **40** (2019) 025004 (8pp) https://doi.org/10.1088/1361-6404/aaf5e4

A double-electrolyte etching method of high-quality tungsten probe for undergraduate scanning tunneling microscopy and atomic force microscopy experiments

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Received 11 September 2018, revised 12 November 2018
Accepted for publication 4 December 2018
Published 28 January 2019

Abstract

We have developed a double-electrolyte etching method to prepare sharp tungsten probes for scanning tunneling microscopy and atomic force microscopy. With the proposed etching method, high-quality tungsten probes can be produced. Furthermore, its simple implementation and easy operability significantly reduces the difficulty for operators and makes it tractable for amateur students. The method can achieve automatic cut off of the current as soon as tip formation occurs without using a cut-off circuit or microcontroller, which reduces the implementation cost and complexity. This is an effective way for students to prepare eligible tungsten probes in undergraduate scanning tunneling microscopy and atomic force microscopy experiments.

Keywords: double-electrolyte etching method, tungsten probes, scanning tunneling microscopy, atomic force microscopy, undergraduate experiments

(Some figures may appear in colour only in the online journal)

1. Introduction

Tungsten probes are widely used as a core part in scanning tunneling microscopy (STM) and atomic force microscopy (AFM) based on quartz tuning forks, where the imaging quality is directly related to tip morphology [1, 2]. In order to achieve high resolution in both STM and AFM images, the tip must have an high aspect ratio and a small curvature radius at the tip apex. If a blunt tip is used in scanning, the obtained image can be seriously distorted by the tip-convolution effect [3–5].

With the development of STM and AFM experiments among undergraduate students, there is a demand for a constant supply of tungsten probes. However, in conventional etching schemes such as the drop-off method and lamellae drop-off method, the etching progress will continue after tip formation [6, 7], which leads to blunt tips. That is why experienced operators are needed to thoroughly monitor the etching process and manually cut off the current as soon as possible after tip formation. For amateur undergraduate students, this agility is hard to acquire. Although a lot of circuit configurations and microcontroller designs have been proposed to cut off the electricity after tip formation [6, 8–11], they are too complex and costly to be applied in undergraduate experiments. Kulawik *et al* [12] proposed a double-lamellae structure to achieve automatic cut off, but the anode liquid lamellae is easy to rupture because of bubble formation in the center of the lamellae.

A double-electrolyte etching method is introduced in this paper. A NaOH lamellae is used to etch the tungsten wire and Na_2SO_4 solution is used to conduct the anode current. The proposed method is not only well-behaved in etching stability but also able to achieve automatic electrical cut off after tip formation. With both simple implementation and easy operation, the proposed method is suitable for amateur undergraduate students to produce high-quality tungsten tips. In addition, a comparison of tip curvature diameter between the conventional manually cut-off lamellae etching method and the proposed method is made to illustrate the superiority of the proposed method in producing sharp tips. The high quality of the produced tips is experimentally confirmed by STM and AFM images.

2. Brief review of etching structures

NaOH solution is commonly used as the reactant in tungsten probe's preparation, where the tungsten wire is etched at the anode under the reaction [13]

$$W + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^-, \tag{1}$$

while the reaction on the cathode can be written as

$$6H_2O + 6e^- \rightarrow 3H_2 \uparrow + 6OH^-. \tag{2}$$

In the early drop-off scheme, the anode and the cathode are immersed collectively in one reaction vessel, as shown in figure 1(a). This kind of device is easy to set up but the liquid level is unstable because of bubble formation on the cathode, which leads to a long and irregular end of the tip [14]. A U-shaped tube instead of a beaker, as shown in figure 1(b), as well as other similar isolating structures, are practicable in reducing the perturbance of cathode bubbles on the liquid level around the tungsten anode [15, 16].

