Anal. Chem. **2005,** *77,* 3013−3017

Fabrication of Ultramicroelectrodes Using A "Teflon-like" Coating Material

Biao Liu,† Jason P. Rolland,‡ Joseph M. DeSimone,‡ and Allen J. Bard*,†

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, and Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712

A new method was developed for the preparation of ultramicroelectrodes (UMEs). In this method, a photocurable fluorinated functionalized perfluoropolyether, a liquid v-like polymer at room temperature, is used as the material for the insulation of metal microwires or carbon fibers. The UMEs prepared by this method were usually conical shaped and could be used both in aqueous solutions and with aprotic solvents. The relatively small thicknesses of the insulating sheath of the "Teflon-like" UME tips make them particularly useful for scanning electrochemical microscopy measurements.

Ultramicroelectrodes (UMEs) have been widely used in electroanalytical chemistry and scanning probe microscopy techniques. In the fabrication of metallic or carbon UMEs for use in solution, the insulation of the metal wires or carbon fibers is key to producing a good electrode. Although most UMEs are encapsulated in a glass capillary, a number of different coating materials and techniques have been employed, including electropolymerization,[1,2] electrophoretic deposition,[3−6] RF sputtering of inorganic insulating materials,[7] dipping the tip in a varnish[8,9] or molten paraffin,[10] and translating the tip through a bead of molten glass,[11] poly(α-methylstyrene),[12] or Apiezon wax[13,14] held on a heated support. These methods have been used successfully, yet many of them are time-consuming and most are not appropriate for measurements in important solvents used in electrochemical measurement, such as acetonitrile.

In this work, a new method is introduced for the preparation of metallic and carbon UMEs utilizing a new polymeric "Teflon-like" (LT) material, a highly fluorinated functionalized perfluoropolyether (PFPE) that has liquidlike viscosity and can be photocured into a tough, highly durable elastomer that exhibits remarkable chemical resistance, similar to fluoropolymers such as Teflon.[15] The LT materials have recently been used for the fabrication of microfluidic devices.[16] Our results demonstrate that the preparation of UMEs using LT as the insulating material is relatively easy because no high temperature or electric field is required in the sealing process. The relative thicknesses of the insulating sheath (RG = r_g/a, where r_g is the radius of the insulating sheath and a is the radius of a metal wire or a carbon fiber) of LT UME tips are smaller than those of tips prepared in glass using conventional methods, i.e., polishing and sharpening. Tips with small RGs are particularly useful in scanning electrochemical microscopy (SECM).[17] Our results also show that the LT UMEs could be used in nonaqueous media.

EXPERIMENTAL SECTION

Materials. Octadecanethiol, $Ru(NH_3)_6Cl_3$, tetrabutylammonium perchlorate, ferrocene, and acetonitrile were purchased from Aldrich (Milwaukee, WI). Pyridine and *N*,*N*-dimethylformamide (DMF) were from Acros Chemicals (Fairlawn, NJ). 1,2-Dichloroethane was from Fisher Chemicals (Fairlawn, NJ). All chemicals were reagent grade and used as received without further purification. The LT materials, which contained ∼1 wt % photoinitiator (2,2-dimethoxy-2-phenylacetophenone), were prepared and cured as described previously.[16] All aqueous solutions were prepared with 18 MΩ cm deionized water (Milli-Q, Millipore Corp.).

Electrochemical and SECM Experiments. Electrochemical experiments were performed in a Teflon cell (3 mL capacity) with a 1 mm diameter Pt wire (Goodfellow, Devon, PA) counter electrode. Unless otherwise mentioned, saturated Hg/Hg_2SO_4, K_2SO_4 (Radiometer, Copenhagen, Denmark), was used as the

* To whom correspondence should be addressed. E-mail: ajbard@mail.utexas.edu.

† University of Texas at Austin.

‡ University of North Carolina at Chapel Hill.

