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R & T Code 4133030

Technical Report No. 010

Characterization of Sub-Micron Sized Carbon Electrodes
Insulated with a Phenol-Allylphenol Copolymer

by

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Prepared for Publication

in

Analytical Chemistry

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January 15, 1992

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REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE January 15, 1992	3. REPORT TYPE AND DATES COVERED Technical	
4. TITLE AND SUBTITLE Characterization of Sub-Micron Sized Carbon Electrodes Insulated with a Phenol-Allylphenol Copolymer		5. FUNDING NUMBERS N00014-90-J-1161	
6. AUTHOR(S) T. G. Strein, A. G. Ewing		8. PERFORMING ORGANIZATION REPORT NUMBER No: 010	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Penn State University Univeristy Park, PA 16802		10. SPONSORING MONITORING AGENCY REPORT NUMBER	
9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Arlington, VA 22217-5000		11. SUPPLEMENTARY NOTES Prepared for Publication in Analytical Chemistry	
12a. DISTRIBUTION AVAILABILITY STATEMENT Unclassified		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) By carefully controlling the copolymerization of phenol and 2-allylphenol onto the outsides of flame etched carbon fibers, a method to construct voltammetric probes with overall physical dimensions as small as 400 nm has been developed. The primary factors controlling the formation of a thin, yet insulating film are relative monomer concentration, polymer electrodeposition time, and electrodeposition solution pH. Optimal conditions for this procedure involve electrodeposition for 12 to 14 min in 60 mM phenol and 90 mM 2-allylphenol (pH = 9.0). Success rates for construction of electrodes with total structural tip diameters below 1.5 μm is approximately 70%, and for construction of electrodes with approximately 400 nm tip diameters it is about 10%.			
14. SUBJECT TERMS submicron carbon electrodes, flame etched carbon fibers,		15. NUMBER OF PAGES 35	
17. SECURITY CLASSIFICATION OF REPORT unclassified		16. PRICE CODE	
18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT	

CHARACTERIZATION OF SUB-MICRON SIZED CARBON ELECTRODES
INSULATED WITH A PHENOL-ALLYLPHENOL COPOLYMER

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UPCOMING RESEARCH

Carbon electrodes with total structural diameters as small as 400 nm having electrochemical diameters less than 200 nm have been fabricated and characterized.

ABSTRACT

By carefully controlling the copolymerization of phenol and 2-allylphenol onto the outsides of flame etched carbon fibers, a method to construct voltammetric probes with overall physical dimensions as small as 400 nm has been developed. The primary factors controlling the formation of a thin, yet insulating film are relative monomer concentration, polymer electrodeposition time, and electrodeposition solution pH. Optimal conditions for this procedure involve electrodeposition for 12 to 14 min in 60 mM phenol and 90 mM 2-allylphenol (pH = 9.0). Success rates for construction of electrodes with total structural tip diameters below 1.5 μm is approximately 70%, and for construction of electrodes with approximately 400 nm tip diameters it is about 10%.

INTRODUCTION

The use of microelectrodes has grown rapidly in the last decade¹⁻³, particularly for analytical determination of electroactive compounds in biological microenvironments.⁴⁻⁷ An interest in our research group has been the measurement of dopamine dynamics at the single cell level in the pond snail *planorbis corneus*.⁸⁻¹⁰ Extension of this technology to voltammetry in still smaller mammalian neurons (approximately 20 micron diameter) has not yet been accomplished. This is primarily due to the relatively large structural dimensions of the electrodes applied to date.

Ultrasmall electrodes have found wide utility for neurochemical analysis. Because many classical neurotransmitters are among the small number of easily oxidized components of brain fluids, electrochemical techniques are well-suited for neurotransmitter analysis. The use of carbon electrodes for *in vivo* electrochemical investigations in the brain was first initiated by Adams.^{11,12} Since that time a great deal of work has been carried out using small carbon paste, graphite epoxy and carbon fiber electrodes for *in vivo* neurochemical analysis.⁴⁻⁷ These electrodes have total tip diameters that typically range from 100 μm down to 20 μm . Carbon electrodes with total structural tip diameters on the order of a few micrometers have been constructed from etched carbon fibers,¹³ and have been used for intracellular voltammetry¹³ and extracellular voltammetry at single adrenal cells.¹⁴ Carbon electrodes with 1-5 μm total tip diameter have been developed in this laboratory¹⁵⁻¹⁷ and have been used for voltammetric analysis of dopamine in the cytoplasm of single large nerve cells.⁸⁻¹⁰

Many reports of electrodes with extremely small electroactive areas can be found in the literature.^{1-3, 18-20} However, most are housed in a rather large support material.

These types of electrodes offer great promise for the investigation of electrode kinetics¹⁸ and for electrochemical microscopy^{19,21}, but cannot be used for neuronal analysis in extremely small microenvironments. Even the extremely small platinum "nanodes" developed by Penner, et al.¹⁸ have a large support material immediately behind the small tip and this inhibits microscopic viewing of the precise manipulations required for analysis in ultrasmall environments.

In this paper we describe the construction of electrodes that are suitably small in both electroactive and structural dimensions for analysis in ultrasmall environments (e.g. single mammalian neurons or perhaps even single synapses). These electrodes have been constructed using carbon fibers which have been etched to tip diameters in the range of 100 nm or smaller. These flame-etched carbon fibers are then electrochemically coated with a thin poly(oxyphenylene) film for insulation. Poly(oxyphenylene) coatings, which have been classically used for corrosion protection of metals²², have more recently been applied as the insulation of carbon-based electrodes.^{23,24} The novel aspect of the polymer used for this work is the merging of the insulating character of 2-allylphenol with the thin films obtainable with phenol. The relative concentration of monomer, electropolymerization time, and the pH of the electrodeposition solution are all critical to the formation of a thin, and insulating polymer film. After coating, the insulating polymer is removed from the exact tip of the electrode, exposing a new carbon surface at only the tip of the low micron to sub-micron total structure.

