Self-Formation and Anisotropic Electrical Conduction of Polypyrrole-Microtubes

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(Received May 24, 2001; CL-010487)

Spontaneous appearance of polypyrrole microtubes was first observed during the electrochemical polymerization of pyrrole in water using sodium *p*-toluenesulfonate as a supporting salt. Almost amorphous microtube showed high electrical conductivity (σ = 498 S cm^{-1}) along an axis of the tube. The tube also revealed extremely high anisotropy in the electrical conductivity. The ratios of the conductivity parallel to the axis (σ) to that perpendicular to the axis in plane (σ') and to that across the plane (σ'') are as high as 10^3 (σ/σ') and 10^5 (σ/σ''), respectively.

Polypyrrole, one of conductive polymers, has attracted considerable attention because of its unique electrical properties and easy preparation of the films coupled with good thermal stability.[1,2] Thus, the synthetic methods and the electronic properties have been extensively studied.[3–7] Its applications have also been investigated for electronic devices such as polymer-LEDs,[5] tantalum solid electrolyte capacitors,[8] secondary polymer batteries,[1] and electrochemical sensors.[9]

Template-guided syntheses of conductive polymers provide the products with versatile shapes based on features of the template. Demoustier-Champagne et al. reported chemical and electrochemical synthesis of polyaniline micro- and nano-tubes using pores of the particle track-etched membrane as a template.[10] They also reported synthesis of polypyrrole nano-tubes using the same template.[11] Han et al. reported a unique method for the preparation of carbon-microtubes through coating polypyrrole on templates of poly(ethylene terephthalate) fibers.[12] On the other hand, conventional or template-free syntheses of conductive polymers can provide such various shapes of target products as grains, fibrils, needles, and films according to the reaction conditions,[13] but not tubes yet.

Recently we have extensively studied polyaniline films as organic thermoelectric materials.[14–16] Polyaniline films show a positive correlation between thermoelectric figure-of-merit and electrical conductivity because the thermal conductivity of polyaniline films is extremely low and almost constant regardless of the electrical conductivity. Therefore, we have postulated that polypyrrole films also have the similar correlation, and tried to electrochemically prepare highly electrically conductive polypyrrole films according to a procedure previously reported by Satoh et al.[6] in order to achieve high thermoelectric performance.[17]

In the process of electrochemical preparation of polypyrrole films, we have fortunately found self-formation (template-free formation) of polypyrrole-microtubes which are highly anisotropic in electrical conduction.

To the best of our knowledge, both such self-formation of microtube-shaped conductive polymers and such high anisotropy of electrical conductivity have not been reported yet.

The electrochemical polymerization was potentiostatically carried out in a one-compartment cell containing an aqueous solution of 0.25 mol dm^{-3} of pyrrole and 0.8 mol dm^{-3} of sodium *p*-toluenesulfonate using an indium–tin-oxide glass (ITO, 1 cm × 2 cm, ca. 10 Ω cm, Toshima Co. Ltd.), platinum net, and Ag/AgCl as an anode, a cathode, and a reference electrode, respectively, at 800 mV vs Ag/AgCl at room temperature under nitrogen atmosphere without stirring.

FT-IR studies were carried out with a JEOL JIR-winspec 50 spectrometer using a pressed KBr-pellet-type sample after making microtubes into powders. Elemental analyses were carried out by a combustion method at Shonan Analytical Center, SBC Co., Ltd. Scanning electron microscopic (SEM) studies were carried out on a JEOL JSM-T100 microscope at 25 kV after covered with a thin layer of sputtered gold. X-ray diffraction (XRD) patterns were recorded on the microtube-shaped sample with a Rigaku Sun MXP X-ray diffractometer, controlled by a Mac Science computer programming system, at 40 kV and 20 mA using copper as a target. Measurement of electrical conductivity along the axis of tube was carried out by a four-point technique under direct current. Otherwise, the measurements were carried out by a two-point technique along any directions of the tube. Subsequently, anisotropies between the electrical conductivity parallel to the axis of the microtube and that perpendicular to the axis in plane or that across the plane were determined.

As mentioned above, the electrochemical polymerization was potentiostatically carried out in an aqueous solution containing pyrrole and sodium *p*-toluenesulfonate using an ITO glass as an anode. In the beginning, usual film formed on the surface of the ITO anode as previously reported.[6] After half an hour of electrolysis, however, 'mustaches' began to grow on the previously formed film of polypyrrole, as shown in Figure 1. The 'mustaches' further grew to several millimeters in length and several hundreds microns in diameter when the electrolysis was carried out for 2.5 h. During the electrolysis the current density gradually increased but there was no drastic change in the current density. In addition, bubbles appeared at the end of the 'mustaches' during the electrolysis. However, it is unlikely considered that the bubbles originate from a decomposition of water due to a depletion of *p*-toluenesulfonate anions because the molar ratio of charged *p*-toluenesulfonate anion to pyrrole (3.2) is significantly larger than that in polypyrrole films or microtubes

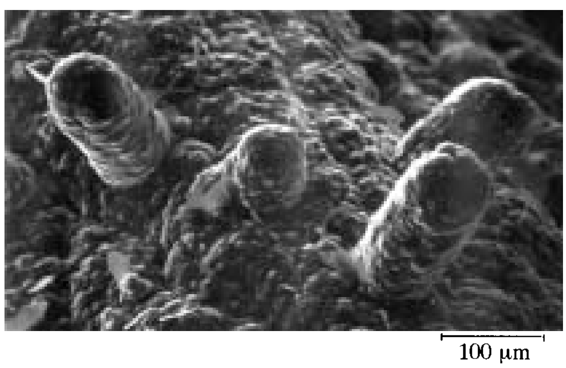

Figure 1. SEM image of capped microtubes grown on polypyrrole film.

