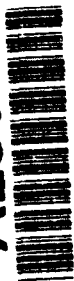OFFICE OF NAVAL RESEARCH
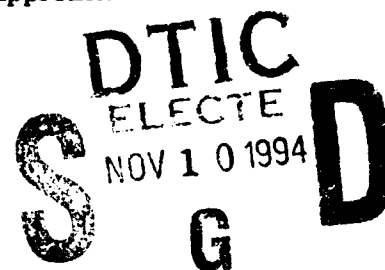
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13. ABSTRACT (Maximum 200 words)

Nanomaterials constitute an emerging, interdisciplinary field of science that deals with the development of methods for preparing nanoscopic bits of a desired material (e.g. a polymer, metal, semiconductor) and with scientific investigations of the nanomaterials obtained. Nanomaterials have numerous possible commercial and technological applications. In addition, this field poses an important fundamental philosophical question—how do the properties of a nanoscopic bit of a material differ from the analogous properties for a macroscopic sample of the same material? We have been exploring a membrane-based approach for preparing nanomaterials. This method entails 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 are obtained. This "template" method for preparing nanomaterials is very general; we, and others, have used it to prepare nanopolymers, nanometals, nanosemiconductors and other nanomaterials.

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NANOMATERIALS - A MEMBRANE-BASED SYNTHETIC APPROACH

Prepared for publication in

Science

by

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Ma⁻ 's with nanoscopic dimensions not only have potential technolog... applications, in areas such as device technology and drug delivery, but also are of fundamental interest in that the properties of a material can change in this regime between the bulk and molecular scales. In this article a relatively new method for preparing nanomaterials, membrane-based synthesis, is reviewed. This method entails synthesis of the desired material within the pores of a nanoporous membrane. Because the membranes employed contain cylindrical ⸱⸱s of uniform diameter, monodisperse nanocylinders of the desired ⸱⸱ᵣ⸱ ⸱,al, whose dimensions can be carefully controlled, are obtained. This "template" method has been used to prepare polymers, metals, semiconductors and ⸱ther materials on a nanoscopic scale.

Nanomaterials have wide-ranging implications to a variety of areas, including chemistry, physics, electronics, optics, materials, and the biomedical sciences. Applications include use in electronic, optical, and mechanical devices (1-5), drug-delivery (6), and bioencapsulation (7). Good reviews of the nanomaterials concept, and of the methods and applications of nanomaterials, can be found in (2, 4).

My research group has been exploring a method, that we call template-synthesis, for preparing micro and nanomaterials [see, for example, (7-19)]. This method entails synthesizing the desired material within the pores of a membrane. Because the membranes employed have cylindrical pores of uniform diameter (see Fig. 1), a nanocylinder of the desired material is obtained in each pore. Depending on the material and the chemistry of the pore wall, this cylinder may be solid (a nanofibril, Fig. 2A) or hollow (a nanotubule, Fig. 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 conductive polymers (7-12), metals (13-18), semiconductors (19), 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 fibrils with diameters of 3 nm (30 Å) (20). 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 tubules or fibrils synthesized within the pores can be freed from the template membrane and collected. Alternatively, an ensemble of micro or nanostructures that protrude from a surface like the bristles of a brush can be obtained (Fig. 2C).

The objective of this article is to give an overview of the template method for preparing nanomaterials. I discuss the types of nanoporous membranes used, and the methods we have developed to do template synthesis within these membranes. I then focus on the two types of template-synthesized materials that we (and others) have investigated in the greatest detail - conductive polymers and metals. I point out interesting fundamental features of the nanostructures obtained (e.g. interesting and unusual electronic and optical properties). In addition, I discuss possible applications of these template-synthesized materials in areas as diverse as bioencapsulation and ultratrace chemical analysis.

Membranes used

Most of the work in this area, to date, has entailed the use of two types of membranes - "track-etch" polymeric membranes and porous aluminas. The track-etch membranes are commercially available in a wide variety of pore sizes. However, these membranes have low porosities and the pores are

randomly distributed across the membrane surface (Figs. 1A and B). The aluminas typically have higher porosities and the pores are arranged in a hexagonal array (Fig. 1C). However, these membranes are available commercially in only a very limited number of pore diameters.

"Track-etch" membranes. A number of companies (such as Nuclepore and Poretics) sell microporous and nanoporous polymeric filtration membranes that have been prepared via the track-etch method (21). This method entails bombarding a nonporous sheet of the desired material with nuclear fission fragments, to create damage tracks in the material, and then chemically etching these tracks into pores. As indicated in Fig. 1A, these membranes contain cylindrical pores of uniform diameter. Membranes with pore diameters as small as 10 nm are available commercially; pore densities approach 10^9 pores per square centimeter. The commercially-available membranes are prepared from polycarbonate or polyester; however, a number of other materials are amenable to the track-etch process (21).

Porous aluminas. Membranes of this type are prepared electrochemically from Al metal (22). Pore densities as high as 10^{11} pores per square centimeter can be achieved (23). If one wanted to mass produce a nanomaterial via the template method, high pore density membranes would allow a greater number of nanostructures to be produced per unit area of template membrane. Although such membranes are sold commercially, only a limited number of pore diameters are available. We have, however, prepared membranes of this type with a broad range of pore diameters (15, 16). We have made membranes with pore diameters 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 with pore diameters as small as 33 nm and pore

densities as high as 3×10^{10} pores per square centimeter (24). Beck, et al. have prepared a new, large-pore-diameter xeolite (20, 25). 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 (26). Finally, Ozin discusses a wide variety of nanoporous solids that could be used as template materials (4).

Template synthesis of conductive polymers

In the 1970s chemists began to prepare new types of organic polymers that are good electronic conductors (27). Some examples of such electronically conductive polymers are shown in Fig. 3. The mechanisms by which these materials conduct electricity have been discussed in some detail [see, for example, (28, 29)]. The most important consideration from a chemical viewpoint is that enhanced electronic conductivities are obtained if polymers with enhanced molecular and supermolecular order can be prepared (29-32). Enhanced molecular order means that the polymer contains fewer conjugation-interrupting defect sites. Enhanced supermolecular order means that the polymer chains are ordered through stretching, crystallization or both. Template synthesis provides a route for enhancing order and therefore conductivity in these materials.

