OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT: N00014-82K-0612

R&T CODE: 4133032
Robert J. Nowak

TECHNICAL REPORT NO. 105

by Charles R. Martin

Prepared for Publication

in Chemistry of Materials

Colorado State University
Department of Chemistry
Fort Collins, CO 80523-1872

******************End page 1
REPORT DOCUMENTATION PAGE

2. June 3 , 1996

3. Interim report

4. "Membrane-Based Synthesis of Nanomaterials "

5. GRANT: N00014-82K-0612 , R&T CODE: 4133032

6. Charles R. Martin

7. Charles R. Martin, Department of Chemistry, Colorado State University,
Fort Collins, CO 80523-1872

8. TECHNICAL REPORT NO. 105

9. Office of Naval Research, Chemistry Division, 800 North Quincy Street,
Arlington, VA 22217-5660

11. To be published in Chemistry of Materials

12. Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.

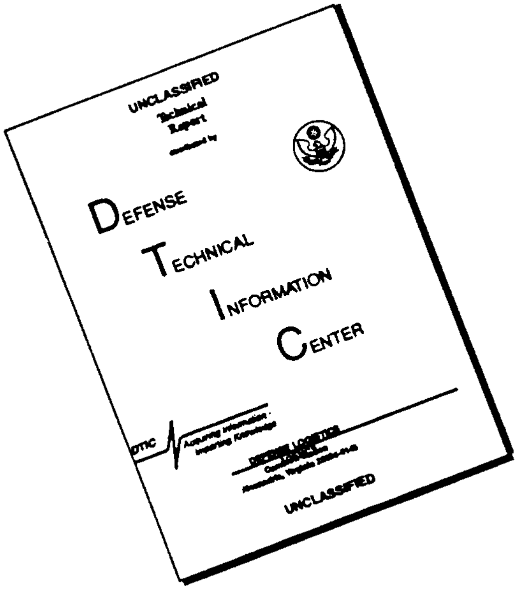
13. Abstract: This article reviews a relatively new method for preparing nanomaterials--membrane-based synthesis. This method entails synthesis of the desired materials within the pores of a nanoporous membrane. Because the membranes employed contain cylindrical pores of uniform diameter, monodisperse nanocylinders of the desired material, whose dimensions can be carefully controlled, are obtained. These nanocylinders may be either hollow (a tubule) or solid (a fibril or nanowire). We call this approach the "template" method for preparing nanomaterials because the pores in the nanoporous membranes are used as templates for forming the desired material. This template method is a very general approach; it has been used to prepare nanotubules and fibrils of polymers, metals, semiconductors, carbons and other materials.

14. Subject terms: Nanomaterials, nanochemistry

17. 18. 19. Unclassified

Membrane-Based Synthesis of Nanomaterials

Charles R. Martin
Department of Chemistry
Colorado State University
Ft. Collins, CO 80523



UNCLASSIFIED

Technical Report

DEFENSE

TECHNICAL

INFORMATION

CENTER

DTIC

UNCLASSIFIED

Abstract

This article reviews a relatively new method for preparing nanomaterials - membrane-based synthesis. This method entails the synthesis of the desired material within the pores of a nanoporous membrane. Because the membranes employed contain cylindrical pores of uniform diameter, monodisperse nanocylinders of the desired material, whose dimensions can be carefully controlled, are obtained. These nanocylinders may be either hollow (a tubule) or solid (a fibril or nanowire). We call this approach the "template" method because the pores in the nanoporous membranes are used as templates for forming the desired material. This template method is a very general approach; it has been used to prepare nanotubules and fibrils of polymers, metals, semiconductors, carbons, and other materials.

INTRODUCTION

There are now numerous chemical methods for preparing nanomaterials.[1,2] My research group has been exploring a method we call "template-synthesis" (for recent reviews see[3,4]). This method entails synthesizing the desired material within the pores of a nanoporous membrane. The membranes employed have cylindrical pores of uniform diameter (Figure 1). We view each of these pores as a beaker in which a particle of the desired material is synthesized. Because of the cylindrical shape of these pores, a nanocylinder of the desired material is obtained in each pore. Depending on the material and the chemistry of the pore wall, this nanocylinder may be solid (a fibril, Figure 2A) or hollow (a tubule, Figure 2B).

The template method has a number of interesting and useful features. First, it is very general; we have used this method to prepare tubules and fibrils composed of electronically conductive polymers,[5-12] metals,[9,13-19] semiconductors,[20] carbons,[21] and other materials. Furthermore, nanostructures with extraordinarily small diameters can be prepared. For example, Wu and Bein have recently used this method to prepare conductive polymer nanofibrils with diameters of 3 nm (30 Å).[22] It would be difficult to make nanowires with diameters this small using lithographic methods. In addition, because the pores in the membranes used have monodisperse diameters, analogous monodisperse nanostructures are obtained. Finally, the tubular or fibrillar nanostructures synthesized within the pores can be freed from the template membrane and collected. Alternatively, an ensemble of nanostructures that protrude from a surface like the bristles of a brush can be obtained.

This article gives an overview of the template method for preparing nanomaterials. Nanoporous membranes used as the template materials are first described. Methods used to deposit polymeric and metallic nanostructures within the pores of these membranes are then reviewed. Finally applications of template synthesized fibrils and tubules in bioencapsulation, electrochemistry, and membrane science are discussed.

MEMBRANES USED

"Track-Etch" Membranes. A number of companies (e.g. Nuclepore and Poretics) sell micro- and nanoporous polymeric filtration membranes that have been prepared via the "track-etch" method.[23] As indicated in Figures 1A and B, these membranes contain cylindrical pores of uniform diameter. The pores are randomly distributed across the membrane surface. Membranes with a wide range of pore diameters (down to 10 nm) and pore densities approaching 10^9 pores per cm^2 are available commercially. The most commonly used material to prepare membranes of this type is polycarbonate; however, a number of other materials are amenable to the track-etch process.[23]

Porous Alumina Membranes. Membranes of this type are prepared electrochemically from aluminum metal.[24] As indicated in Figure 1C, the pores in these membranes are arranged in a regular hexagonal lattice. Pore densities as high as 10^{11} pores per cm^2 can be achieved.[25] While such membranes are sold commercially, only a limited number of pore diameters is available. We have, however, prepared membranes of this type with a broad range of pore diameters.[15,17,18] We have made membranes with pores as small as 5 nm, and we believe that even smaller pores can be prepared.

Other Nanoporous Materials. Tonucci et al. have recently described a nanochannel array glass membrane.[26] Membranes of this type containing pores with diameters as small as 33 nm and densities as high as $3x10^{10}$ pores per cm^2 were prepared. Beck, et al. have prepared a new class of mesoporous zeolites.[27] Polyaniline and graphitic nanowires have recently been template synthesized within the pores of these new zeolites.[22,28] Douglas et al. have shown that the nanoscopic pores in a protein derived from a bacterium can be used to transfer an image of these pores to an underlying substrate.[29] Finally, Ozin discusses a wide variety of other nanoporous solids that could, in principle, be used as template materials.[1]

POLYMERIC MICRO AND NANOSTRUCTURES

Most of our work has focused on the electronically conductive polymers polypyrrole, poly(3-methylthiophene) and polyaniline (Figure 3). For a recent review of this work see.[3] We have shown that template-synthesized nanotubules and nanowires of these materials have higher electronic conductivities than bulk samples of the same material. Furthermore, the mechanism of electronic conduction in these template-synthesized nanostructures can be varied at will by changing their diameter.[30] We have also shown that capped versions of these polymeric microtubules can be used for enzyme immobilization.[12] This work will be briefly reviewed below. Finally, we have prepared graphitic tubules by template synthesis of a precursor polymer (polyacrylonitrile) within the pores of an alumina template membrane.[21]

