1-Dimensional structures of poly(3,4-ethylenedioxythiophene) (PEDOT): a chemical route to tubes, rods, thimbles, and belts

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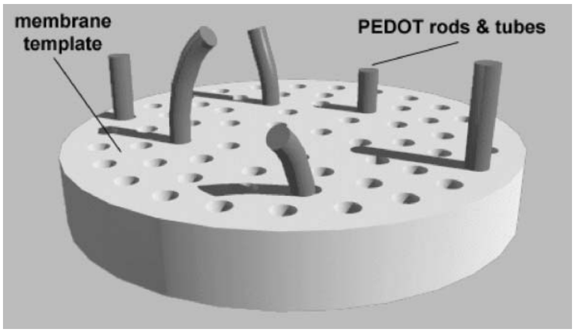
The chemical synthesis of 1-dimensional (1-D) PEDOT nanostructures in the form of tubes, rods, thimbles, and belts has been successfully accomplished through the use of a "hard template".

Since the first discovery of conducting polymers three decades ago,[1] a multitude of research has been done to replace traditional metallic or semiconducting materials with these polymers.[2,3] In recent years, 1-dimensional (1-D) nanostructures (*e.g.*, nanotubes and nanofibers) composed of conducting polymers, have attracted considerable interest due to their unique electronic and optical properties, such as their high surface-to-volume ratio and enhanced current carrying ability, which are a result of their low dimensionality. A number of potential applications exist in chemical sensors, membranes, polymer wires, displays, electrical nanodevices, and drug delivery systems.[4–7] These lower dimensional conducting polymer structures have been developed by introducing "structural directors" during their synthesis, including "hard templates" such as an anodized alumina membrane, track-etched polymer porous membrane, and a zeolite channel,[8–10] while "soft templates", such as surfactants and organic dopants, have also been explored.[11–13] In addition, recent efforts have been presented for creating nanofibers of polyaniline and polypyrrole by interfacial polymerization methods, seeded polymerization methods, and through electrospinning techniques.[14–16]

PEDOT is one of the most promising conducting polymers due to its high environmental stability, low band gap, high conductivity, and excellent transparency in the doped state.[17,18] A number of research efforts and final applications involving PEDOT have utilized the commercial product PEDOT-PSS (Bayer AG) due to its excellent coating properties and reasonable conductivity.[19–21] However, only a few reports of nano- and meso-scale PEDOT structures, such as nanoparticles, nanocomposite particles, and colloidal core-shell particles, have been presented,[22–25] while in the case of polyaniline and polypyrrole, there are a range of methods to prepare 1-D nanostructures.[9–16] Though there have been several reports on the preparation of PEDOT nanotubes by electrochemical methods,[26,27] there has been a lack of chemical-based synthetic approaches presented in the literature. Therefore, in this communication, we report on the first chemical synthesis of nanostructured PEDOTs (*e.g.*, tubes, belts, rods, and thimbles) in an aqueous solution using an Al_2O_3 membrane (AAO, Whatman Anodisc 47, pore size 250 nm, thickness 60 μm) as a template (*cf.* Scheme 1). A high level of control could be exerted on the geometric characteristics of the PEDOT structures through a variation in synthetic conditions.



Scheme 1 Schematic illustrating the use of an Al_2O_3 membrane as a template in the synthesis of 1-D PEDOT structures.

The preparation of the PEDOT 1-D structures was performed inside the membrane pore and was challenging due to the lack of an interaction between the PEDOT and AAO, the poor solubility of the 3,4-ethylenedioxythiophene (EDOT) monomer in water, and the difficulty in controlling the reaction rate. To overcome these drawbacks, the AAO membrane was first filled with EDOT monomer under negative pressure, and then the EDOT-filled AAO membrane was quickly transferred to an aqueous oxidant solution to initiate the polymerization. Due to the extremely low solubility of EDOT in the reaction solution, the monomer was retained in the pore of the AAO. In addition, the solvophobic properties of the PEDOT polymer led to its preferential growth on the pore wall. After polymerization, the nanostructured PEDOT was separated from the AAO membrane by dissolving the AAO in a 20 vol.% hydrofluoric acid (HF) aqueous solution and washing the residue with an excess of HF, deionized water, methanol, and then again with deionized water.

