Using Template-Synthesized Micro- and Nanowires as Building Blocks for Self-Assembly of Supramolecular Architectures

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There has been considerable recent interest in using chemical interactions to self-assemble particles and structures—on the nanometer to millimeter scale—into organized assemblies. Natan's group has used various chemical and biochemical strategies to self-assemble colloidal Au particles onto surfaces.[1,2] Mirkin's group used thiol linkers to bind colloidal Au particles to single-stranded oligonucleotides; these nanoparticles were subsequently self-assembled into a polymeric network by addition of the complementary oligonucleotide.[3,4] Thiol linkers have also been used to attach Au nanoparticles to Fullerene pipes.[5] Whitesides' group has used hydrophobic interactions to self-assemble millimeter-scale objects into a variety of highly organized structures.[6]

To date, template-synthesized micro- and nanostructures have not been self-assembled in this way. Template synthesis is a general and versatile method for preparing micro- and nanomaterials; this method entails synthesizing the desired material within the pores of a microporous template membrane.[7−11] The membranes employed have cylindrical pores, with monodisperse diameters (nanometers to micrometers), that extend through the entire thickness of the membrane. Because of cylindrical pore geometry, corresponding cylindrical micro- and nanostructures are obtained. These may be high aspect-ratio solid nanowires,[12] hollow nanotubules,[13] smaller aspect-ratio nanoplugs,[14] and even pancake-like nanostructures with aspect ratios less than unity.[15] Micro- and nanostructures of these types composed of metals, semiconductors, electronically conductive polymers, carbons, and other materials have been prepared.[7−11]

These micro- and nanostructures should be useful as building blocks for self-assembly of supramolecular architectures. We have recently taken the first steps toward using template-synthesized materials in this way. We have shown that template-synthesized polymeric and metallic micro- and nanowires can be self-assembled with commercially available colloidal particles to prepare colloid/wire supramolecular assemblies. The results of these investigations are described here.

We show, first, that biotin/streptavidin chemistry can be used to self-assemble latex particles onto the ends of template-synthesized conductive polymer microwires (Figure 1). The template membrane employed was a commercially available (Poretics) polyester filter with 600-nm diameter pores. The conductive polymer microwires were deposited into the pores of this membrane using an electropolymerization method.[16] This method yields both the microwires in the pores and a surface polymer film, which was removed by polishing the surface with alumina powder. The microwires were composed of poly[*N*-(2-aminoethyl)-2,5-di(2-thienyl)pyrrole] (poly(AEPy))[17] (see Figure 1), which was chosen for this application because its available amine groups. These amine groups were reacted via amide coupling to yield biotinylated microwires. This was accomplished by simply immersing the microwire-containing membrane into a 1 mM solution of biotinyl-*N*-hydroxysuccinimide in *N*,*N*-dimethyl formamide.

The latex particles employed were commercially available (Spherotech) streptavidin-coated polystyrene (900-nm diameter). These streptavidin-coated particles were self-assembled to the ends of the biotinylated microwires by simply immersing the microwire-containing membrane into the latex suspension and allowing the coupling reaction to proceed for 12 h. The membrane was then removed from the suspension and rinsed extensively with water.

Figure 2a shows that this approach does, indeed, yield microwire/latex supramolecular assemblies. The inset shows a higher magnification image, which demonstrates that the latex particles are attached to the ends of the poly(AEPy) microwires. Counting the latex particles in images such as Figure 2a, shows that there are approximately 1.3×10^7 particles cm^{-2} of membrane area. This may be compared to the pore density which is 3×10^7 cm^{-2}. Membranes treated in the same way, but omitting the biotinylation step, show no surface-bound latex particles (Figure 2b).

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(1) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.

(2) Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, *67*, 735.

(3) Elghanian, R.; Storhoff, J. J.; Mucic, R. C.; Letsinger, R. L.; Mirkin, C. A. *Science* **1997**, *277*, 1078.

(4) Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607.

(5) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y.-S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253.

(6) Bowden, N.; Terfort, A.; Carbeck, J.; Whitesides, G. M. *Science* **1997**, *276*, 233.

(7) Martin, C. R. *Science* **1994**, *266*, 1961.

(8) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739.

(9) Marinakos, S. M.; Brousseau, L. C.; Jones, A.; Feldheim, D. L. *Chem. Mater.* **1998**, *10*, 1214.

