Preparation and Characterization of Carbon Powder Paste Ultramicroelectrodes as Tips for Scanning Electrochemical Microscopy Applications

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S Supporting Information
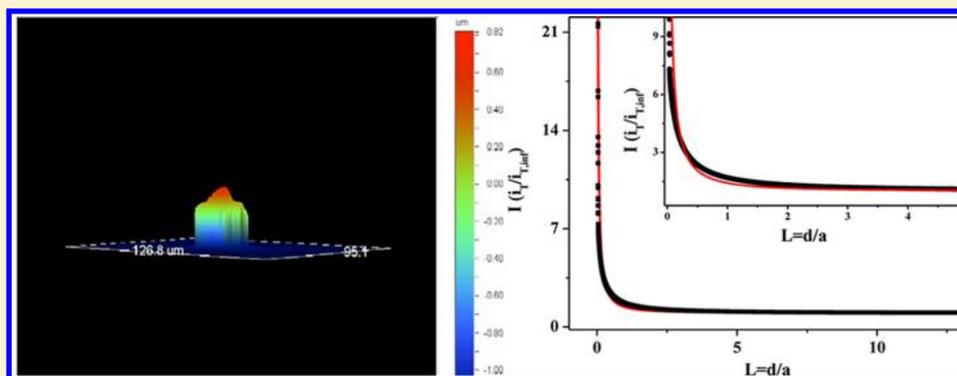
ABSTRACT: We report a simple method of preparation of carbon paste ultramicroelectrodes (UMEs) for use as probe tips in scanning electrochemical microscopy (SECM). Carbon paste UMEs were prepared by packing the carbon paste into a chemically etched tip of a Pt-UME or a pulled glass capillary. Carbon-based UMEs are attractive in micrometer to nanometer gap experiments and in electrodeposition of single metal nanoparticles for electrocatalytic studies because of their high overpotential in proton and oxygen reduction. We have demonstrated the preparation of conically shaped carbon paste UMEs, appropriate for SECM measurements and micrometer to nanometer gap experiments.

Scanning electrochemical microscopy (SECM) has been widely used for the study of surface processes and structures. An important factor in such studies is the availability of easily fabricated and rugged ultramicroelectrode (UME) tips, and many reports on how to construct these have appeared.[1] A significant problem is the difficulty in fabricating and maintaining SECM tips, especially with radii in the sub-micrometer regime, with a small enough insulating sheath (RG value) to allow close approach to a substrate. For example, as we show below, carbon paste tips can be fabricated simply by packing a pulled capillary with no polishing, and we demonstrate this with a tip with a radius below 150 nm.

For high spatial resolution and measurements of fast heterogeneous and homogeneous rate constants, tips with small radii, a, are required. For example, heterogeneous kinetics at the electrode surface can be measured either by recording an approach curve or recording voltammograms by placing the tip electrode at a small distance, d, from the substrate electrode. Because the mass transfer rates at the UMEs are very fast, measurements of fast kinetics are possible without interference from mass transfer effects. For an ultramicrodisk electrode far from a surface the relation between the mass transfer coefficient (m) and the radius of the electrode (a) is taken as[2−4] $m = (4D/\pi a)$, where D is the diffusion coefficient of the species

