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Technical Notes

Preparation of Reliable Probes for Electrochemical Tunneling Spectroscopy

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We present a new procedure to prepare Pt/Ir probes for electrochemical scanning tunneling microscopy (STM) and spectroscopy applications. We detail the experimental setup and the improvements over previous methods. The probes have been used successfully for measurements of tunneling spectroscopy under electrochemical control, which requires scanning the potential of the tip at high velocity.

Since its introduction 20 years ago,[1] scanning tunneling microscopy (STM) has been found to be of use in a wide range of applications: high-resolution images of the surfaces of conductors[2] and semiconductors,[3] study of local electronic properties,[4] and modification of surfaces through local oxidation[5] or deposition.[6] More recently, it has been applied to chemical recognition of extended molecular moieties,[7] real-space imaging of organic monolayer structures with submolecular resolution,[8] and the induction of conformational changes.[9] For many of these applications, STM requires well-defined surfaces, and it must be operated either in ultrahigh vacuum (UHV) or in an environmental gas chamber. In the past decade, STM has been applied to the study of solid−liquid interfaces,[10] which entails the immersion of the STM probe into the liquid media and its corresponding electrochemical control (ECSTM) for in situ monitoring of redox processes on the sample electrode.

ECSTM has advantages over classical or conventional STM operated either in air or in a vacuum. It allows precise and independent control of both tip potential and sample electrode potential through the use of a bipotentiostat and a true reference electrode. This control is essential when studying semiconductor surfaces to obtain quantitative information on the electronic energy levels.

In a vacuum, the STM microscope allows one to perform electronic spectroscopy by recording the tunneling current (I_t) vs. the bias potential (V_b). Known as scanning tunneling spectroscopy (STS), the technique has also been implemented in the electrochemical environment, giving rise to the electrochemical scanning tunneling spectroscopy (ECSTS) technique.[11] Despite becoming a powerful spectroscopic tool, ECSTS is still not widely used because the systems in which it can be applied are rather limited and sophisticated tip preparation methods are required.[12] Here we present a method to facilitate tip preparation in order to extend STS to a wide range of systems.

In ECSTS, the measured current flowing through the tip has several components: the STM tunneling current itself, a faradaic current caused by an eventual electrochemical reaction at the tip/electrolyte interface, and a capacitive current generated by the charge−discharge process of the electrochemical double layer in the tip−electrolyte interface. If the last two contributions are larger than the set-point tunneling current, the STM measurement will no longer be possible.

Methods have been proposed to eliminate these two electrochemical contributions to the measured tip current.[11] The most effective alternative, taking advantage of the fact that faradaic/capacitive currents are directly proportional to the exposed area of the electrode, consists of coating the tip[13] except for the very apex so that tunneling current can flow while faradaic and capacitive currents are minimized. In STM, the tunneling current is usually set to between 1 and 10 nA. For precise measurement,

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coated tips must yield faradaic and capacitive currents ≤ 0.1 nA at the end of the STS curve when ramping at the highest tip potential scan rate (up to 10 V/s) needed to minimize drift, whereas the STS curve is recorded out of feedback. Various methods and materials have been proposed for coating purposes, such as Apiezon wax,[14] melt glass,[15] copolymers,[16] and a combination of glass and polymer,[13,17] and in all these coating procedures, the faradaic and capacitative contributions are too large to be subtracted from the measured tip current, and thus, they do not allow STS spectra to be under electrochemical control.

We propose a procedure for tip fabrication that provides both tip sharpness and coating with the appropriate specifications for ECSTS applications. The procedure consists of sharpening a Pt−Ir wire[18,24] and then coating it with electrophoretic paint. Electrophoretic paints are increasingly used as chemically and electrochemically inert insulators for Pt−Ir tips,[19] electrodes,[20] sensors,[21] AFM tips,[22] or combined SECM/OM (SNOM) probes.[23]

Among the various protection methods available, Apiezon wax is used for ECSTM tip isolation, despite its disadvantages. In our hands, the success rate was only ~10%, and the lifetime of the coating was short. Our electrophoretic painting decreased the nontunneling current by at least 1 order of magnitude, and around 60% of the fabricated tips were suitable for STS experiments after only one coat.

