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Layer-by-Layer Nanotube Template Synthesis

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There is increasing interest in template-synthesized nanotubes. Recent examples include templated carbon nanotubes for electrochemical energy production,[1] phospholipid nanotubes for biochip and biosensor applications,[2] silica nanotubes for biocatalysis and biorecognition,[3] and nanotube-containing membranes for bioseparations.[4] An important feature of the template synthesis method[5] for all of these applications is the ability to control the dimensions of the nanotubes obtained. The outside diameter of the nanotubes is determined by the diameter of the pores in the template, and the length of the nanotubes is determined by the thickness of the template. It is, however, more difficult to control the inside diameter (i.d.), or correspondingly the wall thickness, of template-synthesized nanotubes, and, for some applications, precisely controlling the i.d. is absolutely essential. Nanotube membranes for bioseparations are a good example, because it has been shown that the transport selectivity observed is profoundly influenced by nanotube i.d.[4,6]

Electroless deposition of gold on the pore walls of polycarbonate templates is currently the best known method for controlling nanotube i.d.[6] However, this method is limited to nanotubes composed of Au or other metals. It would be useful to have alternative template-synthetic chemistries that yield nanotubes composed of other materials, but which still allow for precise control over the nanotube wall thickness and i.d.

A film-formation process that is based on layer-by-layer deposition of the film-forming material along the pore walls of the template membrane might provide this alternative synthetic chemistry. In this case, the wall thickness, and correspondingly the i.d., of the nanotubes would be determined by the number of layers of the material deposited along the pore wall. This was attempted, using the well-known layer-by-layer polyelectrolyte film-deposition process in the pores of a nanopore alumina template.[7] However, the polyelectrolyte deposition process in the pores was found to be different than that on flat surfaces. As a result, the ability to control nanotube i.d. was not demonstrated, and only thick-walled nanotubes were obtained.[7] In related work, Guo et al. have used this method to coat the outer surfaces of Au nanowires.[8] In addition, Kovtyukhova et al. have used a method based on alternate $SiCl_4$/H_2O deposition/reaction cycles to make silica nanotubes.[9]

We describe here an alternative layer-by-layer film-forming method, Mallouk's alternating α,ω-diorganophosphonate/Zr chemistry,[10] for preparing nanotubes within the pores of alumina template membranes. This simple method entails alternate emersion of the nanopore template into a solution of the α,ω-diorganophosphonate and then into a solution of ZrO^{2+} to deposit layered α,ω-diorganophosphonate/Zr nanotubes along the pore wall. We have found that, in complete analogy to films formed on flat surfaces,[10] this method allows for accurate, quantitative, and predictable control over the wall thickness, and thus i.d., of the layered nanotubes obtained.

The alumina template membranes were prepared in-house by anodic oxidation of Al foil;[11] these templates were 38 μm thick and had 126 ± 10 nm-diameter pores. Prior to template synthesis, both faces of the alumina membrane were sputtered with ultrathin (~5 nm) films of Au. These Au films are too thin to block the pores at the membrane surfaces; however, they prevent the adsorption of the first layer of the α,ω-diorganophosphate to the faces of the membrane. As a result, layered α,ω-diorganophosphonate/Zr films (the nanotubes) are deposited only along the pore walls and not on the faces of the membrane. Without these Au films, the faces become preferentially coated, and nanotubes are not obtained.

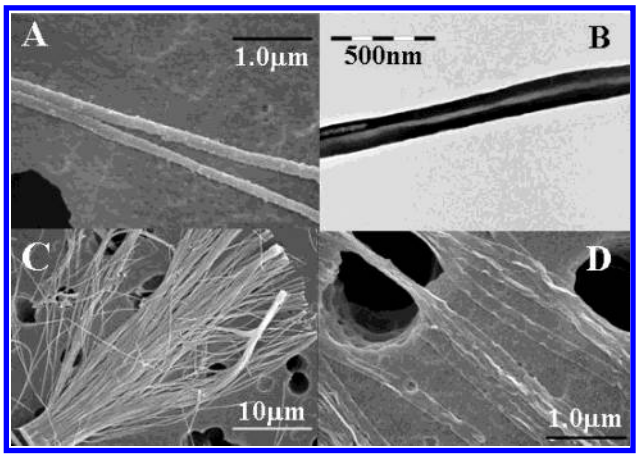

Figure 1. (A) SEM of nanotubes with $N = 25$ wall layers. (B) TEM of nanotube with $N = 25$ wall layers. (C) SEM showing nanotube length. (D) SEM of collapsed nanotubes with thin ($N = 5$ layer) walls.

1,10-Decanediylbis (phosphonic acid) (DBPA) was prepared as described previously.[10] A 1.25 mM solution of DBPA (adjusted to pH = 6 with NaOH) was used to deposit the DBPA layers. A 5.0 mM solution of $ZrOCl_2 \cdot 8H_2O$ was used to deposit the alternating Zr layers.[10] After the desired number of alternate DBPA/Zr emersion cycles, the alumina template was dissolved in 27% H_3PO_4, and the layered DBPA/Zr nanotubes were collected by filtration (Figure 1). We denote these nanotubes by the number (N) of DBPA/Zr layers that make up the walls of the tubes.

Nanotubes with wall thicknesses of $N = 5$, 15, 25, and 30 DBPA/Zr layers were examined by both scanning (SEM) and transmission (TEM) electron microscopy. Nanotubes with walls composed of 10 or more layers have outside diameters equivalent to the pore diameter of the template (Figure 1A, B), and the hollow core and wall thickness can be seen in the TEM images (e.g., Figure 1B). Furthermore, low magnification SEM images show that the length of these nanotubes is equivalent to the thickness of the template membrane (38 μm, Figure 1C). Interestingly, nanotubes whose walls are only $N = 5$ layers thick collapse when collected by filtration (Figure 1D).

