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Nanotubes Prepared by Templating Sacrificial Nickel Nanorods

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ABSTRACT

We present a versatile method, based on the electrostatic self-assembly of oppositely charged species onto sacrificial templates, for the preparation of nanotubes. Polymer and polymer composite nanotubes were prepared by the layer-by-layer (LbL) deposition of polyelectrolytes and/or a charged inorganic molecular precursor onto nickel nanorods, followed by removal of the core by dissolution. Surface charge reversal of the nanotubes was observed at the end of each deposition step, which facilitated the multilayer buildup. The precursor core–shell nanorods prepared and the resulting nanotubes obtained upon dissolution of the core were characterized using transmission electron microscopy. The LbL approach is facile, adaptable, and able to be performed from aqueous-based solutions, thereby opening new avenues for the preparation of a broad range of nanotubes with tailored composition and wall thickness.

Interest in high aspect ratio nanomaterials stems mainly from their geometry dependent properties and from their use as attractive basic building blocks for larger superstructures that can be applied in a variety of applications.[1−5] Since the first report on the discovery of carbon nanotubes by Ijima et al.,[6] nanotubes of different composition have been synthesized in an attempt to create tubular structures with novel and tailored properties. Among the non-carbon nanotubes synthesized thus far, metal oxides such as MoO_3,[7] Al_2O_3,[7] V_2O_5,[7−9] TiO_2,[10] and SiO_2[7,11,12] have received considerable attention. Such nanotubes have mainly been synthesized by template-based strategies, with templates including metal and organic crystals,[11,13,14] the tobacco mosaic virus,[15] and carbon nanotubes.[7,8] Porous membranes have also widely been used to prepare nanotubes:[16] Typically, a track-etched micro/nanoporous membrane has been used as a template for the deposition of a variety of materials composed of metals, semiconductors, polymers, and carbon.[17−20] The ability to create nanotubes with defined properties (e.g., catalytic, magnetic, optical) and surface characteristics are two important aspects that will open new opportunities concerning their areas of application.

Herein, we report the preparation of polymer and inorganic-based nanotubes by utilizing the layer-by-layer (LbL) deposition of oppositely charged polyelectrolytes and/or a titania molecular precursor on sacrificial nickel nanorods and subsequently removing the template. This strategy has the advantage that it allows the facile preparation of a variety of nanotubes by using preformed nanorods as templates. One of the primary advantages of the layer-by-layer-colloid-templating (LbL-CT) approach[21,22] over other methods is that it permits nanoscale control over the nanotube wall thickness by variation of the number of layers deposited, while the final nanotube size and shape are determined by the template. In addition, nanotubes of varied and defined composition with prescribed, functionalized interior and exterior surfaces can be prepared by judicious choice of the layer components. We have previously applied this technique to coat colloids and to generate capsular colloids of various compositions.[21,22] The method described in this report serves not only as a facile route for the construction of nanotubes but also as an efficient method to coat rods with the desired materials (e.g., insulators), which is one of the main concerns for employing these anisotropic materials for different applications.[23,24] Two recent reports have employed the LbL-CT technique to *coat* lipid nanotubules for imaging nanoscale patterns[23a] and arrays of gold nanowires to obtain polymer-insulated gold nanowires with reactive ends.[23b] The current study is the first report on the preparation of nanotubes based on the LbL-CT strategy.

A schematic representation of the LbL-CT approach applied to nanorods to form nanotubes is illustrated in Figure 1.[25] Polymer nanotubes were obtained by coating nickel nanorods with polyelectrolyte multilayers (route A), followed by core dissolution. Similarly, nickel nanorods were coated alternately with positively charged polyelectrolyte and the inorganic molecular precursor, titanium(IV) bis(ammonium lactato) dihydroxide (TALH) (route B) to obtain nickel-core TALH/polymer-shell nanorods. The composite nanorods were then heated under reflux to hydrolyze the titania precursor, and after nickel core dissolution, titania-based nanotubes were obtained.