undergoing reaction at the UME surface. When the UME in an SECM is very close to the substrate electrode, the mass transfer rate of the electroactive species is further increased and the mass transfer coefficient becomes inversely proportional to d, i.e., $m = D/d$ for $d \ll a$.[5,6] Homogeneous kinetics of the electrochemically generated unstable species can be measured if the species lifetime is of the order of the diffusion time, $d^2/2D$, across the gap between the two electrodes. Thus, to investigate a fast heterogeneous or homogeneous kinetics using SECM, it is desirable to have a micrometer to nanometer gap. This can be achieved by closely approaching the UME tip to another UME or a substrate electrode. For this purpose the radius of the glass-insulating sheath around the disk electrode, usually designated RG (ratio of the outer diameter of the glass to the diameter of the metallic wire), has to be small. Another problem is the recession of the metallic ultramicrodisk slightly beneath the insulating glass. Such problems hinder the closest possible approach of the metallic disk electrode to another electrode, either a larger electrode or a tip.
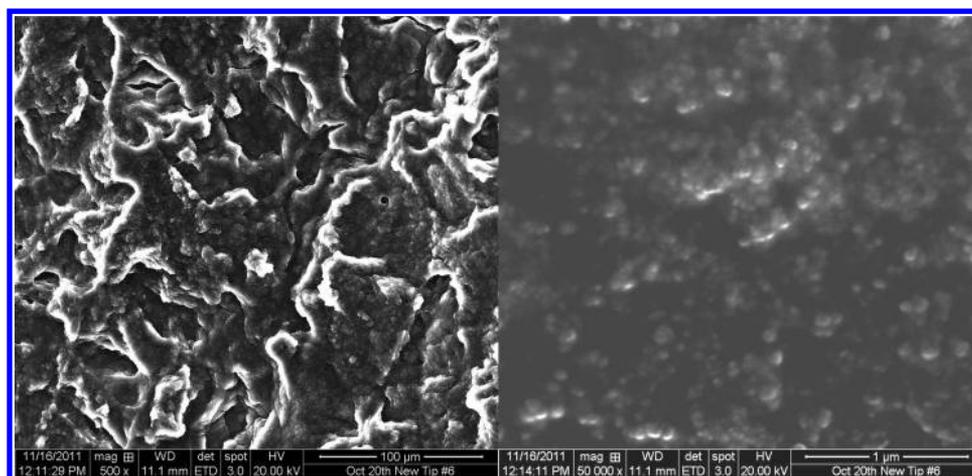
Figure 1. SEM micrograph at two different resolutions of the carbon paste prepared using VULCAN XC72R carbon powder and mineral oil.

Another application of UMEs in SECM is in the study of electronic transport properties of single molecules which bridge a nanogap, e.g., DNA, nanotubes.[7,8] Nanogaps with fixed dimensions are prepared using many different methodologies, but in most cases a nanogap with a controlled dimension of the order of 100 nm is difficult to achieve.[9−11] Our group has been interested in nanogaps with the possibility of controlled variation of its dimension in connection with the studies of single-molecule electrochemistry and in the investigation of rapid homogeneous reactions coupled to electron-transfer reactions at the electrodes.[12,13] SECM with a conical UME is often a good choice for this purpose and has been investigated in previous reports.[14−17] A conical carbon paste UME was prepared in the present study for some of the special advantages of the carbon as electrode material over metallic electrode: (1) carbon particles of diameter 10−20 nm are available in pure form to make the electrode; (2) carbon-based materials are biocompatible, and some biomolecules show special activity with carbon electrodes compared to the metallic electrodes; (3) carbon materials show high overpotentials for proton and oxygen reduction and can be employed over a wide potential window compared to Au and Pt.

Adams first introduced carbon paste as the electrode material.[18] Since then, over the past 5 decades, carbon paste has been widely used as a material for the preparation of detectors, sensors, and electrodes.[19−23] Carbon paste has advantages over the other electrode materials because of simplicity in preparation, easy surface renewal, a nontoxic and biocompatible nature, and relatively low background current characteristics.[19] An advantage over the conventional Pt tips is much wider available potential limits, since the carbon paste surface is not a good electrocatalyst for proton reduction or oxygen evolution. A number of reviews and books describe the preparation, characterization, and use of carbon paste electrodes for various purposes.[24−29] In spite of its wide variety of applications as the electrode material or as sensor substrate, reports on carbon paste UMEs are limited. The first report of a carbon paste microelectrode was by Kissinger et al.[30] Later, Martin and co-workers reported the preparation of carbon paste microelectrode arrays.[31,32] In some recent reports carbon paste UMEs were used as sensing electrodes.[33−36] Carbon paste UMEs modified with a biological sensing molecule should be useful in imaging biological substrates when used as the tip in an SECM. To our knowledge only two reports deal with the

carbon paste UMEs with ≤10 μm diameters.[34,35] No reports show well-defined steady-state cyclic voltammograms with carbon paste UMEs or its application in SECM measurements, especially with the formation of micrometer to nanometer gaps using the SECM approach. There have been reports on electrodes based on ultramicro-/nanocavity formation in glass.[37−42] The cavities were filled with electrocatalyst materials, and catalyst UMEs were prepared; these were used for the evaluation of the catalytic activity and studying active sites in the catalyst materials.[37,39] Nanopore electrodes in glass have also been described for investigation of molecular transport through the pores.[40−42] In a recent report, carbon was deposited by burning butane inside a glass nanopore to produce a carbon nanoelectrode for SECM applications.[43]