When this DBPA/Zr deposition chemistry is used to deposit films on flat surfaces, each layer is 1.70 ± 0.03 nm thick, and the total film thickness (in nanometers) is 1.7 × N.[10] Correspondingly, our

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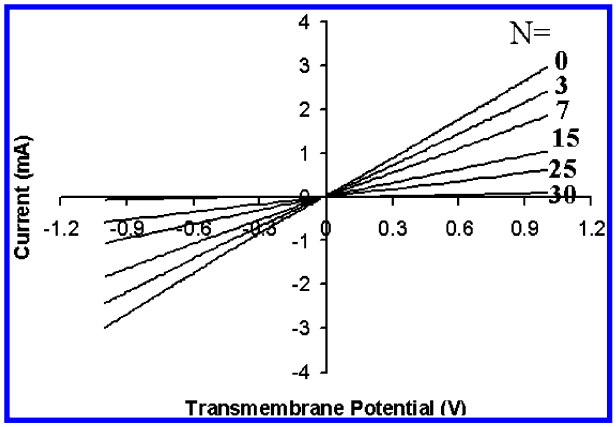

Figure 2. Current−voltage curves for nanotubes with the indicated number of layers comprising the nanotube walls.

TEM images show that the wall thickness for the DBPA/Zr nanotubes increases with the number of layers deposited on the pore walls. However, it is difficult to quantify the nanotube wall thickness from such images. We have used a simple electrochemical method[12] to prove that the wall thicknesses of our nanotubes (in nanometers) increase as $1.7 \times N$, exactly as per films deposited on flat surfaces.

This method entails measurement of current−voltage curves associated with ion-transport through electrolyte-filled DBPA/Zr nanotube membranes.[12] For these experiments, the alumina template membrane was not dissolved away. Instead, the nanotubes were left embedded within the pores of the template membrane, and the nanotube-containing membrane was mounted between the two halves of a U-tube permeation cell.[12] Each half-cell was filled with 0.5 M KCl, and a Ag/AgCl electrode was immersed into each half-cell solution. A potentiostat was used to sweep the potential difference applied between these two electrodes between values of −1 and +1 V (sweep rate = 100 mV s^{-1}) and measure the resulting transmembrane ion current.[12] This current is carried by ionic migration through the nanotubes within the membrane.

In agreement with our studies on gold nanotube membranes, the current−voltages curves are linear (Figure 2), and the slopes of these lines are the inverse of the membrane resistance (R_m).[12] That the wall thickness increases with the number of DBPA/Zr layers deposited is clearly seen by the increase in R_m with increasing N (Figure 2). If we define the resistance of the as-synthesized membrane (no DBPA/Zr within the pores) as R_{bare}, it is easy to show that the ratio R_m/R_{bare} is related to the radius of the pores in the as-synthesized membrane ($r_o = 63$ nm) and the number of layers making up the nanotube wall via

$$R_m/R_{bare} = r_o^2/(r_o - (1.7 \times N))^2 \qquad (1)$$

Equation 1 assumes that each DBPA/Zr layer making up the nanotube wall is 1.7 nm thick, as per films deposited on flat surfaces.[10]

Figure 3 shows the experimental data obtained from the slopes of the current−voltage curves (points) plotted as per eq 1. The standard deviations were obtained from replicate measurements made on at least five different membranes. The inset in Figure 3 is

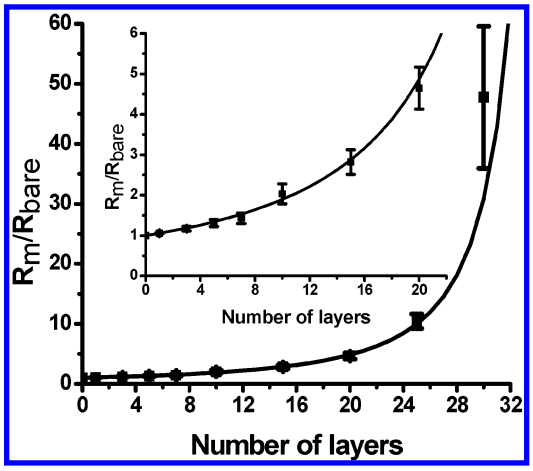

Figure 3. Nanotube−membrane resistance data plotted as per eq 1. Points = experimental data. Solid curves were calculated using eq 1.

an expanded version of the data for low values of N. The solid curves in Figure 3 were calculated from eq 1, and there are no adjustable parameters in this calculation. These data prove that the layer-by-layer film deposition process on the pore walls of the alumina template is identical to deposition on a flat surface. These data also show that this new nanotube synthesis method allows for quantitative and predictable control over the wall thickness and inside diameter of the nanotubes obtained. In addition, nanotubes with very small inside diameters, for example, as small as 23 nm in Figure 3, can be obtained.

This α,ω-diorganophosphonate/Zr chemistry should prove to be a very versatile method for preparing template-synthesized nanotubes. This is because both the chemistry of the segment between the terminal phosphonates and the length of this segment can be varied at will. In addition, nanotubes with one chemistry on the outer nanotube walls and a second chemistry on the inner walls should be possible by simply forming the first layers of the nascent nanotube using one α,ω-diorganophosphonate and changing to a second α,ω-diorganophosphonate to deposit the subsequent layers.

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