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Self-assembly of composite nanotubes and their applications[☆]

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ABSTRACT

Combination of the layer-by-layer (LbL) technique with the porous template method has attracted significant interest as a versatile approach that has been used to prepare tubular nanomaterials with tailored properties. The process involves the sequential deposition of different species, such as polymers, nanoparticles, lipids, proteins, dyes and organic or inorganic small molecules into various porous templates, which are subsequently removed to yield free-standing nanotubes. At the same time, this approach permits the formation of composite nanotubes with the engineering features, including size, shape, composition and function. In this review, we summarize the synthesis and properties of various LbL-assembled composite nanotubes based on electrostatic attraction, hydrogen bonding, and covalent bonding. These assembled nanotubes possess potential application in biomedical fields such as bioseparations, biocatalysis, biosensor, and drug delivery.

1. Introduction

Controlled self-assembly is a growing field of research merging chemistry, physics and biology, with implications for new technologies [1–4]. One particular topic of interest within this field is the assembly and application of tubular nanomaterials. Besides carbon nanotubes, more and more researchers begin to pay attention to non-carbon nanotubes, especially those with multicomponents or multifunctional properties [5–14]. Of the various methods available for producing multicomponent non-carbon nanotubes, the layer-by-layer (LbL) assembly technique combined with the porous template method is recently known as a convenient and versatile method [14–16]. In fact, since Martin et al. first introduce the growth of one-dimensional nanomaterials in the template pores, various nanotubes or nanowires of polymers, metals, semiconductor and other materials prepared by template method have been widely reported [1,9,17]. An important feature of the template method is its capability to control the dimensions and structure of the obtained nanotubes. The outside diameter of the nanotubes is determined by the diameter of the template pores, and the length is limited by the thickness of the template. With a narrow diameter distribution and nearly parallel porous structure, porous membranes such as alumina and polycarbonate are commonly used as templates in the preparation of nanotubes. On the other hand, since the LbL concept was first realized and established by Decher and coworkers [18,19], the LbL technique has led to a number of advances in material science, ranging from the development of novel optical and electronic properties and the formation of high strength materials which mimic nature to stimuli-responsive materials [18–20]. The LbL technique was introduced initially for the preparation of multilayer composite films, largely due to its low cost, simplicity, and versatility. This technique, which primarily exploits the electrostatic attraction between oppositely charged species, has been widely used to prepare multilayer films on planar supports and colloid particles [21–25]. It allows coating of species in various shapes and sizes with uniform layers and controllable thickness. Recently, we first developed the combination of LbL assembly and the porous template method to prepare polyelectrolyte multilayer nanotubes [14]. The study indicates that this new method cannot only control the length, wall thickness, outside and inner diameters of the resulting nanotubes, but also conveniently vary the wall components and properties. Thus, various functional or stimuli-responsive nanotubes can conveniently be prepared by assembling the corresponding components, such as polymers, nanoparticles, proteins, inorganic or organic functional molecules, etc. On the other hand, many non-charged materials cannot be assembled into the wall of the composite nanotubes through the conventional electrostatic LbL technique. Therefore, a range of significant approaches for constructing multilayer films on the basis of non-electrostatic interactions have been introduced to prepare nanotubes. In particular, the use of hydrogen bonding and

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DNA hybridization for assembling multilayer nanotubes that are responsive to changes in the local chemical environment is examined. Further, LbL multilayer nanotubes prepared by use of covalent linkages formed via sequential chemical reactions are discussed. Finally, the potential applications of these nanotubes are also included in the review.

2. Preparation of composite nanotubes via LbL technique

The process of the preparation of composite nanotubes via LbL technique is simple and versatile. Briefly, a piece of porous membrane template such as alumina or polycarbonate (PC) is first immersed into a solution containing component A for a certain time. The templates were then rinsed with suitable solvent three times in different beakers. Next, the component B is alternately adsorbed in the pores of the membrane and then washed three times. This cycle can be repeated until the desired number of layers is obtained. After multilayers depositing on the top and bottom surface of the membrane were removed, nanotubes are released by dissolving the template in certain condition. Herein, we describe the preparation and properties according to their interaction between different components.

2.1. Electrostatic LbL-assembled nanotubes

Electrostatic interaction is the most common driving force to fabricate polyelectrolyte multilayers. For example, polyallylamine hydrochloride (PAH)/sodium polystryrenesulfonic (PSS) is a classically assembly pair which has been widely applied to prepare polyelectrolyte multilayer films on the planar and colloid templates. After the removal of the substrates or templates, the free-standing PAH/PSS multilayer or hollow PAH/PSS multilayer capsules can be released. The properties of PAH/PSS multilayer film has been investigated in detail with regard to temperature, salt concentration, pH value and mechanical strength. About the free-standing and three-dimensional polyelectrolyte multilayer structures by LbL technique, readers can reference several good reviews [16,20,22,24,26]. In this review, we only focus on the preparation and properties of composite nanotubes by LbL technique.