Template-synthetic methods. Most of our work has focused on polypyrrole, poly(3-methylthiophene) and polyaniline (Fig. 3). These polymers can be synthesized by oxidative polymerization of the corresponding monomer. This may be accomplished either electrochemically (8, 12) or with a chemical oxidizing agent (7, 10, 30, 33). 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 (12). Chemical template synthesis can be accomplished by simply immersing the membrane into a solution of the desired monomer and its oxidizing agent (7, 11, 33). Such methods have since been used by other groups (34-37).

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 (7, 9, 10, 33, 38, 39). As a result, polymeric tubules are obtained (Fig. 2B). By controlling the polymerization time, tubules with thin walls (short polymerization times) or thick walls (long polymerization times) can be produced (33). For polypyrrole, the tubules ultimately "close-up" to form solid fibrils. In contrast, the polyaniline tubules will not close-up, even after long polymerization times (33).

The reason the polymer preferentially nucleates and grows on the pore walls is straightforward (39). 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. There is also an electrostatic component because the polymers are cationic, and there are anionic sites on the pore walls (39). This illustrates an important point - if a "molecular anchor" (17) 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. This molecular anchor concept provides a general route for template synthesis of tubular micro and nanostructures (17).

Enhanced conductivity. A plot of conductivity versus diameter for template-synthesized polypyrrole fibrils is shown in Fig. 4 (10). Whereas the

large-diameter fibrils have conductivities comparable to those of bulk samples of polypyrrole, the conductivity of the smallest diameter nanofibrils is more than an order of magnitude greater. Analogous enhancements in conductivity have been observed for template-synthesized polyaniline (11, 33) and poly(3-methylthiophene) (9). The template-synthesized materials show higher conductivities because the polymer chains on the outer surfaces of the tubules or fibrils are aligned. This can be proven using a technique called polarized infrared absorption spectroscopy (PIRAS) (10, 40, 41).

PIRAS entails measurement of the absorption, by a polymeric sample, of two orthogonally-polarized beams of infrared radiation. These absorption data are used to calculate a parameter called the dichroic ratio (R) for the polymeric sample. An R value of unity means, in general, that the polymer chains in the sample show no preferred spatial orientation. In our case, an R value of less than unity means the polymer chains are aligned, and the lower the value of R, the greater the extent of chain alignment (10, 41).

By controlling the polymerization time we can prepare tubules with very thin walls or tubules with thick walls (33). Hence, if PIRAS data are obtained as a function of polymerization time, we can explore the extent of polymer chain alignment in the layer of conductive polymer that is deposited directly onto the polycarbonate (short polymerization times) and in subsequently-deposited layers (longer polymerization times). Fig. 5 shows the results of such an experiment for template-synthesized polyaniline tubules (33). We find that the layer of polyaniline that is deposited directly on the pore wall is ordered (low dichroic ratio) but that the extent of order decreases in subsequently-deposited layers (dichroic ratio increases with polymerization time). Analogous results were obtained with polypyrrole tubules (42).

The chains on the outer surface of the conductive polymer tubules and fibrils are ordered because the polycarbonate chains that make up the pore walls in the template membranes are likewise ordered (33). Hence, the first layer of conductive polymer chains deposits in registry with the polycarbonate chains on the pore wall. This idea of inducing order in a polymer film by synthesizing it on an ordered polymeric substrate has been demonstrated with other systems, including growth of ordered films on oriented fluoropolymer surfaces (43). The disordered central core results because the order-inducing influence of the pore wall is ultimately lost in subsequently deposited layers. An analogous effect has been observed when polypyrrole is electrochemically deposited on an electrode surface (44). Finally, the narrowest template-synthesized fibrils have the highest conductivity (Fig. 4) because they contain a relatively higher proportion of the ordered material (and less of the disordered material) than the large-diameter fibrils. For a review of this work, see (45).

Enzyme immobilization in template synthesized microtubules. There has been considerable technological interest in tubular structures of the type discussed above for applications that include drug delivery and microelectronics (46). We have recently shown that capped versions of our tubules can be loaded with enzymes to make a new type of enzymatic bioreactor. A combination of electrochemical and chemical template-synthetic methods is used (Fig. 6). The surface of the polycarbonate template membrane is first sputtered with a ~ 50 nm layer of gold (Fig. 6A) 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 (Fig. 6B). Polypyrrole tubules are then chemically polymerized within the pores of the plugged membrane (Fig. 6C). 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 (Fig. 6D) (7). 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 (Fig. 6E). After curing, the entire assembly is immersed into methylene chloride to dissolve the membrane. This yields the desired array of enzyme-loaded capsules (Fig. 6F).

Transmission electron microscopy has shown that the walls of these capsules are extremely thin, ~ 25 nm thick (7). 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 (7).

Five enzymes - glucose oxidase, catalase, subtilisin, trypsin, and alcohol dehydrogenase - have been encapsulated and tested to date (7). The enzymatic activity of glucose oxidase (GOx)-loaded capsules is demonstrated in Fig. 7. Curves a and b in Fig. 7 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 (7). A comparison of the slopes of curves c and d with the slope of curve a shows that higher enzymatic activity can be achieved with the capsules.

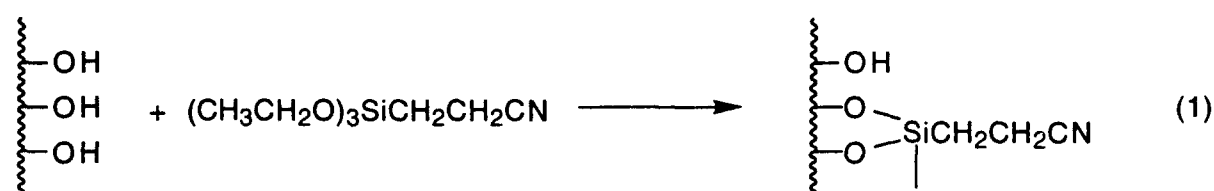## Template synthesis of nanometals

Nanometals have interesting optical (15, 16, 47), electronic (48), and (for appropriate metals) magnetic (23, 49) properties. The concept of using the pores in a nanoporous membrane as templates for preparing nanoscopic metal fibrils was first demonstrated by Possin (50). Earlier work in which nanometals were used to colorize alumina is also of interest (51). Nanometal-containing membranes of this type have also been used as selective solar absorbers (52). Finally, magnetic metals have been deposited within the pores of such membranes to make vertical magnetic recording media (53).