Pt−Ir 80−20 alloy wires were chosen because STS requires a metal that is chemically inert in a wide range of potentials and mechanically stable during the operation. In early STS experiments in UHV, cut-wire Pt tips were used. However, the results were not reproducible, so STM tips are now mainly prepared by electrolytic etching. Our procedure yields Pt−Ir tips with small radii of curvature; it is fast and low cost and does not require sophisticated equipment.[16] In addition, the procedure, which runs in AC current,[24] uses innocuous chemicals ($CaCl_2$, HCl, H_2O),[25] avoiding the more hazardous alternatives (cyanide, NaCN/KOH, or molten $NaNO_3$/NaCl salt).

Finally, the application of the fabricated tips is demonstrated in the acquisition of reproducible, low-noise, wide electrochemical potential range STS spectra of the iron(III) oxide film grown in a borate buffer solution at pH 7.5.
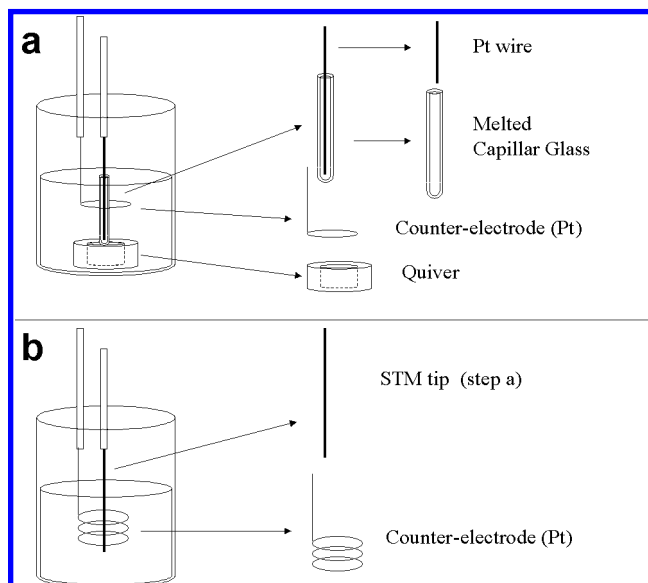
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Figure 1. Schema of the experimental setup used in the two processes involved in tip preparation. (a) Etching process. The wire is partially isolated by a glass capillary and dipped into the solution. (b) Electrophoretic deposition paint process.

EXPERIMENTAL SECTION

Materials. Platinum−iridium 80−20 alloy wires (purity 99.999%, Advent, Oxford, U.K.) were used as tip material. Clearclad HSR (LVH coating) cathodic electrophoretic paint was used to coat the wires.

All chemicals used, $Na_2B_2O_7$, H_3BO_4, $CaCl_2$, KCl, and HCl, were of reagent grade purity (Merck, Darmstadt, Germany) and were used without further purification. The supporting electrolyte was a borate buffer solution of pH 7.5 made from 0.3 M H_3BO_3 and 0.0375 M $Na_2B_4O_7 \cdot 10H_2O$. Aqueous solutions were prepared using Milli-Q deionized water (Milli-Q, Millipore Corp. Bedford, MA), resistivity >18 MΩ cm^{-1}.

Conductive Filled Phenolic Mounting Compound (Buehler Konductomet) was used to mount coated wires to be characterized by scanning electron microscopy (SEM) and optical microscopy. Further mechanical grinding and polishing was performed with silicon carbide grinding paper (Buehler) and polishing cloth with 1-μm diamond compound (Aerosol spray, Buehler Metadi).

Apparatus. All electrochemical experiments were carried out using an Autolab PGSTAT12 (EcoChemie) in a three-electrode configuration with a home-built Ag/AgCl reference electrode. All potentials are quoted versus this reference electrode. A home-built Faraday cage was used to reduce electrical noise. Scanning tunneling spectroscopy (STS) experiments were conducted using a scanning tunneling microscope (PicoSPM, Molecular Imaging Co.) working in the electrochemical STM mode with a low-noise bipotentiostat/galvanostat Picostat (Molecular Imaging Co.) controlled by Nanoscope IIIa electronics (Digital Instruments, Santa Barbara, CA). The STM head was placed on a bench isolated against vibrations, and the cell was shielded by the Faraday cage. SEM images were acquired using a Leica Cambridge Stereoscan S360 (Cambridge Instruments).

