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Preliminary note

Fabrication and characterization of microtips for in situ scanning tunneling microscopy

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INTRODUCTION

We report a new method of preparing tips suitable for atomic resolution scanning tunneling microscopy (STM) imaging in redox active solutions and further characterize these tips as ultramicroelectrodes

STM imaging of surfaces in redox active solutions is a rapidly developing area [1]. One feature that differentiates this application of STM from others performed in air or vacuum is the need to insulate all but the very end of the STM tip to minimize faradaic currents. These currents, which can be several orders of magnitude larger than the tunneling current (ca. 1 μA vs. ca. 1 nA), will prevent precise positioning of the tip and make atomic resolution unfeasible. One way to eliminate this electrochemical background is to subtract it off electronically; however, even modest electrochemical currents can be highly variable and thus the tunneling current set point will also vary, causing instability in the imaging.

Several papers describe the construction of insulated STM tips for use with samples immersed in liquid [2]. The early in situ STM efforts with atomic resolution [3] used commercially available glass coated tips [4] where the Pt + Ir metal surface was exposed by high frequency discharge. While these tips have enjoyed subsequent popularity, they suffer from a number of drawbacks that limit their effectiveness. First, the exposed metal area is fairly large and background currents around 5 nA have been reported [3], implying that STM tunneling currents must be almost two orders of magnitude larger than those generally used in air or vacuum to ensure that the tunneling current contribution is not overwhelmed by the faradaic background. Second, these tips are costly and their availability limited. Finally, the tips must be heated to over 1000 °C to melt glass onto them, and this procedure places restric-

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tions on the material that can be used for the tip and the kind of mounting employed. For example, we have used very short tips soldered into IC pin socket holders, which melt at the glass coating temperatures. While it is possible to use a set screw apparatus to hold longer, more easily handled tips, the exposed threads are hard to seal and provide additional weight at the end of the piezo, which decreases the STM's stability.

Several other tip coating materials have been proposed. Gerber [5] described a tip coating made from a silicone rubber material. While atomic resolution on HOPG in *M* KCl was obtained with this tip, its electrochemical behavior was uncertain. Lustenburger et al. [6] and Behm and co-workers [7] have used Ta and W tips, where a thick oxide layer formed over the etched tip limits the electrochemical background to few pA. Unfortunately, the oxide layer also prevents atomic resolution. Hansma [8a] and Lewis [8b] have proposed using tips that have been sputter-deposited with SiO_2. This coating is then punctured by field emission with the tip close to the sample. This technique, while promising, does require sputtering apparatus and can possibly damage the sample surface during the field emission process.

An additional problem with coated tips for in situ STM work is that their characterization is difficult. While surface scientists working in high vacuum have utilized field emission microscopy to look at the tip structure [9], such methods are not available in aqueous environments. Alternatively, electrochemical characterization of ultramicroelectrodes has been standard for many years, and these techniques can be used to quantitate the degree of exposed tip area and describe some aspects of the coating.

EXPERIMENTAL

The method of preparation of the tips is illustrated in Fig. 1. STM tips were prepared from a 125 μm diameter Pt + Ir rod (FHC Co., Brunswick, ME) which was soldered into an IC pin socket holder and cut to length (typically 3–5 mm). A tip was formed by electrochemical etching in a solution of saturated $CaCl_2$ (60% by volume), H_2O (36%), and HCl (4%) against a carbon rod at 20 V RMS ac by using a Voriac until the tip was completely out of the solution. This was followed by a subsequent 3 s etch at 5 V RMS ac to produce a slightly rounded smooth finish. After etching, some tips were plated with Au (Special Gold SG-10, Transene Corp., Billerica, MA) or cleaned by 15 s immersion into an aqua regia bath.

Tips were coated by dipping into a solution containing 5 parts (by volume) Epoxylite 6001 varnish and one part Epoxylite 6001-s solvent (Epoxylite Corp., Irvine, CA). The tips were returned to an upright position and the varnish allowed to run off the tip. The surface tension of the coating material is such that it adheres to the Pr + Ir rod everywhere except in the vicinity of a sharp radius, i.e., the tip itself. We could thus control the degree of coating by varying the dilution of the varnish and the sharpness of the tip (see below). The coated tips were hardened by 1 h of drying at room temperature followed by 2 h at 80 °C and 1 h at 170 °C.

