



Electrochemical Etching of Tungsten for Fabrication of Sub-10-nm Tips with a Long Taper and a Large Shank

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Abstract

From the perspective of maximizing the practicability of tungsten nano-tips, a sharp tip, long taper, and large shank are usually expected. However, simultaneously satisfying the requirements for tip radius, taper length, and shank diameter is theoretically impossible with the conventional drop-off tip fabrication method, which is based on lamellae electrochemical etching. In this study, a two-step etching method is proposed to fabricate a sub-10-nm tungsten tip directly from a 1-mm rod. First, a floating electrolyte-based drop-off process is carried out to fabricate a tungsten needle with a long length taper of 10 mm. Then, an inversed lamellae drop-off process is conducted to realize fine etching of the needlepoint. As a result, an ultra-sharp tungsten nano-tip with a radius of 5.5 nm and taper length of 10 mm is successfully fabricated from a 1-mm tungsten rod.

Keywords Tungsten tip · Nano tip · Drop-off etching · Liquid metal · Electrochemical etching

1 Introduction

Miniaturization is an important issue for the development of science and technologies in micro- and nanoscales. As a typical case of miniaturization, the fabrication of nano-tips has drawn increasing attention because of their numerous applications in various fields like high-resolution microscopy [1, 2], micro- and nano-machining [3], and nanolithography [4]. Although several materials can be used for the fabrication of nano-tips [5], tungsten has been most widely studied and utilized owing to its superior mechanical and chemical properties, such as high hardness, high melting temperature, strong oxidation resistance, and that it does not mix readily with other metals [6].

For the fabrication of micro- or nano-tungsten tips, electrochemical etching has been widely utilized owing to its good reliability, simplicity of operation, and high efficiency [7]. As an electrochemical etching process, the lamellae drop-off method proposed by several groups has been proven useful for the fabrication of tungsten nano-tips

[8–11]. However, there are several unsolved problems in the conventional lamellae drop-off method. According to its mechanism, the tungsten tip drops when the etching neck cannot sustain the weight of the lower part. Therefore, the radius of the tungsten nano-tip is determined by the mass of the lower part. Ibe et al. [12] proposed the quantitative relationship between the mass of the lower part and the radius of the tip. For a tungsten wire with a diameter of 0.2 mm, the radius is about 32 nm, 110 nm, or 230 nm for a wire with 2 mm, 4 mm, or 6 mm of length below the electrolyte film, respectively. As demonstrated in Fig. 1, the radius of the dropped nano-tip is determined by shank diameter, shank length, and taper volume. Theoretically, tips can be etched as sharp as possible if the lower part is light enough. However, when the lower dropped tip is the targeted tip, it is difficult to be practically utilized if the shank of the lower tip is too small in diameter or length. Tungsten wires with a diameter of 0.2 mm and a lower part length of several mm are the compromised conditions to manufacture tungsten tips [13]. Thus, the radius of tungsten tips made by the conventional drop-off method is usually no sharper than 10 nm, and the shank is usually no bigger than 1 mm.

To solve the mentioned problems in the conventional drop-off method in which the lower parts are the targeted tips, some approaches based on making use of the upper tips have been recently proposed [6, 10, 14–16]. Theoretically,

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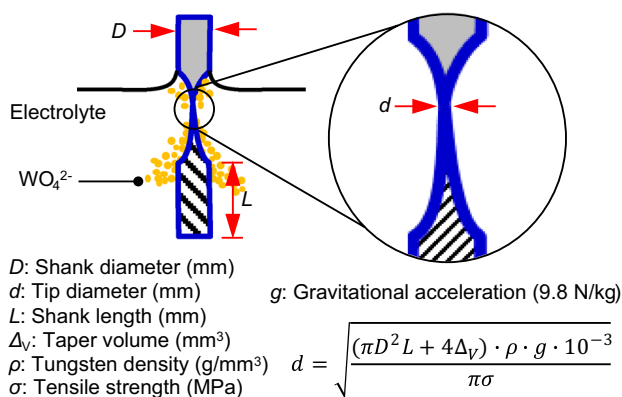


Fig. 1 Schematic diagram of the conventional lamellae drop-off process

if the upper tip and the lower tip have the same radius, then it is possible to make the lower wire as light as possible to make a sharper upper tip, and the shank of the upper tip can be much larger and longer. However, this approach is faced with other challenges. First, the positive potential is applied on the upper tungsten wire. When the lower tip drops and is cut off from the circuit, the upper tip keeps reacting with the electrolyte. Hence, the upper tip is usually blunt compared with the lower tip [13, 17]. Moreover, the wire usually breaks at the air–liquid interface, so the upper tip usually has a short and fixed taper length, which restricts its practical applications to some specific areas [18].

