Nanotubes from dendrimers

Formation of Dendrimer Nanotubes by Layer-by-Layer Deposition

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Non-carbon nanotubes (NTs) are regarded as promising building blocks for a multitude of applications, for instance, in the fields of nanoelectronics, photonics, separation, and...

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catalysis. A versatile approach for their preparation introduced by Martin involves the use of porous materials as templates.[2] Dendrimers[3] synthesized by the stepwise addition of further generations of low-molar-mass building blocks, represent a class of functional materials that can be customized with an unrivaled precision. They contain a well-defined number of terminal functional groups that can reside at the surface. Several examples for applications[4] have been demonstrated, including the encapsulation of guest molecules,[4a] their use as a micellar host for extraction,[4b] optoelectronics,[4c] and catalysis.[4d] Specific reactions may be catalyzed within the cavities provided by dendrimers. If the dendrimers are attached to the pore walls of a porous support, the transport of the reactants to the catalytic site and the removal of the products could occur in a very controlled manner, and no extra processing step for recovering the dendrimers is necessary. Moreover, it would be highly interesting to immobilize specific guest molecules within the pores of porous membranes for applications in the fields of separation and controlled drug release. Trapping analytes within dendritic hosts in the interior of aligned channels may allow the design of a sensing device with a high lateral resolution. Therefore, it is an intriguing task to build up non-carbon NTs from this fascinating class of macromolecules.

To accomplish this objective we employed direct layer-by-layer (LbL) deposition of charged dendrimers within the pores of ordered porous alumina.[5] The LbL approach involves the alternate adsorption of oppositely charged polyelectrolytes (PEs) driven by electrostatic attraction. This methodology allows the fabrication of well-defined multilayer structures consisting of PEs in a very controlled manner.[6] Their thickness can be adjusted on the nanometer scale by the number of performed deposition steps. Combining the LbL technique with nanoporous templates is a straightforward route toward non-carbon NTs, which offers several advantages: since the non-carbon NTs are a replica of the template pores, their dimensions can easily be tailored by using templates with respective pore diameters and depths. Moreover, coating the pore walls provides functionalized channels or cavities. LbL deposition of linear PEs has already been shown to yield non-carbon NTs.[7]

The dendrimer NTs were fabricated using ordered porous alumina templates, 400 nm in diameter with a pore depth of 80 μm. It should be noted that the pores were open only at one end (Figure 1a). At first, the pore walls were coated with 3-aminopropyl dimethylethoxysilane (3-APDMES) by placing the membranes in a closed glass vessel with a 3-APDMES reservoir at a temperature of 135°C for 3 h (Figure 1b). The 3-APDMES layer provides a positively charged surface, on which the first negatively charged dendrimer was directly deposited. As model compounds we used globular-shaped, N,N-disubstituted hydra-

![Figure 1. Schematic of the preparation of the dendrimer tubes: a) Self-ordered porous alumina is used as a template; b) the pore walls are coated with 3-APDMES to provide a positively charged surface; c) at first the negatively charged dendrimer is deposited, followed by alternate oppositely charged dendrimers; d) the dendrimer tubes may be released by selectively etching the template.](image)

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![Scheme 1. Structures of G4(CH-COO−Na+)-96 and G4(NH2EtCl−)-96.](image)


Additional dendrimer layers were added by alternately immersing the templates into the corresponding solutions for 1 h (Figure 1c). Without 3-APDMES, only short tube segments with many defects were obtained (not shown). The non-carbon NTs may be released by applying a solution of chromium(III) oxide in phosphoric acid, in which the samples were kept overnight at a temperature of 37°C, or aqueous potassium hydroxide (Figure 1d).

Figure 2a represents an array of tubes 400 nm in diameter with a length of 80 μm consisting of 20 bilayers. Their well-aligned tube segments adjacent to the pore openings have a cylindrical cross section (see the right-hand side of Figure 2a and Figure 2b). The lower half of the array ini-
tially adjacent to the pore bottoms (left-hand side of Figure 2a) consists of flattened tube segments. Their structure collapsed; a phenomenon that is commonly attributed to the drying during preparation of the samples for SEM investigations. An individual tube having a length of 80 μm (corresponding to the depth of the template pores) is represented in Figure 2c. Energy-dispersive X-ray (EDX) spectroscopy recorded at an accelerating voltage of 20 kV gave qualitative evidence of the presence of phosphorus (Kα at 2.0 keV, the tubes were released from the template by etching with KOH) and sulfur (Kα at 2.3 keV) as shown in Figure 2d. A carbon and a weak oxygen peak also appear. We attribute the relatively low intensity of the oxygen and the absence of a nitrogen peak to irradiation-induced degradation of the dendrimer during the EDX measurements.