(10) Schönenberger, C.; van der Zande, B. M. I.; Fokkink, L. G. J.; Henny, M.; Schmid, C.; Krüger, M.; Bachtold, A.; Huber, R.; Birk, H.; Staufer, U. *J. Phys. Chem. B* **1997**, *101*, 5497.

(11) Routkevitch, D.; Tager, A. A.; Haruyama, J.; Almawlawi, D.; Moskovits, M.; Xu, J. M. *IEEE Trans. Electron Devices* **1996**, *43*, 1646.

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

(13) Jirage, K. B.; Hulteen, J. C.; Martin, C. R. *Science* **1997**, *278*, 655.

(14) Cepak, V. M.; Martin, C. R. *J. Phys. Chem. B* **1998**, *102*, 9985.

(15) Hornyak, G. L.; Martin, C. R. *Thin Solid Films* **1997**, *300*, 84.

(16) Parthasarathy, R.; Martin, C. R. *J. Appl. Polym. Sci.* **1996**, *62*, 875.

(17) Rockel, H.; Huber, J.; Gleiter, R.; Schuhmann, W. *Adv. Mater.* **1994**, *6*, 568.

(18) Cepak, V. M.; Hulteen, J. C.; Che, G.; Jirage, K. B.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Chem. Mater.* **1997**, *9*, 1065.

10.1021/cm990001u CCC: $18.00

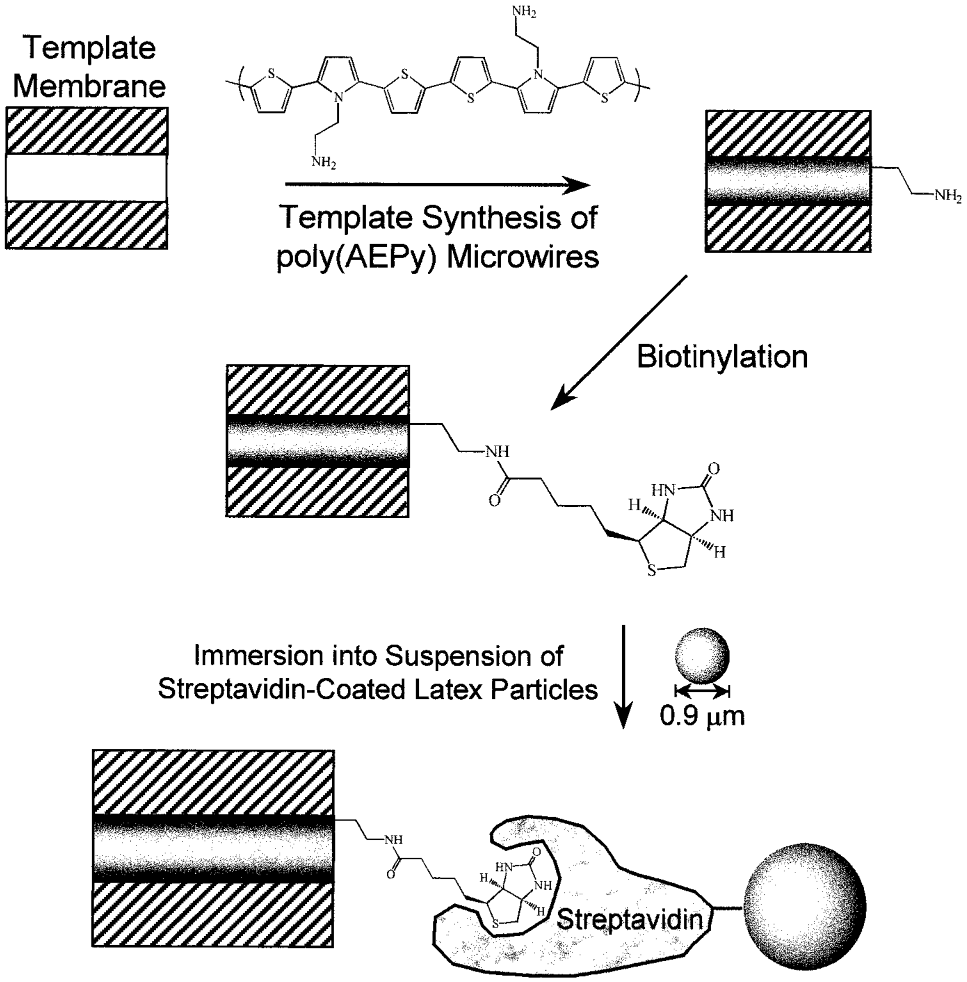

Figure 1. Schematic diagram showing the template synthesis of the poly(AEPy) microwires and the self-assembly, using biotin/streptavidin chemistry, of latex particles to the ends of these microwires.