The manual lamellae drop-off etching method employs a thin NaOH solution film as the reaction environment [7], as shown as figure 1(c). Because the lamellae is more stable than the solution in the beaker, the tip length can be much shorter compared with those immersed in liquid. Another advantage in using the lamellae is the symmetrical tip morphology of the upper and lower end of the longitudinal fracture. If the lower section can be well kept, both

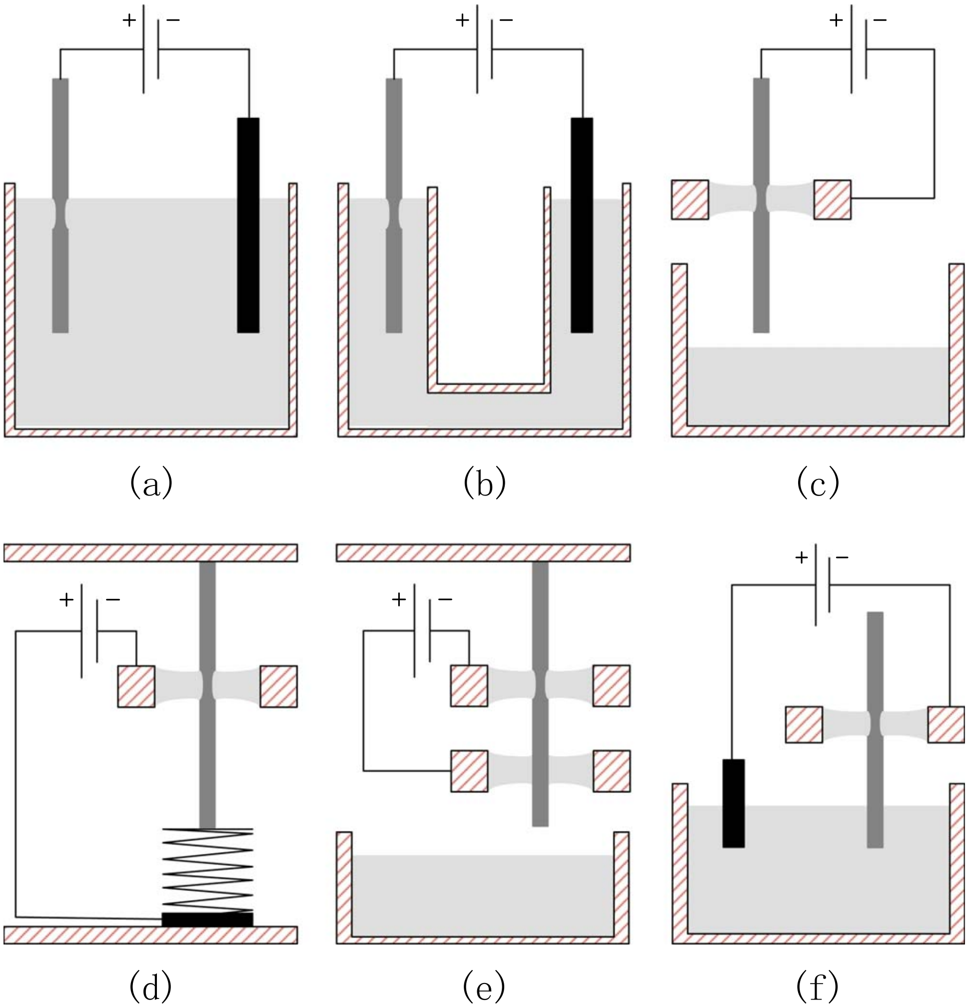


Figure 1. Basic structures for tungsten probe etching: (a) early drop-off method, (b) drop-off method based on an U-shaped tube, (c) manual lamellae drop-off method, (d) lamellae drop-off method based on spring, (e) double-lamellae drop-off method, and (f) lamellae drop-off method based on one electrolyte.

ends can serve as probes. The lower section of the wire fragment is immediately cut off from the electrical circuit while in the upper wire fragment the etching process continues. For inexperienced undergraduate students, the cut-off time is often delayed, which leads to excessive etching at the upper wire fragment. A mechanical automatic cut-off design adopts a spring connecting the anode with the lower section of the tungsten wire, as shown in figure 1(d). However, this approach is unreliable because the wire can easily be snapped by the spring tension before thoroughly etched.