The experimental setup (Figure 1) was used for both electrochemical etching and paint deposition. It consisted of a vertical stainless steel capillary tube attached to a vertical micrometer screw. The Pt−Ir wire to be sharpened or coated was introduced

into the capillary by friction and fed into a 25-mL beaker containing the solution (etching solution or electrophoretic paint). The capillary was connected to one lead of the power supply, and the return lead was connected to a 7-mm-diameter ring auxiliary electrode made of platinum. In both cases, the beaker was a one-compartment electrochemical cell in a two-electrode configuration, working at room temperature.

Etching Procedure. Figure 1a shows the arrangement of elements for the etching process. The lower end of the capillary tube is melted. The Pt−Ir wire is inserted into the glass capillary tube, isolating it from the solution. The Pt−Ir wire melted capillary is immersed into the electrolyte, adjusting the immersion depth with a micrometer screw until ∼1 mm of the uncovered wire is in contact with the solution. The wire is etched along the area that is in contact with the electrolyte, becoming thinner and breaking down.

The electrochemical etching bath consists of an unstirred aqueous solution of 66% $CaCl_2$ and 4% HCl. Immediately before the wire is immersed, several milliliters of Milli-Q water are added to the etching solution without stirring to establish two phases. The amount added should be ∼10% of the volume of the initial solution. The black platinum chloride formed[26] at high temperatures during the etching process accumulates in the upper aqueous phase, thus leaving the etching solution (bottom phase) free of this black component. The solution can be used for the next two stages. Nevertheless, it is advisable to refresh the solution for each tip, since Cl_2 is given off during the process. To ensure symmetric distribution of the electric field around the tip and thus symmetric etching, the wire must be at the center of the Pt auxiliary electrode ring.[19a]

The procedure has three sequential stages. Starting with a fresh solution, we set a potential bias of 27 V AC, which supplies an initial current of 250 mA. The current may fluctuate due to the strong Cl_2 evolution and the increase in temperature at the Pt−Ir−electrolyte interface. When the registered current drops to ∼130 mA, we stop the process, and the upper phase containing the black platinum complex is removed.

In the second stage, the same volume of clean Milli-Q water is added to the solution and the applied AC voltage is stepped to 8 V, and so the etching becomes smoother. The initially vigorous gas evolution ceases, and only a few bubbles are observed. In this second stage, the initial current is ∼100 mA, and in no more than 3 min it decreases to ∼80 mA. Finally, in the third stage, the AC applied voltage is reduced to ∼3 V, which remains until the tip breaks down.

The electrolytic reaction cuts the wire, the lower portion falls off, and thus, now we have two tips. The lower tip has a better aspect ratio, as observed at SEM, so the lower tip is used for STM measurements. To protect the sharpened end from damage when it falls, it is caught in a quiver. The upper wire portion, which is still in contact with the electrolyte surface, will be further etched and the end will be blunted.[27] Indeed, because this upper portion is useless, there is no need to stop the etching process quickly, since the response time is less critical. The lower part is recovered from the quiver. The tip is removed from the capillary tube and is now ready to be used for STM experiments or to be coated for ECSTM/STS applications requiring electrical isolation.

The total etching time depends on the length of the wire immersed in the solution, the area exposed during the etching, and the $CaCl_2$ concentration in the electrolyte, which in turn also changes with time. But for most of our runs, the etching process lasts ∼15 min.

Paint Deposition. The etched tip is insulated in the experimental setup shown in Figure 1b. The etched wire is held vertically in the stainless steel capillary tube with the tip downward and immersed in the electrophoretic deposition paint (EDP) solution. To achieve a homogeneous distribution of the electric field and, thus, a continuous defect-free coating, the tip must again be in the center of the auxiliary electrode ring. Prior to use, the electrophoretic paint is diluted (1:3) in Milli-Q water. Ten milliliters of EDP solution is sufficient to cover efficiently several STM tips without further refreshment.