As shown in Figure 1, self-assembly was done on poly(AEPy) microwires that were embedded within the pores of the template membrane. An alternative strategy would be to dissolve the template membrane and do the self-assembly on the liberated microwires. This method was not used because, due to the porous nature of conductive polymers, these microwires are undoubtedly biotinylated along their entire length. As a result, there would be no reason to expect that the latex particles would self-assemble to only the ends of the microwires. This would, however, be possible if a strategy for masking the sides of the microwires could be developed such that only the amine sites on the ends were available for self-assembly.

We have developed such a strategy, which is based on the concept of concentric–tubular microstructures described previously by this lab.[18] A polyester template membrane (1-μm-diameter pores) was first exposed to an electroless gold plating solution to deposit hollow Au microtubules within the pores.[12] These gold tubules were then used as the electrodes to electropolymerize poly(AEPy) microwires within the Au tubules. This yielded composite microstructures consisting of an outer tubule of Au surrounding an inner microwire of poly(AEPy). Note that now the sides of the microwires are masked by the outer Au tubule and are not available for streptavidin binding.

After preparation of these concentric–tubular microwires, the microwire-containing membrane was attached to a Cu tape surface and immersed into 1,1,1,3,3,3-hexafluoro-2-propanol to dissolve the membrane. This yielded an ensemble of the liberated Au-coated microwires that protruded from the Cu surface like the bristles of a brush. This ensemble was then immersed into the biotinylation solution and then into the latex suspension. A scanning electron micrograph of this assembly is shown in Figure 2c. As anticipated, the latex particles are self-assembled to only the ends of these concentric–tubular microwires.

While the self-assembled structures described thus far have dimensions in the micrometer regime, there is no fundamental reason that this strategy cannot be applied to much smaller nanowires and nanoparticles. An alternative self-assembly chemistry was used to prove this point. This entailed the use of 1,9-nonanedithiol to assemble colloidal Au particles (20-nm diameter) to the ends of 30-nm-diameter template-synthesized Au nanowires.

A Au film was sputtered onto one face of a polycarbonate template membrane (30-nm-diameter pores); this film served as the working electrode for deposition of Au nanowires within the pores of this membrane.[14] The nanowire-containing membrane was then immersed (overnight) into a 1 mM solution of the dithiol in