EXPERIMENTAL

Chemicals and Solutions. I. Polymer Bath Formulation.

Solutions for electropolymerization were prepared daily by dissolving phenol and 2-allylphenol in a 2% by weight solution of butyl cellosolve in 25.0 mL of a 1:1 methanol:water mixture. 2-Allylphenol, liquefied phenol (90%), and butyl cellosolve (2-butoxyethanol) were obtained from Aldrich Chemical. II. Solutions for Analysis.

Voltammetry was carried out in pH 7.4 citrate/phosphate buffer. This solution consisted of 0.0099 M citric acid (Aldrich Chemical), and 0.181 M sodium phosphate, dibasic (Baker Scientific). Dopamine hydrochloride (DA), 4-methylcatechol (4-MC), and 3,4-dihydroxyphenylacetic acid (DOPAC), were obtained from Sigma Chemical. Tris(2,2'-bipyridyl) ruthenium(II) chloride hexahydrate and potassium ferrocyanide trihydrate were obtained from Aldrich Chemical. Reagent grade methanol was obtained from Fischer Scientific. All chemicals were used as received without further purification.

Electrodes. Electrodes were constructed by aspirating 11 μm carbon fibers (Thornell P-55S, 4K pitch based carbon fibers, Amoco Systems, Inc.) into standard glass capillaries (A-M Systems, Inc.) and pulling the capillaries to a tip around the fiber with a glass capillary puller (Harvard Bioscience). Carbon fibers, stretched between the two pulled glass segments, were cut to produce two pulled glass structures with protruding 11 μm carbon fibers. The capillaries were filled with gallium (Aldrich Chemical Co.), and a nichrome wire was inserted for electrical contact. For each electrode, the protruding fiber was etched in an oxygen/methane flame. Electrodes were then insulated with a copolymer of 2-allylphenol and phenol by potentiostating (Bioanalytical Systems CV-1A) at 4.0 volts vs a platinum

wire counter/reference electrode. As many as six electrodes were coated at once by connecting their leads together in parallel. Polymer curing was then accomplished by placing the electrodes in an oven at 150°C for 30 min.

Apparatus. All voltammetry was performed using an Ensmann Instruments EI400 microelectrode potentiostat, and recorded on a Hewlett Packard X-Y recorder. The potentiostat was operated in the two electrode mode with a saturated sodium calomel reference/counter electrode. Scanning electron microscopy was carried out on either an ISI 60 or a Joel 5400. All errors are reported as standard error of the mean (S.E.M.). Electrochemical reversibility for voltammetric analysis was calculated for each voltammogram by plotting $-\log\{(i_{lim}-i)/i\}$ vs potential (E) to check for deviation from Nernstian behavior.

RESULTS AND DISCUSSION

I. Electrode Construction. A schematic of the polymer-coated flame-etched electrode is shown in Figure 1. The carbon fiber is etched in a methane/oxygen flame, and coated with an insulating copolymer film of phenol and 2-allylphenol. Carbon fibers can be etched to approximately 100 nm by simply passing the fiber slowly through a flame.²⁵ The smallest tips are achieved with hotter flames. Figure 2 illustrates the electrode construction with a series of scanning electron micrographs. Figure 2A is an etched carbon fiber with a tip diameter of approximately 100 nm. Figure 2B shows a polymer insulated electrode tip, and Figure 2C shows a structure that has been polymer coated and then cut with a scalpel blade to expose the electroactive carbon surface.

Coating the flame etched carbon fibers with an extremely thin insulating film is the key step in constructing these electrodes. At an applied potential of 4.0 V, the phenolic group on the monomers is oxidized via a one electron, one proton transfer, generating a free radical. This free radical can then initiate a free radical, step-growth polymerization. The rate at which new chains are generated reaches a steady state, which is indicated by the leveling out of the current response. Upon heating, these discrete chains are apparently cross-linked via the allyl groups, creating a network polymer system which electrically insulates the electrode.

Following insulation of the carbon fiber, removal of the polymer from the exact tip of the electrode can be accomplished in several ways. The simplest way is to cleave or scratch the extreme electrode tip with a scalpel. This is carried out with the aid of a microscope, and offers speed of removal, but relies on a steady hand. A more elegant way to remove polymer from the electrode tip involves the use of a field emission arc.²⁶ This method

uses a potential field applied between the electrode tip and a metal plate to induce an arc of current which desorbs the polymer. We have found the field emission method of polymer removal to give the smallest electroactive areas, but often it is too harsh and destroys the electrode. Use of a scalpel to cut the very tip has proven to be the faster, and more consistent method for removal of polymer from the tip of the electrode.

The thickness and integrity of the co-polymer film is critical to the production of a suitable electrode for use in ultrasmall environments. Potje-Kamloth, et al.²³ have obtained insulating films with a thickness of several micrometers by polymerization of only 2-allylphenol onto electrode surfaces. Addition of phenol to the polymerization solution, and careful control of the electrodeposition of the co-polymer results in sub-micron film thicknesses. We have found three factors to be critical for the formation of a thin, yet insulating co-polymer film: 1) relative concentration of phenol and 2-allylphenol, 2) polymer deposition time, and 3) pH of the electrodeposition solution. These parameters have been investigated by coating flame-etched carbon fibers under varied conditions to obtain insulating films, testing the electrodes for voltammetric response, and subsequently examining them with scanning electron microscopy.

