

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

Jyongsik Jang\* and Joon Hak Oh

Hyperstructured Organic Materials Research Center and School of Chemical Engineering, College of Engineering, Seoul National University, Shinlimdong 56-1, Seoul 151-742, Korea.

E-mail: [jsjang@plaza.snu.ac.kr](mailto:jsjang@plaza.snu.ac.kr); Fax: 82 2 888 1604; Tel: 82 2 880 7069

Received (in Cambridge, UK) 9th December 2003, Accepted 23rd February 2004

First published as an Advance Article on the web 5th March 2004

**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.<sup>1</sup> To date, the fabrication of conducting polymer nanotubes has been largely conducted with solution-based approaches using inorganic or organic templates.<sup>2</sup> 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.<sup>3</sup> 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 films<sup>4</sup> and filled composite materials,<sup>5</sup> 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  $\mu\text{m}$  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 reaction vessel (100 mL) equipped with a sealing apparatus and a monomer loading reservoir. The reaction chamber was evacuated at room temperature until the pressure inside reached about  $10^{-1}$  Torr. Then, a variable amount of pyrrole monomer was injected into the closed reservoir. The monomers were partially vaporized as soon as they were injected inside the reactor at room temperature. The monomer reservoir valve was open and the monomers were completely vaporized by heating the reactor at 70  $^{\circ}\text{C}$ .

As the vaporized pyrrole monomer was polymerized into the channels of the AAO membrane, the color of the AAO membrane was changed from white to black. After 12 h of chemical vapor polymerization, the AAO templates were dissolved in NaOH aqueous solution (3 M). Excess water was added to dilute the solution, and the PPy nanotubes were precipitated. The upper solution containing the AAO salts and residual oxidants was discarded, the PPy nanotube precipitates were dried in a vacuum oven at room temperature.

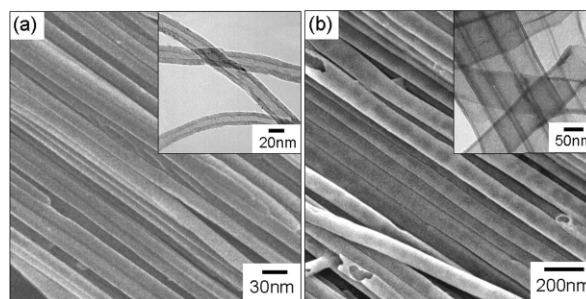
In the carbonization procedure, the collected PPy nanotubes were placed in an alumina tube, and heated to carbonization temperature at a heating rate of 3  $^{\circ}\text{C min}^{-1}$  under Ar gas flow (0.2 L  $\text{min}^{-1}$ ). The AAO membrane containing PPy nanotubes could also be used for carbonization directly. After 3 h of carbonization, the quartz tube was naturally cooled to room temperature.

The FT-IR spectrum of the polymer nanotubes indicated a ring stretching band at 1548  $\text{cm}^{-1}$ , a conjugated C–N stretching at 1486  $\text{cm}^{-1}$ , and a C–H wagging vibrations at 783  $\text{cm}^{-1}$ . Elemental analysis showed the presence of C (61.5%), H (4.0%), and N (18.2%). The ratio of H/N/C was 1.0/4.6/15.4, which is very similar to the composition of pure PPy.<sup>6</sup> 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 PPys is about 3.43. These results indicate that the product consists of the PPy doped with iron complex anion.

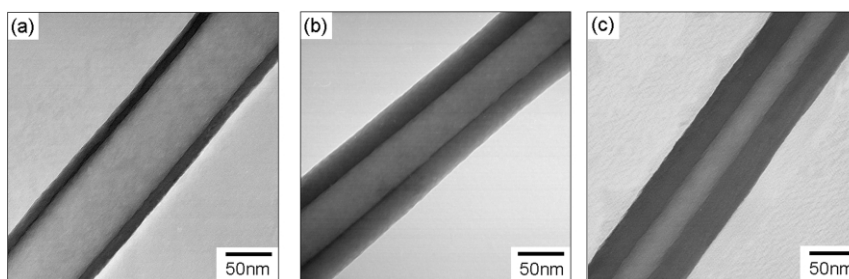
Fig. 1a and b represent scanning electron microscopy (SEM) and transmission electron microscopy (TEM, inset) images of PPy nanotubes synthesized using AAO membranes with pore diameters of 20 and 100 nm, respectively. The VDP provided a remarkably uniform and smooth wall surface, irrespective of the template 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  $^{\circ}\text{C}$ . While the average diameter of PPy nanotubes was  $22 \pm 4$  nm, that of carbonized PPy nanotubes was  $15 \pm 3$  nm. The size reduction originated from the formation of more compact structures accompanied by dehydrogenation, denitrogenation, and aromatization in the carbonization process.<sup>7</sup> According to EDX analysis, the PPy nanotubes carbonized at 1000  $^{\circ}\text{C}$  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  $^{\circ}\text{C}$ , and polycondensed graphitic species are