(1) Strein, T. G.; Ewing, A. G. *Anal. Chem.* **1992**, *64*, 1368.
(2) Pojte-Kamloth, K.; Janata, J.; Josowicz, M. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *93*, 1480.
(3) Bach, C. E.; Nichols, R. J.; Beckman, W.; Mayer, H.; Schulte, A.; Besenhard, J. O. *J. Electrochem. Soc.* **1993**, *140*, 1281.
(4) Schulte, A.; Chow, R. H. *Anal. Chem.* **1998**, *70*, 985.
(5) Slevin, C. J.; Gray, N. J.; Macpherson, J. V.; Webb, M. A.; Unwin, P. R. *Electrochem. Commun.* **1999**, *1,* 282.
(6) Conyers, J. L.; White, H. S. *Anal. Chem.* **2000**, *72*, 4441.
(7) Abe, T.; Itaya, K.; Uchida, I. *Chem. Lett.* **1988**, 399.
(8) Gewirth, A. A.; Craston, D. H.; Bard, A. J. *J. Electroanal. Chem.* **1989**, *261,* 477.
(9) Vitus, C. M.; Chang, S. C.; Weaver, M. J. *J. Phys. Chem.* **1991**, *95*, 7559.
(10) Zhang, B.; Wang, E. *Electrochim. Acta* **1994**, *39*, 103.
(11) Penner, R. M.; Heben, M. J.; Longin, T. L.; Lewis, N. S. *Science* **1990**, *250*, 1118.
(12) Penner, R. M.; Heben, M. J.; Lewis, N. S. *Anal. Chem.* **1989**, *61*, 1630.
(13) Nagahara, L. A.; Thundat, T.; Lindsay, S. M. *Rev. Sci. Instrum.* **1989**, *60*, 3128.
(14) Mirkin, M. V.; Fan, Bard, A. J. *J. Electroanal. Chem.* **1992**, *328*, 47.
(15) Scheirs, J. *Modern Fluoropolymers*; John Wiley & Sons, Ltd.: New York, 1997; pp 435−485.
(16) Rolland, J. P.; Van Dam, R. M.; Schorzman, D. A.; Quake, S. R.; DeSimone, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 2322.
(17) Bard, A. J., Mirkin, M. V., Eds. *Scanning Electrochemical Microscopy*; Marcel Dekker: New York, 2001.

10.1021/ac0482918 CCC: $30.25
Published on Web 03/24/2005

reference electrode. A CH Instruments (Austin, TX) model 900 SECM instrument was used to perform all steady-state voltammetry and SECM measurements. A 2 mm diameter Pt disk (CH Instruments) served as the substrate electrode in SECM measurements. Approach curves were obtained either over the Pt conductor (positive feedback) or over the insulation surrounding the Pt disk (negative feedback). The substrate was mounted onto an adjustable platform so that compensation for any substrate tilt could be made. All experiments were performed at room temperature.

Fabrication of Pt and Au Ultramicroelectrodes. The glass capillary was prepared by pulling a borosilicate glass tube (o.d. = 1.2 mm, i.d. = 0.69 mm) with a micropipet puller (model P-2000, Sutter Instrument Co., Novato, CA). A one-line program was used in the pulling with typical parameters heat = 450, filament = 5, velocity = 30, delay = 150, and pull = 0. To fill the glass capillary with LT, one end of the glass capillary was immersed into LT and the other end of the capillary was connected with a 10 mL syringe. LT was drawn into the capillary using the syringe. A 2 cm length 10 μm diameter platinum wire or 12.5 μm diameter gold wire (Goodfellow) was connected to a copper wire with silver epoxy (Epotek, H20E, Epoxy Technology, Inc., Billerica, MA). The gold wire was soaked in ethanol containing 2 mM octadecanethiol for 2 days, while the platinum wire was soaked in the mixture of ethanol and pyridine (1:1 by volume) overnight. The platinum or gold wire was inserted into one end of a pulled glass capillary filled with LT such that 3−5 mm of the microwire protruded from the tip of the capillary. The metal wire was sealed into the glass capillary after exposure of the LT to UV radiation (Photochemical Reactor, The Southern New England Ultraviolet Co,, Hamden, CT) under nitrogen for 1 h. As suggested by the SECM approach experiments (see below), the LT coating process should be repeated at least three times to get a good insulating coating. The repeat coating was performed by dipping the LT-coated tips into LT solution and exposing the LT to UV for 1 h. This process can be repeated as many times as desired.