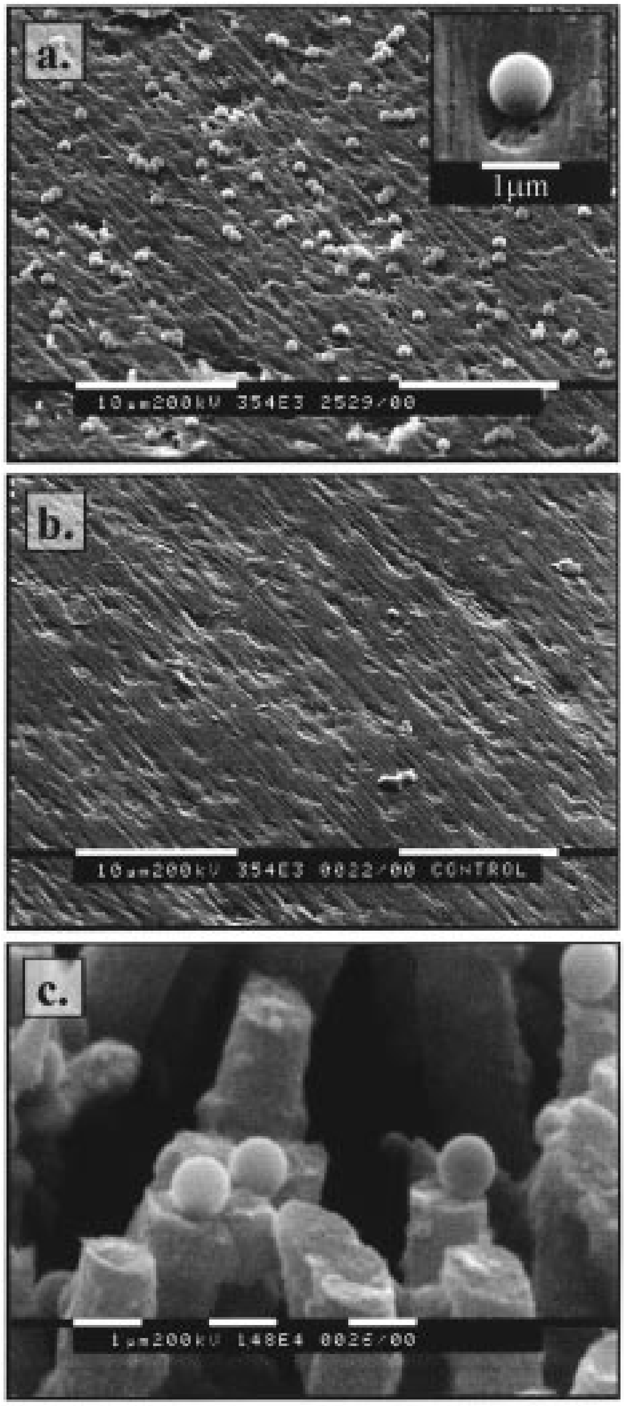

Figure 2. Scanning electron micrographs: (a) the surface of a poly(AEPy) microwire-containing membrane after self-assembly (see Figure 1) of the latex particles to the ends of the microwires; the inset shows a higher magnification image of a single microwire/latex assembly; (b) the surface of an analogous membrane treated in the same way as in panel a but omitting the biotinylation step; and (c) Au/poly(AEPy) concentric tubular microwires after dissolution of the template membrane and self-assembly.

ethanol. This resulted in chemisorption of the dithiol onto the ends of the Au nanowires and also onto the sputtered Au surface film. The Au film was removed by polishing with a laboratory tissue. The membrane was then immersed (overnight) into an aqueous suspension of the colloidal Au nanoparticles and rinsed with water. The template membrane was dissolved away by immersion in $CHCl_3$ to yield a suspension[14] of the Au nanowire/colloidal particle assemblies. A drop of this suspension was applied to a transmission electron microscopy grid.

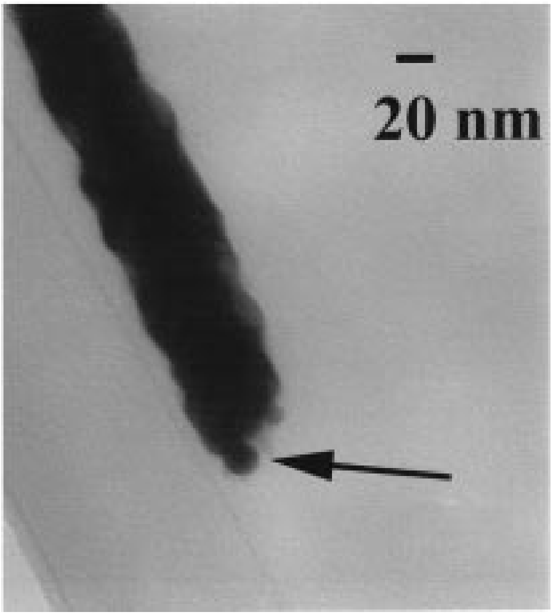

Figure 3. Transmission electron micrograph of a template-synthesized Au nanowire showing the self-assembled colloidal Au particle attached to the end of the nanowire.

Figure 3 shows a transmission electron micrograph of a Au nanowire/Au colloidal assembly. Note, again, that because the nanowires were embedded within the template when they were exposed to the colloidal/Au suspension, the Au particles are self-assembled to only the ends of the Au nanowires. Only about 10% of the nanowires in such images were terminated with colloidal Au particles. However, we have as yet made no attempt to optimize the assembly chemistry and conditions. Currently the ends on the Au nanowires are recessed somewhat within the pores of the membrane. We have previously shown that an oxygen plasma can be used to burn away, in a controlled manner, the surface of the polymeric template membrane. This should leave the ends of the Au nanowires protruding from the surface of the membrane. These nanowires can then be dithiolated. We hope that this approach will allow for greater access to the nanowire ends and thus greater yields. In addition we are investigating other dithiols to see if the length of the carbon chain affects the capping yield. Au colloid-terminated nanowires were exceedingly rare in suspensions prepared in the same way but omitting the dithiol treatment.

We have shown that template-synthesized micro- and nanostructures can be used as building blocks for the self-assembly of supramolecular architectures. It is clear, however, that we have just scratched the surface of this interesting field.

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