Template-synthetic methods. The polymers shown in Figure 3 can be synthesized by oxidative polymerization of the corresponding monomer. This may be accomplished either electrochemically[5,7] or with a chemical oxidizing agent.[10,12,31,32] Both of these methods can be used to do template synthesis of conductive polymers. The easiest way to do electrochemical template synthesis is to coat a metal film onto one surface of the template membrane, and then use this metal film as an anode to electrochemically synthesize the polymer within the pores of the membrane.[7] Chemical template synthesis can be accomplished by simply immersing the membrane into a solution of the desired monomer and its oxidizing agent.[11,12,32]

In developing these template synthetic methods, we made an interesting discovery. When these polymers are synthesized (either chemically or electrochemically) within the pores of the track-etched polycarbonate membranes, the polymer preferentially nucleates and grows on the pore walls.[6,10,12,32,33] As a result, polymeric tubules are obtained (Figure 2B). By controlling the polymerization time, tubules with thin walls (short polymerization times) or thick walls (long polymerization times) can be produced.[32]

The reason the polymer preferentially nucleates and grows on the pore walls is straightforward.[9] Although the monomers are soluble, the polycationic forms of these polymers are completely insoluble. Hence, there is a solvophobic component to the interaction between the polymer and the pore wall. We have recently exploited such solvophobic interactions to prepare graphitic tubules.[21] In this case polyacrylonitrile was first synthesized from the monomer within the pores of the template membrane using water as the solvent. While the monomer is soluble in water, the polymer is not. As a result, polymerization within the pore yielded a tubule of polyacrylonitrile on the pore wall. These tubules were subsequently graphitized by heating at elevated temperatures.[21]

In the case of the conductive polymers there is also an electrostatic component to the interaction between the nascent polymer and the pore wall. This is because the polymers are cationic, and there are anionic sites on the pore walls.[9] This illustrates an important point - if a "molecular anchor"[14] that interacts with the material being deposited is present on the pore wall, a hollow tubule (as opposed to a solid fibril) will be obtained. For example, we showed that Au tubules can be electrochemically deposited into the pores of alumina template membranes if a silane that contains a -CN functionality is first bonded to the alumina pore wall.[14] If the -CN containing silane is not attached to the pore wall prior to Au deposition, solid Au fibers are obtained in the pores. We have also prepared Au tubules in polycarbonate template membranes using an electroless deposition method; in this case, the sensitizer for the electroless deposition (Sn^{2+}) is first applied to the pore walls.[34] This molecular anchor concept provides a general route for template synthesis of tubular structures.[14,19,34]

Finally, by controlling the polymerization time, conductive polymer tubules with thin walls (short polymerization times) or thick walls (long polymerization times) can be obtained.[32] For polypyrrole, the tubules ultimately "close-up" to form solid fibrils. Hence, by controlling the polymerization time we can make hollow polypyrrole tubules or solid fibrils. In contrast, the polyaniline tubules will not close-up, even at long polymerization times.[32] This is an interesting observation for which we currently do not have a definitive explanation.

Enzyme immobilization in template synthesized microcapsules. There has been considerable technological interest in tubular structures of the type discussed above for applications that include drug delivery and microelectronics.[35] We have recently shown that capped versions of our tubules can be loaded with enzymes to make a new type of enzymatic bioreactor.[12] A combination of electrochemical and chemical template-synthetic methods is used (Figure 4). The surface of the polycarbonate template membrane is first sputtered with a ca. 50 nm layer of gold (Figure 4A) which is used to electropolymerize a polypyrrole film across the face of the membrane. Short (1 μm) polypyrrole "plugs" are also deposited within the pores (Figure 4B). Polypyrrole tubules are then chemically polymerized within the pores of the plugged membrane (Figure 4C). The electrochemically polymerized plugs become caps for the chemically polymerized tubules.

The capped tubules (capsules) are then filled with the desired enzyme by vacuum filtering a solution of the enzyme through the capsule-containing membrane (Figure 4D).[12] The solvent molecules (H_2O) can pass through the polypyrrole plugs, whereas the much larger enzyme molecules are retained within the capsules. After addition of the enzyme, Torrseal epoxy is applied to the upper surface of the membrane (Figure 4E). After curing, the entire assembly is immersed into methylene chloride to dissolve the polycarbonate template membrane. This yields the desired array of enzyme-loaded capsules (Figure 4F).

Transmission electron microscopy has shown that the walls of these capsules are extremely thin, ca. 25 nm thick.[12] This is important because small molecules (such as the substrate and product of the enzymatic reaction) must diffuse through the walls in order to access the enzyme within the capsules. The thinness of the walls insures that these mass-transport processes will be facile. Diffusion is also facilitated by the fact that polypyrrole is a nanoporous polymer. However, the pores in polypyrrole are too small to allow the protein molecules inside to leach out.[12]

Five enzymes - glucose oxidase, catalase, subtilisin, trypsin, and alcohol dehydrogenase - have been encapsulated and tested to date.[12] The enzymatic activity of glucose oxidase (GOx)-loaded capsules is demonstrated in Figure 5. Curves a and b in Figure 5 compare catalytic activities for capsule arrays containing two different loading levels of GOx. As would be expected, the capsules with the higher GOx content show higher enzymatic activity. Curves c and d are from a competing encapsulation method, incorporation into a thin polymer film.[12] A comparison of the slopes of curves c and d with the slope of curve a shows that higher enzymatic activity can be achieved using the template-synthesized capsules.

TEMPLATE SYNTHESIS OF NANOMETALS

Nanometals have interesting optical,[15,18,36] electronic,[37] and (for appropriate metals) magnetic[25,38] properties. The concept of using the pores in a nanoporous membrane as templates for preparing nanoscopic metal fibrils was first demonstrated by Possin.[39] Earlier work in which nanometals were used to colorize alumina is also of interest.[40] Nanometal-containing membranes of this type have also been used as selective solar absorbers.[41] Finally, magnetic metals have been deposited within the pores of such membranes to make vertical magnetic recording media.[42]

My research group[15,18] and others[36] have been investigating the fundamental optical properties of template-synthesized nanometals. We are also using the template method to prepare ensembles of nanoscopic electrodes for fundamental and applied electrochemistry.[43] Finally, we have recently described a template-based method for preparing membranes with cylindrical metal nanotubules with diameters that approach the sizes of molecules (i.e. less than 1 nm).[34]

Template methods. Metals can be deposited within the pores of the template membranes by either electrochemical or chemical ("electroless") reduction of the appropriate metal ion. Electrochemical deposition is accomplished by simply coating one face of the membrane with a metal film and using this metal film as a cathode for electroplating;[14,16,19,44,45] this method has been used to prepare copper, platinum, gold, silver, and nickel fibrils. Typical gold nanofibrils are shown in Figure 2A. The lengths of these fibrils can be controlled by varying the amount of metal deposited. By depositing a small amount of metal, short, squat fibrils can be obtained; alternatively, by depositing large quantities of metal, long, needle-like fibrils can be prepared.[15,18] This ability to control the aspect ratio (length to diameter) of the metal fibril is especially important in our optical investigations because the optical properties of nanometals are dependent on aspect ratio.[15,18]

In order to conduct electroless deposition of metal within the pores of the template membrane, a catalyst must be applied to the pore walls.[43] As a result, we have a "molecular anchor" and, metal tubules are obtained after brief deposition times. These tubules close up to form solid metal fibrils at longer deposition times. Unlike the electrochemical method, where the length of the metal fibril can be controlled at will, the electroless method yields fibrils or tubules that run the complete width of the template membrane. Finally, Huber et al.[46] have recently described an alternative template method that entails injection of the metal melt into the pores of a template membrane.