The platinum or gold wire that extended from the capillary was then electrochemically etched, with microscopic monitoring of the process, in a solution containing saturated $CaCl_2$ (60 vol %), H_2O (36%), and concentrated HCl (4%). The microwire was placed on an ITO electrode that was used as a large-area counter electrode. A drop of etching solution was added onto the ITO electrode to cover the microwire, and an ac voltage of ~1.5 V rms, 1 kHz, was applied. This assembly was placed on the microscope stage. The etching process was monitored optically (Olympus, BH-2 microscope). After etching was completed, the wire was thoroughly rinsed with deionized water. The construction of the metallic UMEs is schematically shown in Figure 1.

Fabrication of Carbon Ultramicroelectrodes. To prepare carbon UMEs, a 10 μm diameter carbon fiber (Goodfellow) was etched in a 3 M NaOH solution by applying a dc voltage of 3 V between the carbon fiber and a large-area carbon plate electrode. About 1 mm of the carbon fiber was immersed in the solution.As the etching proceeded, the current decreased gradually, and then decreased abruptly when the etching was complete. At this stage, the carbon tip was sharp (aspect ratio about 15). To decrease the aspect ratio of the cone, the conical tip was moved into the etching solution by 30−40 μm using the SECM positioner, and the etching process described above was repeated. After etching was complete, the carbon fiber was thoroughly rinsed with deionized water and dried at 100 °C for several hours. The etched carbon fiber was inserted into one end of a pulled glass capillary filled with LT such that the conical part of the fiber protruded from the tip of the capillary. Subsequent photocuring of LT was accomplished following the same procedure described above.

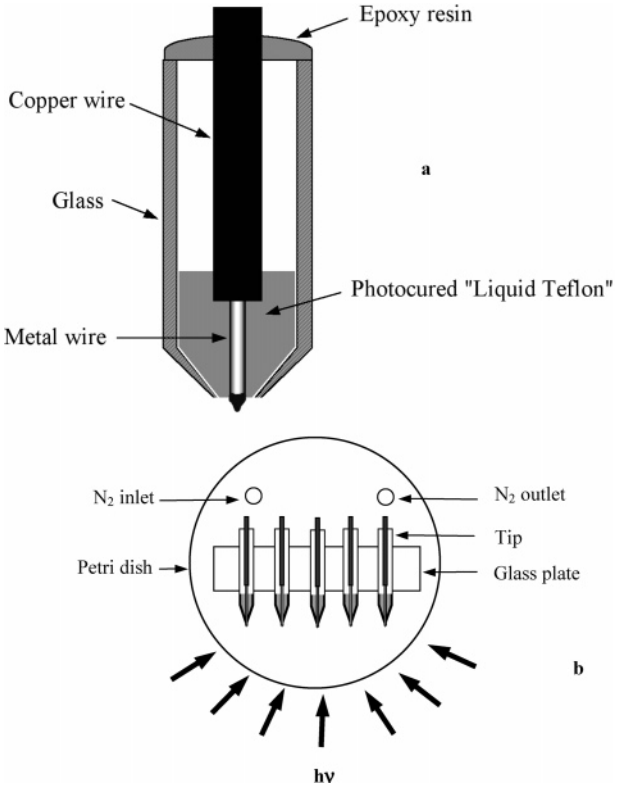

Figure 1. Construction of UMEs prepared using LT (a) and the setup for photocuring the UMEs under nitrogen (b). The dimensions of the glass and polymer are exaggerated for clarity.

RESULTS AND DISCUSSION

Fabrication and Characterization of the Teflon-like Ultramicroelectrodes. Figure 2 shows optical images for two representative UMEs prepared with 10 μm diameter Pt wire. After electrochemical etching, the shapes of the tips may vary. Usually, conical-shaped tips were obtained as shown in the top image in Figure 2. On the basis of the optical measurements, the aspect ratio of the tip, H, is between 0 and 1 ($H = h/a$, where a and h are the base radius and the height of the cone, respectively). The RG is between 1.2 and 2.