A constant DC voltage of −7 V is applied for 3 min between the tip (cathode) and the platinum auxiliary electrode (anode)[28] until the current drops to ∼0. The tip is taken from the solution and rinsed in distilled water to remove any excess nonattached particles.

The wire is then placed in a holder with the tip pointing upward and heated in an oven at 200 °C for 30 min. The tip is then taken from the oven and cooled at ambient temperature. Finally, a rough coating of Apiezon is applied to the nonetched part of the tip to improve mechanical stability and to prevent damage to the electrophoretic layer when it is being handled.

RESULTS AND DISCUSSION

Tip Geometry and Isolation Characterization. Scanning electron microscopy is used to characterize the geometry, radius, and shape of the etched tips. Figure 2 shows low- and high-magnification micrographs of an electrochemically etched tip. The tips have a low aspect ratio[27] and a radius of curvature at the apex of ∼50 nm. Note the smooth surface, characteristic of tips fabricated by electrochemical etching.[25]

To achieve a low curvature radius, the third stage of the etching procedure must be done at low ac voltage (∼3 V), thus promoting an accurate and smooth microetching of the wire. This stage makes the etching process smoother, thus avoiding the melting of Pt at the tip.[29] Our three-stage procedure (27, 10, and 3 V) results in a faster and more reliable method than the one presented elsewhere,[29] in which the final 2 V micropolishing stage in cyanide solution is very slow.

The homogeneity and thickness of the isolation polymer layer was assessed by optical micrographs (Figure 3). Hardened coated Pt−Ir wires were embedded in a conductive resin, well molted, then ground, and finally, polished with 1-μm diamond compound cloth to a mirror finish. The embedding process does not damage the coating, most probably because the working temperature is below 150 °C. Optical micrographs of such sections show a homogeneous polymer film well adhered to the metal surface. The concentric coating has an average thickness of 15 μm, with a smooth decrease as the tip end is approached because of vertical hardening.

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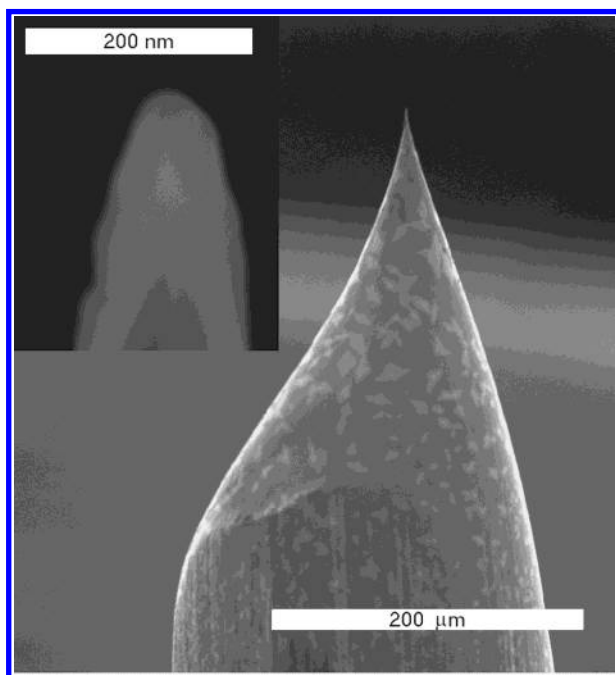(29) Zhang, B.; Wang, E. *Electrochim. Acta* **1994**, *39* (1), 103−106.

Figure 2. Scanning electron micrograph of an etched Pt−Ir tip showing the tip shape against the wire diameter. Inset: Magnification of the above micrograph showing the radius of the tip apex.
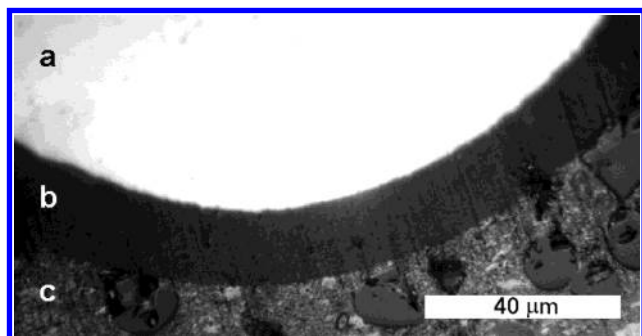

Figure 3. Optical microscope image of a section corresponding to an embedded electropainted tip once insulated. Platinum−iridium wire diameter is 250 μm. (a) Pt−Ir wire. (b) Electrodeposited insulating paint. (c) Embedding mounting compound used for polishing.