A broken tube segment and an open end of an individual tube are depicted in Figure 3. The outer diameter of the cylindrical tube segments was on the order of 400 nm, which corresponds to the diameter of the template pores, and their wall thickness was on the order of 40 nm, as estimated from several SEM images of broken tube segments. This corresponds to a thickness increment of 2 nm per double layer.

For comparison, the alternating deposition of the cationic and anionic dendrimers on a flat solid substrate was investigated by surface plasmon resonance (SPR) spectroscopy in the Kretschmann configuration. For this purpose, a 50-nm-thick Au film was evaporated onto a glass substrate, which was then optically matched to the base of a 90° glass prism (n = 1.85 at λ = 632.8 nm). The first functional layer consisting of 3-mercaptopropionic acid (3-MPA), which provides a negatively charged surface on which the first cationic dendrimer layer readily adsorbs, was self-assembled onto the Au surface from an aqueous solution. The consecutive repetition of the dendrimer deposition led to the stepwise formation of multilayers along with a very regular shift of the resonance angle, as demonstrated by scan-mode SPR spectroscopy (Figure 4). The corresponding geometrical thickness was determined from the mean value of the shift of the resonance angle by assuming a refractive index of 1.5. The thickness increment per deposited double layer was calculated to be ≈ 22 ± 3 Å. This is in reasonable agreement with the results obtained from the SEM investigations.

Dendrimer tubes prepared by the LbL templating of pores having one open and one closed end may show a gradient of their mechanical stability, which indicates that the effective number of deposition steps near the pore bottom is smaller than the actual value. The most probable explanation for this is the occurrence of diffusive limitations because of the one-dimensional pore geometry. If, however, uniform tubes are desired, templates having pores open at both ends may be used.

Dendrimer tubes with a high number of functional groups exposed to their environment are potential candidates for various applications, either released from or attached to the walls of a template. Porous membranes could be functionalized by coating the pore walls with dendrimers acting as hosts for guest molecules. Such architectures might...
be useful for applications in the fields of sensing and separation. The dendrimer tubes can be further functionalized chemically, or by incorporation of other types of nanoparticles into the tube walls. This is currently under investigation.

Experimental Section

Ordered porous alumina was prepared according to the method of Masuda and Fukuda. In a first anodization step, pores were etched under conditions where self-assembly occurred. The electrolyte, the temperature, and the applied voltage have to be selected in such a way that the 10% porosity rule is obeyed. As a result, a porous alumina layer attached to the aluminum substrate is obtained, which is disordered at the surface, whereas the pore bottoms are arranged in a hexagonal lattice. The interface between alumina and aluminum adapts the hemispherical shape of the pore bottoms. After removing the alumina layer, the aluminum substrate thus exhibits regularly arranged pits, acting as seeds for the generation of ordered pores during a second etching step.

The templates were carefully washed twice with deionized water after each deposition step. Prior to releasing the tubes we cleaned the undersides of the aluminum substrates, on which the porous alumina layers were attached, with a scalpel. The templates were placed in polypropylene cuvettes, and the etching solution was added. We applied either aqueous KOH (20%) at room temperature for 30 min (on longer exposure Al(OH)3 may be formed), or a mixture of H3PO4 (85%, 7.1g) and CrO3 (1.8g) at 37°C to selectively remove the alumina. The residual aluminum substrates were removed with tweezers after the alumina layer had been dissolved. Then, the samples were washed by centrifuging, removing the supernatant liquid, and adding deionized water; this procedure was repeated for four times. The suspensions eventually obtained were sonicated and then placed on highly doped and conductive silicon wafers for SEM investigations. We used a scanning electron microscope JEOL JSM 6300F at an accelerating voltage of 1.5 keV for recording the micrographs. EDX spectra were measured at an accelerating voltage of 20 keV. We obtained the same spectra for samples released with KOH or H3PO4/CrO3 apart from the presence of a chromium peak in the latter case.

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