Electrodes could also be constructed without an external glass capillary, by coating the bare wire (treated with octadecanethiol) with the polymer and curing. To gain information about the quality of the LT insulation on these electrodes, a SECM approach curve was obtained at the air/solution interface, where the solution

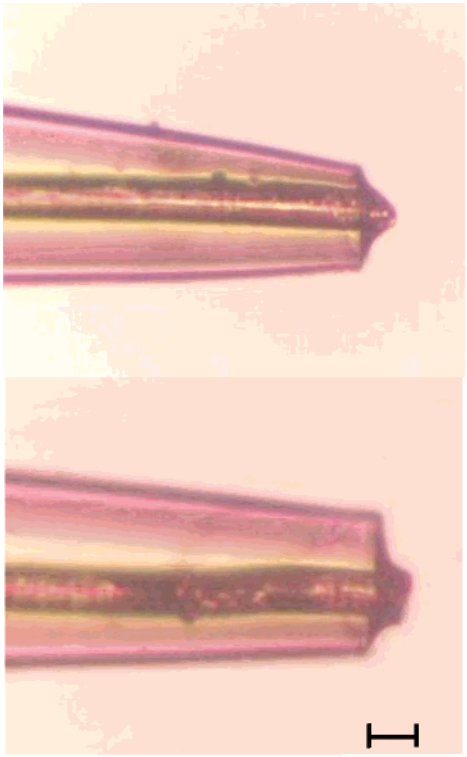

Figure 2. Optical micrographs of platinum UMEs with different aspect ratios. The UMEs were prepared by sealing a 10 μm diameter Pt wire into a glass capillary with LT, followed by electrochemical etching.

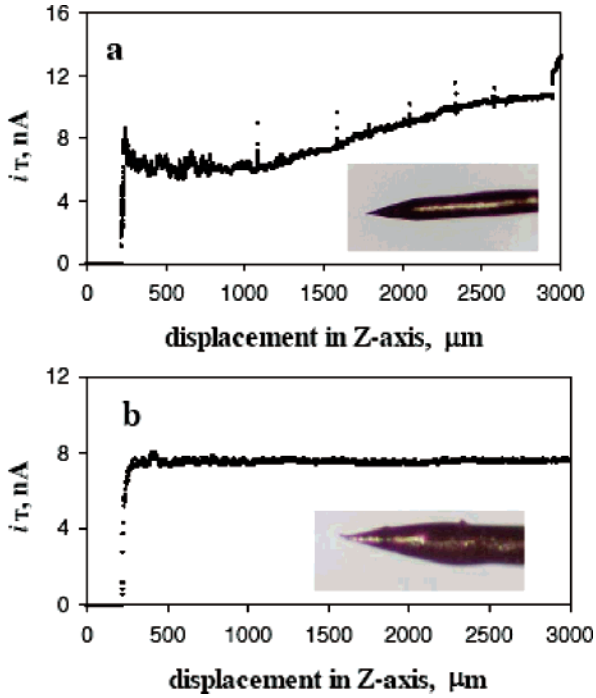

Figure 3. Electrochemical approach curves of a Pt UME insulated with LT to an air/solution interface. The conical Pt UME was prepared by electrochemically etching a 10 μm diameter Pt wire followed by coating the wire with LT. (a) The Pt wire was insulated with LT only once. (b) The insulating procedure was repeated three times. The solution contained 2 mM $Ru(NH_3)_6Cl_3$ and 0.1 M KCl. The tip potential was −0.7 V vs Hg/Hg_2SO_4. The approach speed was 10 μm/s. The insets show the optical images of the Pt wires coated with LT.

contained a redox mediator such as $Ru(NH_3)_6^{3+}$.[18] A conical Pt UME coated with LT was used as the SECM tip. A potential sufficient to reduce $Ru(NH_3)_6^{3+}$ was applied to the tip, and the tip current was monitored as the tip was moved from air into an aqueous 2 mM $Ru(NH_3)_6^{3+}$ solution. For a completely insulated tip, no current flowed until the tip entered the solution, where the current then rose sharply in a UME transient, which decayed to a constant steady-state current value. This constant value was maintained as more of the tip was immersed in solution. When the metal wire was coated with LT only once, a noisy and gradually increasing tip current was observed as the tip entered the solution (Figure 3a), indicative of poor insulation. Because of pinholes in the insulating film, a poorly insulated tip showed leaks along the sides as more of the tip was immersed into the solution.