Optical properties of nanometals. Nanoscopic metals have interesting (and beautiful) optical properties.[47] For example, colloidal suspensions of gold can be red, purple or blue depending on the size of the spherical gold particles.[47] Analogous colors are obtained after electrochemical plating of gold within the pores of the alumina template membranes.[15,18] This is illustrated in Figure 6, which shows photographs of pieces of our alumina membranes after deposition of gold fibrils into the pores. The membranes, themselves are optically transparent; hence, the colors are due to the gold fibrils.[15,18]

Electrochemistry at ensembles of nanometal electrodes.[43] When the electroless deposition procedure is used, metal fibrils that run the complete width of the polycarbonate template membrane are ultimately obtained. In addition, both faces of the membrane are covered with thin metal films. If one of these metal films is removed, an ensemble of nanodisk electrodes (the ends of the metal fibrils) is exposed at the surface of the membrane (Figure 7). These nanodisk electrodes are connected at their bases to a common current collector (the metal film that was not removed). Hence, it is trivial to make electrical contact to this ensemble of nanodisk electrodes.

Electrochemistry at nanoscopic electrodes constitutes one of the most exciting frontiers of modern electrochemical science. In fundamental electrochemistry, nanoelectrodes offer the opportunity to explore the kinetics of heterogeneous electron transfer reactions that are too fast to study at electrodes of conventional dimensions.[48] Our nanoelectrode ensembles (Figure 7) can be used to conduct studies of this type.[43] In applied electrochemistry, ensembles of nanoscopic electrodes offer the possibility of using electrochemical methods of chemical analysis to detect ultratrace levels of electroactive species. For example, we have recently shown that ensembles of 10 nm-diameter Au disk electrodes prepared via the template method show electroanalytical detection limits that are three orders of magnitude lower than detection limits at Au disk electrodes of conventional diameters (i.e. 1 mm).[43] Hence, electroanalytical chemistry becomes a more powerful method of chemical analysis when conducted at ensembles of nanoscopic electrodes.

Metal Nanotubule Membranes.[34] If the electroless deposition method discussed above is stopped before the pores are completely filled with gold, hollow Au tubules that run the complete thickness of the membrane are obtained. The resulting metal nanotubule membranes show selective ion-transport analogous to that observed in ion-exchange polymers.[49] Ion permselectivity[50] occurs because excess charge density can be present on the inner walls of the tubules. The tubes reject ions of the same sign, and transport ions of the opposite sign, as this excess charge. This is only possible when the inside radius of the tubule is small relative to the thickness of the electrical double layer[34] within the tubule. These membranes can be either cation selective or anion selective, depending on the potential applied to the membrane. Hence, these metal nanotubule membranes can be viewed as universal ion exchange membranes.

The pores in a commercially available polycarbonate filtration membrane (Poretics) were used as templates to form the gold nanotubules. These membranes contain cylindrical nanopores of uniform diameter (50 nm, 6×10^8 pores per cm^2) that run through the complete thickness (6 μm) of the membrane. Gold was electrolessly plated[43] onto the walls of these pores to yield a gold nanotubule within each pore. Gold films are also deposited on both faces of the membrane. These gold surface layers allow us to make electrical contact to the nanotubules within the pores. The thickness of the gold layers deposited on the pore walls can be controlled by varying the plating time. As a result, the inside diameter of the gold nanotubules can be varied at will (as determined from measurements of gas (He) flux across the tubule-containing membrane).[34]

We have explored the transport properties of these membranes using a simple U-tube concentration cell in which the membrane to be studied separates two aqueous solutions. In the simplest experiments of this type, solutions of differing KCl activity are placed on either side of the membrane, and reference electrodes are inserted into each solution in order to measure the membrane potential. We have shown that when the diameters of the Au nanotubules are small (less than 2 nm), the membranes show almost ideal cation permselectivity; that is, these membranes transport cations but reject anions. This cation permselectivity results because Cl^- chemisorbs to Au, resulting in nanotubules with excess negative surface charge.[34]

We have also demonstrated a more interesting concept - controlling the ion permselectivity by applying a potential to the metal nanotubule membrane. For these studies, it is essential to use an anion that does not adsorb to gold because we do not want the excess charge to be determined by adsorption. Because F^- does not adsorb to Au, KF was chosen as the electrolyte. A U-tube cell was assembled in which a gold nanotubule membrane separated solutions that were 1 mM and 10 mM in KF. This membrane was connected (through the Au surface layers) to the working electrode lead of a potentiostat and the potential applied to the membrane was varied over the range from -0.5 V to + 0.5 V vs. Ag/AgCl. The membrane potential (E_m) values were measured at each applied potential (Figure 8).

The dashed lines at the top and bottom of Figure 8 are the E_m values that would be achieved if the nanotubule membrane showed ideal cation and ideal anion permselectivity, respectively. At negative applied potentials, the nanotubule membrane shows ideal cation permselectivity, whereas at positive applied potentials the membrane shows ideal cation permselectivity. This selectivity occurs because at negative applied potentials, excess electrons are present on the walls of the tubes, and excess positive charge (K^+) accumulates within the tubes. As a result, anions (F^-) are excluded and cations (K^+) are transported by the membrane. At positive applied potentials the opposite situation occurs, and cations are excluded and anions are transported.

For any combination of metal and electrolyte, there is a potential called the potential of zero charge (pzc) where there is no excess charge on the metal. At this potential the nanotubule membranes should show neither cation nor anion permselectivity, and E_m should approach 0 mV. E_m for the tubule-containing membrane does, indeed, go from the ideal cation permselective value, through zero to the ideal anion permselective value (Figure 8). Furthermore, the potential at which E_m approaches zero is close to the reported pzc (-4 mV for Au in 1 mM NaF).[51]

We have demonstrated that these metal nanotubule membranes can be cation permselective, anion permselective or nonselective, depending on the potential applied to the membrane. These membranes can be as permselective as the commercially relevant Nafion® polymer and should have applications in both fundamental and applied electrochemistry. In addition, because the gold tubules have radii that approach molecular dimensions, these membranes might have applications in chemical separations, for example, biomedical separations or industrial gas separations.

An interesting question remains to be resolved - do these tubular structures have a uniform nanoscopic diameter throughout the length of the tube, or are there nanoscopic constrictions at the mouths of the tubes, with the inner part of the tube having a larger diameter. In fact, from a practical point of view, this possibility would be much more attractive than a uniform nanoscopic diameter. This is because flux through a tube of uniform nanoscopic diameter would be significantly lower than flux through a tube that had nanoscopic constrictions at both ends. We are currently attempting to definitively answer this interesting question.

CONCLUSIONS

The template method is proving to be a powerful approach for preparing nanomaterials. What does the future hold for this technology? From a fundamental viewpoint, we are interested in producing nanostructures with even smaller diameters in order to explore more thoroughly the effects of size on the properties of materials. In addition, we are using the template approach to prepare composite nanomaterials. Applications for the template-synthesized nanomaterials are also being developed. With help and support from a number of industrial partners, we are exploring applications in biosensors, bioencapsulation, energy production, and electronic and electro-optical devices. We are also developing new ways to do template synthesis, so that tubules and fibrils composed of other types of materials can be prepared. Finally, it is clear that if practical applications are to be realized, methods for mass-producing template-synthesized nanostructures will be required.