1) **Relative Monomer Concentrations.** The effect of phenol concentration on film thickness is summarized in Table I. At a pH of 9.0, 40 μ L aliquots of liquefied phenol (90%) have been added to a 90 mM 2-allylphenol solution. As the ratio of phenol to 2-allylphenol is increased, the resulting polymer thickness decreases, eventually to the point of compromising the insulating character of the co-polymer film. The insulating properties of the polymer films appear to be the result of crosslinking provided by the allyl functional groups. Inadequate

crosslinking due to lowered allyl content of the co-polymer results in a noninsulating film. The data in Table I do not include ratios of phenol to 2-allylphenol equalling or exceeding unity. When the phenol concentration exceeds that for 2-allylphenol, the majority of the polymer films formed are not insulating. Scanning electron microscopy images of a naked carbon fiber, and fibers coated with non-insulating as well as one coated with an insulating film are shown in Figure 3. Non-insulating films are characterized by either large charging currents (greater than 10 pA between anodic and cathodic scans in supporting electrolyte), or by an ohmic response (greater than 5 pA per 100 mV) to a linear potential scan. Figure 3A is an etched carbon fiber with no polymer coating, and Figures 3B-3D are polymer-coated electrodes which have been cleaved with a scalpel. Figure 3B shows an electrode that has been coated by electrolysis in a solution containing only 60 mM phenol. Figures 3C and 3D show electrodes coated in solutions with a ratio of 2:1 and 1:2.5 phenol to 2-allylphenol, respectively. Only the conditions used to obtain the electrode shown in Figure 3D provide electrodes with insulating polymer coatings. A reasonable compromise between film thickness and insulating character is obtained when solutions of 60 mM phenol and 90 mM 2-allylphenol (or a 2:3 ratio of phenol to allylphenol) are used. Data obtained with this monomer formulation have been used for the remainder of the discussion in the paper, and this formulation will be referred to as the normal monomer formulation.

2) Anodic Polymerization Time. A parameter that is very important for the formation of a suitable polymer film is the electrodeposition time. There is an obvious correlation between electrolysis time and film thickness, and this is shown in Table II. Using the normal monomer formulation at pH 9.0, deposition times have been varied from 4 to 14 min. At least 6 minutes is required to achieve

a 50% success rate of polymer film insulation, and 14 min. electrodeposition times provide a high success rate for polymer insulation and film thickness within the desired range (less than 250 nm).

3) **Electrodeposition Solution pH.** Perhaps the most pronounced effect on polymer thickness is observed when the pH of the electrodeposition solution is varied. The one electron, one proton transfer to initiate the free radical polymerization is a pH dependent reaction, thus, the pH apparently influences the polymer film thickness. Using the normal monomer formulation and 14 minute polymerizations, the pH has been varied from 8.9 to 9.6 via addition of ammonium hydroxide to the electrodeposition solution. Film thickness increases markedly with elevated pH as illustrated in Figure 4, and summarized in Table III. Representative scanning electron microscopy images of three similarly sized electrodes shown in Figure 4 compare the effect of polymerizing at a pH of 9.0, 9.2 and 9.5. These three images are at the same magnification, and the large scale bar represents 1 μm . In each case, the outer smooth portion of the image is the insulating polymer and the roughened core material is the carbon electrode surface. It is readily apparent that the polymer coating is larger at elevated pH, so the electroactive area of carbon comprises a smaller portion of the total diameter. Polymer films deposited in solutions with pH between 9.0 and 9.5 are very similar in terms of successful insulation. Hence, polymerization at the lower pH (9.0), where thinner films are formed, is clearly superior for construction of structurally small electrodes.

The current monitored during electropolymerization in pH 9.0, 9.3, and 9.6 solutions is shown in Figure 5. The apparent dip in the response at higher pH, is due to a higher steady-state current eventually reached. This deflection in the current response is typical of this type

of polymerization onto conducting surfaces.²² The higher steady-state values correspond with the bubble-like polymer formations as seen in Figures 4B and C. Apparently, higher pH results in an enhanced steady state current and the formation of bubbles, which interfere to some degree with visualization of the electrode tip with a microscope. It is evident that the lower pH value of 9.0 is optimal for the formation of a more uniform, as well as thinner film.

II. Voltammetric Characterization of Electrodes.

Cyclic voltammograms for several electroactive species are shown in Figure 6. Dopamine, 4-methylcatechol, and 3,4-dihydroxyphenylacetate have been examined as examples of two electron transfer reactions. Ruthenium tris bipyridine and ferrocyanide undergo one electron transfer reactions. Table IV summarizes the average halfwave potentials and wave slopes obtained for a series of electrodes for the oxidation of these electroactive species. These data are consistent with previously reported^{27,28} values at carbon fiber electrodes, indicating that the voltammetric integrity of the carbon fibers has been retained following flame etching and polymer coating.

III. Determination of Electrode Size. Determination of the total structural diameters of the electrodes has been accomplished by optical, video enhanced and electron microscopy. One of the smallest electrodes we have constructed is shown in Figure 7. The total tip structure (including the electrode and insulation), is approximately 400 nm.