Here we report a simple method of preparing carbon paste UMEs by packing the carbon paste into the ultramicrocavity formed by chemically etching the tip of a platinum UME (Pt-UME) or into a pulled glass capillary.[34,35] The electrochemical behavior of the carbon paste UME was investigated by cyclic voltammetry and SECM measurements. The carbon paste UME can be formed in a conical shape, thereby minimizing the problem of interference of the glass insulator in a close approach of the tip to the substrate. Well-defined probe approach curves were obtained with carbon paste UMEs as tips and indium−tin oxide (ITO)-doped glass as the substrate electrode. Controllable gaps of micrometer to nanometer dimension between the carbon paste UME and the ITO-doped glass substrate could be formed using SECM approach curves. Most of the experiments describe the preparation of 10 μm carbon paste UMEs. However, we also demonstrate carbon paste UMEs based on packing inside a recessed Pt-UME of 600 nm diameter and also into a pulled glass capillary to form a 285 nm diameter electrode. Both the Pt-UME and the glass capillary were made with a commercial laser puller. Generally, on pulling, the metal wire broke apart before the glass and the metal wire were recessed from the tip of the electrode. Such electrodes are not suitable for the SECM applications. We have investigated the preparation of the carbon paste electrodes in submicrometer dimension by packing the recessed Pt electrode with carbon paste.

■ EXPERIMENTAL SECTION

Reagents and Chemicals. Mineral oil from Fischer Scientific, U.S.A. and Vulcan XC-72R carbon powder from

Cabot Corporation were used to prepare the paste. All acids and other chemicals were from Fisher Scientific and used as received. Deionized (Milli-Q) water was used for all experiments.

Instrumentation. A BAS 100A electrochemical analyzer (West Lafayette, IN) was used for the cyclic voltammetry measurements. SECM experiments were carried out using CHI 920C instrument from CH Instruments, Inc. (Austin, TX). A white light interference profiler model WYCO NT9100 from VEECO Instruments, Inc. (Plainview, NY) was used for the microscopic characterization of the UMEs. A microelectrode puller from Stoelting Co. (Wood Dale, IL) was used for the sealing of UMEs. Capillaries for the nanometer electrodes were made on a laser puller model P2000 (Sutter Instruments, Novato, CA). An Olympus optical microscope was used frequently during the preparation and polishing steps of UMEs. An Olympus confocal laser scanning microscope (OLS 4000) was used for the measurement of the depth of the ultramicrocavity.

Preparation of the Carbon Paste. Carbon paste was prepared by thoroughly mixing Vulcan carbon XC-72R powder with 15 wt % mineral oil using a mortar and pestle. After mixing, the paste was kept under vacuum (rotary pump) for 2 h to remove any adsorbed gases. It was then stored in a vial and used as the material for making the UMEs. The morphology of the carbon paste was investigated with scanning electron microscopy (SEM) measurements; typical results are shown in Figure 1. The carbon particles were well-dispersed and well-mixed with mineral oil used as the pasting medium. High-resolution SEM showed individual carbon particles along with some agglomerations. The individual particle size was about 10−20 nm, as specified for Vulcan XC72R.

Preparation of the Pt Tip Carbon Paste UME. A schematic representation of the preparation of the ultramicrocavity from the Pt-UME and the packing of the ultramicrocavity with carbon paste to form the carbon paste UME is shown in Scheme 1. A platinum UME of 10 μm