After the coating procedure was repeated three times, the insulation greatly improved as shown in Figure 3b. In this case, the tip was completely insulated with only the very end of the tip uncovered. For this reason, all UMEs used in this work were coated with LT at least three times. It was necessary to precoat the metal wires with alkanethiols (for Au) or pyridine (for Pt) before the wires were insulated with LT. Otherwise, the insulation was poor (data not shown). The organic film on the metal wires increased adhesion of the cured film to the metal surface. Carbon fibers, however, did not need to be precoated. Good insulation was confirmed by voltammetric measurements (see below).

(18) Lee, Y.;. Bard, A. J. *Anal. Chem.* **2002**, *74*, 3626.

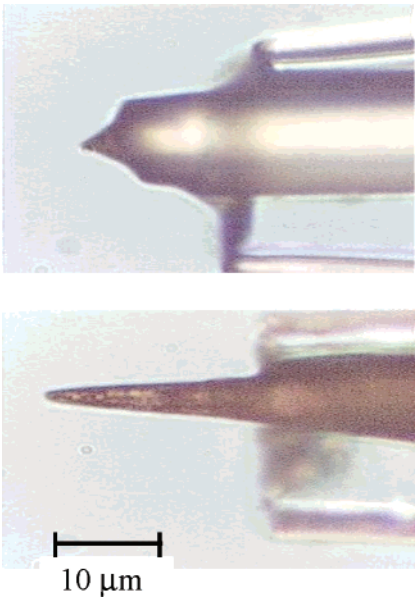

Figure 4. Optical images of LT-insulated carbon UMEs with different aspect ratios. A 10 μm diameter carbon fiber was electrochemically etched to obtain the conical-shaped carbon UME.

Figure 4 shows the optical images of two carbon UMEs with different aspect ratios. Etched 10 μm diameter carbon fibers were sealed into a glass capillary using LT. Unlike the metallic UMEs, the carbon UMEs were prepared by etching a carbon fiber first and then coating it with LT. Good insulation could not be obtained if the carbon fiber was coated first and then etched, suggesting

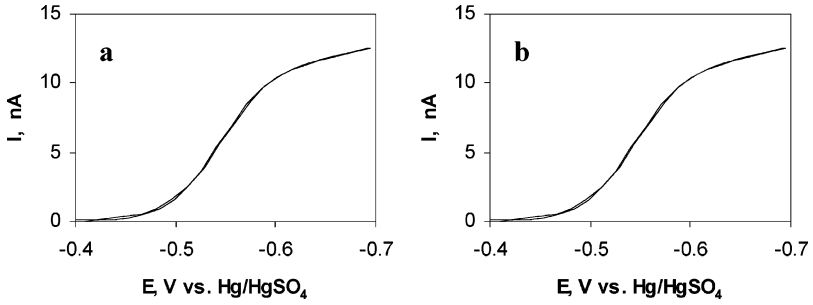

Figure 5. Cyclic voltammograms of the LT-insulated UMEs prepared using (a) 12.5 μm diameter gold wire and (b) 10 μm diameter platinum wire. The aqueous solution contained 2 mM $Ru(NH_3)_6Cl_3$ and 0.1 M KCl. The potential scan rate was 20 mV/s.

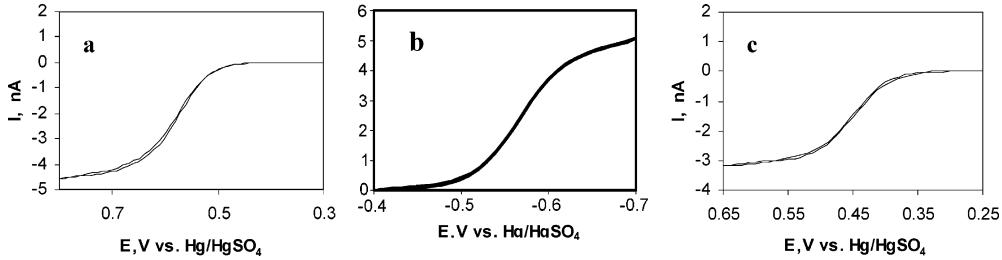

Figure 6. Cyclic voltammograms of an LT-insulated UME prepared using a 10 μm diameter platinum wire. The solution contained 2 mM ferrocene and 0.1 M $TBAClO_4$. The solvent was (a) acetonitrile, (b) *N*,*N*-dimethylformamide, and (c) 1,2-dichloroethane. The potential scan rate was 20 mV/s.

that the etching processes could destroy the LT coating layers on carbon.