Klein et al. [19] proposed an improved lamellae etching method. They interrupted the etching process at a suitable time and turned the tungsten wire upside down. By the upside down reversal, the cut-off time for the upper tip was greatly shortened, and a sharper tip was fabricated, though the taper was very short. As reported, a tungsten tip with a radius of 12.5 nm was produced [19]. Guise et al. [15] developed an instantaneous cut-off device, which could turn the power off within a minimal delay of about 500 ns. On the basis of this instrument, an ultra-sharp tungsten tip with a radius of 3.6 nm has been successfully achieved with a shank of 0.35 mm. Although these modified drop-off methods have successfully minimized the tip radius, they rely on specialized setups, and the taper length of the tip has not been considered [17, 18]. Furthermore, the fabrication of tungsten nano-tips with a shank larger than 1 mm has not yet been reported.

In this communication, we propose a combined electrochemical etching process to fabricate tungsten nano-tips with a long taper and a large shank. The process consists of two steps. First, a floating electrolyte-based drop-off process is carried out to fabricate a tungsten needle with a long taper from a large rod. Then, an inversed lamellae drop-off process in which the needle is further etched by applying the positive

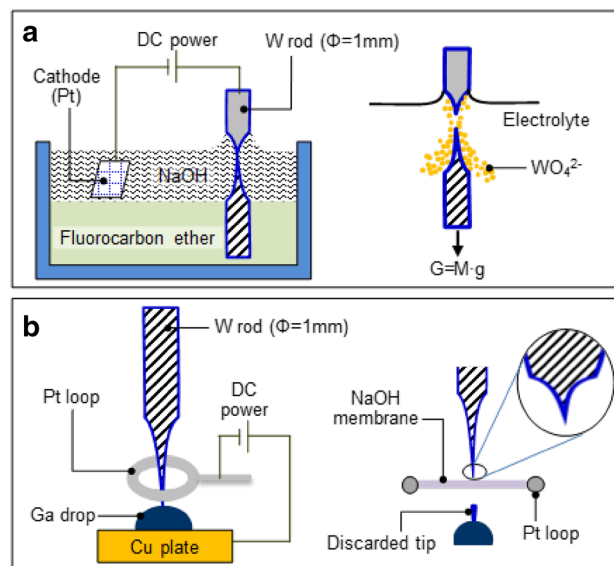
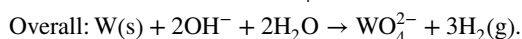
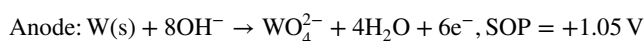
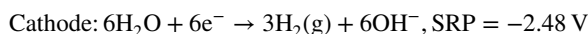


Fig. 2 **a** Schematic diagram of the floating electrolyte-based drop-off process. **b** Schematic diagram of the inversed lamellae drop-off process

potential on the lower tip (rather than the upper tip as in the conventional drop-off method) is conducted to minimize the tip radius. It is expected that nano-tungsten tips with a long taper and a large shank can be fabricated using this two-step etching method.

2 Experimental

Tungsten rods with a diameter of 1 mm and purity of 99.9999% were used in this work. First, a floating electrolyte-based drop-off process was conducted, as shown in Fig. 2a. The vertically fixed tungsten rod was stretched into a layered solution with 5 M sodium hydroxide (NaOH, EMD Millipore Corporation, purity $\geq 99\%$) electrolyte floating on inert fluorocarbon ether (3 M HFE-7100, purity $> 99.5\%$). The electrochemical reactions were as follows:



In the tungsten drop-off etching process, the taper was formed owing to the nonuniformly distributed thickness of the mucous layer [6, 13]. Thus, in the first step, the thickness of the floating NaOH electrolyte determined the taper length of the needle, and it was set to about 10 mm in this study. The inert and nontoxic fluorocarbon ether beneath the electrolyte was used to protect the tungsten shank. The

length of the tungsten rod immersed in the inert solution was about 5 mm.