Scheme 1. Simplified Scheme of the Preparation Steps of the Carbon Paste UMEs
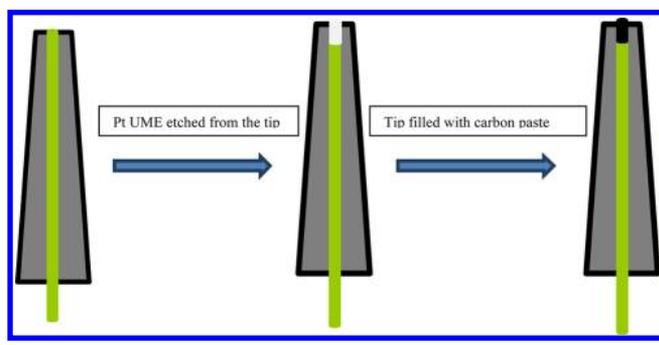
diameter was prepared using the method described in the literature.[1] The tip of the electrode was polished and the radius of the glass was reduced by hand polishing with sandpaper of size 240, 600, and 1200. The ratio of the radius of glass to the radius of the electrode (RG) was maintained at ∼2. Finally, the electrode was polished using micro fine polishing cloth and alumina in water suspension of different sizes (typically 1.0, 0.30, and 0.05 μm) to produce a final shiny metal electrode and surrounding glass. The Pt-UME was then dipped into warm (80 °C) freshly prepared aqua regia for 20 min. The electrode

was ultrasonicated in water and in acetone solvents sequentially for 2 min each and then dried in an oven at 120 °C for 30 min. On microscopic examination of the tip, the Pt wire was etched back from the tip of the electrode. The tip was then examined using laser confocal microscopy; the image and the cross-sectional diagram are shown in Figure 2. The tip of the glass was flat, and the RG was ∼2. A cross-sectional view of the ultramicrocavity, after dissolving Pt, showed a maximum depth of the cavity of 4.2 μm. At the mouth of the tip, the Pt wire was completely dissolved and the ultramicrocavity was uniform; it narrowed down toward the bottom of the cavity. The ultramicrocavities were also investigated with the optical profiler, and the images are shown in Figure 3. A uniform ultramicrocavity of 10.2 μm diameter (marginally higher than that of the dissolved Pt wire) was observed. The bottom of the cavity was not seen by the profiler, so it was not possible to measure the depth from these measurements. However, Pt wire in the UME dissolved for a shorter time (10 and 15 min) showed reflection from some portions of the cavity shown in Figures S1 and S2 in the Supporting Information. The average depth of the ultramicrocavities formed with 10, 15, and 20 min of dissolution were 1.8, 3.1, and 4.2 μm, respectively. Thus, after an initial incubation time of about 2 min the Pt wire dissolved at the rate of about 0.24 μm/min. The ultramicrocavities were then filled with carbon paste by carefully pressing the electrode tip over the carbon paste spread on a glass slide. The packing process was repeated many times for uniform packing of the paste inside the ultramicrocavity. This also ensured a good contact between the Pt wire and the carbon paste. The packed electrode tip was tapped against the glass slide, and the sides were carefully wiped with superfine tissue paper. The surface finish of the electrode was periodically monitored under an optical microscope and the profiler. A profiler image of the carbon paste UME (Figure 4) shows the carbon paste protruding above the glass substrate by about 200 nm. Electrodes with deeper cavities (Pt wire dissolved for 20 min) were easier to pack with carbon paste compared to those dissolved for 10 or 15 min, and all of the results here involve 20 min dissolution times.

Preparation of Capillary Filled Carbon Paste Nanoelectrodes. Borosilicate glass capillaries (outer diameter 1.5 mm, inner diameter 0.75 mm) were pulled with the laser puller. Carbon paste was filled inside the capillary using a standard glass syringe from the backside of the capillary. For these electrodes 25% mineral oil was used to make the carbon paste less viscous for easier filling of the capillary. A copper wire was inserted into the back of the capillary tube for making electrical contact.