Voltammetric Behavior. Figure 5 shows the cyclic voltammograms of two metal wire LT UMEs in aqueous solutions. Sigmoidal steady-state voltammograms with little hysteresis between the forward and reverse potential sweeps, as shown in Figure 5, are an indication of a good seal between the polymer insulation and the metal wire in these UMEs.

To test solvent resistance, voltammetric measurements of the LT UMEs were also performed in acetonitrile, *N*,*N*-dimethylformamide, and 1,2-dichloroethane. In all these solvents, stable voltammetric responses were observed, as shown in Figure 6. Stable voltammetric responses in both aqueous and nonaqueous media were also obtained with carbon UMEs, as shown in Figure 7. The LT UMEs were reusable, giving similar voltammetric responses over a period of at least several weeks.

After immersion in these solvents for 4 h, no appreciable change in the polymeric coatings was observed. This is in agreement with classic swelling measurements. Cross-linked PFPE shows negligible swelling after immersion in dichloromethane for 94 h.[16] The remarkable resistance to organic solvents makes LT a suitable material for UME fabrication.

SECM Measurements. In SECM measurements, to bring the UME tip very close to the substrate surface, the tip should be sharpened so that the tip has a small RG.[17] Conventionally, the glass-encapsulated SECM tips are manually polished and sharpened with a polishing wheel. Although the tips prepared in this way are relatively robust, the polishing and sharpening processes are tedious. As mentioned previously, the RG of an LT tip is usually smaller than 2, which is very difficult to accomplish using conventional polishing methods. Thus, the LT tips should be particularly useful for SECM measurements. Figures 8 and 9 show SECM approach curves (normalized current, $i_T/i_{T,\infty}$, vs normalized distance, d/a)[17] on conducting and insulating substrates, respectively, obtained with LT Pt tips. As shown in the optical images, the UME tips prepared with LT are usually of conical geometry. Therefore, the experimental SECM approach curves do not fit the theoretical SECM approach curves for disk-shaped tips, but fit well the theory for conically shaped tips.[19] The geometry of a conical electrode is described by

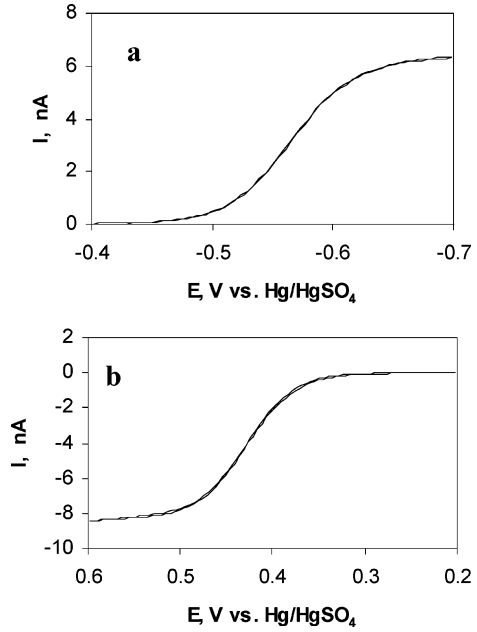

Figure 7. Cyclic voltammograms of a carbon UME in aqueous (a) and nonaqueous (b) media. The aqueous solution contained 2 mM $Ru(NH_3)_6Cl_3$ and 0.1 M KCl. The nonaqueous medium consisted of 2 mM ferrocene and 0.1 M $TBAClO_4$ in *N*,*N*-dimethylformamide. The reference electrode used in the organic solution was a 1 mm diameter Ag wire. The potential scan rate was 20 mV/s.