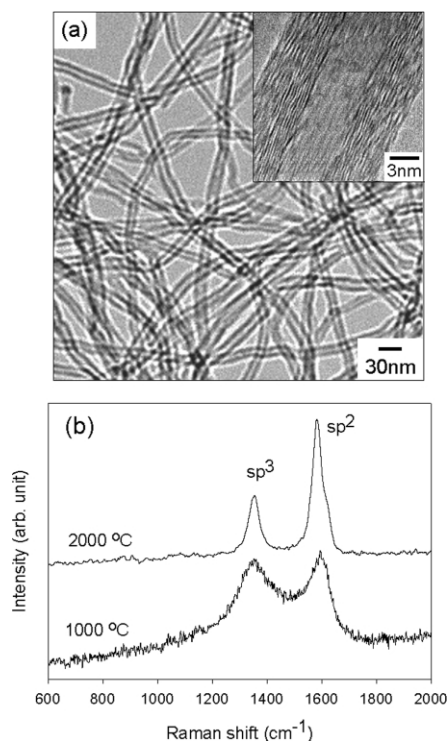
**Fig. 1** SEM and TEM (inset) photographs of PPy nanotubes prepared using AAO membranes with pore diameters of (a) 20 nm and (b) 100 nm, at a fixed amount of monomer (0.05 mL).



**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.

generated.<sup>8</sup> The HRTEM image (inset in Fig. 3a) confirms the formation of partially ordered graphitic layers. In addition, iron complex dopants lose most of the halogen atoms at over 800 °C and form iron oxides.<sup>9</sup> The source of oxygen is considered to be the moisture picked up by the iron complex dopants. XRD analysis revealed that the carbon nanotube consists of an intermediately ordered graphite impregnated with iron oxides. The carbon nanotubes had an average length of *ca.* 29 μm with a broad distribution. The diminution in the length mainly arose from the fracture during the experimental procedure.

Fig. 3b represents the Raman spectral change of the carbonized PPy nanotubes according to carbonization temperature. The Raman spectrum exhibited two distinct peaks at 1582 and 1355 cm<sup>-1</sup>. The band at 1582 cm<sup>-1</sup> (G band) is assigned to the E<sub>2g</sub> vibration of graphitic carbon with an sp<sup>2</sup> electronic configuration. On the other hand, the peak at 1355 cm<sup>-1</sup> (D band) is attributable to the A<sub>1g</sub> mode of diamond-like carbon with an sp<sup>3</sup> configuration.<sup>10</sup>



**Fig. 3** (a) Bright field TEM and high resolution TEM (inset) images of the PPy nanotubes (*ca.* 22 nm diameter) carbonized at 2000 °C, and (b) Raman spectra of the carbonized PPy nanotubes.

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.<sup>11</sup> 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 semi-crystalline 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.

This work was supported by the Brain Korea 21 program of the Korea Ministry of Education and Korea Science and Engineering Foundation through the Hyperstructured Organic Materials Research Center.

## Notes and references

- X. Duan, Y. Huang, Y. Cui, J. Wang and C. M. Lieber, *Nature*, 2001, **409**, 66; J. Kong, N. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho and H. Dai, *Science*, 2000, **287**, 622; D. Normile, *Science*, 1999, **286**, 2056.
- V. P. Menon, J. Lei and C. R. Martin, *Chem. Mater.*, 1996, **8**, 2382; S. D. Vito and C. R. Martin, *Chem. Mater.*, 1998, **10**, 1738; C. R. Martin, *Acc. Chem. Res.*, 1995, **28**, 61; M. Fu, Y. Zhu, R. Tan and G. Shi, *Adv. Mater.*, 2001, **13**, 1874; S. Demoustier-Champagne and P.-Y. Stavaux, *Chem. Mater.*, 1999, **11**, 829; M. Goren, Z. Qi and R. B. Lennox, *Chem. Mater.*, 2000, **12**, 1222; Y. Long, L. Zhang, Y. Ma, Z. Chen, N. Wang, Z. Zhang and M. Wan, *Macromol. Rapid Commun.*, 2003, **24**, 938.
- J. Jang and B. Lim, *Angew. Chem., Int. Ed.*, 2003, **42**, 5600.
- J. Kim, D. Sohn, Y. Sung and E.-R. Kim, *Synth. Met.*, 2003, **132**, 309; F. Cacialli and P. Bruschi, *J. Appl. Phys.*, 1996, **80**, 70.
- K. Kurachi and H. Kise, *Macromol. Chem. Phys.*, 1995, **196**, 929; S. N. Tan and H. Ge, *Polymer*, 1996, **37**, 965; J. Jang, B. Lim, J. Lee and T. Hyeon, *Chem. Commun.*, 2001, 83.
- J. Jang, J. H. Oh and G. D. Stucky, *Angew. Chem., Int. Ed.*, 2002, **41**, 4016; J. Jang and J. H. Oh, *Chem. Commun.*, 2002, 2200.
- K. Kim and J.-I. Jin, *Nano Lett.*, 2001, **1**, 631.
- E. Ando, S. Onodera, M. Iino and O. Ito, *Carbon*, 2001, **39**, 101.
- C. Hung, *Carbon*, 1995, **33**, 315.
- F. Tuinstra and J. L. Koenig, *J. Chem. Phys.*, 1970, **53**, 1126.
- M. S. Dresselhaus, P. C. Eklund, G. Dresselhaus and M. J. Pelletier, *Analytical Application of Raman Spectroscopy*, Blackwell Science, Oxford, 1st edn., 1999, ch. 9.