Combination of the electrostatic LbL technique with the porous template method was initially developed so that polymeric tubular structures with complex but well-controlled wall morphologies and adjustable wall thickness can be prepared. In order to obtain continuous tubes and avoid clogging the template, a so-called pressure-filter-template method was employed by our group in 2003 (Fig. 1A) [14]. Thus, one can overcome the difficulty to allow the components to smoothly filter through and completely deposit along the pore wall of the template. With this method, PAH as the anionic and PSS as the cationic component from aqueous solution containing 0.5 M NaCl was deposited into a nanoporous anode alumina oxide (AAO) membrane with a diameter of about 200 nm. After etching the AAO membrane with aqueous NaOH solution, flexible $(PAH/PSS)_3$ complex nanotubes were obtained. The length and outer diameter of these nanotubes correspond to the used AAO template (Fig. 1B). However, the polyelectrolyte deposition process in the nanopores of AAO membrane was found to be different with that on flat substrates. The thickness of the nanotube walls with 50–80 nm was one order of magnitude lager than that of corresponding multilayer structures prepared on flat surfaces in which a bilayer has a thickness of a few nanometers. Caruso et al. deposited poly(ethylenimine), poly(acrylic acid)/poly(allylamine hydrochloride) multilayers onto the pores of polycarbonate (PC) membranes with a diameter of 400 nm in the presence of Cu^{2+} and then thermally cross-linked [27]. Whereas the wall thickness of the nanotubes thus obtained could be adjusted by the number of successive deposition cycles, the functionality of the embedded inorganic nanoparticles was preserved. The wall thicknesses of the nanotubes reported in this study were only slightly larger than those in smooth configurations, and the mechanical stability of as-prepared nanotubes depended on the number of the assembled bilayers [28–31].

Polyelectrolyte multilayers have been proven to have excellent hosts for electrical, optical and electrochemically active materials systems, therefore various functional nanotubes with multilayer films can be obtained after removal of the template. In a report by our group [32], the conductive polymer, negatively charged polypyrrole (PPy) was used to fabricate conductive nanotubes through the alternating adsorption with positively charged polyallylamine hydrochloride (PAH) onto the inner pores of polycarbonate (PC) template. Here, positively charged polyelectrolyte PAH is used as a counterion [33]. The assembled PPy/PAH nanotubes are rather stable without the requirement of adjusting pH values to provide charge density. The obtained nanotubes replicated the shape of the template with diameter as 400 nm and length as 10 μm. The electro-property of the assembled nanotubes has been characterized by the cyclic voltammetry (CV) measurements. It showed that PPy has a stable oxidation state in organic acid. With the alternating current (AC) impendance measurement, the conductivity of the PPy/PAH nanotubes was measured as 0.008 s/cm, which has a good agreement with the results obtained for the PPy/PAH microcapsules or films at a flat substrate, indicating the conductive property of the assembled nanotubes [33]. A six bilayer (PPy/PAH) is reported as a critical condition for constructing stable nanotubes. Below six, the nanotubes will collapse for this assembly pair.

Lee et al. also prepared PAH/PSS nanotubes at neutral condition by using same method [28]. While at a high pH condition ($pH > 9.0$), the PAH/PSS multilayers in the PC membrane behaved different discontinuous swelling/deswelling transitions and demonstrate the membrane possess pH reduced hysteretic gating property. The flux of pH-adjusted water was used to detect the transitions and showed that the (PAH/PSS) multilayers in the confined geometry swelled to smaller extents compared to the same multilayers on planar substrates under the same conditions. And the average bilayer thickness of multilayers in the cylindrical pores of PC membranes was showed greater than that of planar substrates. The hysteretic gating property of the multilayer-modified PC membrane was utilized to achieve either a “closed” or “open” state at one pH condition depending on the pretreatment history, thereby enabling either the retention or passage of high-molecular weight polymers by varying the membrane pretreatment condition as a stimuli-responsive mechanochemical valves.

Another advantage of the LbL technique is the ability to incorporate a number of different materials into the multilayer films, as long as alternating charge is maintained. These materials included smaller organic molecules and nanoparticles. Several inorganic materials can be prepared as charged nanoparticles, which are also useful as wall components in the LbL process. Metal and metal oxide nanoparticles have been used for the preparation of hybrid nanotubes [27, 34–39]. Incorporating of a stable colloidal dispersion of nanoparticles as one of the wall components led to composite organic–inorganic hybrid nanotubes with a regular coating and a controllable thickness at the nanometer. Semi-conductor CdTe nanoparticles had been used to fabricate fluorescent nanotubes and Au nanoparticles used to synthesize composite nanotubes through assembling with polyelectrolyte [27]. For the LbL synthesis nanotubes, the presence of nanoparticles can enhance the structural stability of the nanotubes: a lower total number of layers were required to form intact nanotubes when nanoparticles form part of the nanotubes.

Interestingly, we found that the phenomenon of Rayleigh instability occurs when (PSS/PAH) multilayer nanotubes are hydrothermally treated above 121 °C (Fig. 2) [40]. It is well-known that a fluid cylinder with a circular cross-section breaks up into small spherical droplet with the same volume but less surface area if its