Scanning Tunneling Spectroscopy Applications. Figure 4 show an ECSTS experiment to assess the quality of the tips. The tip current was recorded while the tip potential was scanned twice versus the reference electrode: once, far away from the surface at 5 nm, and the second time at a tunneling distance of a few angstroms, corresponding to 6 nA of tunneling set point[11] (Figure 4a). The first experiment measures the electrochemical current, which incorporates the faradaic and capacitive currents, and it is subtracted from the total tip current recorded in the second experiment, the result being the pure tunneling current. To obtain a commensurate value of the pure tunneling current, the electrochemical current subtracted should be less than 10% of the total, thus minimizing the subtraction error. A representation of the pure tunneling current as a function of the tip potential characterizes the electronic structure of the studied sample. Figure 4b shows an STS spectrum for a semiconducting iron oxide film in a borate buffer medium at pH 7.5. In this experiment, the potential of the iron oxide layer/iron electrode is fixed within the electrochemical potential range corresponding to the passive region while the
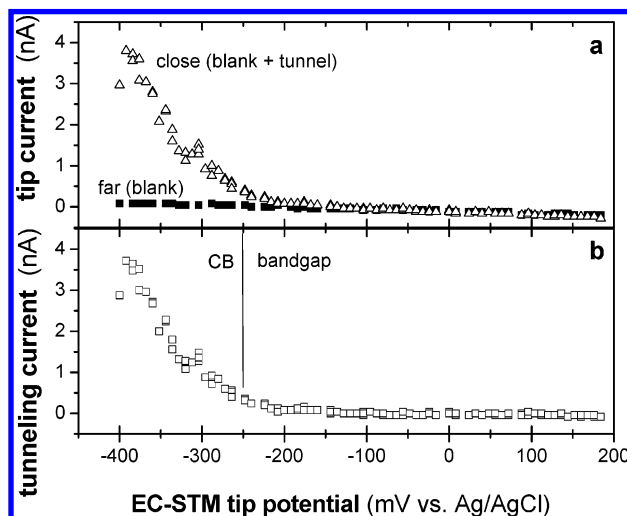

Figure 4. ECSTS spectra of the Fe (III) oxide film/iron electrode held at +500 mV in a borate buffer solution at pH = 7.5. (a) Spectra corresponding to total tip current (close distance tunneling) and the nontunneling current components (far away). (b) Pure tunneling current component.

spectra are registered. The iron(III) oxide film has been grown at the prefixed potential within the passive layer and presents n-type semiconducting properties.[30] The interfacial potential keeps the semiconductor band bending and, hence, the interfacial charge density at the electrode surface, as well as the energetic position of the conduction and valence band edges. The tip potential is scanned versus the potential reference electrode from −0.5 to +0.5 V at 10 V/s. The electronic structure of the oxide film can then be inferred from the STS spectra. Two different regimes are observed: a low-current electrochemical range (faradaic background of ∼10 pA for the probe used) corresponding to the band gap, and an exponential current growth as U_{tip} approaches the conduction band edge ($U = -0.3$ V/SSC).[4]

In STS applications, our coated tips present several improvements with respect to the Apiezon wax coatings, as indicated by the results shown in Figure 5. First is the high efficiency of the coating method using the electrodeposition paint (Figure 5a). Up to 50% of the coated tips are well-isolated, giving a maximum current flow of <0.2 nA for an STS curve recorded at 10 V/s. Second, up to 80% of such coated tips present a current flow of <1 nA, as compared with only 10% of the tips coated with Apiezon wax, even after three coatings (Figure 5b). Indeed, 5% of the prepared tips have a current flow of <20 pA. Third, fine insulation with Apiezon wax requires several coatings, but unfortunately, the tip apex is also frequently insulated. In our case, 60% of the Apiezon-coated tips were completely isolated after three coats. This percentage varies over a wide range due to the poor reproducibility of the method itself. The area finally exposed depends on poorly controlled parameters, such as the temperature of the melted wax or the tip velocity through the melted wax.

