Synthesis of Long Polypyrrole Micro/Nanotubules with Rectangular Sections

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Novel rectangular-sectioned micro/nanotubules of polypyrrole (PPy) were synthesized via a self-assembly method by using 5-acetamido-4-hydroxy-3-(phenyldiazenyl)naphthalene-2,7-disulfonic acid (Acid Red G) as dopant and $FeCl_3$ as oxidant. Investigation results indicated that the average length of these tubules could be around 530 μm at a certain reaction temperature. Iron(II) 5-acetamido-4-hydroxy-3-(phenydiazenyl)naphthalene-2,7-isulfonate (ARG-Fe(II) salt) with cubic crystal structure was expected to play a template-like role in forming the rectangular-sectioned micro/nanotubules.

Long micro/nanotubules of conducting polymers are attracting more and more attention in current materials science because of their unique properties and potential applications in molecular electronics, optics, and molecular devices. "Template synthesis"[1–3] and self-assembly method[4–11] are two common and effective ways to synthesize micro/nanotubular conducting polymers. Compared with "template synthesis," self-assembly method is simpler and less expensive because no microporous membrane is required to serve as the template in the polymerization and has to be removed afterwards. So far, most reported micro/nanotubules of conducting polymers synthesized via self-assembly method are cylindrical ones and the length of them is only several to one hundred micrometers.[4–6] Few rectangular microtubules were exhibited in the article of Wan,[5] but with no interpretation in detail.

In this letter, we report, for the first time, the synthesis of massive rectangular-sectioned micro/nanotubules of polypyrrole (PPy) with an approximately average of 530 μm in length by using 5-acetamido-4-hydroxy-3-(phenyldiazenyl)naphthalene-2,7-disulfonic acid (Acid Red G) as the dopant and $FeCl_3$ as the oxidant via a self-assembly method. The synthetic procedure was as follows: Pyrrole monomer was distilled under reduced pressure. Other reagents were used as received without further treatment. 2.04 g (4 mmol) of Acid Red G was dissolved in 30-mL deionized water and then mixed with 1.34 g (20 mmol) of pyrrole (Py) with magnetic stirring for 30 min at room temperature. Subsequently, 33.4 mL of 1 M aqueous $FeCl_3$ solution was added dropwise in 2 h. The whole polymerization was maintained for 24 h with gentle stirring (stirring rate $\leq$ 200 rpm) or without any stirring at 5 °C. Precipitated PPy was filtered and washed by deionized water and followed by methanol several times until the used methanol became colorless. The product was then dried in a vacuum oven at 25 °C for 12 h.

The SEM images were used to characterize the morphology of product by using a Hitachi-530 scanning electron microscope and a field emission scanning electron microscope (FESEM, JEOL, JSM-6700F). The Fourier-transform infrared (FTIR, Nicolet, FT-IR6000) spectra data were used to analyze the molecular structure of the obtained PPy. The crystalline phases of the sample were identified by an X-ray diffraction (XRD, Rigaku, D/MAX-2400X) using graphite monochromized Cu Kα radiation (45 kV, 15 mA). The conductivity of these tubules at room temperature was measured by a four-probe conductivity meter (SZ85).

The morphology of prepared PPy micro/nanotubules was shown in Figure 1. Figure 1a presented a cluster of PPy micro/nanotubules in a regular arrangement. Figure 1b showed that these tubules had obvious arrises. Figure 1c proved that these tubules were rectangular. The average length of these PPy micro/nanotubules was about 530 μm. The side length of tubule section and the thickness of tubule walls were estimated to be 150 nm–2 μm and 50 nm, respectively. Figures 1c and 1d also revealed that these tubules were hollow.

The FTIR spectra of the rectangular micro/nanotubules showed the characteristic PPy structure. For instance, the pyrrole-ring fundamental vibration centered at 1547 and 1460 cm^{-1}, the =C–H in-plane deformation at 1295, 1093, and 1038 cm^{-1} as well as the N–H stretching vibration at 3429 cm^{-1}, were observed. This result was consistent with the literature.[11,12] At the same time, two peaks at 2921 and 2853 cm^{-1} corresponding to the C–H stretching vibration in $–CH_3$ group and the peak at 1638 cm^{-1} assigned to the C=O vibration in acylamino group were also observed. These three peaks indicat-

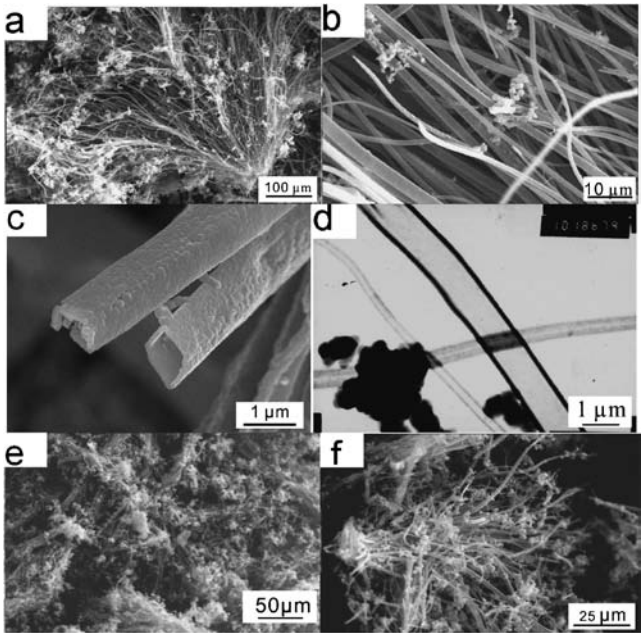

Figure 1. (a), (b), (c), (e), (f) SEM and (d) TEM images of PPy micro/nanotubules. [Py] = 0.31 M, [Acid Red G] = 0.062 M, [$FeCl_3$] = 0.51 M, no stirring, (a), (b), (c), (d) 5 °C; (e) 0 °C; (f) 15 °C.