Determination of electroactive area of these voltammetric electrodes has been accomplished by cyclic voltammetry. Microdisk electrodes of very small dimension have been modeled with hemispherical diffusion, and are characterized by sigmoidal voltammetry with a limiting current described by²⁰:

$$i_{lim} = 2\pi rnFDC$$

where r is the radius of the electrode, n is the number of electrons transferred in the electrode reaction, F is the Faraday constant, D is the diffusion coefficient ($6 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ for dopamine), and C is the concentration. For the electrodes described here, the limiting currents obtained in 10^{-4} M solutions are in the picoampere range, corresponding to electrode radii in the nanometer range.

Voltammograms have been obtained at a 400 nm structural diameter electrode in solutions of dopamine ranging from $9.9 \times 10^{-5} \text{ M}$ to $1.00 \times 10^{-3} \text{ M}$ (Figure 8). Equation I predicts an electrode radius of 62 nm and the total structural radius observed by electron microscopy is approximately 200 nm. Hence, a good correlation is observed, and the difference in radius further predicts that the insulating film thickness is approximately 140 nm (also consistent with the data shown in Table III).

As with most microelectrode construction techniques, one does not expect a 100% success rate for construction. With practice, it is possible to reach a success rate of about 70% for construction of well-insulated electrodes with total structural diameter of 1.5 μm or less. Electrodes as small as that shown in Figure 7 and characterized with the voltammetry in Figure 8 are presently constructed with a significantly lower success rate. However, this low rate is acceptable, because the development of electrodes this small should allow electrochemical measurements in ultrasmall environments. Experiments are presently in progress in our laboratory attempting to use the electrodes described here to monitor neurotransmitter dynamics in and around single human neuroblastoma cell synapses.

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ACKNOWLEDGMENTS

This work was supported by a grant from the Office of Naval Research. T.G.S. acknowledges support from an American Chemical Society Analytical Division Fellowship sponsored by the Proctor and Gamble Company. A.G.E. is the recipient of a Presidential Young Investigator Award from the National Science Foundation (CHE-8657193) and is a Camille and Henry Dreyfus Teacher Scholar. The authors wish to thank Rosemary Walsh for her assistance in obtaining the scanning electron microscope images presented in this paper.

**Table I. Effect of Phenol Concentration on Copolymer
Film Thickness.¹**

Amount of Phenol ² Added (μ L)	Solution Conc. of Phenol (mM)	Resulting Film Thickness (nm)	Success in Insulation (%)	N
0	0	283 \pm 23	80%	5
40	15	219 \pm 29	92%	12
80	30	209 \pm 31	100%	6
120	45	200 \pm 33	71%	7
160	60	182 \pm 20	71%	7
200	75	118 \pm 28	57%	7

1. Initial solution was 90 mM 2-allylphenol in a volume of 25.0 mL.

2. Phenol concentration was 90% by volume.

Table II. Effect of Electrodeposition Time on Copolymer Film Formation.¹

Time of polymer Deposition (min)	Resulting Film Thickness (nm)	Success in Insulating (%)	N
6	104 ± 38	50	4
8	173 ± 27	67	3
10	184 ± 56	50	2
12	200 ± 50	100	2
14	200 ± 75	100	3
17	208 ± 22	75	4

1. Solution used for electrodeposition was 90 mM
2-allylphenol and 60 mM phenol (pH 9.0).

Table III. Effect of Electrodeposition Solution pH on Copolymer Film Thickness.¹

pH ²	Resulting Film Thickness (nm)	Success in Insulating (%)	N
8.9	158 ± 35	75%	4
9.0	236 ± 36	100%	5
9.1	265 ± 14	83%	6
9.2	344 ± 8	100%	4
9.3	410 ± 3	100%	3
9.4	511 ± 97	67%	3
9.5	658 ± 55	67%	3
9.6	760 ± 72	50%	4

- Solutions were 90 mM 2-allylphenol and 60 mM phenol and electrodeposition time was 14 min in all cases.
- pH was adjusted by addition of ammonium hydroxide.

**Table IV. Halfwave Potentials and Waveslopes Obtained with
Polymer-Insulated Flame-Etched Carbon Fiber
Electrodes.**

Analyte	Halfwave Potential (mV vs SSCE)	Waveslope (mV/decade)	N
Dopamine	163 ± 14	75 ± 11	12
4-methylcatechol	188 ± 14	126 ± 9	12
3,4-dihydroxy- phenylacetate	327 ± 24	155 ± 9	10
Ferrocyanide	373 ± 50	171 ± 29	7
Tris(2,2'-bipyridyl) Ruthenium	1022 ± 35	68 ± 3	14

Supporting electrolyte: pH 7.4 citrate/phosphate buffer

FIGURE LEGENDS

Figure 1. Schematic of an electrode constructed from a flame-etched carbon fiber and insulated with a thin copolymer. W, nichrome wire; Ga, Gallium; C, flame-etched carbon fiber; P, poly(oxyphenylene) insulating polymer coating. Inset: end-on view of the electrode tip.

Figure 2. Scanning electron micrographs of A) a carbon fiber which has been etched in a hot oxygen/methane flame; B) an etched fiber which has been coated with an insulating layer of poly(oxyphenylene); and C) a coated fiber which has been cut with a scalpel blade to expose the carbon electroactive surface. In each case the large scale bar represents 1 μm .

Figure 3. Scanning electron micrographs comparing the texture and thickness of noninsulating (B,C), and insulating (D) polymer films on etched carbon fibers. A) An etched carbon fiber with no polymer coating, B) an etched fiber coated in 60 mM phenol only, C) an etched carbon fiber coated in 60 mM phenol and 60 mM 2-allylphenol, and D) an etched fiber coated in 60 mM phenol and 150 mM 2-allylphenol.

