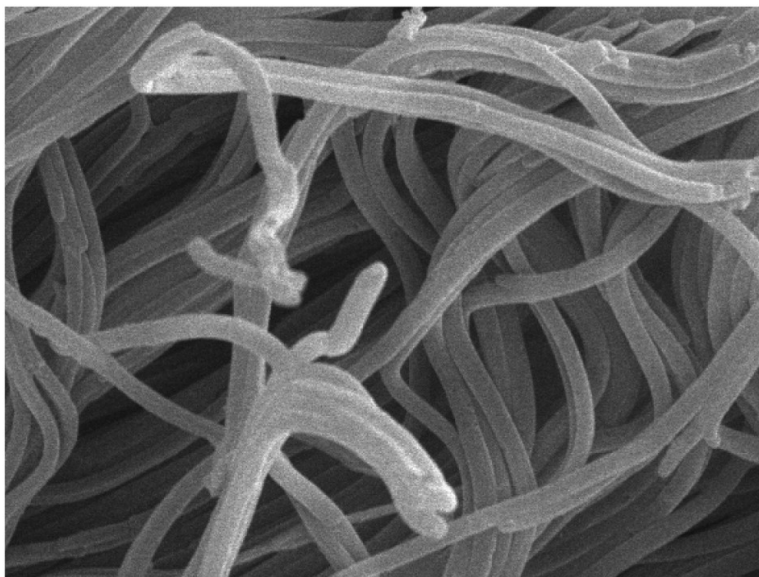


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Highly Flexible Polyelectrolyte Nanotubes

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Since Iijima first found carbon nanotubes in 1991,¹ a great deal of attention has been paid to the preparation of nanotubes. Meanwhile, various nanotubes or nanofibrils made of conductive polymers, metals, semiconductor, and other materials, prepared in different ways, have been reported.^{2–4} The template method is regarded as a simple and very effective way for preparing micro- and nanotubes.^{5–7} For example, Steinhart et al.⁸ used porous alumina and oxidized macroporous silicon templates to prepare polymer nanotubes from polymer melts or from polymer solutions. Because of the adhesive force with the pore walls, a thin polymer film can cover the pore walls. After the removal of the template, a tube structure is preserved. Thus, if the template has a monodisperse pore size distribution with regular arrays (e.g., anodic aluminum oxide), even aligned or ordered nanotubes can be obtained after the removal of the template.

This simple adsorption technique usually does not work with water-soluble, charged polymers (polyelectrolytes). The polyelectrolytes strongly adsorb to the (oppositely) charged template surface. They cover and clog the entrance of the pores. This prevents the polyelectrolyte molecules from entering the pores and adsorbing to the inner template walls. The polyelectrolytes remain outside the template membrane.⁹ As a consequence, polyelectrolyte nanotube structures cannot be formed inside the pores of alumina template membranes. In a modification of the simply unsuccessful adsorption approach, Mayya et al.¹⁰ used the layer-by-layer (LbL) deposition method of oppositely charged polyelectrolytes. This technique is a well-established approach to build composite multilayer assemblies. It is based on the electrostatic attraction between the consecutively deposited, oppositely charged species.¹¹ Mayya et al. successfully fabricated polyelectrolyte nanotubes by LbL deposition on sacrificial nickel nanorods (contrary to pores, rods cannot be clogged) and the following removal of the template. As expected, the size and shape of the nanotubes strongly depended on the nanorod template. However, it turns out to be very difficult to use the LbL method directly to fabricate long polyelectrolyte nanotubes with high flexibility.

Here, we report on the successful preparation of polyelectrolyte nanotubes with a pressure-filter-template technique. Basically, the technique uses the inner walls of pores as template and overcomes the problem of pore blocking by external pressure. Polyelectrolyte solutions are squeezed through a porous membrane. The pressurized flow of solutions with alternately charged polyelectrolytes (and neutral washing steps between) results in the LbL deposition of a polyelectrolyte multilayer on the inner walls of the membrane. To stabilize the template membrane mechanically, it is sandwiched between commercially available Millipore filters. The filters may also induce some hydrodynamic alignment/stretching of the polyelectrolyte molecules, which possibly improves their adsorption properties on the inner pore walls (this is currently under investigation). At the end, the membrane is removed and nanotubes are

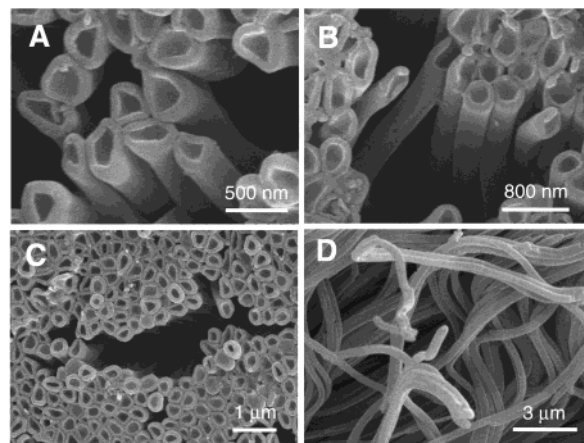


Figure 1. Scanning electron micrograph of polyelectrolyte nanotubes via layer-by-layer assembly. (A) High magnitude SEM image of the polyelectrolyte tubes through the (PAH/PSS) assembly. (B) The (PAH/PSS) nanotubes with very thick wall structure and smooth surface. (C) Ordered array of polymer tubes after the complete removal of the alumina template. (D) The highly flexible tubes.

obtained. This method allows the preparation of comparatively thick tube walls (tens of nanometers) with a high flexibility.