A positive potential varying from 2 to 8 V was applied on the tungsten rod while the platinum plate (10 mm × 10 mm × 0.1 mm) worked as the cathode. As the etching process continued, the diameter of the tungsten rod around the air–solution interface decreased. Finally, the lower part fell off, and a tungsten needle was formed. Through this process, tungsten needles with tapers of different lengths were supposed to be achieved by regulating the thickness of the floating NaOH electrolyte.

In the second step, to further reduce the tip radius of the tungsten needle, an inversed lamellae drop-off process in which etching of the upper tip could be instantaneously cut off was conducted. A schematic of the experimental setup is shown in Fig. 2b. A closed platinum loop with a diameter of 4 mm served as the counter electrode and the supporter of the lamellae NaOH electrolyte. To avoid violent bubble release, 2 M NaOH electrolyte was used in this step. The tungsten needle penetrated the center of the membrane without contacting with the platinum loop, and a droplet of 1 ml of liquid metal gallium (Ga) sustained on a copper plate was used as the connector of the vulnerable tip and the power supply.

In the second fine etching step, the vertical position of the tungsten needle was precisely adjusted using a numerically controlled Z axis with stepping accuracy of 1 μm . A detection potential of 0.1 V was charged between the needle and the copper plate and the downward movement of the needle was stopped immediately once it made contact with the Ga droplet to complete the electric loop. Then, the position of the Pt loop was manually adjusted to be close to the gallium droplet without contact. With this approach, the length of the lower tip, which was finally discarded, could be minimized. A positive potential of 3 V relative to the platinum loop was applied on the copper plate. In this process, the weight of the lower part of the needle was extremely small owing to its small radius and length. Meanwhile, once the lower tip dropped off from the tungsten needle, the electric loop (Pt loop—NaOH membrane—W needle—Ga droplet—Cu plate) became disconnected immediately. Thus, etching of the upper tip was immediately terminated as it was completely separated from the etching circuit. Thus, nano-tips were fabricated using this method.

3 Results and Discussion

Figure 3a, b show the low-magnification full-view scanning electron microscope (SEM) images of the tungsten needles fabricated by the floating electrolyte-based drop-off process with applied potentials of 8 V and 2 V, respectively. The needle etched with 8 V was much bigger than that etched with

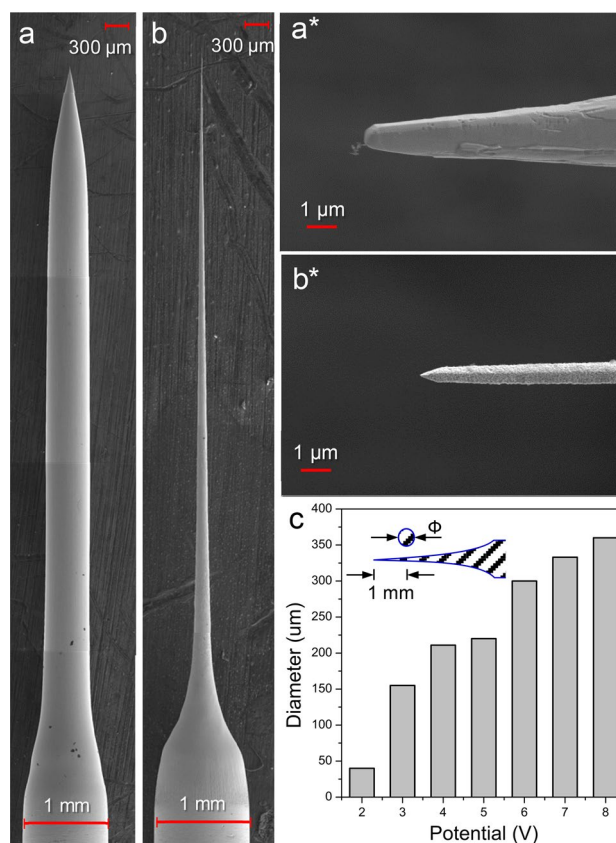


Fig. 3 Full-view SEM images of the tungsten needles etched with applied potentials of **a** 8 V and **b** 2 V. **a***, **b*** SEM images of tips of needles shown in **(a, b)**. **c** Cross-sectional diameters of the needles at the location of 1 mm from the top of the tip versus the applied potential