Acknowledgments. This work would not have been possible without the efforts of a number of hardworking and highly-motivated graduate students and post docs. They include Vinod P. Menon, Zhihua Cai, Junting Lei, Wenbin Liang, Ranjani V. Parthasarathy, Charles J. Brumlik, Gabor L. Hornyak, Leon S. Van Dyke, Colby Foss, Matsuhiko Nishizawa and Reginald M. Penner. Financial support from the Office of Naval Research is also gratefully acknowledged.

References

(1) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612-649.

(2) "Engineering a Small World: From Atomic Manipulation to Microfabrication," special section of *Science* **1991**, *254*, 1300-1342.

(3) Martin, C. R. *Acc. Chem. Res.* **1995**, *28*, 61-68.

(4) Martin, C. R. *Science* **1994**, *266*, 1961-1966.

(5) Penner, R. M.; Martin, C. R. *J. Electrochem. Soc.* **1986**, *133*, 2206-2207.

(6) Cai, Z.; Martin, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 4138-4139.

(7) Van Dyke, L. S.; Martin, C. R. *Langm.* **1990**, *6*, 1123-1132.

(8) Liang, W.; Martin, C. R. *J. Am. Chem. Soc.* **1990**, *112*, 9666-9668.

(9) Martin, C. R. *Adv. Mater.* **1991**, *3*, 457-459.

(10) Cai, Z.; Lei, J.; Liang, W.; Menon, V.; Martin, C. R. *Chem. Mater.* **1991**, *3*, 960-966.

(11) Martin, C. R.; Parthasarathy, R.; Menon, V. *Synth. Met.* **1993**, *55-57*, 1165-1170.

(12) Parthasarathy, R.; Martin, C. R. *Nature* **1994**, *369*, 298-301.

(13) Penner, R. M.; Martin, C. R. *Anal. Chem.* **1987**, *59*, 2625-2630.

(14) Brumlik, C. J.; Martin, C. R. *J. Am. Chem. Soc.* **1991**, *113*, 3174-3175.

(15) Foss, C. A. J.; Hornyak, G. L.; Stockert, J. A.; Martin, C. R. *J. Phys. Chem.* **1992**, *1992*, 7497-7499.

(16) Brumlik, C. J.; Martin, C. R.; Tokuda, K. *Anal. Chem.* **1992**, *64*, 1201-1203.

(17) Foss, C. A. J.; Hornyak, G. L.; Stockert, J. A.; Martin, C. R. *Adv. Mater.* **1993**, *5*, 135-136.

(18) Foss, C. A. J.; Hornyak, G. L.; Stockert, J. A.; Martin, C. R. *J. Phys. Chem.* **1994**, *98*, 2963-2971.

(19) Brumlik, C. J.; Menon, V. P.; Martin, C. R. *J. Mater. Res.* **1994**, *9*, 1174-1183.

(20) Klein, J. D.; Herrick, R. D. I.; Palmer, D.; Sailor, M. J.; Brumlik, C. J.; Martin, C. R. *Chem. Mater.* **1993**, *5*, 902-904.

(21) Parthasarathy, R. V.; Martin, C. R. *Adv. Mater.,* 1995, 7, 896.

(22) Wu, C.-G.; Bein, T. *Science* **1994**, *264*, 1757-1759.

(23) Fleischer, R. L.; Price, P. B.; Walker, R. M. *Nuclear tracks in solids*; University of California Press: Berkeley, 1975.

(24) Despic, A.; Parkhutik, V. P. In *Modern aspects of electrochemistry*; J. O. Bockris, R. E. White and B. E. Conway, Eds.; Plenum Press: New York, 1989; Vol. 20.

(25) AlMawiawi, D.; Coombs, N.; Moskovits, M. *J. Appl. Phys.* **1991**, *70*, 4421-4425.

(26) Tonucci, R. J.; Justus, B. L.; Campillo, A. J.; Ford, C. E. *Science* **1992**, *258*, 783-785.

(27) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834-10843.

(28) Wu, C.-G.; Bein, T. *Science* **1994**, *266*, 1013-1015.

(29) Douglas, K.; Devaud, G.; Clark, N. A. *Science* **1992**, *257*, 642-644.

(30) Spatz, J. P.; Lorenz, B.; Weishaupt, K.; Hochheimer, H. D.; Menon, V. P.; Parthasarathy, R. V.; Martin, C. R.; Bechtold, J.; Hor, P.-H. *Phys. Rev. Lett.* **1994**, *50*, 14,888-14,892.

(31) Lei, J.; Cai, Z.; Martin, C. R. *Synth. Met.* **1992**, *46*, 53-69.

(32) Parthasarathy, R. V.; Martin, C. R. *Chem. Mater.* **1994**, *6*, 1627-1632.

(33) Martin, C. R.; Van Dyke, L. S.; Cai, Z.; Liang, W. *J. Am. Chem. Soc.* **1990**, *112*, 8976-8977.

(34) Nishizawa, M.; Menon, V. P.; Martin, C. R. *Science* **1995**, *268*, 700-702.

(35) Pool, R. *Science* **1990**, *247*, 1410.

(36) Preston, C. K.; Moskovits, M. J. *J. Phys. Chem.* **1993**, *97*, 8495-8503.

(37) Masden, J. T.; Giordino, N. *Phys. Rev. B* **1987**, *36*, 4197-4202.

(38) Whitney, T. M.; Jiang, J. S.; Searson, P. C.; Chien, C. L. *Science* **1993**, *261*, 1316.

(39) Possin, G. E. *Rev. Sci. Instrum.* **1970**, *41*, 772-774.

(40) Asada, T. *Japanese Patent No.* **1960**, *310,401*,

(41) Patel, R. D.; Takwale, M. G.; Nagar, V. K.; Bhide, V. G. *Thin Solid Films* **1984**, *115*, 169-184.

(42) Kawai, S. In *Symposium on Electrochemical Technology in Electronics*; Electrochemical Society, Pennington, N.J.: 1987; p 389.

(43) Menon, V. P.; Martin, C. R. *Anal. Chem.* **1995**, *67*, 1920-1928.

(44) Chakarvarti, S. K.; Vetter, J. *J. Micromech. Microeng.* **1993**, *3*, 57-59.

(45) Chakarvarti, S. K.; Vetter, J. *Nucl. Instrum. Meth. Phys. Res.* **1991**, *B62*, 109-115.

(46) Huber, C. A.; Huber, T. E.; Sadoqui, M.; Lubin, J. A.; Manalis, S.; Prater, C. B. *Science* **1994**, *263*, 800-802.

(47) van de Hulst, H. C. *Light scattering by small particles*; Dover: New York, 1981, pp 397-400.

(48) Oldham, K. B.; Zoski, C. G. *J. Electroanal. Chem.* **1988**, *256*, 11.

(49) Dotson, R. L.; Woodard, K. E. in*Perfluorinated Ionomer Membranes*; A. Eisenberg and H.L Yeager Eds.; ACS Symposium Series, American Chemical Society: Washington, D.C., 1982; Vol. 180.

(50) Koryta, J. *Ion-Selective Electrodes*; Cambridge Univ. Press: Cambridge, 1975, pp pp. 21-23.

(51) Clavilier, J.; Huong, C. N. V. *J. Electroanal. Chem.* **1977**, *80*, 101.