My research group (15, 16) and others (47) have been investigating the fundamental optical properties of template-synthesized nanometals. My group is also using the template method to prepare arrays of microscopic and nanoscopic electrodes for fundamental and applied electrochemistry (13, 14, 54). This approach has since been adopted by other researchers (55). Finally, my group has shown that attachment of an appropriate "molecular anchor" (see above) to the pore wall allows hollow metal tubules to be prepared (17, 18).

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 (14-18, 56, 57); this method has been used to prepare copper, platinum, gold, silver, and nickel fibrils. Typical gold nanofibrils are shown in Fig. 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, 16). 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 critically dependent on aspect ratio (15, 16).

Electrochemical template-synthesis can also be used to prepare arrays of metal tubules (Fig. 2C) (17, 18). In order to obtain tubules, the pore walls must be chemically derivatized so that the electrodeposited metal preferentially deposits on the pore wall; that is, a "molecular anchor" must be applied (17, 18). This is accomplished by reacting hydroxyl groups on the alumina pore wall with a cyanosilane (17, 18, 58) . This chemistry can be represented as

$$\begin{array}{l} \xi\!-\!OH \\ \xi\!-\!OH \\ \xi\!-\!OH \end{array} + (CH_3CH_2O)_3SiCH_2CH_2CN \longrightarrow \begin{array}{l} \xi\!-\!OH \\ \xi\!-\!O \\ \xi\!-\!O \end{array}\!\!\!\searrow\!\!SiCH_2CH_2CN \qquad (1)$$

This chemistry is important because a large number of silanes of this type is commercially available. Hence, this provides a general route for chemically tailoring the pore walls in the alumina membrane.

In order to conduct electroless deposition of metal within the pores of the template membrane, a catalyst must be applied to the pore walls (18). As a result, we have a "molecular anchor" and, again, metal tubules are obtained after brief deposition times (18). 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. (59) 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 (60). For example, colloidal suspensions of gold can be red, purple or blue depending on the size of the spherical gold

particles (60). Analogous colors are obtained after electrochemical plating of gold within the pores of the alumina template membranes (15, 16). This is illustrated in Fig. 8, 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.

The colors in Fig. 8 result from the plasmon resonance band of the nanometal, which corresponds to the wavelength of light that induces the largest electric field on the nanometal particle (15, 16). As discussed above, the template method allows both the diameter and aspect ratio of the metal fibrils to be controlled, so fundamental investigations of the effect of aspect ratio on the optical properties of nanometals can be made (15, 16). The effect of aspect ratio is clearly shown in Fig. 8.

Electrochemistry at ensembles of nanometal electrodes. When the electroless deposition procedure is used, metal fibrils that run the complete width of the polycarbonate template membrane are 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 (Fig. 9). 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 microscopic and 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 (61). Nanoelectrode ensembles

(Fig. 9) can be used to conduct studies of this type (62). In applied electrochemistry, ensembles of micro and nanoscopic electrodes offer the possibility of using electrochemical methods of analysis to detect ultratrace levels of electroactive species (54, 62). Hence, electroanalytical chemistry becomes a more powerful method of analysis when conducted at ensembles of micro and nanoscopic electrodes (54, 62).

Template synthesis of other materials

Sailor et al. have shown that II-VI semiconductor films can be prepared electrochemically (63). In a collaborative effort, my research group and Sailor's group have adapted this method so that it can be used to deposit these materials into the pores of an alumina template membrane (19). First nickel fibrils were deposited into the membrane and then semiconductor fibrils were deposited on top of the nickel fibrils. Hence, this approach produces an array of metal-semiconductor diodes which were shown to be rectifying (19). Chakarvarti and Vetter have also used the template method to prepare arrays of such metal-semiconductor heterostructures (56). We have also prepared semiconductor/semiconductor junctions with this approach. This was accomplished by depositing CdSe fibrils on top of the nickel and then depositing CdTe fibrils on top of the CdSe. We are currently using this method to deposit semiconductors into membranes with pores that are less than 10 nm in diameter to see if evidence for electron quantum confinement (64) can be obtained.

Finally, we are also developing template methods for preparing graphitic nanotubules. This entails template synthesis of polyacrylonitrile tubules followed by graphitization of this polymer at high temperatures. There is considerable current interest in graphitic nanotubules of this type (65). With the

template approach, we should be able to prepare monodisperse graphitic tubules of any desired diameter and wall thickness.

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. We are also interested in developing applications for our template-synthesized micro and nanomaterials, especially the polymeric capsules. For example, we are developing biosensors based on these capsules and we are investigating the possibility of using such capsules for waste water remediation. We are also exploring new ways to do template synthesis so that tubules and capsules composed of other polymeric 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 (66).

References

1. R. T. Bate, *Sci. Amer.* **259**, 96 (1988).

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

3. J. L. Jewell, J. P. Harbison, A. Scherer, *Sci. Amer.* **265**, 86 (1

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

5. M. H. Devoret, D. Esteve, C. Urbina, *Nature* **360**, 547 (1992).

6. R. Gref, et al., *Science* **263**, 1600 (1994).

7. R. Parthasarathy and C. R. Martin, *Nature* **369**, 298 (1994).

8. R. M. Penner and C. R. Martin, *J. Electrochem. Soc.* **133**, 2206 (1986).

9. Z. Cai and C. R. Martin, *J. Am. Chem. Soc.* **111**, 4138 (1989).

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

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

12. L. S. Van Dyke and C. R. Martin, *Langm.* **6**, 1123 (1990).

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

14. C. J. Brumlik, C. R. Martin, K. Tokuda, *Anal. Chem.* **64**, 1201 (1992).

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

16. C. A. Foss, Jr., G. L. Hornyak, J. A. Stockert, C. R. Martin, *J. Phys. Chem.* **98**, 2963 (1994).

17. C. J. Brumlik and C. R. Martin, *J. Am. Chem. Soc.* **113**, 3174 (1991).

18. C. J. Brumlik, V. P. Menon, C. R. Martin, *J. Mater. Res.* **9**, 1174 (1994).

19. J. D. Klein, et al., *Chem. Mater.* **5**, 902 (1993).

20. C.-G. Wu and T. Bein, *Science* **264**, 1757 (1994).

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

22. A. Despic and V. P. Parkhutik, in *Modern aspects of electrochemistry* ; J. O. Bockris, R. E. White, B. E. Conway, Eds. (Plenum , New York, 1989), vol. 20, Chap. 6.

