A facile synthesis of polypyrrole nanotubes using a template-mediated vapor deposition polymerization and the conversion to carbon nanotubes

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Polypyrrole (PPy) nanotubes with highly uniform surface and tunable wall thickness were fabricated by one-step vapor deposition polymerization (VDP) using anodic aluminium oxide (AAO) template membranes, and transformed into carbon nanotubes through a carbonization process.

Conducting polymer nanotubes have been attracting considerable attention because of their potential applications as nano-sized transistors, displays, sensors, and molecular wires.1 To date, the fabrication of conducting polymer nanotubes has been largely conducted with solution-based approaches using inorganic or organic templates.2 In a solution-based approach, it is relatively difficult to tune the wall thickness due to the possible capillary condensation and the strong interfacial tension between monomer and template. Recently, our group reported that a vapor deposition technique allows powerful control of the shell thickness of inorganic–polymer core–shell nanostructures, and creates a smoother and more uniform surface by consecutive polymerization of vaporized monomer under vacuum onto the desired surface.3 In addition, it provides experimental simplicity and accessibility such as solvent-free system and no recovering process. So far, the vapor phase polymerization of conducting polymers has been mainly performed to fabricate conductive thin films4 and filled composite materials,5 whereas considerably less attention has been paid to the preparation of tubular nanostructures. Herein, we report on the facile synthesis of polypyrrole (PPy) nanotubes using a template-mediated VDP and the conversion into carbon nanotubes through the carbonization process.

In a typical synthesis of PPy nanotubes, AAO template membranes having a thickness of 60 μm and pore diameters of 20 and 100 nm were soaked in ferric chloride aqueous solution (0.21 M). After wetting the template thoroughly, residual ferric chloride on the top and bottom surfaces of the AAO membrane was removed to reduce the possible closing and interconnection of the nanotubular edges. The dried AAO membranes were moved into a closed reservoir. The monomers were partially vaporized as the feeding amount of monomer increased from 12 to 34 nm. As the loading amount of monomer increased, the vapor pressure inside the reaction chamber increased and the conversion into carbon nanotubes through a carbonization process.

The FT-IR spectrum of the polymer nanotubes indicated a ring stretching band at 1548 cm⁻¹, a conjugated C–N stretching at 1486 cm⁻¹, and a C–H wagging vibrations at 783 cm⁻¹. Elemental analysis showed the presence of C (61.5%), H (4.0%), and N (18.2%). The ratio of H/N/C was 1.04/6.15.4, which is very similar to the composition of pure PPy.6 Energy dispersive X-ray (EDX) analysis provided the composition, i.e. C (59.8%), N (17.1%), Fe (7.3%), and Cl (15.8%). The ratio of C/N was 3.4 and 3.5 for elemental analysis and EDX analysis, respectively. Since a pyrrole has one N and four C, the C/N weight ratio of PPy's is about 3.43. These results indicate that the product consists of the PPy doped with iron complex anion.

Fig. 1a and b represent scanning electron microscopy (SEM) and transmission electron microscopy (TEM, inset) images of PPy nanotubes synthesized using AAO membranes with pore diameters of 20 and 100 nm, respectively. The VDP provided a remarkably uniform and smooth wall surface, irrespective of the template pore diameters.

The wall thickness was easily controlled by injecting different amounts of pyrrole monomers. The variation in the wall thickness of the PPy nanotubes as a function of the feeding amount of pyrrole monomers is illustrated in Fig. 2. For comparison, the PPy nanotubes were fabricated using AAO membranes with ca. 100 nm pore diameter. As the feeding amount of monomer increased from 0.07 to 0.21 mL, the average wall thickness increased gradually from 12 to 34 nm. As the loading amount of monomer increased, the vapor pressure inside the reaction chamber increased and the adsorption of monomers onto the surface of AAO channel was facilitated, which resulted in the increment in wall thickness. The chemical oxidation polymerization of vaporized pyrroles started exclusively from the channel surface owing to the adsorbed ferric chloride, and grew towards the center of the channel.

Fig. 3a shows TEM images of the PPy nanotubes carbonized at 2000 °C. While the average diameter of PPy nanotubes was 22 ± 4 nm, that of carbonized PPy nanotubes was 15 ± 3 nm. The size reduction originated from the formation of more compact structures accompanied by dehydrogenation, denitrogenation, and aromatization in the carbonization process.7 According to EDX analysis, the PPy nanotubes carbonized at 1000 °C were composed of C (82.7%), N (1.2%), Fe (6.3%), Cl (1.1%), and O (8.7%). In the carbonization process of a doped PPy, the loss of nitrogen occurs between 400 and 600 °C, and polycondensed graphitic species are
Fig. 2 TEM images showing the wall thickness variation of PPy nanotubes with increasing the loading amount of monomers: (a) 0.07 mL, (b) 0.14 mL, and (c) 0.21 mL, at a fixed pore size (100 nm) of AAO membrane.

The relative intensity ($I_D/I_G$) of carbonized PPy nanotubes at 1000 °C is 0.86. This ratio indicates a semicrystalline carbon structure containing some lattice edges or plane defects within the analyzed carbon nanotube. When carbonized at 2000 °C, the Raman spectra of the carbon nanotube exhibited an increased intensity and a decreased half width at half maximum (HWHM) of the G band, and also a decreased intensity and decreased HWHM of the D band [$I_D/I_G = 0.43$]. The decreased intensity value of $I_D/I_G$ arose from the reduced fraction of defects within graphite-like domains. This means that structural development from a semicrystalline to a highly crystalline carbon material occurs through the carbonization process.

In conclusion, a template-mediated VDP technique is found to be a facile and effective method to fabricate polymer and carbon nanotubes. The vapor phase polymerization provided a highly uniform nanotubular surface as well as easier control over the wall thickness. This novel approach might be expanded to allow the preparation of various nanostructures, which are intended to mimic the morphological characteristics of templates.

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Notes and references