Figure Captions

Figure 1. Electron micrographs of polycarbonate (**A** and **B**) and alumina (**C** and **D)** template membranes. For each type of membrane, an image of a larger pore membrane is presented (**A** and **C**) so that the characteristics of the pores can be clearly seen. An image of a membrane with extremely small pores is also presented (**B** and **D**). **A.** Scanning electron micrograph of the surface of a polycarbonate membrane with 1 µm-diameter pores. **B.** Transmission electron micrograph (TEM) of a graphite replica of the surface of a polycarbonate membrane with 30 nm-diameter pores. The pores appear "ragged." This is an artifact of the graphite replica. **C** and **D.** TEM's of microtomed section of alumina membranes with 70 nm (**C**) and 10 nm (**D**)-diameter pores.

Figure 2. **A.** Transmission electron micrograph of a microtomed section of an alumina template membrane showing 70 nm-diameter Au nanofibrils within the pores. **B.** Transmission electron micrograph of three polypyrrole nanotubules. The outside diameter is ~ 90 nm; the inside diameter is ~ 20 to 30 nm.

Figure 3. Some electronically conductive polymers.

Figure 4. Schematic diagram of methods used to synthesize and enzyme-load the capsule arrays. **A.** Au-coated template membrane. **B.** Electropolymerization of polypyrrole film. **C.** Chemical polymerization of polypyrrole tubules. **D.** Loading with enzyme. **E.** Capping with epoxy.
F. Dissolution of the template membrane.

Figure 5. Evaluation of the enzymatic activity of GOx-loaded capsules (curves a and b), and empty capsules (curve e). The standard o-dianisidine/peroxidase assay was used. A larger amount of GOx was loaded into the capsules used for curve a than in the capsules used for curve b. Curves c and d are for a competing GOx-immobilization method - entrapment within a polypyrrole film.

Figure 6. Photomicrographs (10x) of pieces of the alumina membranes after deposition of gold fibrils of various aspect ratios into membranes with pores of various diameters. The diameters of the gold fibrils get smaller from the top row (150 nm-diameter) to the bottom row (20 nm-diameter). The aspect ratios of the gold fibrils get larger from left to right.

Figure 7. Schematic of an edge view of a nanoelectrode ensemble. The nanometal fibrils running through the pores of the template membrane are shown. The lower ends of the fibrils define nanodisks which are the electrodes. The opposite (upper) ends of the nanofibrils are connected to a common metal film, which is used to make electrical contact to the nanodisks. We have used this method to make nanoelectrode ensembles containing gold disks with diameters as small as 10 nm.[43]

Figure 8. Variation of E_m with potential applied to the membrane (1 mM KF on the low-concentration (l) side, and 10 mM KF on the high concentration (h) side, of the membrane; tubule radius ~1.1 nm). The potential of the membrane was controlled with a potentiostat vs. a Ag/AgCl reference electrode immersed

in the side-h solution. E_m was measured with the membrane under potentiostatic control.

