Stimuli-Responsive Polymer Nanotube Arrays

by

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Abstract

Nanotube arrays, composed of materials such as carbon, titania, and zinc oxide, have shown potential as conductors, energy conversion devices, actuators, and adhesives. Such nanoscale constructs are particularly novel for their high area-to-volume and length-to-diameter aspect ratios that lead to physical and chemical properties more interesting than their bulk counterparts. However, the stimuli-responsiveness of nanotube arrays has seldom been explored, mostly due to the inertness of the materials typically utilized to create them.

Here I introduce a new concept of designing and synthesizing surface-bound stimuli-responsive polymer nanotubes with dynamic mechanical properties. Polyelectrolyte multilayers (PEMs) composed of poly(allylamine hydrochloride) and poly(acrylic acid) were chosen as the nanotube building blocks for their ability to undergo pH-triggered swelling-deswelling transitions. The swelling behavior was first demonstrated in the *in situ* synthesis of gold nanoparticles in the PEM; upon suitable post-assembly treatment, the PEM undergoes substantial molecular rearrangements that generate free amine groups available for gold salt binding. Characterization of the size and distribution of the gold nanoparticles as a function of assembly condition and post-assembly treatment, and *in situ* ellipsometry thickness measurement of the PEM film during the swelling transition provided further insights into the swelling behavior. These studies ultimately led to the design and synthesis of reversibly swellable PEM nanotube arrays via layer-by-layer assembly on porous templates. The template-based approach allows straightforward control over the length, diameter, orientation and lateral arrangement of the resultant tube array, which can be challenging with other synthesis methods. Activation of the swelling transition resulted in dramatic changes in the length and diameter of the tube arrays as characterized *in situ* via confocal laser scanning microscopy, and in the effective modulus of the nanotube arrays as measured by nanoindentation, conducted by collaborator Lin Han. Parallel to experimental work, finite element analysis of simulated indentation on the nanotube arrays, conducted by collaborator Li Feng Wang, showed deformation mechanisms and a discontinuous stress-and-strain field different than that of a flat film. Template-based nanotube synthesis is further applied to the assembly of nanotubes with thermal- and magnetic-responsiveness, as well as incorporating cell-receptor-interacting biopolymers.

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