Figure 4. Scanning electron micrographs illustrating the effect of monomer bath pH on copolymer film thickness. All electropolymerizations were carried out for 14 min in 60 mM phenol and 90 mM 2-allylphenol. A) pH = 9.0 B) pH = 9.2 C) pH = 9.5. All scale bars represent 1 μm .

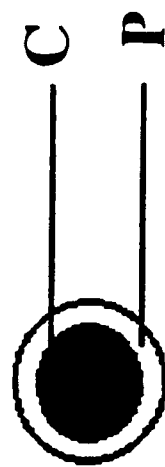
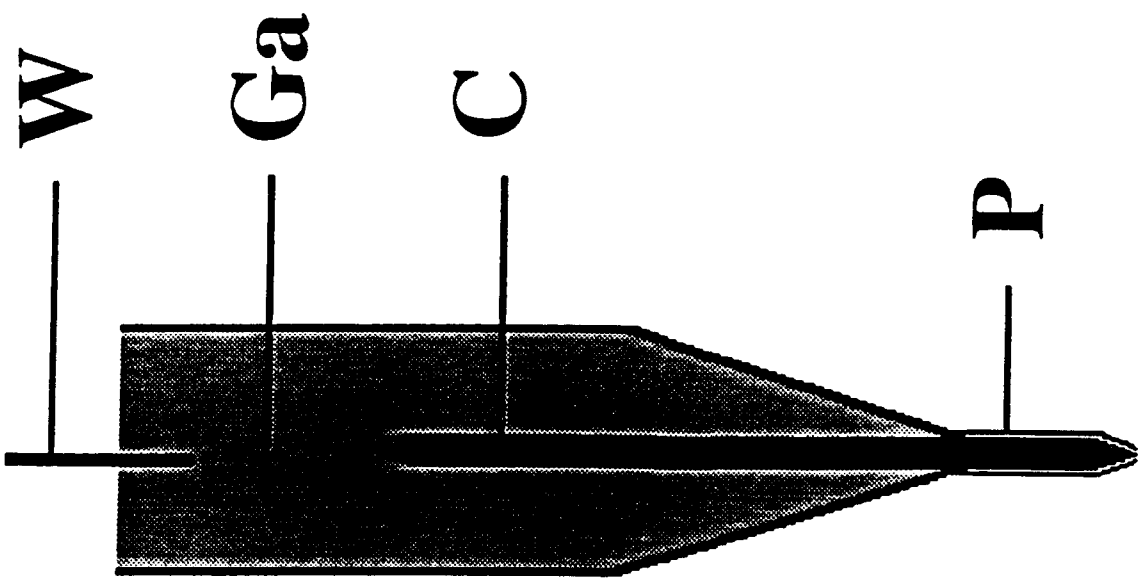
Figure 5. Current response during the electropolymerization of a combined six etched fibers at three different pH values. A) pH = 9.0; B) pH = 9.3; C) pH = 9.6.

Figure 6. Voltammetry using flame-etched, polymer-insulated electrodes. Analytes: A) dopamine, B) 4-methylcatechol, C) 3,4-dihydroxyphenylacetate, D) ferrocyanide, and E) tris(2,2'-bipyridyl)ruthenium. Voltammogram F is for an insulated electrode that has not been cleaved and has been immersed in dopamine solution. Analyte concentration: 10^{-4} M; scan rate: 100 mV s^{-1} .

Figure 7. Scanning electron micrograph of one of the smallest electrodes produced by the method described. The scale bar represents 100 nm, and the entire tip diameter is approximately 400 nm, with a corresponding electroactive diameter of about 200 nm. Electrode construction: normal monomer formulation, pH 9.0, 12 min electrodeposition time.

Figure 8. Voltammograms obtained in solutions of dopamine at an electrode of similar size and construction to that shown in Figure 7. The dopamine concentration was increased via standard additions. Dopamine concentrations:

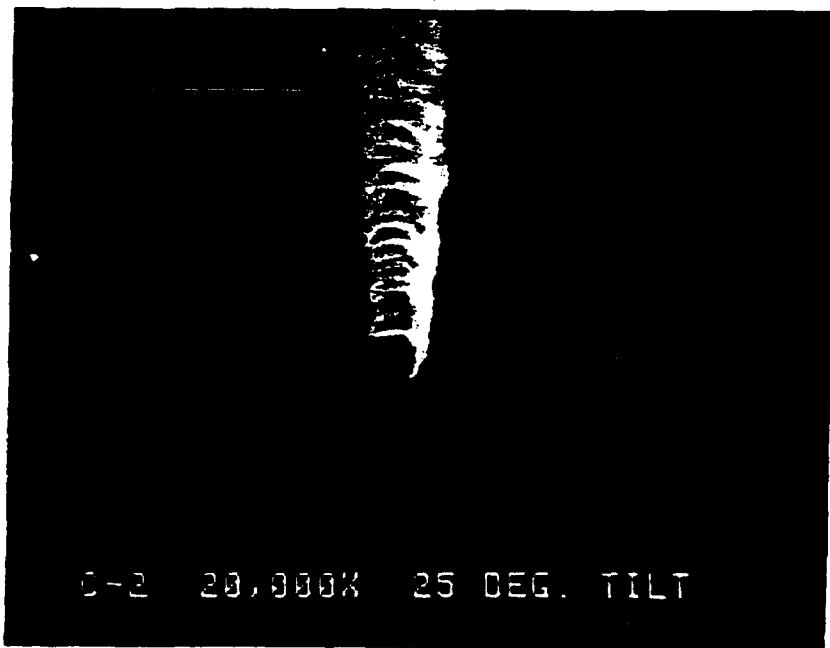
A) 1.00×10^{-3} M; B) 7.66×10^{-4} M; C) 6.76×10^{-4} M;
D) 3.84×10^{-4} M; E) 1.96×10^{-4} M; E) 9.90×10^{-5} M.