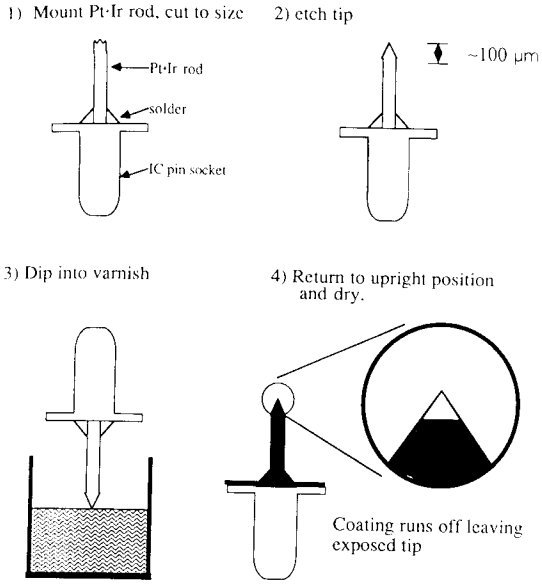

Fig. 1. Procedure for producing STM tips.

STM measurements with both sample and tip under potential control were performed using an instrument described previously [10]. Data were collected by an Arlunya TF6540 image processor, stored on VCR tape, and accessed for plotting via a personal computer.

Ultramicroelectrode characterization was performed using a home-built potentiostat utilizing an OPA128LM op amp (Burr-Brown Corp., Tucson, AZ). Voltage sweeps were performed with a PAR 175 universal programmer. Chemicals were reagent grade and aqueous solutions were prepared with Millipore water.

RESULTS AND DISCUSSION

Tips were characterized both electrochemically and with the STM. On immersion into 1 *M* H_2SO_4 solution with the tip potential held between 0.15 and 0.55 V vs. SCE, the background current was typically between 0.01 and 0.05 nA, rising to between 0.1 and 0.2 nA after several hours immersion. Background currents through the tip remained at this level with an HOPG sample poised at any potential between -0.6 and $+1.0$ V vs. SCE. Equally important, these tips enable atomic resolution at these potentials. Figure 2 shows a 1.5 by 1.5 nm image of a highly oriented pyrolytic graphite surface immersed in 1 *M* H_2SO_4 with the tip held at 0.20 V vs. SCE and the surface at -0.40 V vs. SCE. The tunneling gap was thus 0.6 V and the tunneling current was 2 nA. This image demonstrates that atomic resolution is possible, even under these extreme electrochemical conditions and with a high tunneling gap resistivity (3×10^8 Ω). At these potentials, the barrier height to tunneling, measured

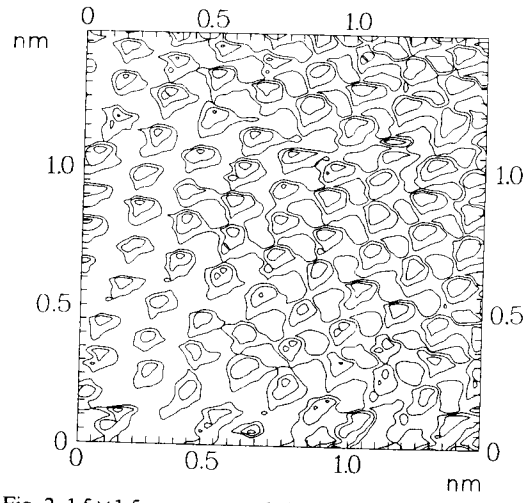

Fig. 2. 1.5×1.5 nm constant height STM image of highly oriented pyrolytic graphite in 1 *M* H_2SO_4 with the surface held at −0.4 V vs. SCE, *V*(tip) = +0.6 V, *i*(tunnel) = 2 nA. Image is uncorrected for sample tilt.

by modulating the tip by 50 pm at 8 kHz relative to the sample surface and locking in on the modulated tunneling current, was between 1 and 2 eV, comparable to results obtained in vacuum. This indicates that the tip is not highly contaminated, as the presence of substantial adsorbates on the tip would be expected to lower its work function and lead to reduced barrier heights. One final indication of the suitability of the tips for in situ work is their behavior on touch-down to the sample surface. We have found that highly contaminated tips "crash" onto the surface and exhibit substantial hysteresis before they tunnel correctly. Alternatively, uncoated tips or the coated tips used in this study approach the surface cleanly and touch down without any hysterisis.