■ RESULTS AND DISCUSSION

Voltammetry with the Carbon Paste UMEs. The capacitance of the carbon paste UMEs was determined from the cyclic voltammetry measurements in 0.1 M KNO$_3$ solution at scan rates from 10 mV/s to 300 V/s (Supporting Information Figure S3), and a linear correlation between the average current magnitude and the scan rate was observed. This fits well with the relation $i = C(dE/dt)$ and yielded a capacitance, C, of 32.5 μF/cm^2. Cyclic voltammograms of ferrocene methanol (FcMeOH) oxidation using the carbon paste UME are shown in Figures 5 and 6 in two scan rate regions. Well-defined steady-state responses for the oxidation of FcMeOH were observed, shown in the inset of Figure 5, for a
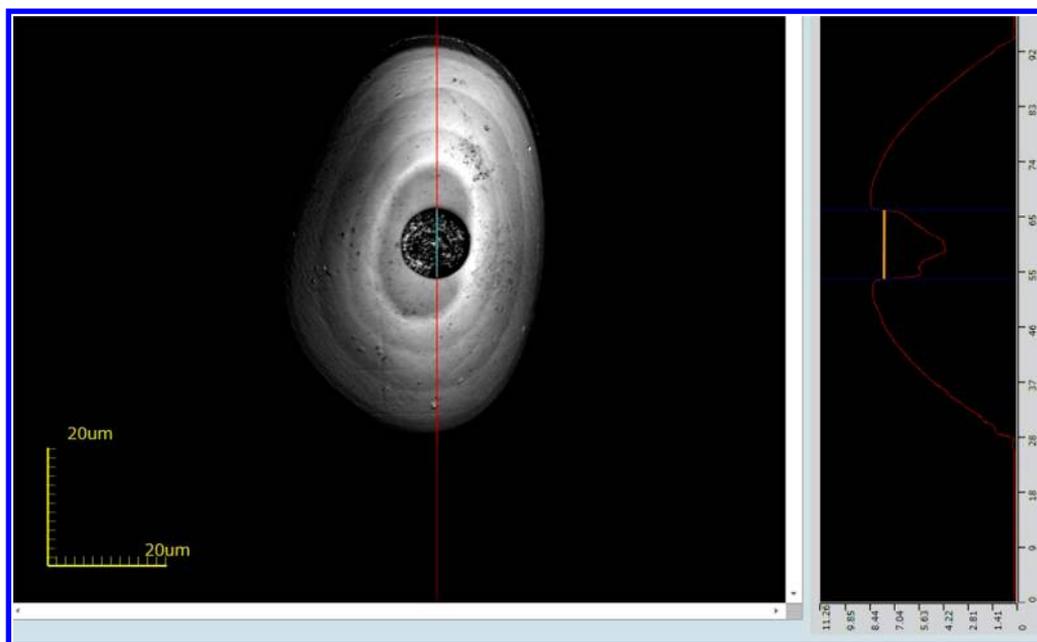
Figure 2. Image from the laser confocal microscope of the ultramicrocavity formed by dissolving the Pt wire from the top of the 10 μm Pt-UME. Diagram to the right shows the cross-sectional view of the ultramicrocavity.
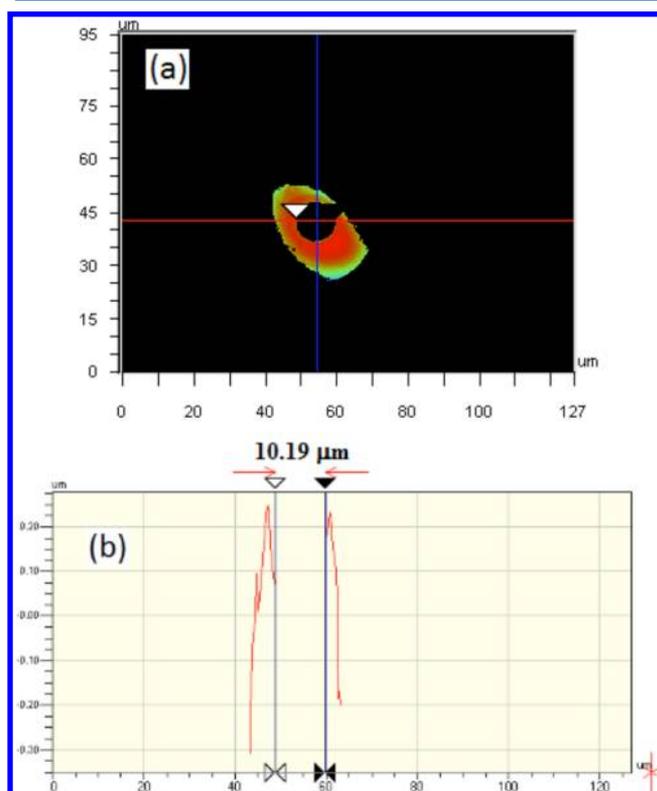
Figure 3. (a) Image from the VEECO profiler of the ultramicrocavity formed by dissolving the Pt wire for 20 min from the top of the 10 μm Pt-UME. (b) Cross-sectional view of x-axes section of the ultramicrocavity.