The double-lamellae structure suggests the idea of connecting the anode with the tungsten wire through the electrolyte [12], as shown in figure 1(e). But in practice, the anodal lamellae often bursts due to the formation of hydrogen bubbles in the center of the lamellae, causing the etching process to stop early. Even by replacing the anodal lamellae with a

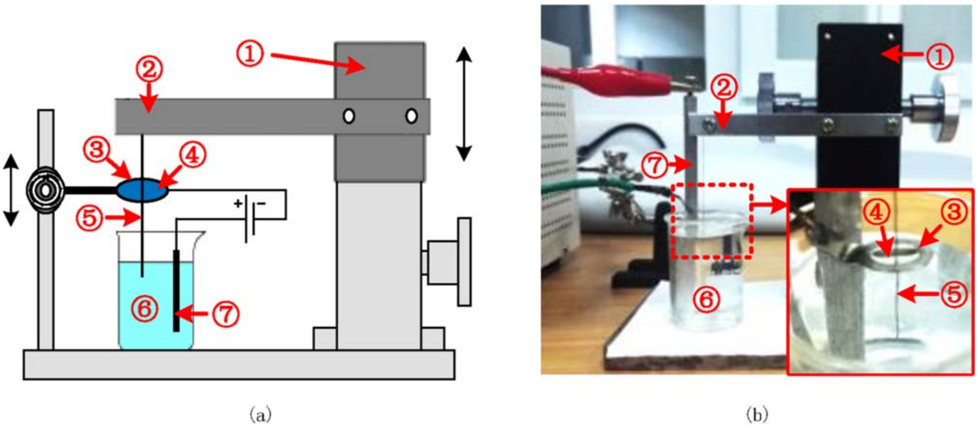


Figure 2. (a) Schematic of the proposed double-electrolyte method. (b) Photo of the double-electrolyte device. For both (a) and (b): ① Z-axis positioning stage, ② wire-holding device, ③ stainless ring cathode, ④ NaOH lamellae, ⑤ tungsten wire, ⑥ Na_2SO_4 solution, ⑦ stainless steel anode.

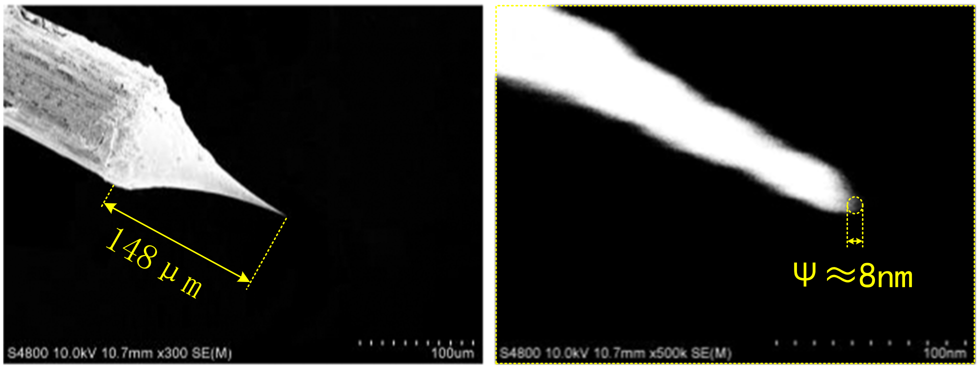
breaker of solution, as shown in figure 1(f), the same NaOH electrolyte contact with the anode and cathode will cause both to react with the tungsten wire. In the case that the solution in the beaker and lamellae has the same concentration, the wire will break at the liquid level in the beaker before it breaks at the lamellae because the electrolyte in the beaker can be replenished more quickly, which would make no difference with the drop-off method [12].

3. Experimental implementation

Based on the lamellae drop-off methods mentioned above, we have developed a novel method to produce high-quality tungsten probes using two types of electrolytes to achieve stable lamellar etching as well as automatic cut-off of electricity. The implementation is shown in figure 2, which differs from figure 1(f) only in using two electrolytes. The device contains a Z-axis positioning stage holding the tungsten wire in a vertical direction and a height-adjustable stainless steel ring holding a 3 mol L^{-1} NaOH solution lamellae, which is connected with the cathode. The tungsten wire passes through the lamellae perpendicularly, whilst its lower end is immersed into a beaker of 1 mol L^{-1} Na_2SO_4 solution. The stainless steel anode is also immersed in the Na_2SO_4 solution, as shown in figure 1(f): the only difference is a different electrolyte in the beaker. The height of the ring is about 1 cm above the liquid level in the beaker and the immersed depth of the wire in the Na_2SO_4 solution is 1–2 mm.