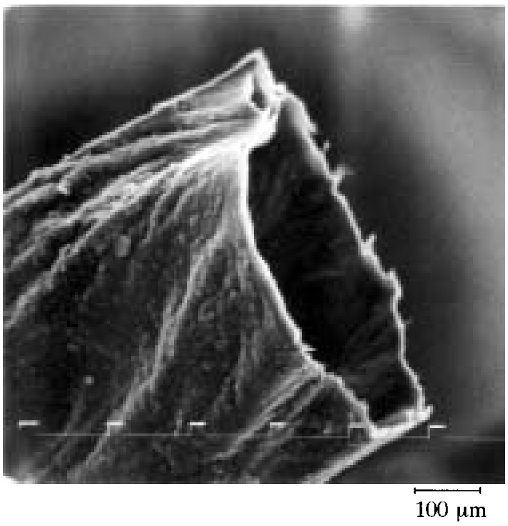

Figure 2. SEM image of a self-formed polypyrrole-microtube.

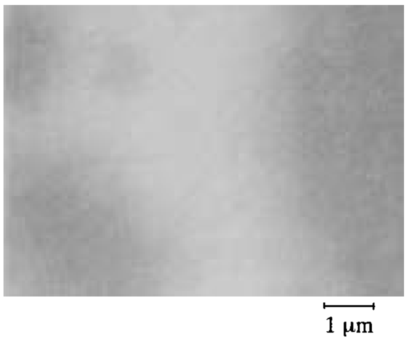

Figure 3. SEM image of the surface of an ITO electrode.

(0.6). As-produced 'mustaches' were removed from the film with a pincette, after being washed with deionized water and acetonitrile, and dried under vacuum. The 'mustache' was observed by SEM after frozen in liquid nitrogen and cutting out the front part of the 'mustache'. The SEM micrograph (Figure 2) shows a perfect microtube with a clear cavity. The microtube can be inserted by a platinum wire of 100 μm in diameter and can be moved along the wire. Since the surface of an ITO electrode is enough smooth as shown in Figure 3, the shape of microtubes could not be attributed to the surface structure of the electrode. The spontaneous production of microtubes was also observed when a platinum plate was used as a working electrode instead of ITO. Therefore, it is reasonable that the production of microtubes is not a specific phenomenon occurring on an ITO electrode.

The IR spectrum of microtubes clearly showed peaks at 1540, 1560, and 3434 cm^{-1}, assigned as stretching vibrations of C–C on pyrrole and benzene rings, and N–H on pyrrole rings, respectively. Elemental analyses indicated that an S/N atomic ratio was 0.6. The results have revealed that polypyrroles in the microtubes are doped by sodium *p*-toluenesulfonate. The XRD pattern of microtubes showed a broad peak centered at 25° of 2θ, indicating a partially crystalline character of microtubes.

Surprisingly and interestingly the microtubes show high electrical conductivity of 498 S cm^{-1} along an axis of the tube in the measurement by a four-point technique. Anisotropy in electrical conductivity was probed by a two-point technique, which is less precise than the four-point one but widely accepted as a technique

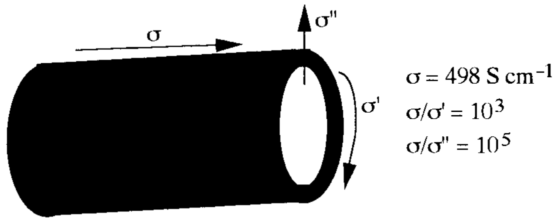

Figure 4. Schematic illustration of anisotropic electrical conduction of the polypyrrole-microtube.

for measurement of such microscopic samples.[10] In the two-point measurement the microtubes show extremely high anisotropy in the electrical conductivity. The conductivity parallel to the long axis (σ) was measured on the microtube. However, those perpendicular to the axis in plane (σ') and across the plane (σ'') were measured for a rectangular sample after cutting the microtube by half along the axis of tube. The electrical conductivities were 131, 2.3×10^{-2}, and 1.2×10^{-3} S cm^{-1}, respectively, for the corresponding directions. Therefore, the ratios of the conductivity parallel to the long axis (σ) to that perpendicular to the axis in plane (σ') and to that across the plane (σ'') are as high as 10^3 (σ/σ') and 10^5 (σ/σ''), respectively, as shown in Figure 4. Such high anisotropy, however, can not be satisfactorily explained by the partial crystalline character of microtubes.

In conclusion we have fortunately first found the spontaneous production of polypyrrole microtubes by electrochemical polymerization of pyrrole in water using sodium *p*-toluenesulfonate as a supporting salt. The partially crystalline microtubes showed high electrical conductivity (σ = 498 S cm^{-1}) along an axis of the tube. The microtubes also revealed extremely high anisotropy in the electrical conductivity. The ratio of the conductivity parallel to the axis (σ) to that perpendicular to the axis in plane (σ') and to that across the plane (σ'') are as high as 10^3 (σ/σ') and 10^5 (σ/σ''), respectively. To the best of our knowledge, the anisotropy could be the highest among spontaneously produced conductive polymers.

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