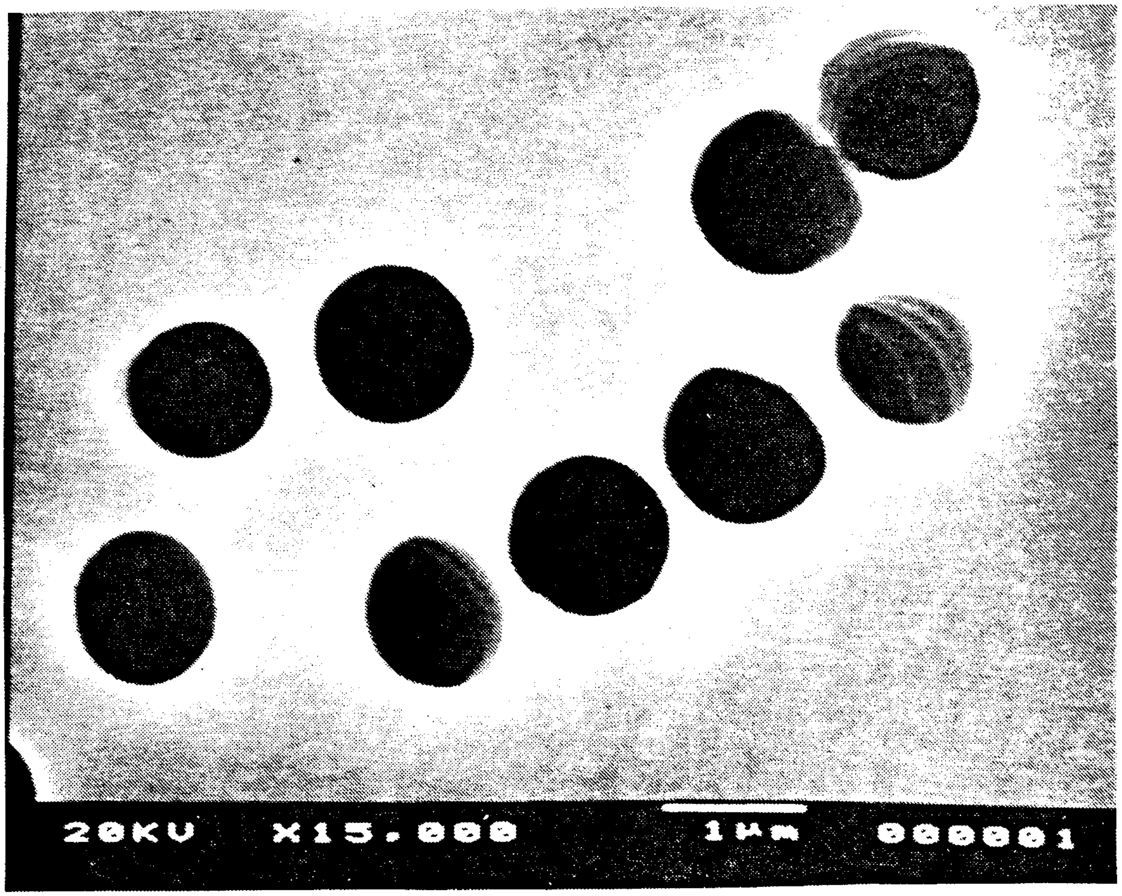


Fig 1A

Fig 1B

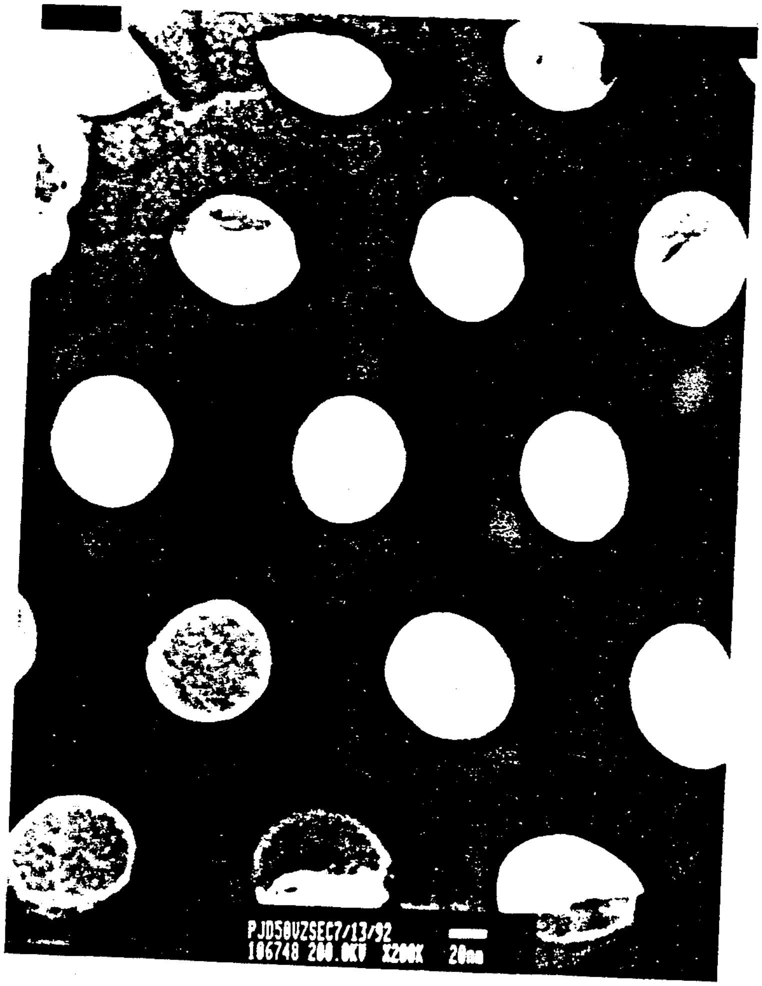


Fig 1C

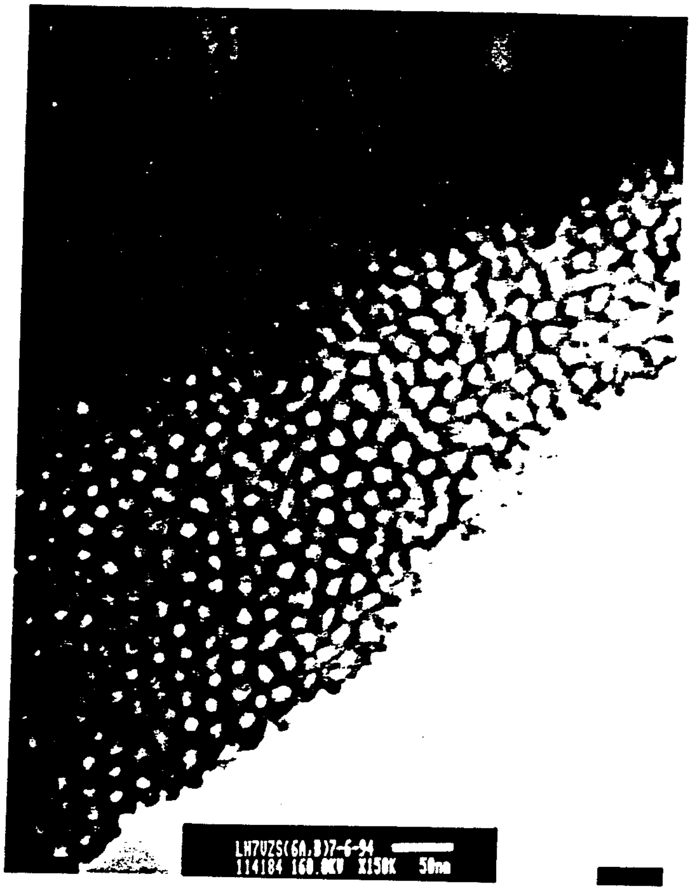
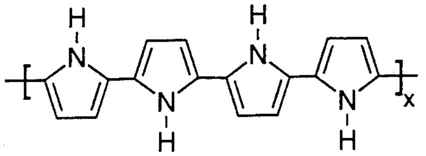


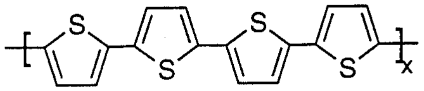
Fig 10

FIG. 2A

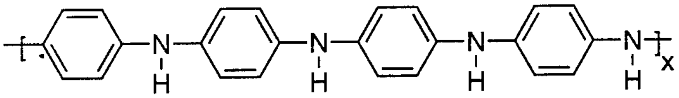
Fig 2B



Polypyrrole



Polythiophene



Polyaniline

Fig 3

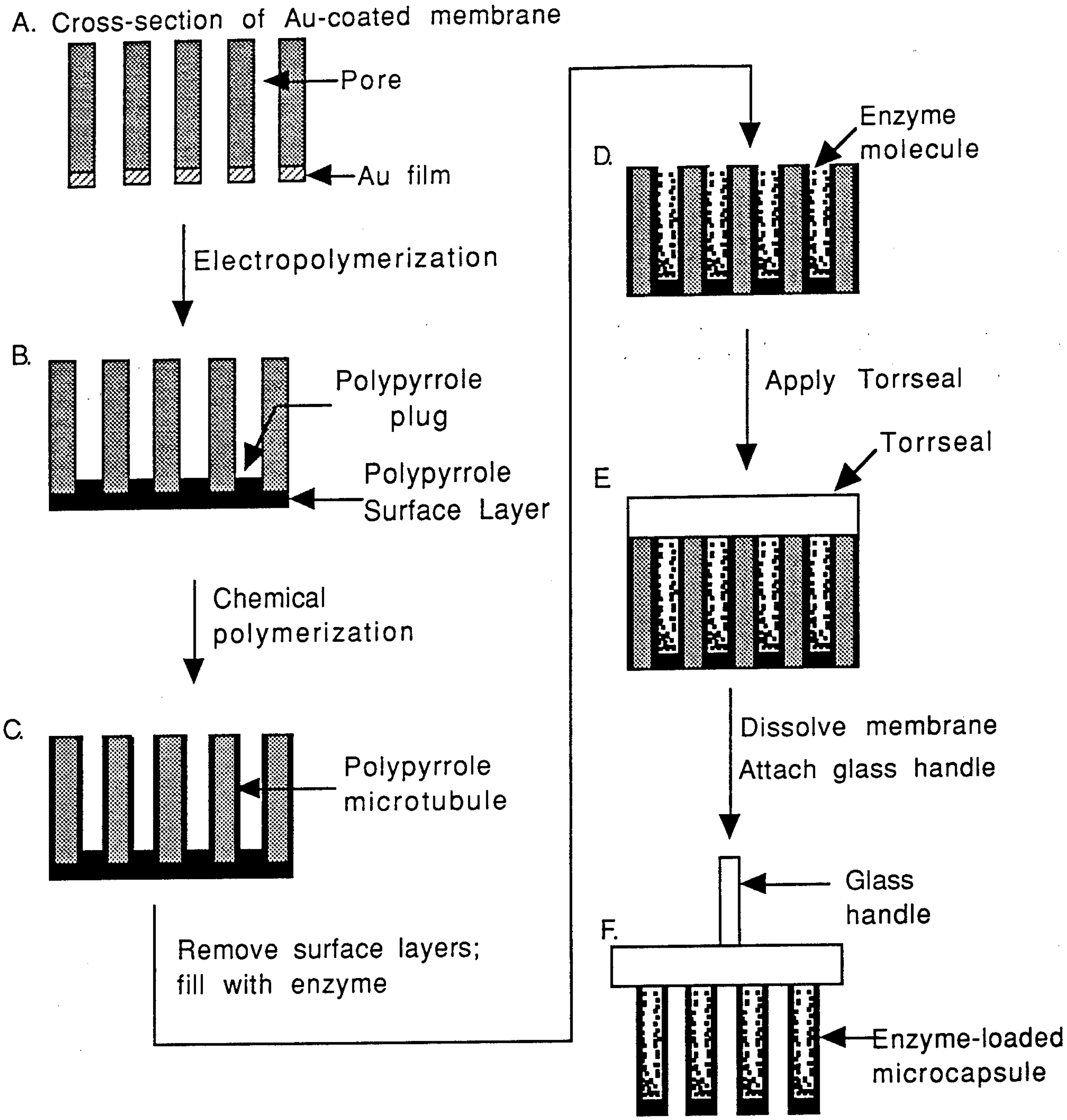

A. Cross-section of Au-coated membrane
Pore
Au film
Electropolymerization
B.
Polypyrrole plug
Polypyrrole Surface Layer
Chemical polymerization
C.
Polypyrrole microtubule
Remove surface layers; fill with enzyme
D.
Enzyme molecule
Apply Torrseal
E
Torrseal
Dissolve membrane
Attach glass handle
F.
Glass handle
Enzyme-loaded microcapsule