A constant DC voltage (9–12 V in our experiment) is applied to perform the etching process. For a typical tungsten wire with a diameter of 0.1 mm and purity over 99.999%, the current is approximately 5 mA at the beginning of etching and less than 1 mA when the wire is nearly fractured. The duration of the whole etching process is about 120–150 s. In this scheme, the tungsten will be etched only in the lamellae. The Na_2SO_4 solution acts as a conducting element between the wire and the anode, ensuring that the wire fracture will only occur in the lamellae.

Once the tungsten wire fractures, the electrical circuit will be automatically cut off with the drop of the lower fragment of the wire. Compared with the cut-off time using complicated



(a) (b)

Figure 3. Scanning electron microscope images of a tip produced by the double-electrolyte etching method: (a) $\times 300$, (b) $\times 500$ k.

control circuits or microprocessors (often at the nanosecond to microsecond level) [6, 8, 9, 11], the cut-off time of the proposed method can be regarded as zero. In addition, the method is not only low cost, but also easy to operate. In undergraduate experiments, students no longer need to pay close attention to the whole etching progress and to manually cut off the current as quickly as possible after fracture: all they need to do is wait for the fracture and check it under the optical microscope. If the tip is sharp and well-shaped, it will be suitable for STM or AFM imaging.

It is important to mention that the distance of the lamellae from the tungsten wire-holder bar must stay constant during etching, so the Z-axis positioning devices have to be fastened, and any mechanical oscillation ought to be avoided in the etching process.

4. Tip quality

To observe the tip topography, scanning electron microscope (SEM) (Hitachi S-4800) images of the produced probe are acquired. A typical tungsten probe made through the proposed method is shown in figure 3. The tip length is about 148 μm (figure 3(a)). The sharpness of the tip is evaluated by the tip curvature diameter (the diameter of the curvature circle of the apex curve). In this case, the tip curvature diameter is 8 nm (figure 3(b)).

To compare quality between the tips produced by the double-electrolyte etching method and the conventional manual lamellae drop-off method (figure 1(c)), 50 tips were made respectively by each method. The conventional manual lamellae method relies on supervision by the naked eye to cut off the electricity after fracture. Figure 4 shows the distribution of tip dimension using the two methods. It can be concluded from figure 4 that the proposed double-electrolyte method yields sharper tips (curvature diameter of tip apex under 40 nm) than the conventional lamellae drop-off method.

5. Imaging experiments on STM and AFM

The quality of the tungsten tip is tested in STM and AFM. A 5 mm-long section of the tungsten wire is cut out as the probe, and installed on a commercial STM (Nanosurf Naio). An image of the graphite sample is acquired using the constant current mode, shown in

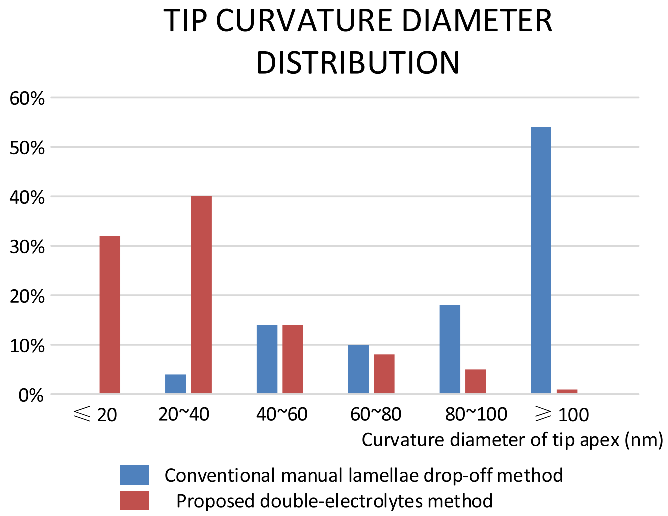


Figure 4. Distribution of tip curvature diameter produced by the double-electrolyte etching method (red) and the conventional manual lamellae etching method (blue).