23. D. AlMawiawi, N. Coombs, M. Moskovits, *J. Appl. Phys.* **70**, 4421 (1991).

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

25. J. S. Beck, et al., *J. Am. Chem. Soc.* **114**, 10834 (1992).

26. K. Douglas, G. Devaud, N. A. Clark, *Science* **257**, 642 (1992).

27. T. A. Skotheim, Ed., *Handbook of conducting polymers* (Dekker, New York, 1986).

28. J. L. Bredas and G. B. Street, *Acc. Chem. Res.* **18**, 309 (1985).

29. S. Kivelson and A.J. Heeger, *Synth. Met.* **22**, 371 (1988).

30. J. Lei, Z. Cai, C. R. Martin, *Synth. Met.* **46**, 53 (1992).

31. A. G. MacDiarmid, in *Conjugated Polymers and Related Materials* W. R. Salaneck, I. Lundstrom, B. Ranby, Eds. (Oxford Univ. Press, Oxford, 1993) pp. 73-97.

32. W. Fosong, T. Jinsong, W. Lixiang, Z. Hongfang, M. Zhishen, *Mol. Cryst. Liq. Cryst.* **160**, 175 (1988).

33. R. V. Parthasarathy and C. R. Martin, *Chem. Mater.*, in press.

34. W. Cahalane and M. M. Labes, *Chem. Mater.* **1**, 519 (1989).

35. C. G. J. Koopal, R. J. M. Nolte, B. De Ruiter, *J. Chem. Soc. Chem. Commun.* , 1691 (1991).

36. M. Granstorm and O. Inganas, *Synth. Met.* **55-57**, 460 (1993).

37. R. P. Burford and T. Tongtam, *J. Mater. Sci.* **26**, 3264 (1993).

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

39. C. R. Martin, *Adv. Mater.* **3**, 457 (1991).

40. W. Liang and C. R. Martin, *J. Am. Chem. Soc.* **112**, 9666 (1990).

41. J. Lei, V. P. Menon, C. R. Martin, *Polym. Adv. Tech.* **4**, 124 (1992).

42. V. P. Menon and C. R. Martin, *Manuscript in preparation.*

43. J. C. Wittmann and P. Smith, *Nature* **352**, 414 (1991).

44. Z. Cai and C. R. Martin, *J. Electroanal. Chem.* **300**, 35 (1991).

45. C. R. Martin, *Accounts of chemical research* , accepted for publication.

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

47. C. K. Preston and M. J. Moskovits, *J. Phys. Chem.* **97**, 8495 (1993).

48.   J. T. Masden and N. Giordino, *Phys. Rev. B* **36**, 4197 (1987).

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

50.   G. E. Possin, *Rev. Sci. Instrum.* **41**, 772 (1970).

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

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

53.   S. Kawai and R. Ueda, *J. Electrochem. Soc.,* **112**, 32 (1975).

54.   I. F. Cheng, L. D. Whiteley, C. R. Martin, *Anal. Chem.* **61**, 762 (1989).

55.   K. Uosaki, K. Okazaki, H. Kita, H. Takahashi, *Anal. Chem.* **62**, 652 (1990).

56.   S. K. Chakarvarti and J. Vetter, *J. Micromech. Microeng.* **3**, 57 (1993).

57.   S. K. Chakarvarti and J. Vetter, *Nucl. Instrum. Meth. Phys. Res.* **B62**, 109 (1991).

58.   C. J. Miller, C. A. Widrig, D. H. Charych, M. Majda, *J. Phys. Chem.* **92**, 1928 (1988).

59.   C. A. Huber, et al., *Science* **263**, 800 (1994).

60.   H. C. van de Hulst, *Light scattering by small particles*. (Dover, New York, 1981).

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

62.   V. P. Menon and C. R. Martin, manuscript in preparation.

63.   A. M. Kressin, V. V. Doan, J. D. Klein, M. J. Sailor, *Chem. Mater.* **3**, 1051 (1991).

64.   M. Sundaram, S. A. Chalmers, P. F. Hopkins, A. C. Gossard, *Science* **254**, 1326 (1991).

65.   O. Zhou, et al., *Nature* **263**, 1744 (1994).

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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. **C.** Scanning electron micrograph of an array of gold microtubules.

Figure 3. Some electronically conductive polymers.

Figure 4. Conductivity vs. diameter for polypyrrole fibrils. Data for two different synthesis temperatures are shown.

Figure 5. PIRAS data for template-synthesized polyaniline tubules. The x-axis is polymerization time. Because tubule wall thickness increases with polymerization time, the x-axis can be viewed as a wall thickness axis (33).

Figure 6. 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 7. 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 (7).