Fig4

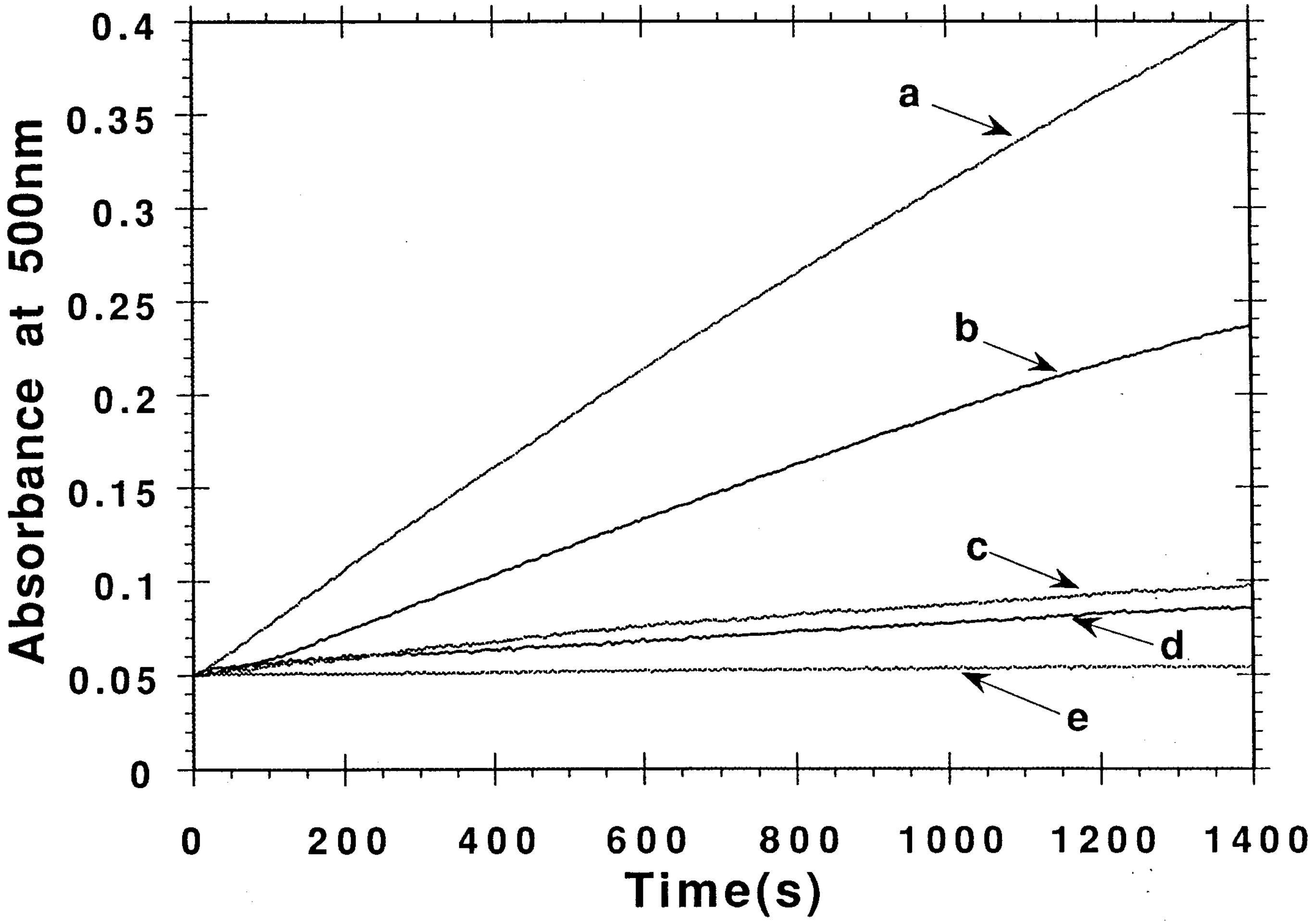

Absorbance at 500nm
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
200
400
600
800
1000
1200
1400
Time(s)
a
b
c
d
e