A



B

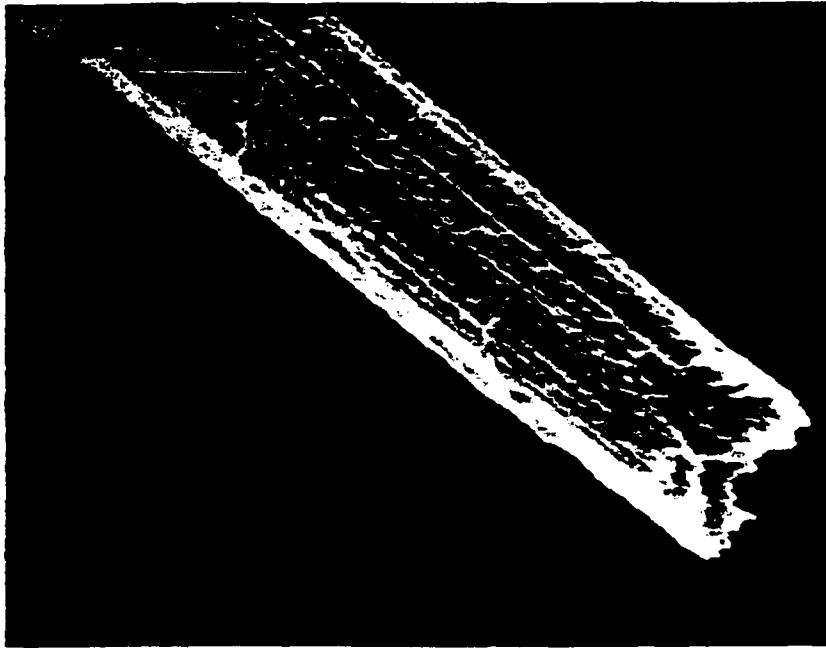


C

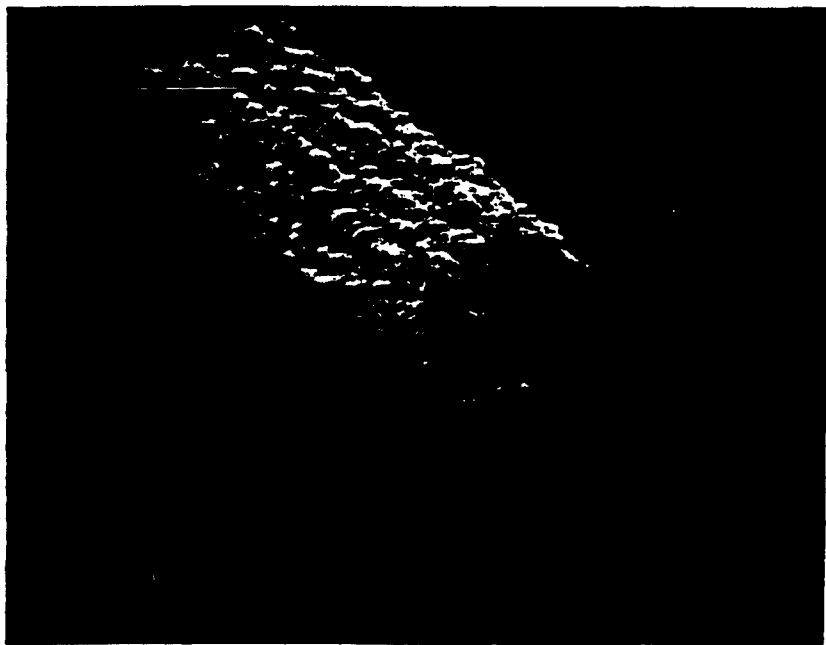


A

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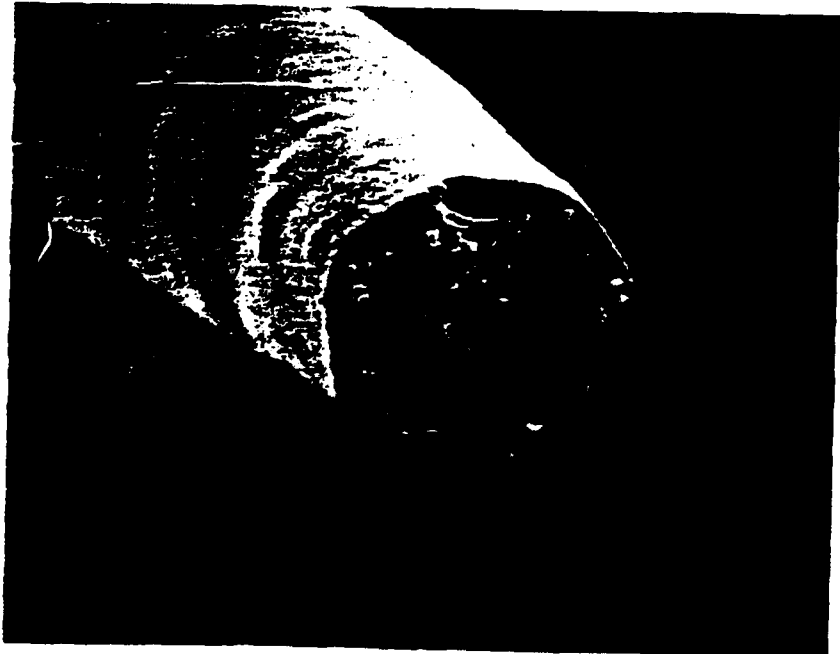
B