Figure 8. 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 9. 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.
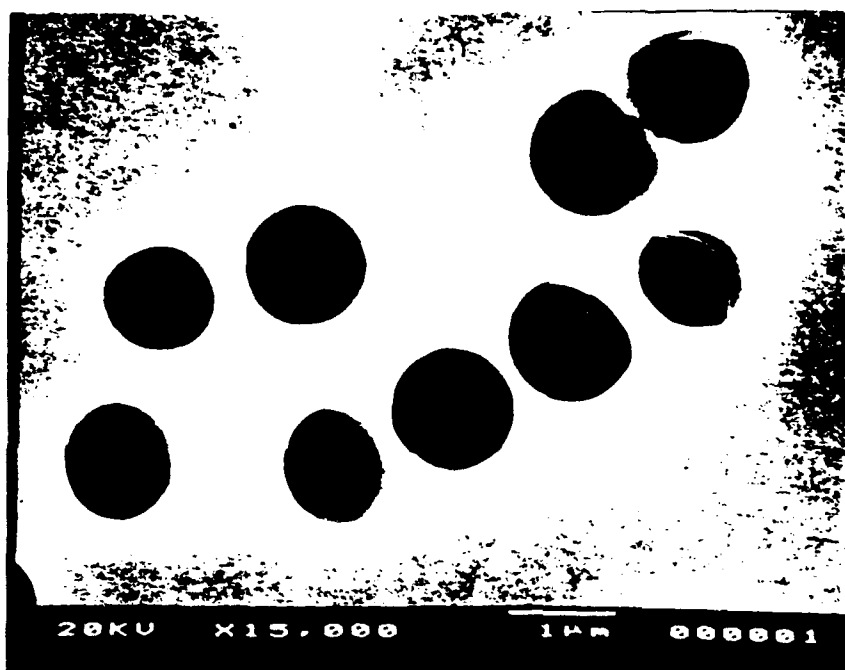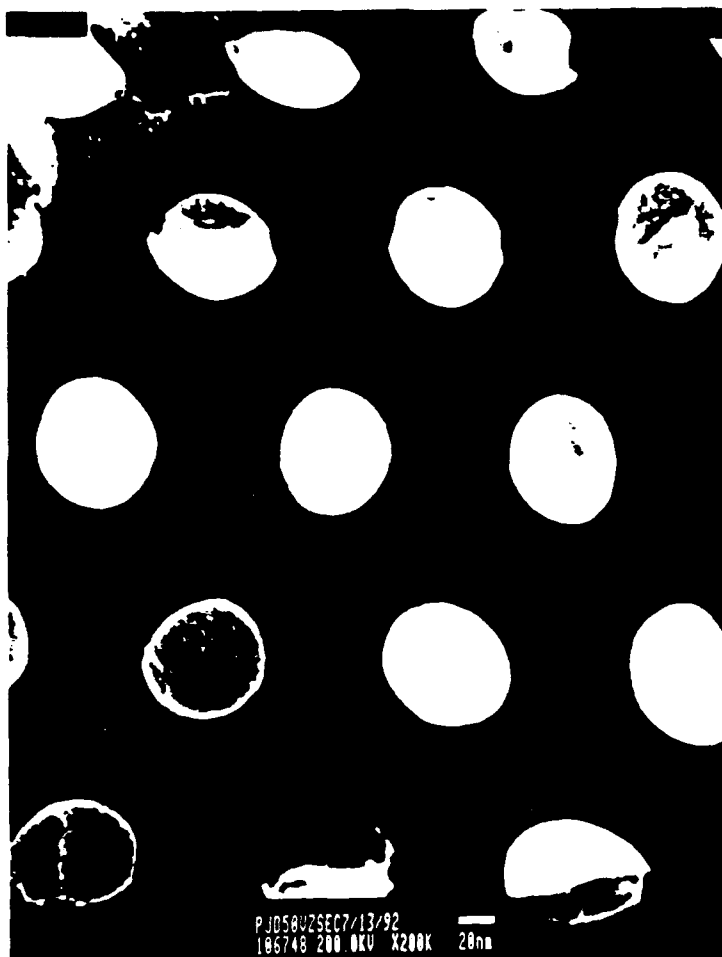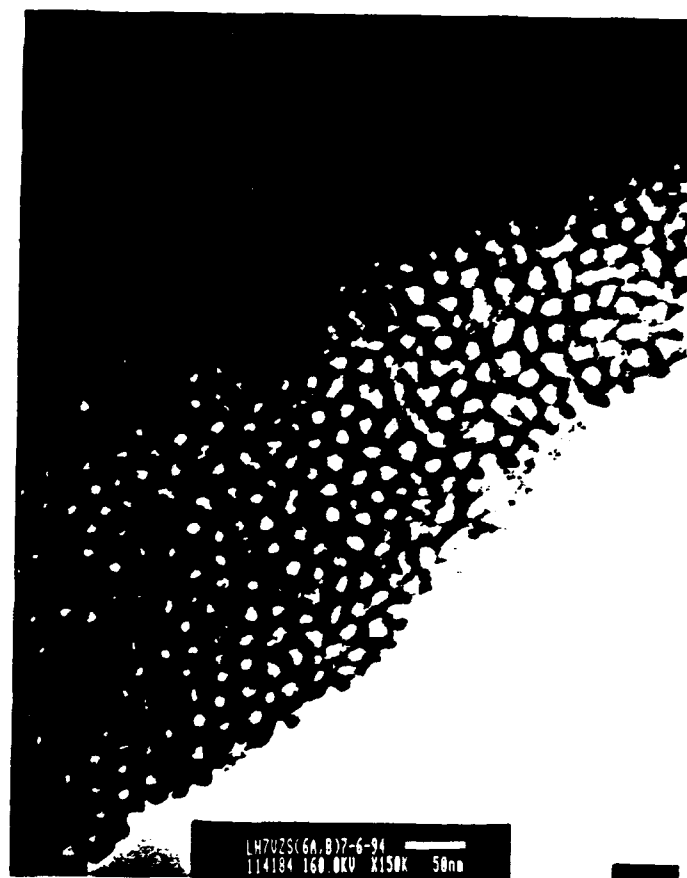
20KU   X15,000   1μm   000001

FIG 1A

PJ050UZSEC7/13/92
106748 200.0KV X200K   20nm

Fig 1C

LH7U2S(6A,B)7-6-94
114184 160.0KU X150K 50nm

LH50V.1C-6/18/92
186279 200.0KV   X20K   200nm

Fig. 2A

15KV X15000   0010   1.0U   TAMU

FIG 2B

1 µm 30.0kV 4.00E4 0961/01 7365330
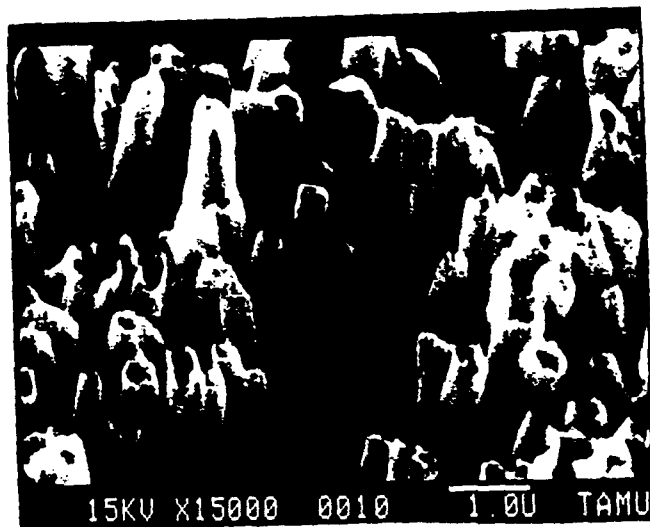
Fig 2.
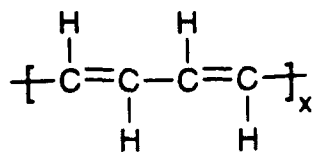
Polyacetylene
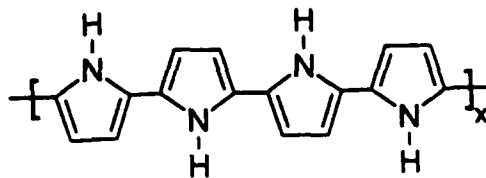
Polypyrrole
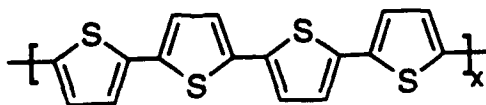
Polythiophene