Scanning electron microscopy (SEM) (*cf.* Fig. 1) clearly indicated the successful formation of PEDOT nanotubes with an

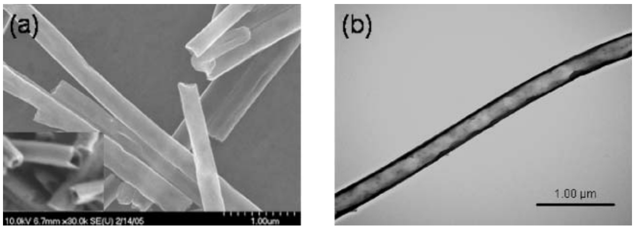


Fig. 1 (a) SEM image of PEDOT nanotube synthesized at 30 °C using 2 M of $FeCl_3$ as an oxidant–dopant; (b) a representative TEM image of a PEDOT nanotube.

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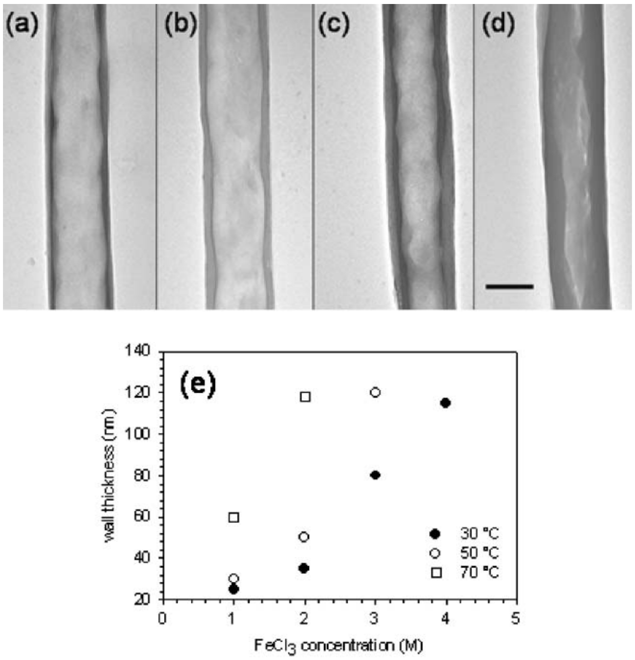

Fig. 2 TEM images of PEDOT nanotubes synthesized under various conditions: (a) in 1 M $FeCl_3$ solution at 30 °C; (b) in 1 M $FeCl_3$ solution at 50 °C; (c) in 2 M $FeCl_3$ solution at 50 °C; (d) in 3 M $FeCl_3$ solution at 30 °C; and (e) tube wall thickness as a function of $FeCl_3$ concentration and polymerization temperature. Polymerization time was 1.5 hours for each sample.

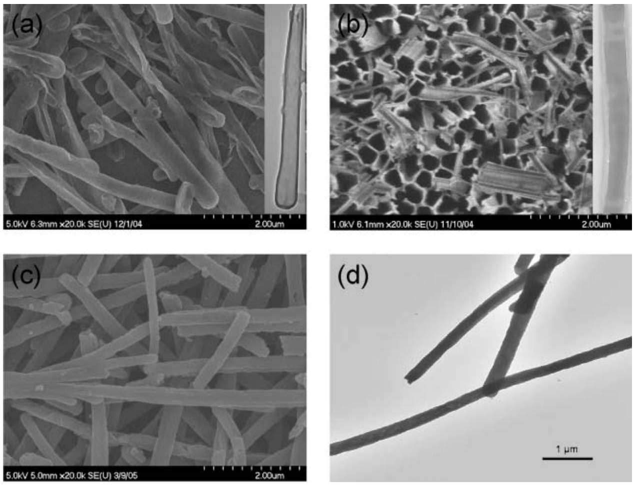

Fig. 3 SEM images of various 1-D PEDOT structures: (a) thimble-like structure synthesized in 1 M $FeCl_3$ at 50 °C; (b) belt-like structure synthesized in 1 M $FeCl_3$ at 30 °C which was grown inside a pore and protruded from the membrane; (c) SEM image and (d) TEM micrograph of PEDOT rod synthesized in 2 M $FeCl_3$ solution at 70 °C. TEM micrographs of corresponding structures are included in the right section of SEM micrographs in (a) and (b).