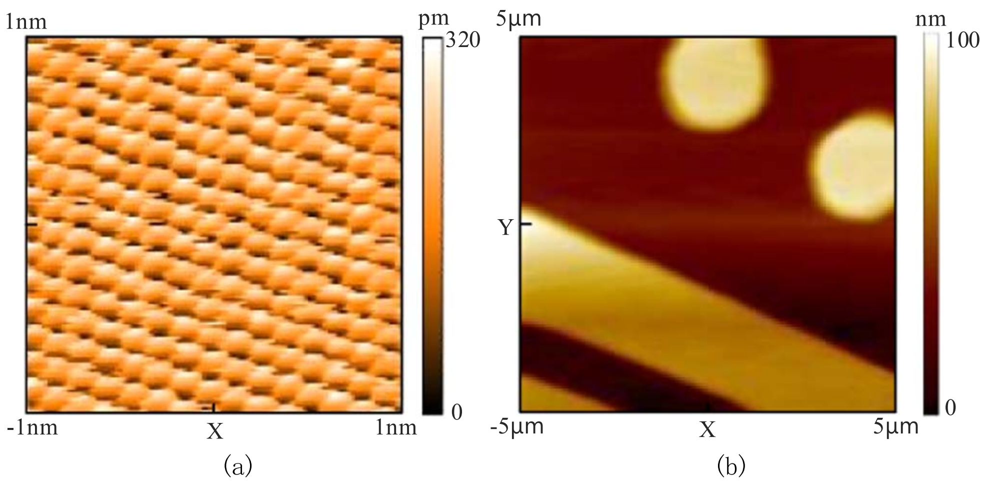


Figure 5. (a) Graphite sample images acquired by STM using one of the probes made through the double-electrolyte method. (b) A border area between different rasters on the standard BudgetSensor HS-100MG calibration sample imaged by AFM using one of the probes made through the double-electrolyte method.

figure 5(a). From the 2 nm $\times$ 2 nm graphite image we can clearly see arrays of carbon atoms, which means lattice resolution can be achieved on STM using a probe made by the proposed method.

To be applied on AFM based on a quartz tuning fork, tungsten probes have to first be assembled on quartz tuning forks. As shown in figure 6, the produced probe is attached on one prong of the fork while an equal-length tungsten wire is attached on the other prong to obtain a high quality factor [17]. A homemade AFM is employed [18]. The balanced fork is implemented on a piezoelectric tube scanner. We use a calibration sample (BudgetSensor HS-

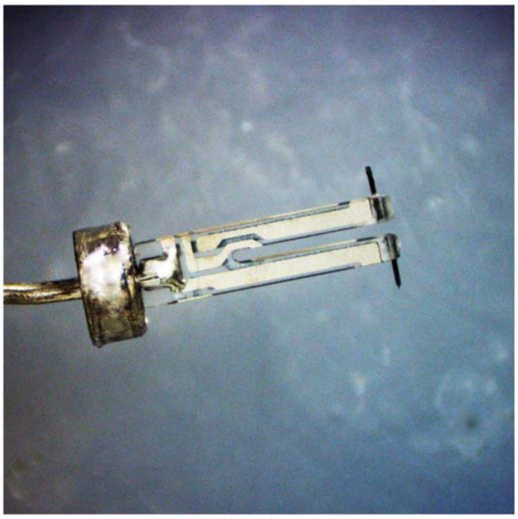


Figure 6. Quartz tuning fork with balanced tungsten probes attached.

100MG, with a 5 micron pitch and 100 nm height) to test the quality of the probe. The AFM is set to scan 256 $\times$ 256 pixels on a 10 μm $\times$ 10 μm area in frequency modulation mode. Figure 5(b) shows the border area between the one-dimensional raster and two-dimensional rounded raster. The edges of the raster are steep on the image, which means the tip is sharp enough to track raster details.

6. Conclusion

We proposed a double-electrolyte method to produce tungsten tips for undergraduate STM and AFM experiments. Benefitting from its easy operation, even amateur students are able to produce high-quality tungsten probes, which guarantees the success of the experiment. In addition, without any cut-off circuit or microcontroller, the implementation is simple and low cost for educational practice. In the method, the NaOH lamellae is used to etch the tungsten wire and the Na_2SO_4 solution serves as the connective medium between the tungsten and the anode. The usage of two types of electrolyte ensures that the tungsten wire is only etched at lthe amellae and that the current is automatically cut off after etching. Through SEM images we have demonstrated that the method is more efficient at producing sharp tips than the conventional manual lamellae drop-off etching method relying on manual current control. The STM and AFM imaging experiments prove the high quality of the probes.

Acknowledgments

The authors gratefully acknowledge support from the National Natural Science Foundation of China (61371067 and 61771033).

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