2 V, which means the total mass removed by etching with 2 V was much larger than that with 8 V. For drop-off etching, the etching duration is determined by the etching speed of the neck region around the air–solution interface [20]. With a higher etching potential, the etching rate is higher and the etching duration prior the drop-off becomes shorter. In this study, etching lasted for 757 s when the potential was 8 V, whereas it lasted for 4184 s when the etching potential was 2 V. The tapering part on the needle was formed by the gradually changed etching rate along the needle, which was governed by several factors, including the thickness of the diffusion layer and the density of OH^- ions [20]. Since the shapes of the needles etched with the potentials of 8 V and 2 V were different, their balancing conditions must have been different during etching [21]. Along the W needle, the thickness of the diffusion layer is determined by two factors: the downward flow of the generated diffusion layer (D_{flow}) and the locally formed diffusion layer by local etching reaction (D_{local}). With a higher etching potential, owing to the high etching rate, D_{local} plays the governing role in the etching process. In contrast, the etching process is slowly

occurring under a small etching potential. Then, owing to the cumulative effect of the downward flow diffusion layer, D_{flow} plays the governing role in the taper formation process. Our results have revealed that a lower applied etching potential is more suitable to fabricate a micro-tungsten needle with a continuous taper, as shown in Fig. 3b.

Figure 3a*, b* shows the high-magnification SEM images of the tungsten needlepoints etched with applied potentials of 8 V and 2 V, respectively. The tip radii were about 418 nm and 60 nm. As shown in Fig. 3a, b, the mass removed with 2-V etching was much larger than that with 8-V etching; thus, a smaller needlepoint was formed. For the following inversed lamellae drop-off process, the smaller the needlepoint, the sharper the tungsten nano-tip that can be achieved. To optimize the etching potential for needle fabrication, tungsten needles etched with a potential varying from 2 to 8 V were fabricated, and their sectional diameters at the point located 1 mm from the needlepoint were measured as a characterization parameter. Figure 3c shows the measured sectional diameters of the tungsten needles etched by different potentials varying from 2 to 8 V. It is obvious that the diameter is positively related to the potential. As a lower etching potential resulted in a tungsten needle with a smaller needlepoint, 2 V was then selected as the potential for the first needle etching step.

Figure 4 shows the curves of current evolution during etching with the applied potential varying from 2 to 8 V. On the whole, the current curves form a platform first, then decrease slowly, and finally drop quickly to zero. The etching process was governed by the inward migration rate of OH^- ions and the surface area available for etching reaction. The formation of current platforms demonstrates that etching had not been restricted by the OH^- ion density or reaction area. It also can be found that with the increase of the potential, the current level at the platform also increased as

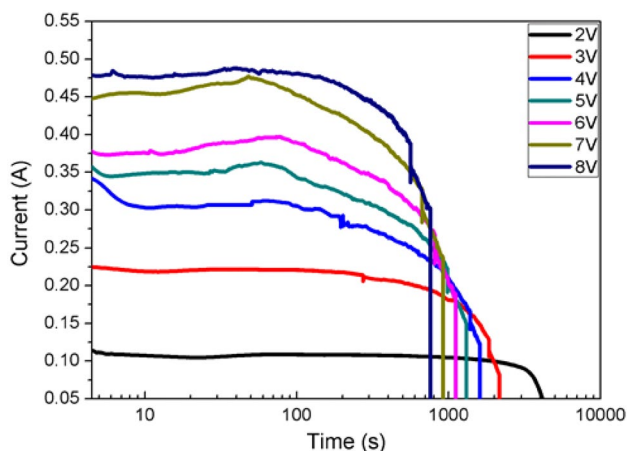


Fig. 4 Curves of current evolution during etching with potentials varying from 2 to 8 V

the increase of potential promoted the migration rate of the OH^- ions. As etching proceeded, the tungsten rod became smaller, and the effective reaction surface area was reduced. Then etching was restricted by the reduced etching reaction area, and the current gradually decreased. Eventually, the current dropped to zero when the lower tip fell from the rod.