Anodic aluminum oxide templates were used to prepare cylindrical nanotubes with a narrow diameter distribution and a uniform and nearly parallel porous structure. The templates are sold as having 0.2 μm pores. Measurements showed that the inner pore diameters were $0.33 \pm 0.04 \mu\text{m}$. The three-layer filters (a commercial product of Millipore company) consisted of a blend of nitrocellulose and cellulose acetate with a highly hydrophilic surface. Polyallylamine hydrochloride (PAH) was chosen as cationic, and polystyrenesulfonic acid (PSS) was chosen as the anionic polyelectrolyte for the multilayer formation.^{12–14} PAH (1 mg/mL) and PSS (1 mg/mL) were dissolved in 0.5 M NaCl aqueous solutions, respectively. With a syringe, the solutions were squeezed alternatively with a pressure of 0.25 bar through the multilayer sequence consisting of a triple layer of Millipore filters, the alumina template membrane, and another Millipore filter. The filters together with the alumina template film were fixed in a stainless steel filter holder.

The oppositely charged PAH is filtrated to form the first layer on the wall of the pores. After a short washing with a solution without polyelectrolyte, the negatively charged PSS was then adsorbed into the surface of PAH as a second layer. The repetition of this procedure leads to the multilayer formation of (PAH/PSS) on the inner walls of the template pores. Finally, the template is dissolved with a concentrated NaOH solution.

Figure 1A shows a scanning electron microscopy (SEM) image of regular polymer nanotube arrays after the complete removal of the template. The tube walls consist of three PAH/PSS layers. They have wall thicknesses of 50–80 nm and lengths of up to 60 μm

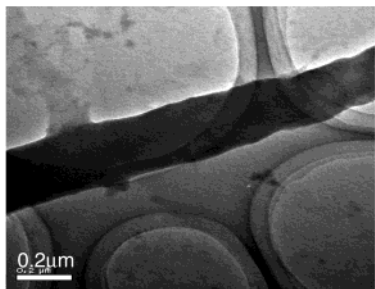


Figure 2. Transmission electron microscopy images of the three layers (PAH/PSS) of nanotube with a diameter of 200–300 nm.

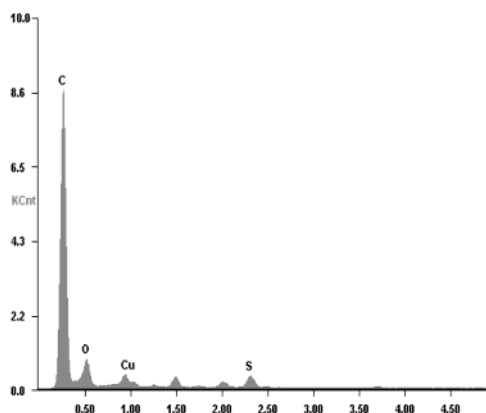


Figure 3. Energy-dispersive X-ray spectra of (PAH/PSS) polyelectrolyte nanotube.

(i.e., the entire thickness of the template, Figure 1B). Figure 1C shows an ordered array of aligned PAH/PSS nanotubes. Every individual tube can be bent without damage (Figure 1D). The high flexibility of the tube is ascribed to the comparatively thick, and thus mechanically stable walls of the nanotubes. The transmission electron microscopy (TEM) image of a selected polyelectrolyte nanotube (Figure 2) shows diameters similar to those obtained by SEM. It also shows that the surface of the polyelectrolyte nanotubes is covered with some residual alumina salt. Figure 3 displays the energy-dispersive X-ray spectra. Atoms of the expected composition including sulfur are detected, indicating that PSS was adsorbed onto the PAH surface. This is further verified by UV spectra analyzing the products (Figure 1 in the Supporting Information). The UV spectrum shows the absorption bands of PSS at 255.5 and 208.5 nm, respectively.

The walls of the nanotubes are 50–80 nm thick. This is much thicker than what is usually expected from a three-layer (PAH/PSS)-polyelectrolyte film (typically only a few nanometers per double layer for this salt concentration^{10,12}). This may be because the diameter of the tubes is nearly in the range of the radius of gyration of the polyelectrolyte molecules. Thus, for the molecules the wall surface is in effect somewhat concave which may lead to a stronger polymer adhesion.^{8,15}

As demonstrated, we successfully fabricated polyelectrolyte nanotubes by replication of pore templates with a special filter-pressure-template technique. The walls of the nanotubes consist of polyelectrolyte multilayers, which are formed by means of the LbL assembly of oppositely charged polyelectrolytes based on electrostatic interactions. The walls are comparatively thick and thus mechanically stable. The polyelectrolyte nanotubes are also very flexible. The pressure-filter-template approach can be applied to any nanotube fabrication of charged polymers in aqueous solution.

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Supporting Information Available: Synthetic materials, UV spectra, and measurements for SEM and TEM (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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