Polyaniline

Fig. 3

Fig 4

Disordered central core

Ordered surface layer

A

B

Direction of polymer chains in ordered surface layer
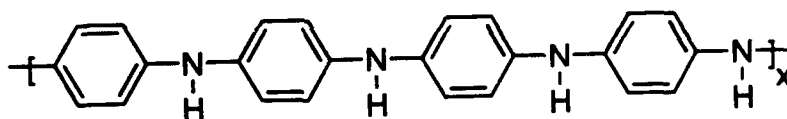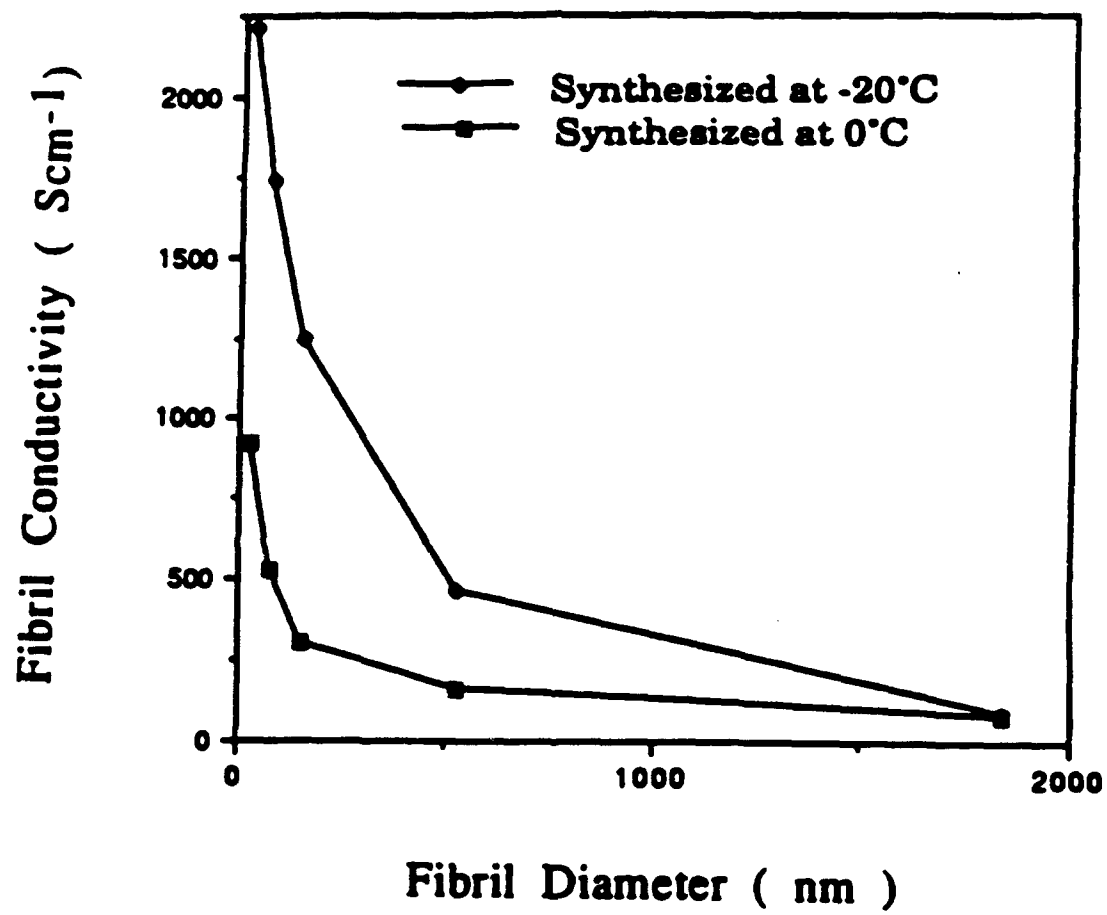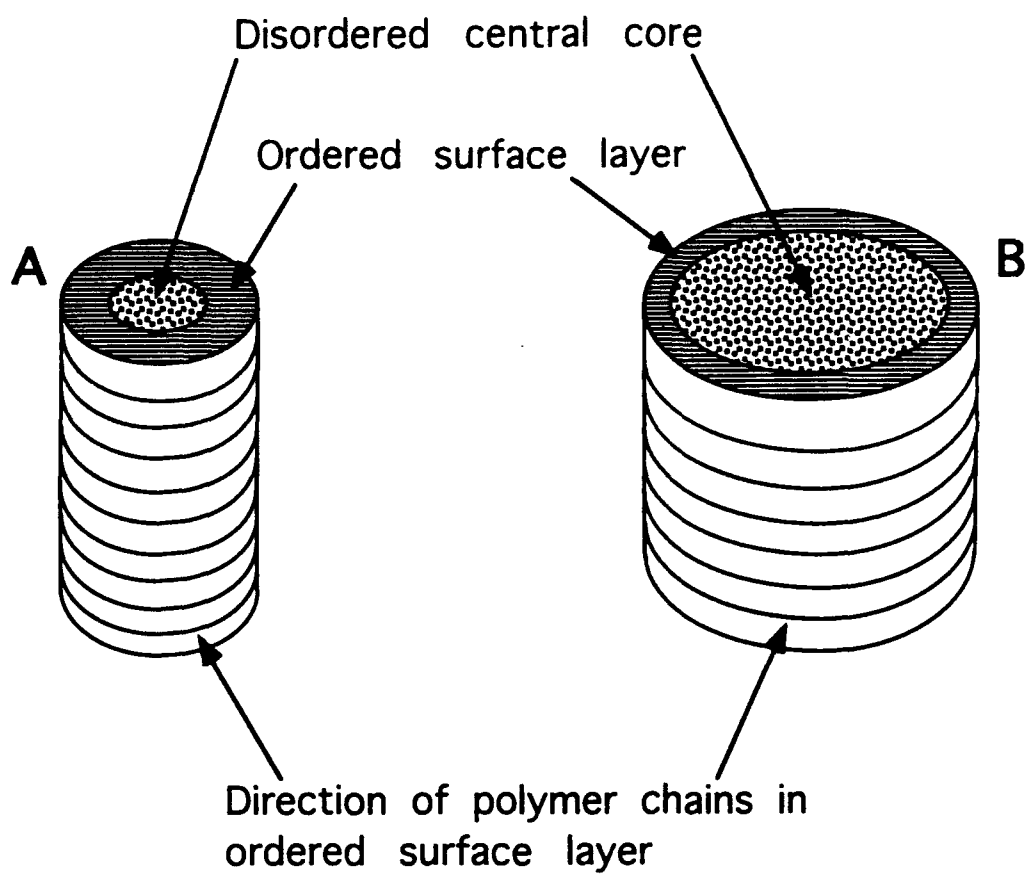
Fig.5