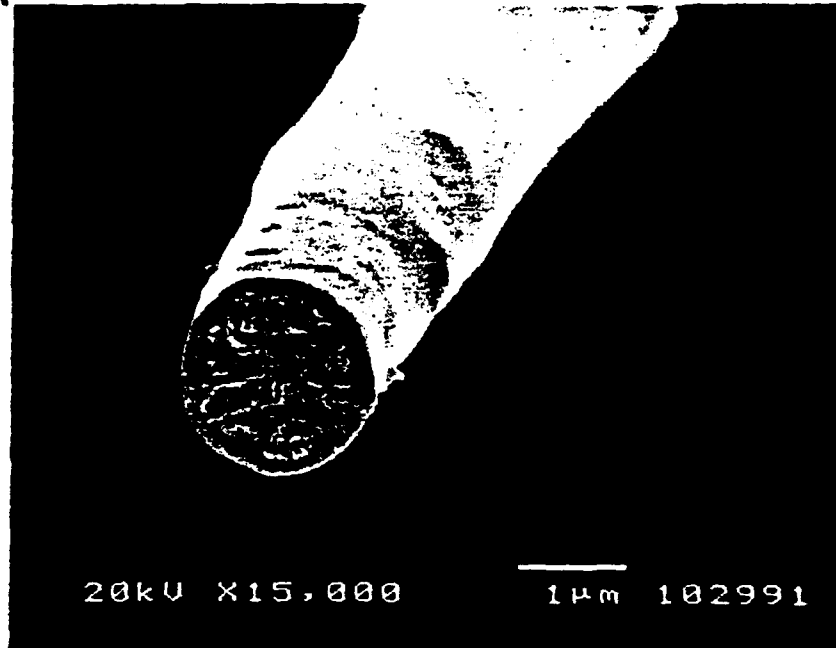
C



D



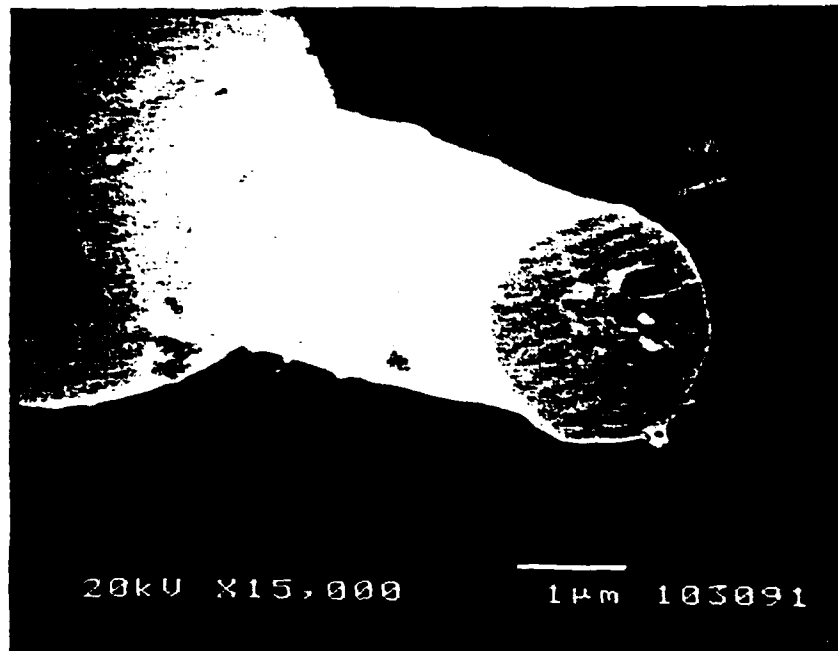
A