Nickel nanorods (average diameter = 65 ± 15 nm, length = 1.5 ± 0.25 μm (Figure 2A)) were coated with eight

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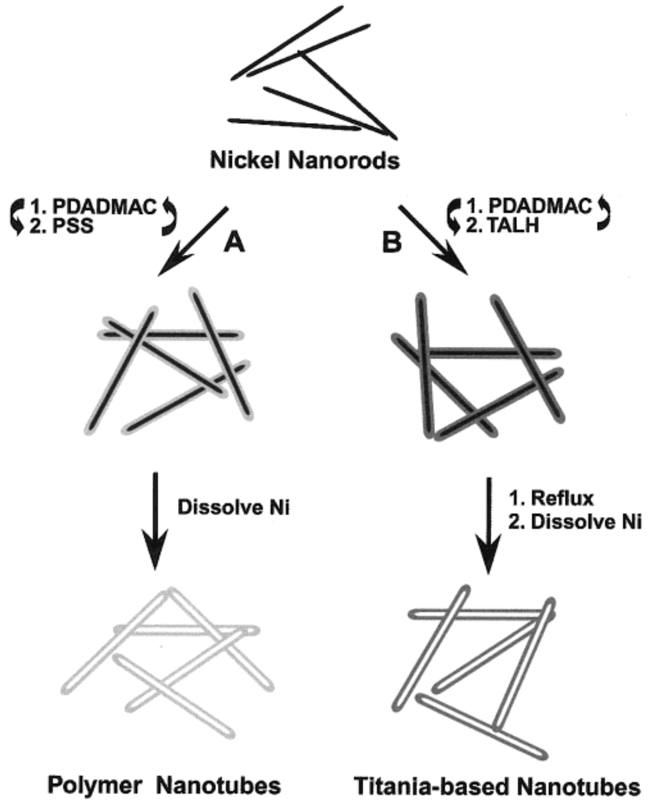

Figure 1. Schematic illustration of the preparation of polymer and inorganic−organic composite nanotubes by the LbL-CT strategy.

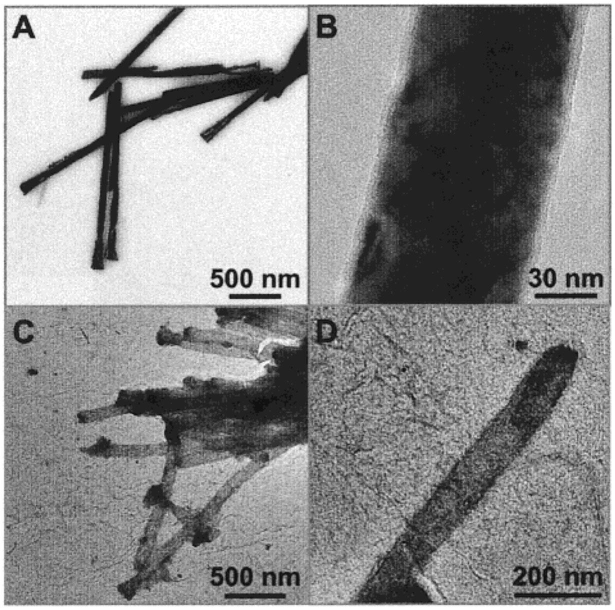

Figure 2. TEM images of (A) uncoated nickel nanorods, (B) a nickel nanorod coated with eight layers of polyelectrolyte [(PDADMAC/PSS)$_4$], (C) polymer nanotubes obtained upon dissolution of the sacrificial nickel nanorod, and (D) a higher magnification image of a polymer nanotube.