As shown in Fig. 3b, a tungsten needle with a long taper of about 10 mm and small needlepoint of about 60 nm was fabricated using the floating electrolyte-based drop-off process with an etching potential of 2 V. Then, the needle was further etched by the inversed lamellae drop-off process to reduce the tip radius. Similar to the conventional drop-off process, the mass of the lower part greatly affected the tip radius. Thus, fine etching with different drop-off lengths was carried out, as shown in Fig. 5a. Though the shorter the drop-off length, the sharper the tungsten tip, the minimum drop-off length is limited by the experimental setup used. In this study, to make the tip fabrication process more reproducible, the position was considered the best when the gap between the Pt loop and the Cu plate was 2 mm (position I).

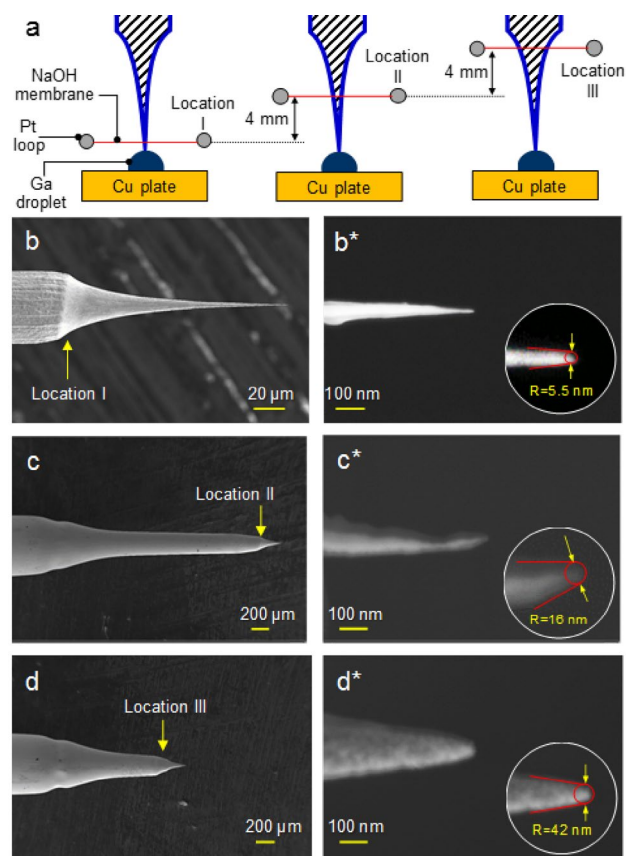


Fig. 5 a Schematic of the second fine etching process. **b, b*** High-resolution SEM images of the prepared tungsten nano-tip etched at location I. **c, c*** SEM images of the prepared tungsten nano-tip etched at location II. **d, d*** SEM images of the prepared tungsten nano-tip etched at location III

Using position I as the reference, the position of the Pt loop was further adjusted to change the drop-off length.

Figure 5b shows the high-resolution SEM image of the tip. A conical nano-tip with a taper length of 120 μm was formed by the fine etching process. Figure 5b* shows the high-resolution SEM image of the tungsten tip. The tip radius was 5.5 nm, which is even smaller than that of the sharpest tungsten tip made by the conventional drop-off method with a radius of 10 nm [11]. In the inversed lamellae drop-off process, the location of the Pt loop is important because it determines the mass of the lower tip. When the loop was at location II, which was lifted by 4 mm relative to location I, the radius of the tip was about 16 nm, as shown in Fig. 5c, c*. When the loop was at location III, which was further lifted by 4 mm, the radius of the tip was about 42 nm, as shown in Fig. 5d, d*. It is obvious that the tip radius increased with the increase of the drop-off length. It is noteworthy that the smallest nano-tips fabricated by the second fine etching step may have different tip radii in different etching operations as the position of the Pt loop was determined by naked-eyes and manually lifted. However, it can be well repeated to fabricate nano-tips with radius of sub-10 nm.

For comparison, a tungsten tip fabricated by the conventional lamellae drop-off method is presented in Fig. 6. The tip was made from a tungsten wire with diameter of 0.1 mm, and the drop-off length below the platinum loop was 2 mm. Figure 6a shows the schematic of the etching setup. The fabricated tip had a radius of 12 nm, as shown in Fig. 6b, b*, which is much larger than the tip prepared with our proposed combined method, though the utilized tungsten wire was much smaller. This result also verifies that our combined etching method has more advantages to produce tungsten nano-tips over the conventional drop-off method.

