Nanomaterials: A Membrane-Based Synthetic Approach

Lien Lee Literature Seminar November 14, 1996

Nanochemistry is an important emerging area in the chemical and material sciences.[1,2] It involves the development of synthetic methods of nanosize materials as well as scientific investigation of these nanomaterials. Materials with nanoscopic dimensions not only have potential technological applications in areas such as electronic, optical, and mechanical devices,[3] drug delivery,[4] and bioencapsulation,[5] but also are of fundamental interest because the properties of a material often change when going from the bulk to the molecular scale.

There are numerous chemical methods for preparing nanomaterials. The template method,[6-11] a membrane-based synthesis approach, involves synthesizing the desired material within the channels of a nanoporous membrane. A nanocylinder of the desired material is obtained in each pore due to the cylindrical shape of these pores. Either solid (nanofibril) or hollow (nanotubule) cylinders may be obtained depending on the material, the chemistry of the pore wall, and the method applied in the synthesis.[11]

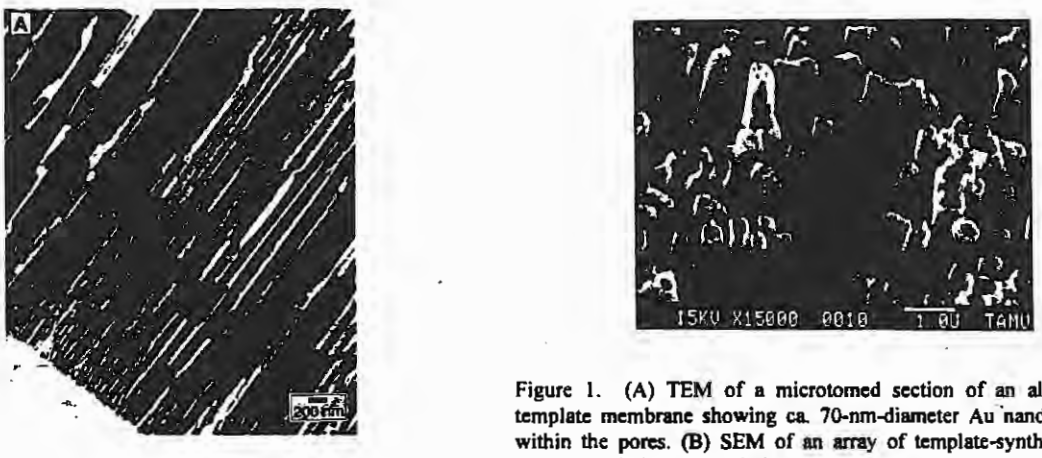

Figure 1. (A) TEM of a microtomed section of an alumina template membrane showing ca. 70-nm-diameter Au nanofibrils within the pores. (B) SEM of an array of template-synthesized poly(N-methylpyrrole) tubules.

The template method has been widely used to prepare tubules and fibrils composed of conductive polymers.[6, 7, 13] Nanotubules or nanofibrils of polypyrrole and polyaniline can be prepared by this method. For example, these polymers can be synthesized via oxidative polymerization of the monomers either electrochemically [9] or chemically [12, 14] using an oxidant. Electrochemical template synthesis can be accomplished by a metal film coating as an electrode on one surface of the membrane and electrochemically synthesizing the desired polymer within the pores of the membrane. In the chemical method, polymers can be prepared by simply immersing the membrane into a solution which separates the desired monomer and an oxidizing agent. The desired polymers are then synthesized within the pores of membranes.[13] When these polymers are synthesized within the pores, they preferentially nucleate and grow on the pore walls.[15] Tubules with thin or thick walls or even solid fibrils can be obtained by controlling the polymerization time. Conductivity measurements[7,16] show that while the large diameter fibrils have conductivities which is comparable to those of bulk samples of the polymer, the conductivity of the smaller diameter fibrils is over an order of magnitude higher.

Nanoporous membrane templates can also be used to prepare nanosize metal fibrils and tubules.[8, 17] Metals can be deposited within the pores of the template by either electrochemical or chemical ("electroless")[18] reduction of the appropriate metal ion. Electrochemical deposition is achieved by coating one face of the membrane with a metal film. Gold nanofibrils[8] can be synthesized in this manner. The lengths of the fibrils can be controlled by

varying the amount of metal deposited. In the electroless chemical method, anchoring molecules such as silanes are used to modify the pore walls. This allows metal tubules to be synthesized after short deposition times.

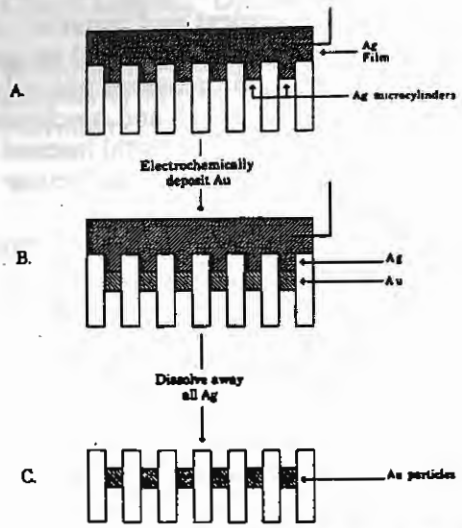

Figure 2. Fabrication of Transparent metal films: A, deposition of silver; B, deposition of gold into the pores; C, dissolution of silver.

Nanometals can exhibit interesting optical properties.[19] For example, several different colors can be obtained after electrochemically plating gold within the pores of alumina template membranes.[20] This is due to the plasma resonance band of the nanomaterials. The length to diameter aspect ratio of the metal fibrils determines the optical properties.[21]

Various electrochemical and chemical template synthetic methods can be employed to prepare microcapsules that encase enzymes.[22] Transmission electron microscopy[22] has shown that the walls of these capsules are very thin (~25nm) so that small molecules, such as the substrate and product, can diffuse through the wall. The thinness of the walls also ensures that the mass-transport processes will be facile.

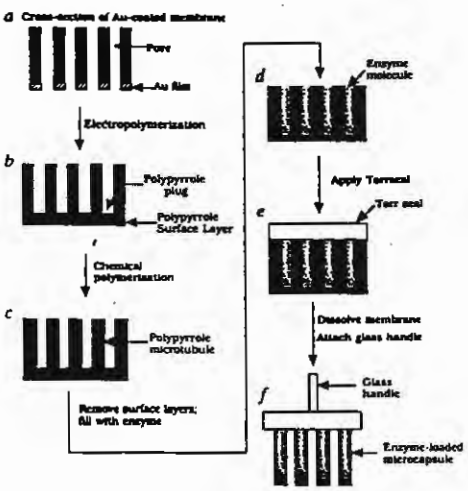

Figure 3. Schematic diagram of methods used to synthesize and enzymeload the microcapsule arrays.

Selective ion transport analogous to that observed in ion-exchange polymers has been exhibited by some nanometals.[23] Gold tubules running the complete thickness of the membrane is one example. These nanoscopic membranes with these tubulus can be either cation or anion selective, depending on the potential applied to the membrane.

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