A. Cross-section of Au-coated membrane

Pore

Au film

Electropolymerization

B.

Polypyrrole plug

Polypyrrole Surface Layer

Chemical polymerization

C.

Polypyrrole microtubule
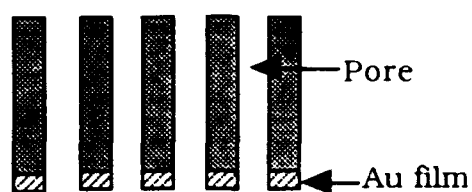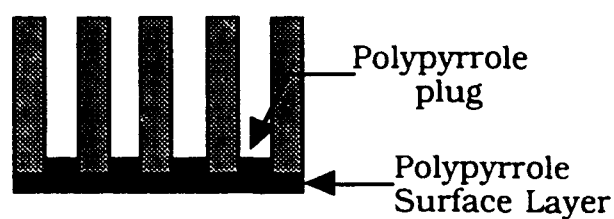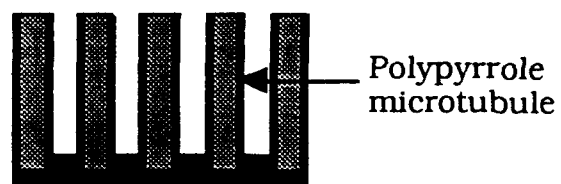
Remove surface layers; fill with enzyme

D.

Enzyme molecule

Apply Torrseal

E.
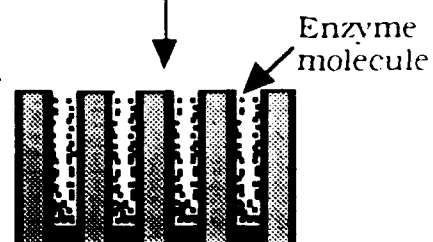
Torr seal
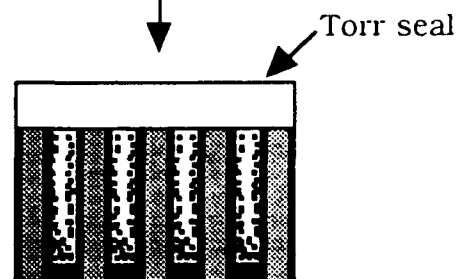
Dissolve membrane

Attach glass handle
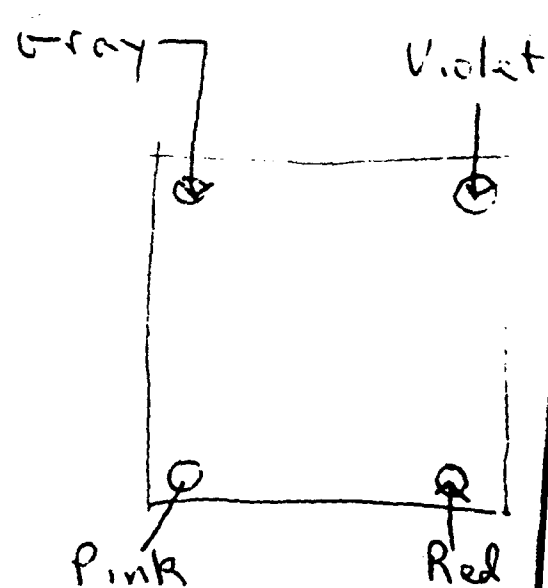
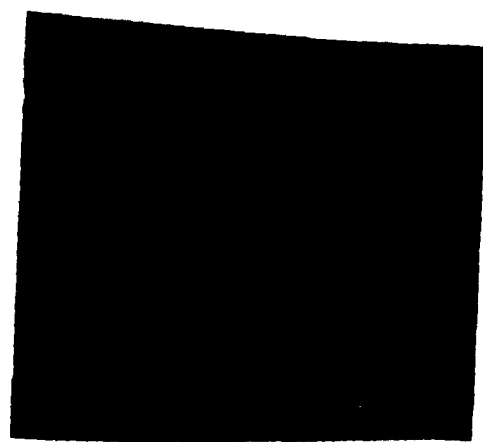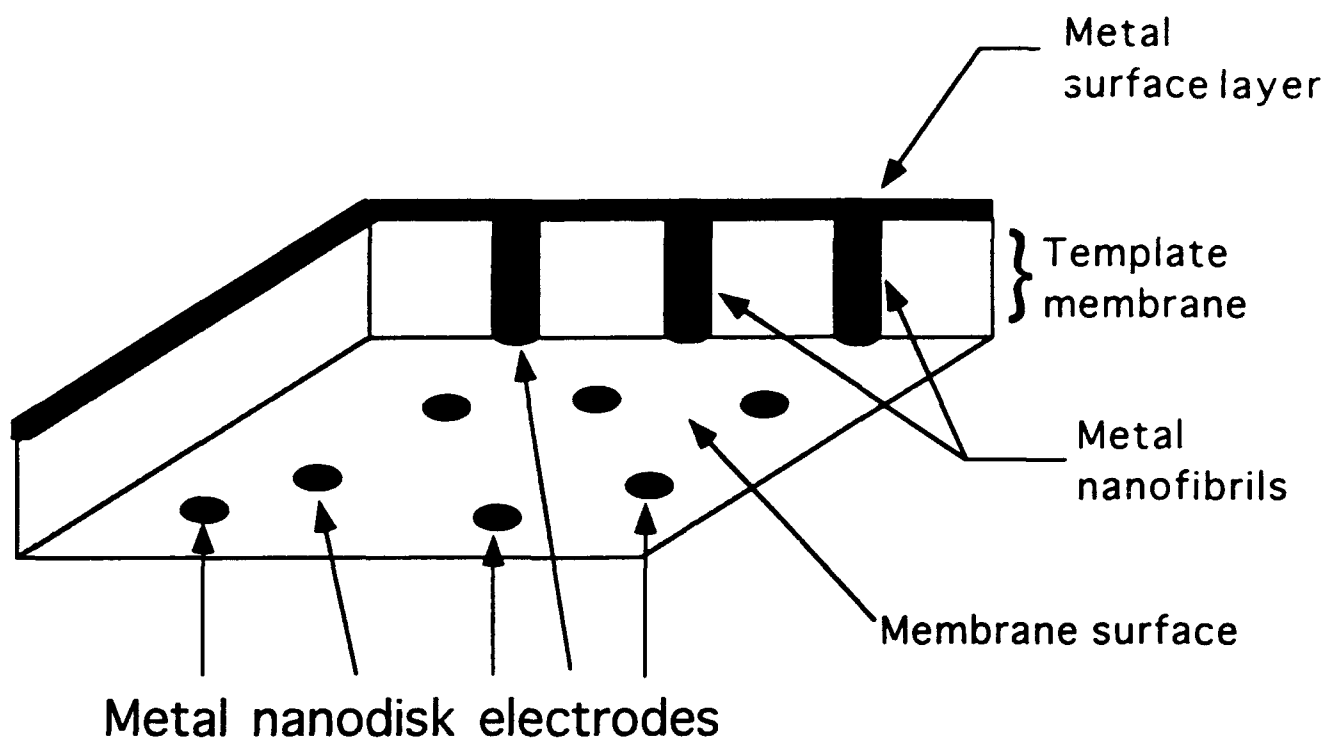**F.**