To fabricate the tungsten nano-tip with a large shank as shown in Fig. 5b, the two combined etching steps are both indispensable. The first floating electrolyte-based drop-off process makes it possible to fabricate tungsten needles with a long taper and a large shank. Meanwhile, the fabricated needle has a small needlepoint, which makes it possible to greatly reduce the drop-off mass in the second fine etching step. As for the second inversed lamellae drop-off step, the key point is the use of liquid metal to apply the positive potential on the lower tip of the tungsten needle instead of the upper tip as in the conventional drop-off process. At the moment of dropping, the upper tip and the lower tip separate from each other under the influence of gravity. The potential on the upper tip vanishes naturally after a very short time, which is similar to what happens to the lower part in the conventional drop-off process. In this way, the problem of the conventional method that the upper tip is usually less sharp than the lower tip owing to the delay of disconnecting the power has been solved. Considering that we do not use any

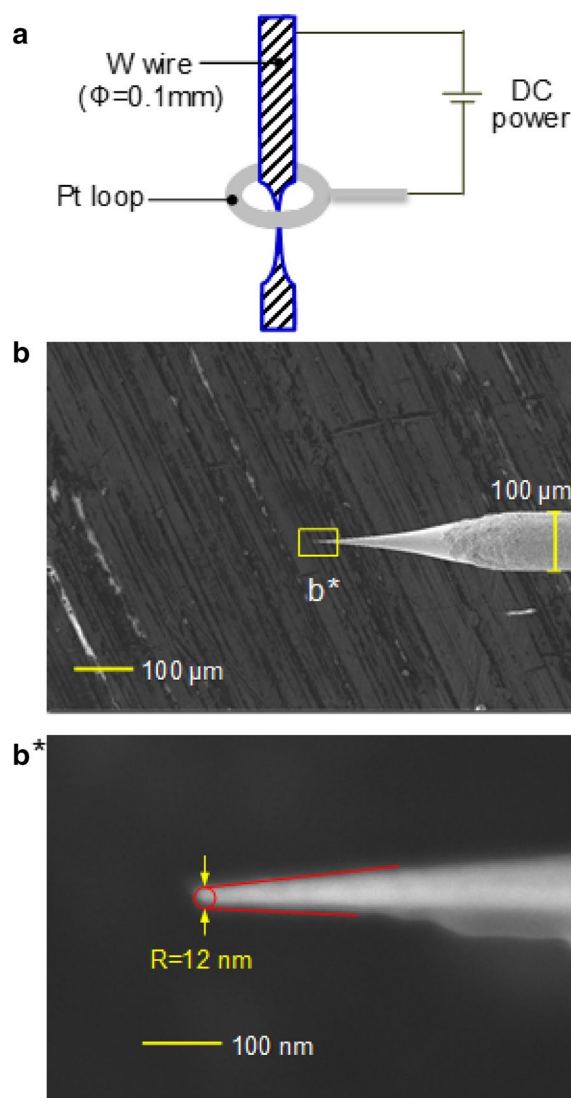


Fig. 6 a Schematic of the conventional lamellae drop-off setup. b, b* SEM images of the fabricated tungsten tip

specialized instruments, we believe this simple, versatile, and cost-saving method can be an alternative approach for the fabrication of tungsten tips with a sub-10-nm radius, a long taper, and a large shank.

4 Conclusions

In conclusion, we proposed a two-step electrochemical etching method to fabricate ultra-sharp tungsten nano-tips with a long taper and a large shank. The first floating electrolyte-based drop-off process was carried out to fabricate tungsten needles with a long taper and a large shank. Then, as the second fine etching step, an inversed lamellae drop-off process further etched the needlepoint to form a sub-10-nm nano-tip. In this way, an ultra-sharp nano-tungsten tip with

a small radius of 5.5 nm, a long taper of 10 mm, and a large shank of 1 mm was finally obtained without the use of specialized instruments. Compared with the tips fabricated by conventional drop-off methods, it is believed that the tungsten tips fabricated by the proposed two-step method have more practical values.

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