(19) Zoski, C. G.; Liu, B.; Bard, A. J. *Anal. Chem.* **2004**, *76*, 3646.

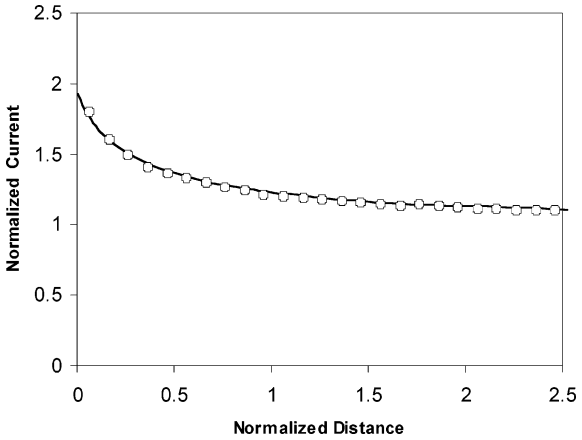

Figure 8. Theoretical (solid line) and experimental (open circles) SECM approach curves at a Pt conductive substrate. The tip was fabricated using a 10 μm diameter platinum wire. The solution contained 2 mM $Ru(NH_3)_6Cl_3$ and 0.1 M KCl. The tip and substrate were held at potentials of −0.7 and −0.35 V, respectively, vs Hg/Hg_2SO_4. The best fit was obtained with $H = 1$ and RG = 1.2.

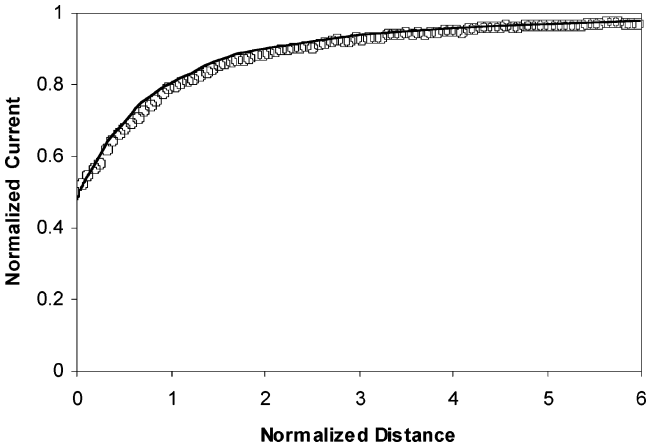

Figure 9. Theoretical (solid lines) and experimental (open circles) SECM approach curves at an insulating substrate. The tip was fabricated using a 10 μm diameter platinum wire. The solution contained 2 mM $Ru(NH_3)_6Cl_3$ and 0.1 M KCl. The tip was held at a potential of −0.7 V vs Hg/Hg_2SO_4. The best fit was obtained with $H = 0.5$ and RG = 2.

three parameters, the base radius (a) of the cone, the height (h), and the radius of the insulating sheath (r_g), or, alternatively, by a, r_g, and the aspect ratio $H = h/a$. The values of H obtained from the fitting are between 0.5 and 1. The RG values ($RG = r_g/a$) obtained from the fitting are between 1.2 and 2, consistent with that obtained from optical measurements. Similar results, obtained with carbon tips prepared with LT, will be reported elsewhere.

Although the tips prepared are conical, they have a small aspect ratio, so that the sensitivity in an SECM experiment is not greatly compromised compared to that of the more widely used disk electrodes. Indeed, such conical tips have the important advantage of allowing an independent assessment of the normalized distance ($d = 0$) by noting the point where the tip contacts a conductive substrate, something that is very difficult with a disk electrode with an insulating sheath.

CONCLUSIONS

In summary, metallic or carbon UMEs can be readily fabricated using PFPEs as the insulating material. The conical-shaped UMEs prepared using the photocurable polymer can be used in aqueous and nonaqueous media. The present work provided an alternative approach for the fabrication of SECM tips.

ACKNOWLEDGMENT

We thank the National Science Foundation (Grant CHE 0109587) for support of this research. We further acknowledge partial support from the Office of Naval Research (Grant N000140210185).

Received for review November 18, 2004. Accepted February 1, 2005.

AC0482918