Glass handle

Enzyme-loaded microcapsule

Fig. 6
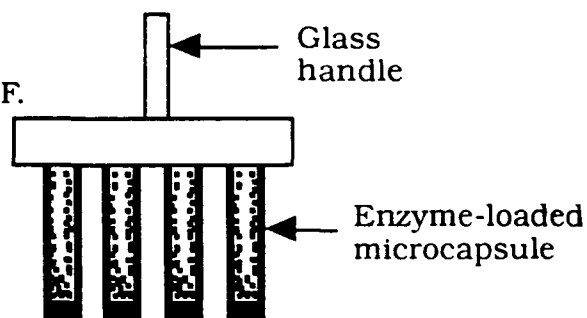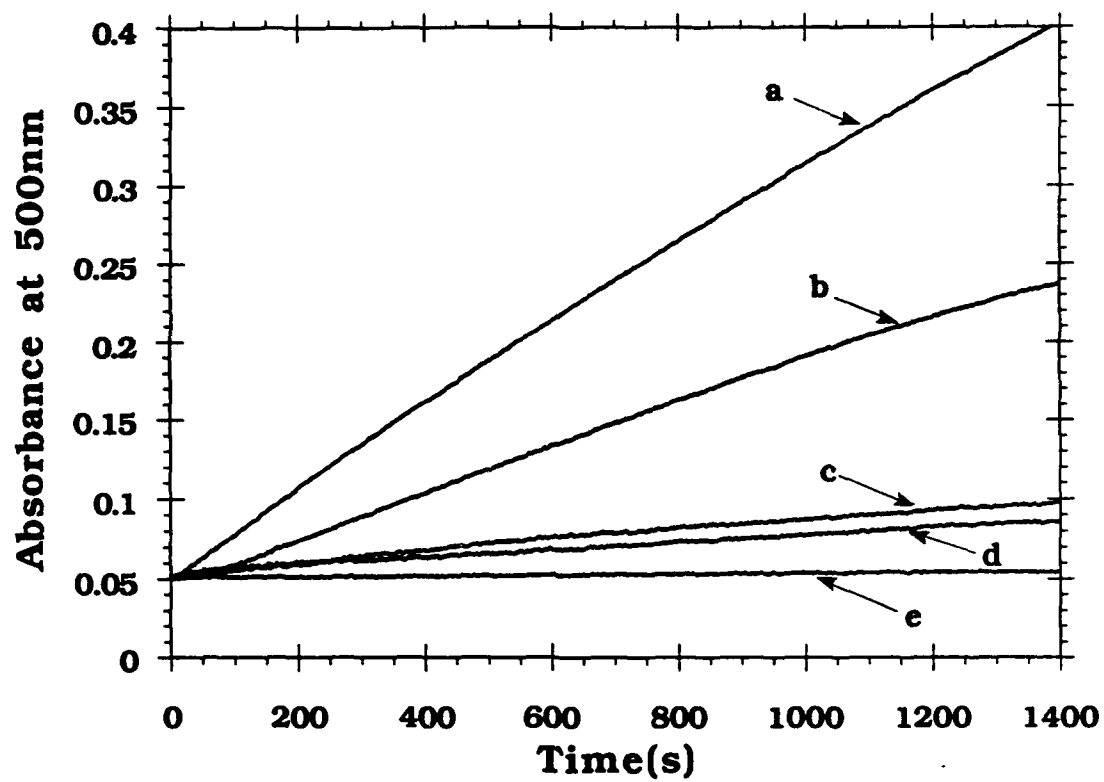
Fig.7

This is Figure 8. Red colors
go at lower right.
Gray colors go at upper left.

Fig. 8

Metal
surface layer

} Template
membrane

Metal
nanofibrils

Membrane surface

Metal nanodisk electrodes

☐ Indicates template membrane

■ Indicates metal

Fig 9