Chen et al.[28] found that, for carbon fibers, the area exposed using electrophoretic paint depends on the thickness of the coating applied. If it is too thin, pinholes appear along the length of the wire, due to shrinkage and protrusions on the surface. In our case,

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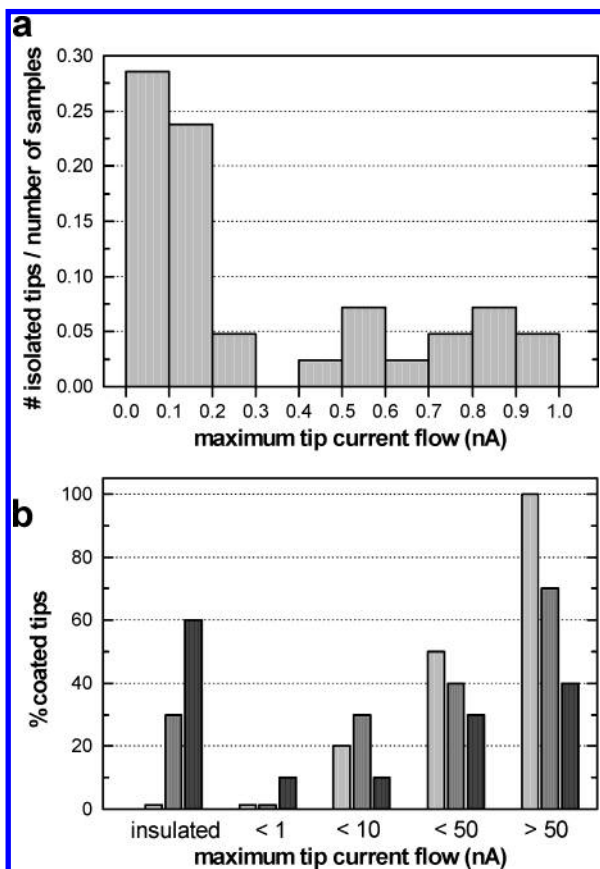
Figure 5. Histogram representing the number of coated tips as a function of the total current flowing through the tip. (a) Electrophoretic paint data. Coated only once. Total number of samples is 30. (b) Accumulative bare diagram. Apiezon data. Several coating layers have been applied: light gray, coated once; grey, coated twice; dark gray, coated three times. Total number of samples is 20.

to avoid this dependence, the heat curing was done with the tip upward, with the exposed area only at the very end of the tip apex. This position allows the paint layer to slide along the tip during the thermal hardening, which means that the thickness of the coat increases from the end of the apex to the cylindrical wire section. The results reported in Figure 5 were always obtained with one deposition/heat cycle.

CONCLUSIONS

Pt−Ir tips have faradaic stability in a wide electrode potential range (up to 2 V). Unfortunately, powerful potential applications have not been developed, because the methods used to prepare such probes are not reproducible. We report a simple method to prepare Pt−Ir STM tips suitable for the classical in situ imaging applications and for sophisticated tunneling current measurements while scanning the tip potential. The new electrochemical etching procedure gives a clear improvement in the reproducibility of both curvature radius (<50 nm) and low aspect ratio (<1.2). In addition, the use of electrophoretic paint for the electrochemical isolation of the Pt−Ir, allows us to achieve a tip noise current in the level of 20 pA at potentiostatic conditions and nice statistics (80%) on isolated tips with 1 nA of maximum current when scanning the tip potential at high scanning potential rates on the order of 10 V/s. All of these specifications demonstrate that the tip fabrication method we propose succeeded in the preparation of STM probes for ECSTM and ECSTS applications.

Note Added after ASAP. This paper was originally posted on March 23, 2004. The primary change was to the first paragraph of the second page. Citation of ref 19 for use of electrophoretic as inert insulators for carbon tips was changed to Pt−Ir tips. This paper was reposted on the Web on July 23, 2004.