Figure 4. Image from the VEECO profiler of the carbon paste UME. The carbon paste protruded at the middle of the electrode from the rest of the glass substrate.

With an increase in the scan rate the cyclic voltammograms deviated from the steady-state behavior, as expected from the inequality showing where transient effects appear:

$$v \gg RTD/nFa^2 \tag{2}$$

For a 10 μm carbon paste electrode the right-hand term is ~600 mV/s with 1 mM FcMeOH, and steady-state behavior was observed up to 100 mV/s.

SECM with Carbon Paste UME Tips. The carbon paste UME was used as the tip electrode in SECM and was held at 0.4 V (Ag/AgCl) in a solution of 1 mM FcMeOH in 0.1 M KNO$_3$. The substrate Pt electrode (5 mm diameter) was held at 0 V (Ag/AgCl). The basic aim was to compare the approach curve to a theoretical positive feedback curve and ascertain the distance, d, of closest approach of the probe to the substrate. The probe approach curve using a 10 μm carbon paste UME (Figure 7) showed the maximum dimensionless currents (i_T/

20 mV/s scan rate. The steady-state current follows the UME equation:[44]

$$i_{T,\infty} = 4nFDCa \tag{1}$$
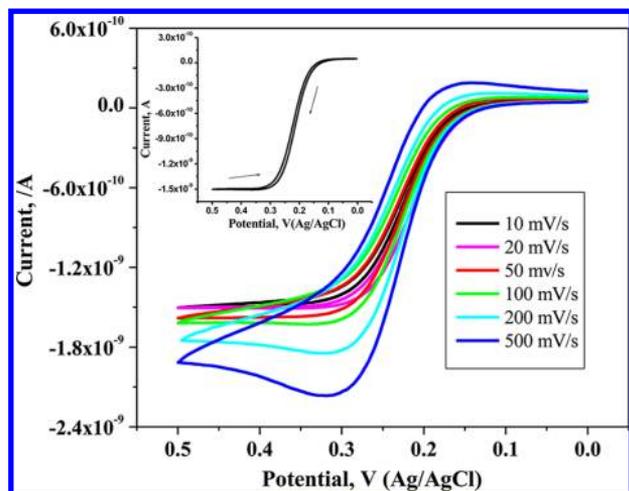
Figure 5. Cyclic voltammogram of 1×10^{-3} M ferrocene methanol solution in 0.1 M KNO$_3$ supporting electrolyte media using a carbon paste UME at different scan rates (lower range). Inset: the cyclic voltammogram at scan rate 20 mV/s.
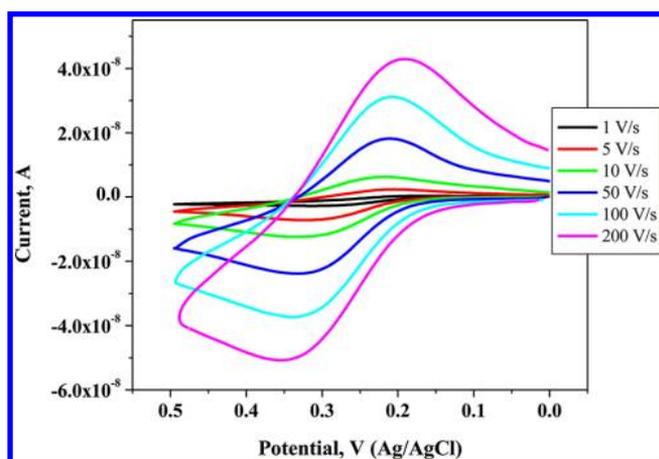
Figure 6. Cyclic voltammogram of 1×10^{-3} M ferrocene methanol solution in 0.1 M KNO$_3$ supporting electrolyte media using a carbon paste UME at different scan rates (higher range).
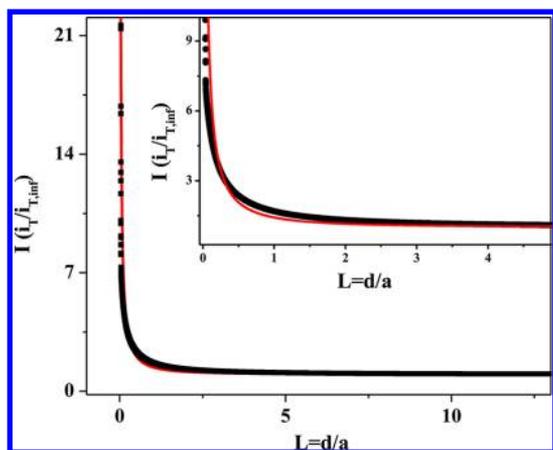
Figure 7. Probe approach curve using a 10 μm carbon paste UME as the tip electrode and ITO-coated glass as the substrate electrode in 1 mM ferrocene methanol and 0.1 M KNO$_3$; probe scan speed, 50 nm/s. Inset: portion of the approach curve at small L. The black points are experimental, and the red line is theory for diffusion-controlled feedback.