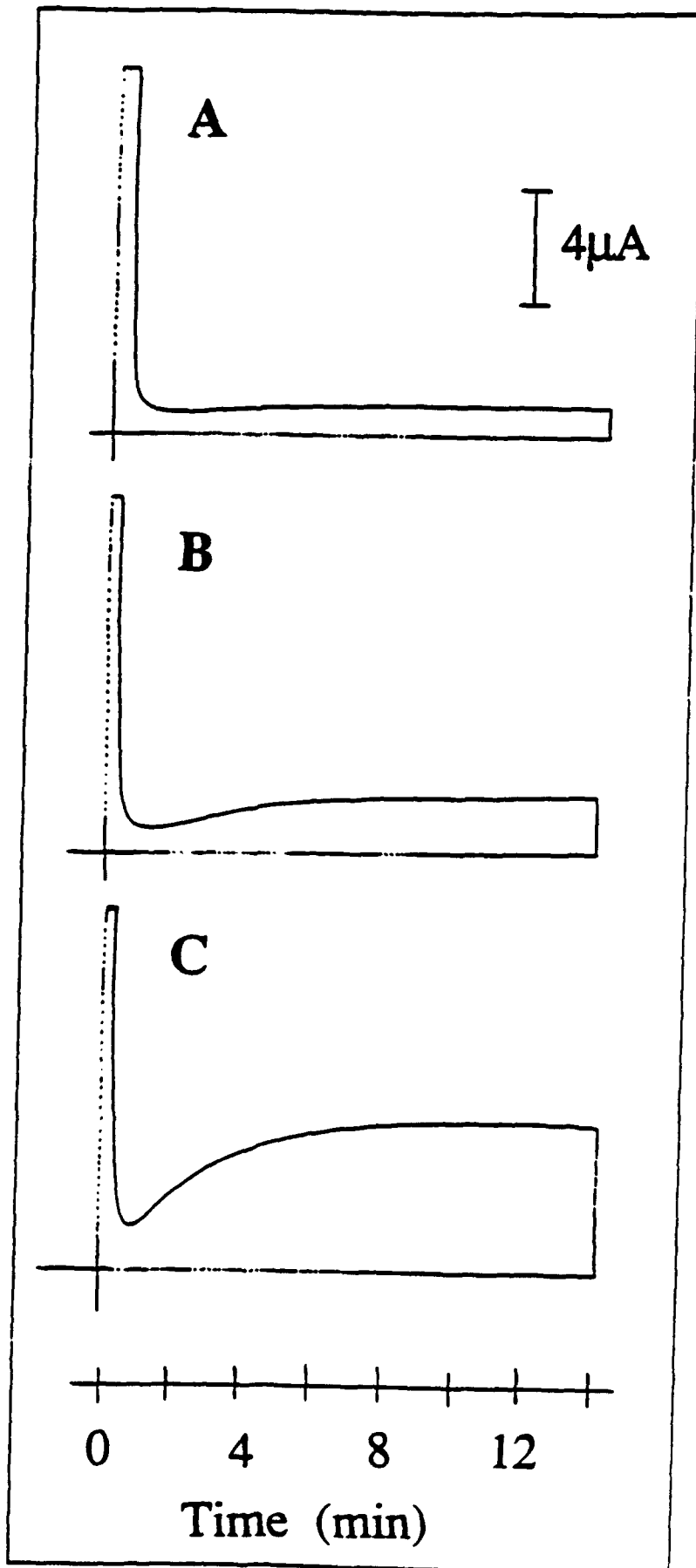


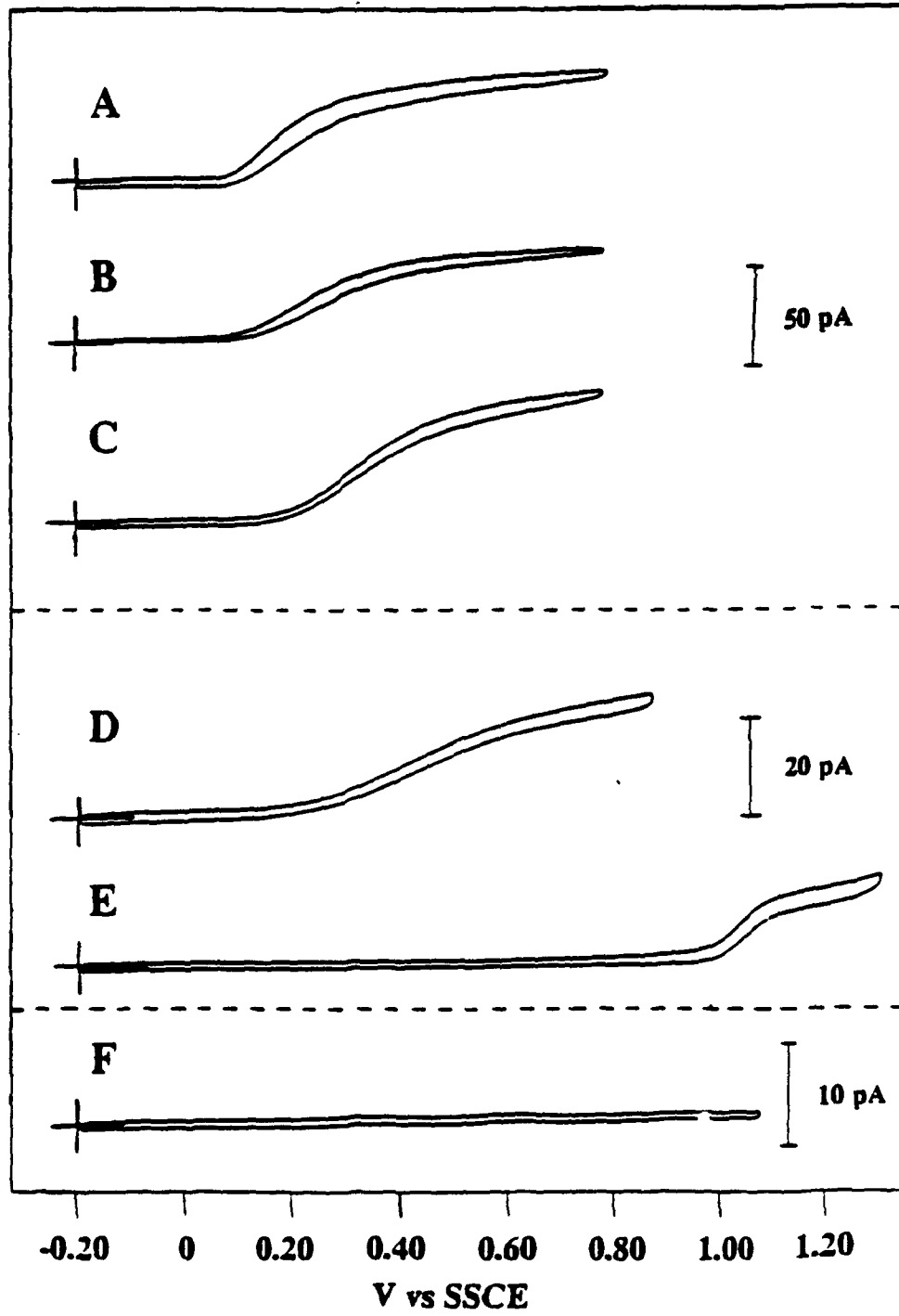
B



C







Strein and Ewing Fig. 7



