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Template Synthesis of Metal Microtubules

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We have recently described a "template" method for the synthesis of organic microtubules. This method entails the use of the pores in a microporous membrane as templates for tubule formation. The key to the tubule-formation process is the presence of "molecular anchors" on the pore walls. These anchors insure that the tubule-forming materials deposits as a thin skin which lines the pore wall. We describe in this paper an electrochemical template method for the synthesis of metal (Au) microtubules. We also present a general paradigm for the formation of molecular anchors on the pore walls of alumina template membranes. We believe that this paradigm should allow for the synthesis of microtubules composed of any desired material.

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TEMPLATE SYNTHESIS OF METAL MICROTUBULES

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Abstract. We have recently described a "template" method for the synthesis of organic microtubules. This method entails the use of the pores in a microporous membrane as templates for tubule formation. The key to the tubule-formation process is the presence of "molecular anchors" on the pore walls. These anchors insure that the tubule-forming material deposits as a thin skin which lines the pore wall. We describe in this paper an electrochemical template method for the synthesis of metal (Au) microtubules. We also present a general paradigm for the formation of molecular anchors on the pore walls of alumina template membranes. We believe that this paradigm should allow for the synthesis of microtubules composed of any desired material.

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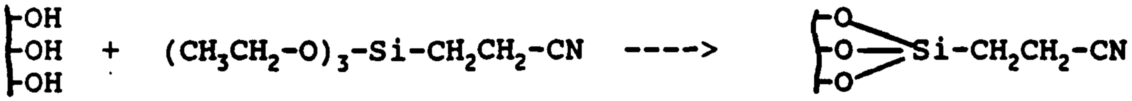
Organic microtubules have recently caused a great deal of excitement in the chemistry, physics, and materials science communities (1). We have developed a novel "template" method for synthesizing such tubules (1c). This method entails using the pores in a microporous membrane as templates for tubule formation. We have used this method to prepare microtubules composed of various heterocyclic polymers (1c). It seems likely that the template method could be used to synthesize microtubules composed of other materials; metals are an obvious choice. We describe, in this paper, an electrochemical template synthesis of gold microtubules (2).

In general, the template method entails synthesis of a material within the pores of a microporous membrane (1c-3). Either solid fibrils (3b) or hollow tubules (1c,2) will be obtained. Tubules will only be obtained if "molecular anchors" are present on the pore wall; these anchors assure that the material forms as a thin "skin" which lines the pore wall (1c). The challenges in synthesizing metal microtubules, then, are 1) To identify chemistry for forming the metal within the pores of the membrane, 2) To identify a suitable molecular anchor, and 3) To develop chemistry for attaching this anchor to the pore walls in the membrane. Numbers 2 and 3, above, are by far the most challenging problems. A general paradign for solving these problems is presented in this paper.

Gold microtubules were prepared by electrochemically depositing Au into the pores of microporous alumina (Anopore, Anotech Ltd.) (3b) membranes. These membranes have 200 nm diameter pores and enormous pore densities (3b). A commercial Au plating solution (Orotemp 24, Technics) was employed. We chose an organocyanide (2-cyanoethyltriethoxysilane) as the molecular anchor to bind the electrochemically-deposited Au to the walls of the template membrane. Soriaga et al. have shown that organocyanides strongly chemisorb to Au (4). This molecular anchor was attached to the pore wall via (5)



$$\begin{matrix}\vdash OH\\ \vdash OH\\ \vdash OH\end{matrix} + (CH_3CH_2-O)_3-Si-CH_2CH_2-CN \;{-}{-}{-}{-}{>}\; \begin{matrix}\vdash O\\ \vdash O\\ \vdash O\end{matrix}\!\!>Si-CH_2CH_2-CN \quad (1)$$

where the -OH's represent hydroxyl groups on the pore wall.

A schematic representation of the procedure used to synthesize the Au microtubules is shown in Figure 1. A 50 nm layer of Au was first sputter-deposited, from an Ar plasma, onto one face of the silane-treated Anopore membrane. This layer was too thin to block the pores in the Anopore membrane but converted the surface of the membrane into an electrode (Figure 1A). The electrochemical cell consisted of this Au/Anopore cathode and a large-area platinized niobium mesh (Technics) anode; the anode faced the Au-coated side of the membrane. Au was deposited galvanostatically at current densities of 0.5 to 2.0 mA cm^{-2}; 0.5 to 4.0 coul. cm^{-2} were passed.

As indicated in Figure 1B, Au is deposited on the surface of the Anopore membrane and along the walls of the pores in this membrane. The gold deposited along the walls forms the Au microtubules. Deposition along the walls continues (i.e. the microtubules grow longer) until the pores become completely blocked by the Au surface layer (Figure 1C); at this point, the rate of tubule growth decreases markedly. To date, we have obtained Au microtubules which are as long as 2 μm.

After tubule synthesis, the Anopore membrane can be dissolved away (6), to expose the Au microtubules. An upright ensemble of microtubules connected via a common Au base layer is obtained (Figure 1D). An electron micrograph of such an ensemble is shown in FIgure 2A. The organocyanide molecular anchor is essential to this tubule formation process. If the electrochemistry illustrated in Figure 1 is conducted at an underivatized Anopore membrane, solid Au fibrils (Figure 2B) are obtained. We are currently exploring the mechanism of this novel tubule formation process.

It is not clear from Figure 2B how far down their lengths the tubules remain hollow. We have conducted several experiments which address this issue. First, electron micrographs of tubules which were broken near the base (i.e. near the Au surface layer) show that the tubules are hollow to within several hundred nm of the base. Second, while solution will not flow through the membrane when the Au surface layer is intact (i.e. Figure 1C), dissolution of the Au layer, in aqua regia, allows for solution flow through the tubule-impregnated membrane. Finally, electron micrographs of the membrane after dissolution of the Au surface layer show that the exposed bases of the tubules are hollow. It is worth noting that dissolution of the Au base layer disconnects the tubules from each other. If the Anopore membrane is then dissolved (6), the isolated fibrils can be collected by filtration (3).

The silanization chemistry illustrated in Equation 1 provides a very general method for attaching many different types of molecular anchors to the Anopore (alumina) pore walls (5). Furthermore, a vast array of silane derivatives is available through commercial sources. Thus, as indicated earlier, we view the procedures outlined above as a general paradigm for synthesis of microtubules composed of any desired material. For example, tubules composed of a vinyl polymer might be synthesized by attaching a silane which contains an active vinyl group to the pore walls, and tubules composed of an ionic polymer might be synthesized by attaching a silane which contains a counterionic group to the pore walls. We are currently using this paradigm to synthesize microtubules composed of a variety of different materials.

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(5) (a) Miller, C.J.; Majda, M. Anal. Chem. 1988, 60, 1168. (b) The Anopore surfaces were silanized by sonicating the membrane for 30 sec. in a 0.1 (v/v) % solution of 2-cyanoethyltriethoxysilane in anhydrous hexadecane. The membrane was removed from this solution and heated overnight at 100° C. The silane probably does not form as a monolayer but as a thin polymer film.

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