polyelectrolyte layers by the electrostatic LbL self-assembly of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium-4-styrenesulfonate) (PSS).[25] A necessary condition for the growth of polymer multilayers by electrostatic LbL assembly is the attainment of surface charge reversal at the end of each deposition cycle.[26] The growth of polyelectrolyte multilayers on nickel rod templates was followed by electrophoresis.[27] A ζ-potential of −48 mV was measured for bare nickel rods (the negative surface charge is likely due to the oxide layer). Hence the nickel rods were coated first with a layer of PDADMAC, followed by a layer of PSS. Subsequently, the rods were coated alternately with PDADMAC and PSS. Electrophoresis measurements showed that the ζ-potential alternated in sign between positive (+40 mV) and negative (−30 mV) values depending on whether PDADMAC or PSS was the outermost layer, respectively, suggesting successful polyelectrolyte multilayer growth.[21,22] The particles were also characterized with transmission electron microscopy (TEM) (Figure 2).[28] The TEM images reveal that the nickel nanorods were coated with polyelectrolyte multilayers. The thickness of the eight-layer polyelectrolyte coating was ca. 8 nm (Figure 2B), corresponding to ca. 1 nm per layer. This thickness is comparable to those observed for similar polyelectrolyte multilayers on polymer colloids.[21a] The nickel core from the nickel-polymer core−shell particles was dissolved by using dilute hydrochloric acid (pH = 2) to obtain polyelectrolyte nanotubes. Traces of nickel were not detected in the energy-dispersive X-ray (EDAX) spectrum of the polymer nanotubes, indicating the dissolution and removal of the nickel core; however, the presence of small amounts of nickel cannot be ruled out. Figure 2C shows a representative TEM image of hollow polymer nanotubes. Comparison of the micrographs in Figure 2 (A and C) reveals that the polymer nanotubes retain the shape of the nickel nanorod template. Unlike previous reports on the synthesis of polymer nanofibrils using water-soluble polymers, the integrity of the polymer tube is retained even after dissolution of the template.[20] The nickel rod template-directed shape of the nanotube is preserved mainly due to the exceptionally strong electrostatic interactions, which keep the polyelectrolyte layers tightly associated. Figure 2D is a high magnification TEM image of a polymer nanotube, the diameter of which is ca. 90 nm. A noticeable increase in diameter (ca. 10%) of the polymer nanotubes was observed, compared with the coated nickel nanorods. This could be due to the effect of drying, as a result of which the polymer nanotubes collapse to form a “sheet” with increased diameter. Similar observations have been made for hollow polymer capsules derived from coated polymer colloids.[21a] Notably, the current approach to polymer nanotube fabrication can be applied to a range of charged polymers, in contrast to currently available template-based methods for the synthesis of (water-soluble) polymer nanotubes, which require the use of conducting polymers.[20]

Titania is known for its desirable photocatalytic properties,[29,30] as well as its wide applications as a pigment[31] and filler[32] in the paint and paper industries. Catalytic applications require titania forms with high surface area, of which titania nanotubes could be potential candidates. Titania-based nanotubes were obtained by the LbL deposition of PDADMAC and TALH, followed by hydrolysis of the titania precursor, and finally dissolution of the nickel core.[25] TALH is a water-soluble titania precursor and is relatively stable at room temperature, as compared to other commonly used titania

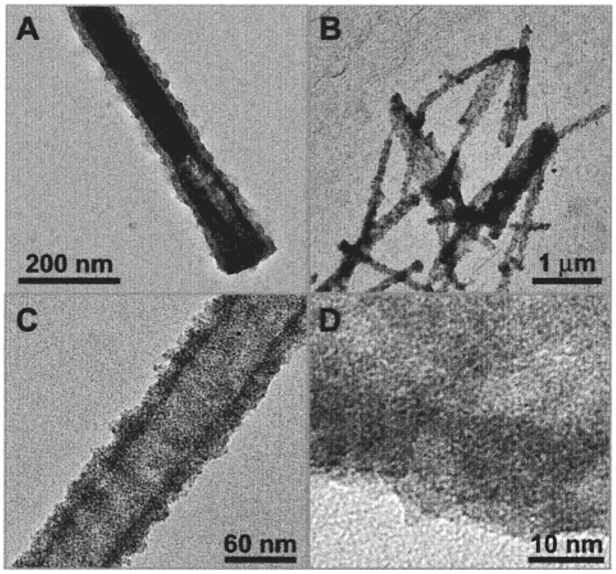

Figure 3. TEM images of (A) a nickel nanorod coated with a titania/PDADMAC coating, (B) titania-based nanotubes obtained on dissolution of coated nickel nanorods, (C) a higher magnification image of a nanotube, and (D) a high-resolution image of a composite (titania/PDADMAC) nanotube showing the titania nanoparticles.