$i_{T,\infty}$), where $i_{T,\infty}$ is the current with the tip far from the substrate, of up to 21. The experimental curve agrees well with the theoretical one for a disk-shaped UME. Although the carbon paste protrudes very slightly, as shown earlier[45] this geometry fits the disk theory quite well. Figure 7 shows the fitting of experimental data points (black dots) with the SECM theory (solid red lines) corresponds to the theoretical fit of positive feedback in SECM as in eq 3.

$$i_{T}(L) = 0.6686 + 0.6973/L + 0.3218 \exp(-1.7446/L)$$
$$(3)$$

The dimensionless parameter $L = d/a$ for the closest approach was 0.035; thus, the closest distance approach between the tip and the substrate was 175 nm. To verify that the current at closest approach did not involve any current resulting from contact between tip and substrate, cyclic voltammetry experiments were carried out after the probe approach experiments. The corresponding cyclic voltammograms (Figure 8) were
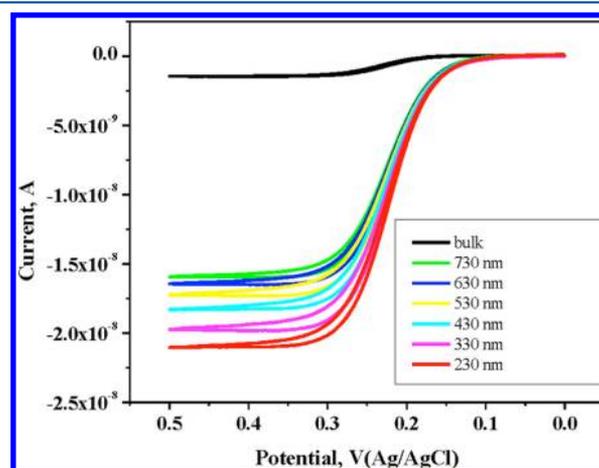
Figure 8. Cyclic voltammetry on a carbon paste UME (10 μm) at the closest approach distance to the ITO-coated glass substrate (from the SECM approach curve ~230 nm). Other distances represent the movement from this point in 1 mM ferrocene methanol in 0.1 M KNO$_3$ medium.

taken from the closest approach and then retracted in steps of 100 nm. In these experiments the maximum enhancement $i_T/i_{T,\infty}$ was 14.6, which corresponds to an approach distance 230 nm. The results demonstrate that minimum gaps of about 200 nm are achievable with an easily constructed carbon paste UME of 10 μm diameter.