average diameter of *ca.* 250 nm and a length of over 5 μm. Transmission electron microscopy (TEM) images (*cf.* Figs. 1b and 2a–d) of the nanotubes indicated a well-defined hollow structure, while the inset in the SEM micrographs (*cf.* Fig. 1a) verifies the tubular structure. The observed wall thickness was *ca.* 35 nm when the tubes were synthesized at 50 °C and with 2 M of $FeCl_3$.

By introducing different concentrations of the $FeCl_3$ oxidant and modifying the polymerization temperatures, the wall thickness of the tubes could be controlled. The wall thickness of the PEDOT nanotubes, as observed by TEM, increased both with higher concentrations of the $FeCl_3$ and with elevated polymerization temperatures due to an increased polymerization yield.[28] The observed wall thicknesses were *ca.* 20, 30, 50, and 80 nm in Figs. 2a–d, respectively. At the highest polymerization temperature and $FeCl_3$ concentrations, the pore of the wall was almost closed off by the quickly growing PEDOT tubes in the typical 1.5 hour synthesis run. The control afforded to the material scientist in synthesizing tubes of a defined wall thickness is highlighted in Fig. 2e.

These 1-D PEDOT structures were readily dispersed in either water or alcohol. If the thickness of the wall was very thin (< 20 nm), or in the case of a nanobelt, transparent continuous films could be obtained by simply dropping these dispersions on a substrate and drying, which can provide a critical component for electronic and photonic devices.[29,30]

Fig. 3 presents various forms of 1-D PEDOT structures prepared under different synthetic conditions. Fig. 3a presents a thimble-like structure which was obtained in the same way as the nanotubes but a layer of monomer was allowed to bridge the pore opening resulting in a PEDOT "plug" on one end of the tube. TEM micrographs clearly indicate the occluded end of the structure, which could be potentially employed as a nanosized container. A PEDOT belt-like structure was also obtained by reducing the reaction rate and vertically inclining the membrane in the $FeCl_3$ solution. Fig. 3b presents a PEDOT belt structure grown in the pore of the AAO membrane and induced to protrude from the void by sonication, evidence that the structure was grown in the pore of the membrane. As indicated previously, the tube walls could be fully filled by PEDOT to produce rod-like structures as indicated in Figs. 3c–d. The AAO pore was fully filled and the PEDOT rod was obtained in either a higher concentration of $FeCl_3$ or at an elevated polymerization temperature (over 3 M at 50 °C or over 2 M at 70 °C for the 1.5 hour polymerization time).

FT-IR spectra of the tubes confirmed the successful formation of the PEDOT as evidenced by the presence of the peaks at 1522 and 1316 cm^{-1} (C–C or C=C stretching of thiophene ring), 1199, 1087, and 1050 cm^{-1} (C–O–C bond stretching in ethylene oxide group), and 976, 838, and 689 cm^{-1} (C–S bond in the thiophene ring).[23,31] Energy dispersive X-ray (EDX) analysis also indicated that the atomic composition of C (64.7%), O (30.1%), S (4.2%), and Cl (1%) was consistent with theoretical values.

In conclusion, various kinds of 1-D PEDOT structures were successfully synthesized through a chemical oxidative polymerization method in an aqueous solution. The exploitation of an Al_2O_3 membrane with a pore diameter of 250 nm as a template resulted in a range of unique 1-D structures. Control of the geometric aspects of the structures was obtained through modifications of the synthetic conditions. These 1-D PEDOT structures can facilitate environmentally friendly processing due to their excellent dispersibility in both water and alcohol, and can be potentially utilized in electronic, photonic devices, and biological applications.

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