precursors. Furthermore, the hydrolysis of TALH can readily be controlled.[33,34] TALH is known to bind electrostatically to PDADMAC and has been used as a precursor to form hollow titania spheres.[21d] Multilayer buildup of PDADMAC/TALH layers on the nickel nanorods was monitored by electrophoresis. The ζ-potential of the coated rods was found to alternate between +30 mV and −25 mV with each deposition cycle, respectively, depending on whether PDADMAC or TALH was the outermost layer. The particles were then heated under reflux for 24 h to effect hydrolysis of the titania precursor.[21d] Figure 3A is a TEM image of a core−shell nickel nanorod with a titania-based coating. The diameter of the core−shell nanorods is ca. 90 nm, with a shell thickness of ca. 15 nm. An increase in thickness per TALH layer (deposited in alternation with PDADMAC) of ca. 5 nm has been observed previously, and this has been partly attributed to the deposition of oligomers from solution.[21d] The core−shell nanorods were then treated with dilute hydrochloric acid (pH = 2) to dissolve the nickel core. Figure 3B-D shows the TEM images of the nanotubes obtained after dissolution of the nickel core. The porous nanotubes are a composite of titania and PDADMAC, as the polymer is retained during the hydrolysis of TALH. There was no evidence for the presence of nickel in the EDAX spectrum of the titania-based nanotubes. As with the polymer nanotubes (see earlier), there is a marginal increase (10 nm) in the outer diameter of the nanotube compared with that measured in the presence of the nickel core. High-resolution TEM analysis (Figure 3D) showed the presence of titania nanoparticles with the lattice spacing corresponding to the anatase phase of titania (0.352 nm).

In conclusion, it has been demonstrated that the LbL-CT strategy can be used to prepare polymer and inorganic−organic composite nanotubes. The main essence of this strategy is that it is a versatile water-based technique, thereby permitting the construction of nanotubes of a broad range of composition (including heterocomposites) with nanoscale control over the thickness of the nanotube wall. This method can be further used to tailor the properties of the nanotube by, for example, decorating the inner surface with catalytically active particles such as platinum,[13] or magnetic particles in an attempt to obtain magnetized nanotubes. The LbL-CT method also offers a promising route for the preparation of nanotubes of different compositions as well as concentric nanotubes (composition on the inside of the nanotube different from that of the surface).

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collected by heating (60 °C) the alumina membrane with nanorods in a 4 mL solution containing 6 wt % phosphoric acid and 1.8 wt % chromic acid. After 30 min at this temperature, the nanorod-loaded membrane in the acid solution was sonicated for 2 min. The orange-colored acid solution turned dark green, indicating the transfer of rods from the membrane to the solution. The nanorod dispersion was then washed three times by repeated centrifugation (1800*g*)/redispersion cycles, and finally the nanorods were dispersed in 1 mL of water. The nanotubes were prepared as follows: 0.1 mL of the nickel nanorod dispersion was placed in a 2 mL Eppendorf tube and diluted to 1 mL with water. Following this, 0.1 mL of PDADMAC (1 mg mL^{-1}, 0.01 M NaCl) was added, and the dispersion was vigorously mixed for 1 min. The solution was allowed to stand for a further 20 min, after which time the excess polymer was removed in the supernatant fraction after centrifugation (1800*g*, 7 min). This washing cycle was repeated two more times. The same solution concentrations and conditions described for the deposition of PDADMAC were used for coating the nanorods with further layers of polyelectrolytes (e.g., PSS, 1 mg mL^{-1}, 0.01 M NaCl). However, salt-free solutions were used during the TALH (5 wt % aqueous solution prefiltered through a 0.2 μm filter) step. For the preparation of the polymer nanotubes, nickel nanorods were coated with a total of 8 polyelectrolyte layers $(\text{PDADMAC/PSS})_4$, while for the titania-based nanotubes, three layers of TALH (alternating with PDADMAC) were deposited. TALH was hydrolyzed by placing the TALH/PDADMAC-coated nanorods in a round-bottomed flask, adding 9 mL of water, and heating the dispersion under reflux for 24 h. The solution was then cooled, and the nanorods were sedimented by centrifugation at 1800*g*. The sediment was redispersed in water, and this washing cycle was repeated two more times. The nanotubes were obtained by centrifuging the core−shell nanorods, redispersing in dilute HCl (pH = 2), and then allowing them to stand for 24 h. The solution containing the nanotubes was then sonicated for 10 s and dialyzed (Spectra/Por, regenerated cellulose) three times against water over 24 h.

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