Similar experiments were carried out with the capillary filled carbon paste electrodes. These were examined microscopically and with the profiler, and micrographs (Figure 9) show an outer diameter of the tip of the electrode of about 395 nm. This capillary filled carbon paste nanoelectrode was tested by cyclic voltammetry measurements in 1 mM FcMeOH solution, and the voltammogram (Figure 10) shows the expected steady-state voltammetric response for ferrocene oxidation. The steady-state current corresponds to an electrode diameter of 285 nm. The size of these electrodes is only limited by the filling of the capillary tip with carbon paste and should be useful in preparing electrodes of even smaller dimensions, especially if stronger quartz capillaries are used.
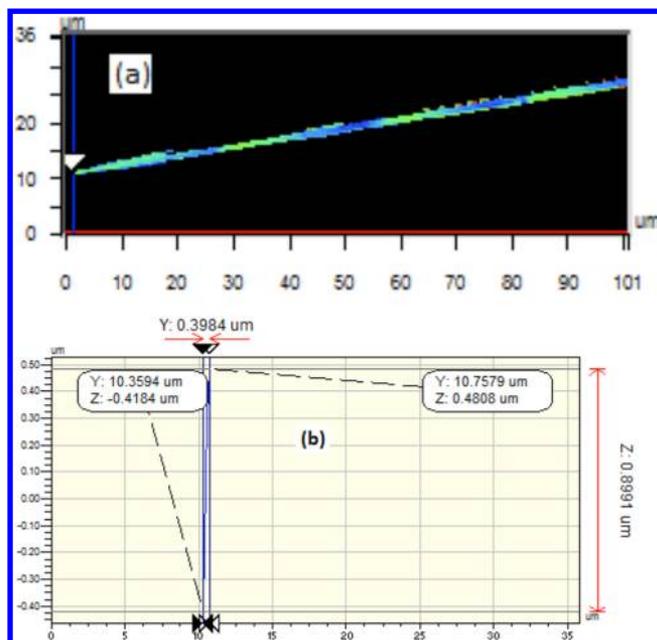
Figure 9. (a) Image from the VEECO profiler of the capillary filled carbon paste electrode. (b) Cross-sectional view along *y*-axes of the tip of the electrode.
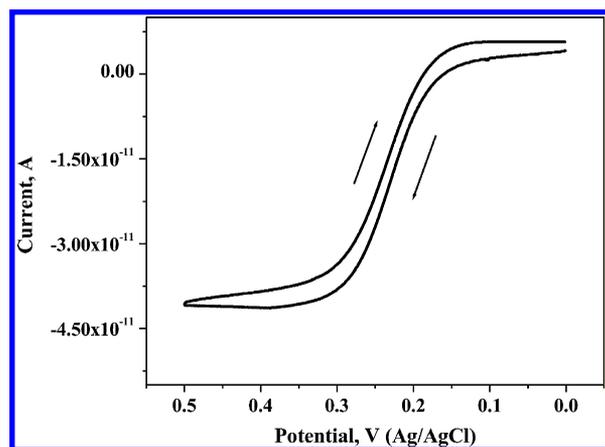
Figure 10. Cyclic voltammetry response of the capillary filled carbon paste UME with diameter of 285 nm. The scan was recorded in 1 mM ferrocene methanol in 0.1 M KNO_3 medium at the scan rate of 20 mV/s.

CONCLUSIONS

Carbon paste UMEs are good alternatives to metallic UMEs in terms of easy preparation and renewability and importantly in solving the recession problem. Another problem with UMEs of nanometer size is fouling by coating relatively small amounts of contaminants in the solution; carbon paste UMEs seem to be less prone to fouling compared to the metallic UMEs. They also seem to be less sensitive to leakage of solution between the glass and the metallic ultramicrowire of imperfectly sealed wires. With carbon paste UMEs the nonpolar binding oil wets the glass well and decreases the possibility of seeping of aqueous solution into nanocracks. Carbon paste UMEs could be renewed by removing the old paste by ultrasonication alternatively in water and in acetone for 5 min each. The electrode body was then dried in an oven at 120 °C for 30 min and repacked with the carbon paste for further use.

We report here the fabrication of two different carbon paste ultramicroelectrodes, one based on etching a Pt-UME and packing with carbon paste and the second based on a pulled glass capillary filled with carbon paste under pressure and then contacted with a wire. Electrodes of diameters ranging from 285 nm to 10 μm are reported. The electrodes show good SECM approach curves and allow approaches to a distance of about 200 nm. A potential problem with carbon paste is its low electrocatalytic activity for many reactions, compared to Pt. However, using the techniques described for cavity electrodes[38,39] mixing catalytic materials with the carbon paste should be possible.

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Notes

The authors declare no competing financial interest.

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