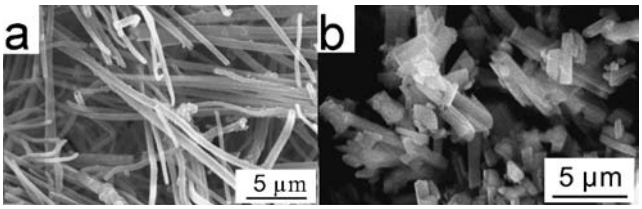

Figure 2. SEM images of (a) PPy micro/nanotubules. [Py] = 0.31 M, [Acid Red G] = 0.062 M, [$FeCl_3$] = 0.51 M, 5 °C, stirring rate = 200 rpm. (b) ARG-Fe(II) salt. The product of Acid Red G reacting with $FeCl_2$.

ed the presence of dopant in prepared PPy micro/nanotubules and thus proved that the PPy rectangular micro/nanotubules obtained were doped.

There was only one broad peak centered at $2\theta = 26.5°$ that could be observed in the X-ray diffraction pattern of the prepared PPy tubules, indicating that these PPy tubules were amorphous. The maximum conductivity of these tubules was measured to be 28.6 S·cm^{-1} by a four-probe conductivity meter at room temperature.

The formation of PPy rectangular micro/nanotubules was strongly affected by reaction conditions. The results revealed that the reaction temperature influenced the length of the PPy rectangular micro/nanotubules. As shown in Figure 1a, the lengths of PPy tubules obtained at 5 °C were approximately 530 μm. When the reaction temperature decreased from 5 °C to 0 °C, it was found from Figure 1e that PPy tubules became shorter, which was only 150 μm in length. On the other hand, when the temperature went up to 15 °C, the length of tubules decreased to 100 μm (Figure 1f), which was also much shorter than the ones obtained at 5 °C.

The influence of temperature on the length of PPy micro/nanotubules could be interpreted by the mechanism of PPy tubules formation. We know that the polymerization rate of pyrrole monomer was affected by the temperature. Wan et al.[7] found that the formation of PPy micro/nanotubules via template-free method was a slow self-assembled process. At a higher temperature (e.g. 15 °C), however, the polymerization accomplished fast, i.e., PPy formed in a very short period. In such a fast polymerization, PPy was very unlikely to aggregate to form micro/nanotubules. On the other hand, while the temperature was lower (e.g. 0 °C), although the polymerization was slow enough for PPy to aggregate, the tubules did not grow as long as the tubules grew at 5 °C during the same reaction time.

Interestingly, when the polymerization process was under vigorous stirring (stirring rate ≥ 200 rpm), the morphology of obtained PPy turned out to be hollow cylindrical tubules (Figure 2a) which were similar to the tubular PPy synthesized with β-naphthalene sulfonic acid (β-NSA) as dopant by Wan et al.[7] In Wan's article, the micelles formed by the dopant which was an anionic surfactant were interpreted to act as templates in forming the cylindrical micro/nanotubules. Acid Red G had both hydrophilic and hydrophobic groups and might tend to form some micelles in the reaction solution. However, micelles are cylindrical or spherical and can not work as the templates of rectangular-sectioned tubules. How did the rectangular tubules form in our experiment? We thought that the formation mechanism is as follows: During the reaction process, Fe^{3+} ions from $FeCl_3$ was reduced into Fe^{2+} ions which then reacted with Acid Red G and produced iron(II) 5-acetamido-4-hydroxy-3-(phenyldiazenyl)naphthalene-2,7-disulfonate (ARG-Fe(II) salt) with cubic crystal structure. As shown in Figure 2b, the morphology and dimensions of ARG-Fe(II) salt matched the ones of rectangular PPy micro/nanotubules. Thus, we speculated that ARG-Fe(II) salt was produced within the micelles formed by the dopant and would play a template-like role in stationary reaction system. PPy aggregated on the surface of micelles with crystals inside and grew along the one-dimensional direction simultaneously to form the rectangular-sectional micro/nanotubules. XRD data of rectangular PPy tubules and ARG-Fe(II) salt revealed that ARG-Fe(II) salt did exist in PPy tubules before washed by methanol. However, violently stirring action disrupted the stationary system and crystals of ARG-Fe(II) salt could not exist in the micelles stably. Thus, micelles of the dopant without crystals of the salt inside were expected to work as the template-like role[7] and cylindrical tubules were formed. On the basis of this idea, further study on formation mechanism is underway currently.

In summary, PPy rectangular-sectioned micro/nanotubules with typical size of 0.15–2.0 μm in side length and about 50 nm in wall thickness were prepared massively via a self-assembly method by using Acid Red G as dopant and $FeCl_3$ as oxidant. The maximum conductivity of obtained tubules is 28.6 S·cm^{-1}. At a certain reaction temperature (about 5 °C), long micro/nanotubules of PPy with an average length up to 530 μm could be obtained. ARG-Fe(II) salt produced during the reaction process was proposed to play a template-like role in determining the rectangular-sectioned morphology of PPy micro/nanotubules.

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