Fig 5

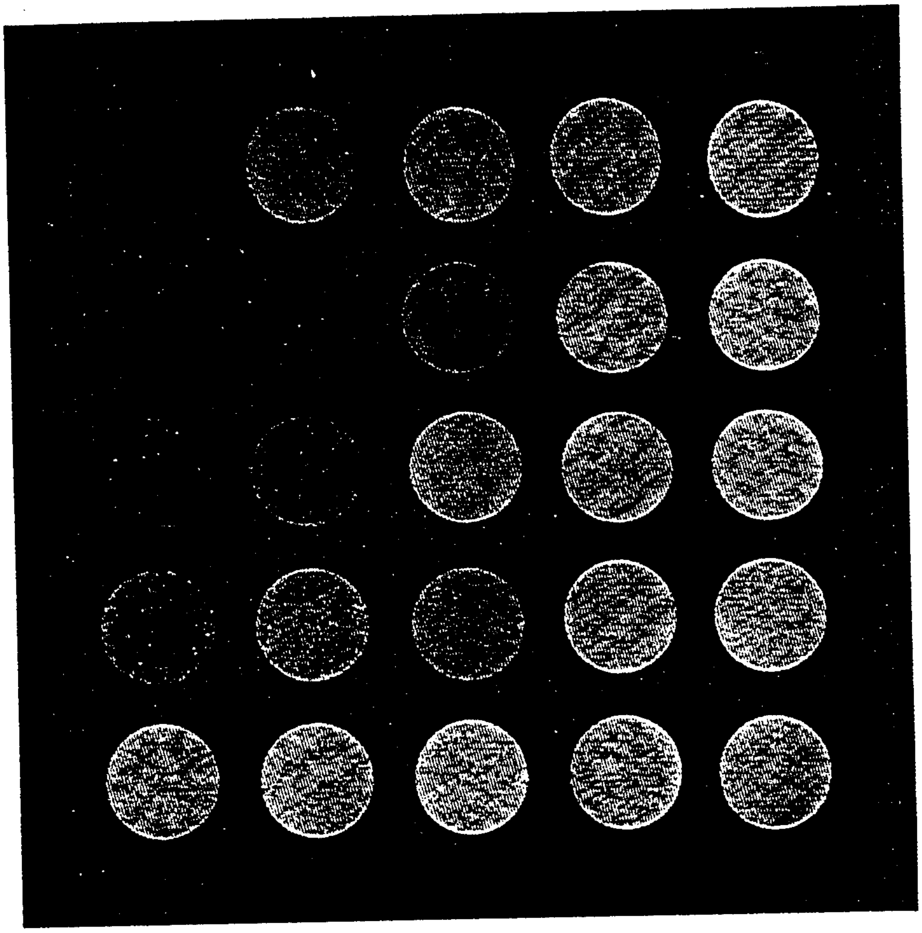


Fig 6

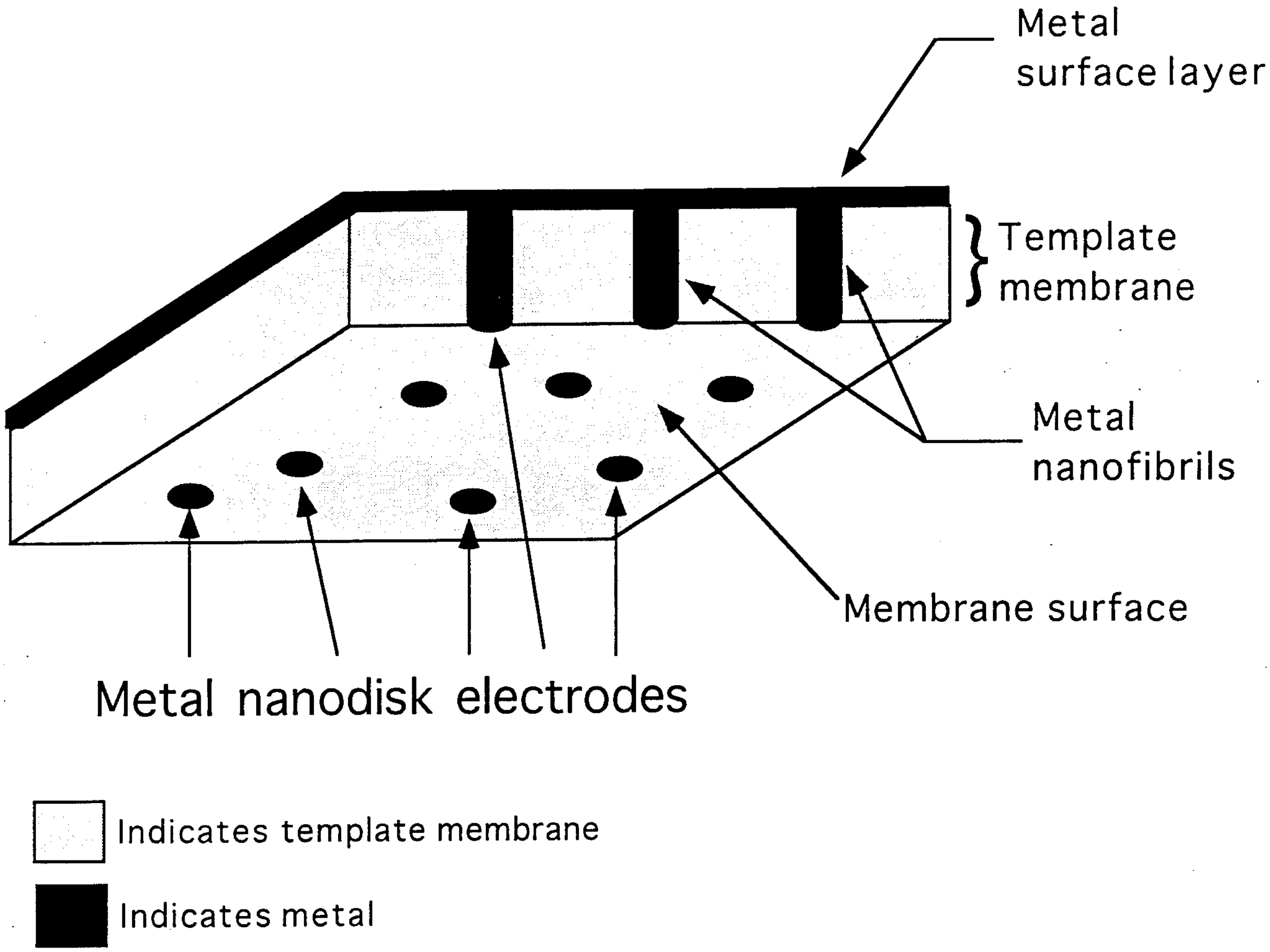

Metal surface layer
Template membrane
Metal nanofibrils
Membrane surface
Metal nanodisk electrodes
▢ Indicates template membrane
■ Indicates metal

Fig7

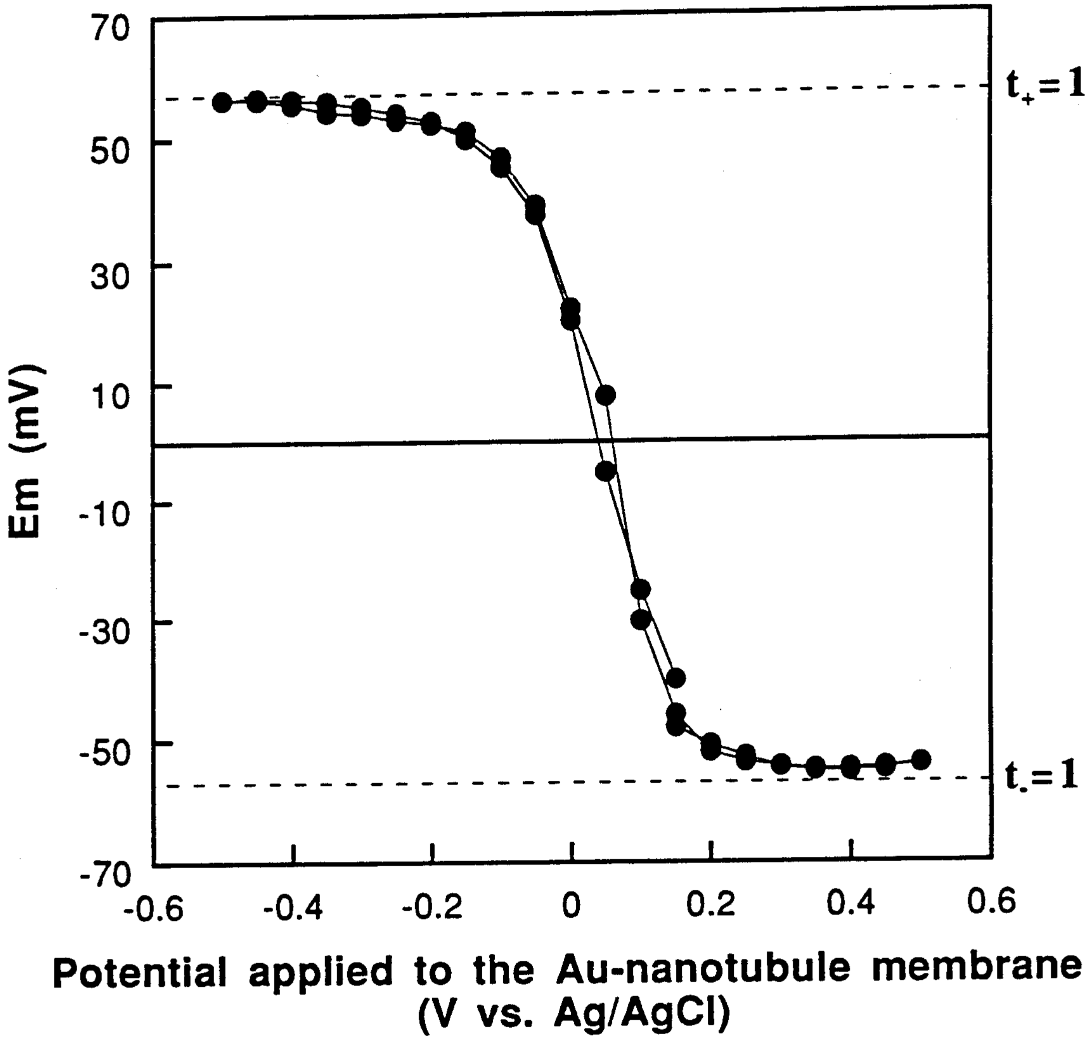

70
50
30
10
-10
-30
-50
-70
Em (mV)
t₊=1
t₋=1
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
Potential applied to the Au-nanotubule membrane
(V vs. Ag/AgCl)

Fig. 8