While STM measurements demonstrate the suitability of these varnish-coated tips for in situ work, they give no indication of the size of the uncoated area.We were unable to distinguish between coated and uncoated areas on the Pt + Ir rod using either optical or scanning electron microscopies. We thus characterized tip electrodes by investigating their electrochemical behavior in a solution containing 10 m*M* ferricyanide with 0.2 *M* KCl as the background electrolyte. The approximate areas of the tip electrodes were calculated using the equation for the steady-state current obtained at an ultramicrodisk electrode given by [11]

$$i_{s,s} = 4\pi FrcD \tag{1}$$

where *c* and *D* are the concentration and diffusion coefficient, respectively, of the electroactive species, *F* is Faraday's constant, and *r* is the radius of the disk electrode. The degree of exposed metal area varied with different coating procedures and different tip preparations, but was fairly constant for tips prepared in the same

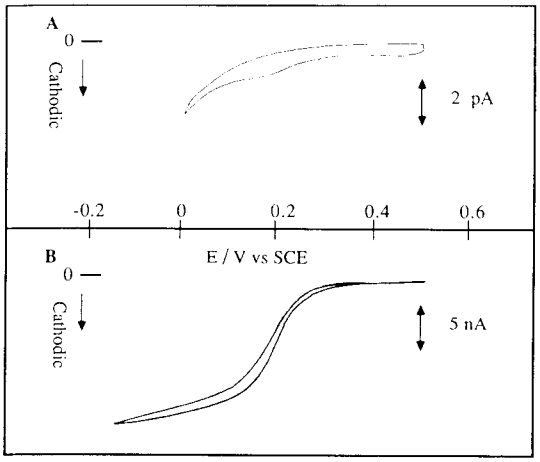

Fig. 3. Cyclic voltammogram of two different tip electrodes in $K_3Fe(CN)_6$ (0.2 *M* KCl) at a scan rate of 5 mV/s. (A) Electrochemically etched Pt + Ir rod coated with Epoxylite varnish (5 m*M* ferricyanide); (B) electrochemically etched Pt + Ir rod cleaned in aqua regia and then coated with Epoxylite varnish (10 m*M* ferricyanide).

manner. Figure 3 shows cyclic voltammograms for tip electrodes prepared in two different manners. For Pt + Ir tips coated with varnish without further treatment (Fig. 3A), exposed tip radii spanned a range from 0.01 to 1 μm. Alternatively, Au-plated tips showed somewhat larger exposed areas with apparent exposed tip radii in the range of 0.1 and 3 μm. Finally, the aqua regia cleaned tips (Fig. 3B) exhibited the largest radii with values between 1 and 5 μm.

Clearly, the smallest exposed areas ($r \leq 0.1$ μm) were found with bare tips coated with the Epoxylite varnish. With this coating technique, a range of exposed tip areas could be obtained with different tip shapes. We found that the best coatings were obtained with tips tapering with a cone ca. 100 μm in length. Longer tapers invariably resulted in poorer STM images and more capacitive electrochemical behavior.

Both the aqua regia and gold plating treatments resulted in substantially larger exposed tip area relative to tips made from untreated Pt + Ir rod. Under an optical microscope, the surfaces of these tips appeared rougher and less well formed than the untreated tips, probably because the coating material does not flow as readily over these surfaces as over the smoother untreated surface.

The cyclic voltammetry also indicates that there are large capacitive currents associated with these tips. This could be due to either the electrolyte leaking between the metal and the coating material, or, less likely, that areas of the tip are coated with only a very thin layer of material which has a low dielectric constant. As can be seen in Fig. 3B, somewhat better electrochemical behavior is observed with the larger aqua regia pretreated tips. We further found a reduction wave at

potentials around −200 mV vs. SCE, possibly due to reductive decomposition of the coating material at this potential.

The exposed area of the tip will be governed by how well the coating solution flows over the etched point of the metal rod. This can be influenced by a number of factors including (a) the shape and topography of the etched point of the metal rod, (b) the surface tension between the coating solution and the metal, and (c) the viscosity of the coating solution. While we have not tried to optimize each of the above factors to produce tips with the best possible microelectrode behavior, it is likely that smaller electrodes can be produced than those described above, by using the same technique.

We have described a simple method for producing STM tips suitable for work in aqueous environments and have demonstrated that these tips can produce atomic resolution images in a 1 *M* H_2SO_4 electrolyte with the HOPG sample poised at any potential between −0.6 and +1 V vs. SCE, as long as the tip is held in the double layer region for Pt. We have used electrochemical measurements to demonstrate that the radius of the exposed area of these tips ranges from 0.01 to 1 μm. The STM tips produced with this coating procedure are small and can be mounted in a variety of different ways to the STM. Further work with different coating materials utilizing this surface tension approach is currently in progress.

ACKNOWLEDGEMENTS

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