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Microtubules of polypyrrole synthesized by an electrochemical template-free method

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Microtubules of polypyrrole (PPy) were synthesized by an electrochemical template-free method in the presence of β-naphthalenesulfonic acid (β-NSA) as a dopant for the first time. The influence of electrochemical polymerization conditions, such as material of the working electrode, the concentration of β-NSA and pyrrole monomer, current density and polymerization time on the tubular morphology of PPy-NSA was systematically investigated. PPy-NSA tubules 0.8–2.0 μm in diameter and 15.0–30.0 μm in length were obtained when a non-corrosive steel plate was used as the working electrode, and the size of the tubules was affected by other polymerization conditions. The molecular structure of the tubules was characterized by FTIR and X-ray diffraction, indicating that their polymer chains are similar to granular PPy synthesized by other chemical or electrochemical methods, and the tubules were amorphous. The conductivity of the tubules at room temperature was found to be about 5.0 S cm^{-1} and the temperature dependence of the conductivity followed a two-dimensional Variable Range Hopping (2D-VRH) model. It was proposed that the absorbed micelles of β-NSA, which result from the surfactant characteristics of β-NSA dopant on the working electrode, act like templates in forming PPy-NSA tubules by this new method.

Introduction

Since the discovery of carbon nanotubes (CNTs),[1] nanoscale materials including nanotubes or nanofibers have attracted considerable attention because of their unique properties and potential applications in molecular electronics, optics and biomedical science.[2,3] Martin *et al.*[4–8] have used commercial membranes as templates, the template-synthesis method, to prepare a nanofibrous composite of metal, semiconductor and conducting polymer. This method has successfully been applied in the synthesis of micro- or nanotubules of polyacetylene (PA),[9] polypyrrole (PPy)[9] and polyaniline (PANI).[10,11] PPy with controlled fibrilar morphology has also been reported in the literature.[12–15] Recently, PPy nanotubules and nanowires have been synthesized using nanoporous particle track-etched membranes (nano-PTM) as templates[16–19] Furthermore, PPy microwires synthesized by electrochemical polymerization with a scanning microneedle as an electrode have been reported.[20] In particular, Wan *et al.*[21] reported that PANI[22] and PPy[23] microtubules could be synthesized by *in-situ* doping polymerization in the presence of β-naphthalenesulfonic acid (β-NSA) as the dopant. This is termed the template-free method because no template is involved. Compared to the template-synthesis method, the template-free method is simple and cheap because no micro- or nano-porous membranes are used as templates. Our previous research proved that the chemical template-free method is a reliable and practical method in the synthesis of PANI and PPy microtubules,[24] but it is not known whether PANI and PPy microtubules could be synthesized by an electrochemical template-free method. It is well known that electrochemical reactions can be easily controlled by adjusting the applied potential or current density and polymerization time. Among conducting polymers, PPy stands out because it has a high conductivity and large variety of applications,[25–29] and the electrochemical method is an effective method in the preparation of large-scale free standing films of PPy with high conductivity.[30–31] Therefore we examined the possibility of synthesizing PPy microtubules by an electrochemical template-free method.

In this article, the synthesis of microtubules of PPy-NSA by an electrochemical template-free method is reported for the first time. The influence of electrochemical polymerization conditions, such as working electrode (materials, smoothness of surface and distance between working electrode and counter-electrode), current density, concentration of β-NSA and pyrrole monomer and polymerization time, on the tubular morphology of PPy-NSA was systematically investigated. The characteristics of molecular structure, electrical properties and the formation mechanism of the PPy-NSA microtubules are discussed.

Experimental

The pyrrole monomer was distilled under reduced pressure. β-NSA as a dopant was used as received. The concentration of β-NSA ranged from 0.05 mol L^{-1} to 1.0 mol L^{-1}, while the concentration of pyrrole monomer varied from 0.25 to 1.0 mol L^{-1} at a given molar ratio of β-NSA to pyrrole (*i.e.* 1 : 1). Electrochemical template-free polymerization was performed in a conventional one-compartment cell with two electrodes (15×25 mm^2) at room temperature. Non-corrosive steel plate, indium tin oxide (ITO) coated glass, and highly ordered polylytic graphite (HOPG) were used as the working electrodes, non-corrosive steel plate was used as a counter-electrode. The distance of the two electrodes was changed from 5 mm to 15 mm. Current density between 0.05 mA cm^{-2} and 1.0 mA cm^{-2} was applied. A typical synthesis of the microtubules was as follows: 0.76 ml pyrrole monomer and 3.147 g β-NSA dissolved in 20 ml deionized water was mixed with stirring at room temperature for 20 minutes to form a pyrrole–β-NSA solution. The resulting mixture looked like an emulsion

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which may be due to surfactant characteristics of the β-NSA dopant. The above solution was pulled into the electrochemical cell with stirring, then 1.2 V was applied between the two electrodes for 1 minute in order to accelerate electrochemical polymerization of pyrrole to obtain the doped PPy-NSA. Consequently, a black thin film of PPy-NSA was coated on the working electrode after polymerization for 1 minute, then a constant current polymerization was performed.

The applied voltage and current were provided by Advanst R1642 programmable DC Voltage/Current generator. The morphology of PPy-NSA was measured with scanning electron microscopy (SEM, Hitachi 530) and transmission electron microscopy (TEM, JEM-200 CX). The molecular structure of PPy-NSA was characterized by FTIR spectra (Perkin-Elmer System) and X-ray diffraction spectra (RINT-2000 wide-angle goniometer). The conductivity of PPy-NSA at room temperature was measured by a four-probe method using a Keithley 196 System DMM Digital Multimeter and Advanst R1642 Programmable dc-voltage/current generator as the current source. Temperature dependence of the conductivity was carried out on a CT1 Cryogenics Refrigerator controlled by a DRC-91 CA temperature controller.

Results and discussion

1. Morphology

In order to find the optimal conditions for formation of PPy-NSA microtubules by the electrochemical template-free method, we first studied the influence of the working electrode (materials, surface smoothness and distance between working electrode and counter-electrode), on the tubular morphology of PPy-NSA. Fig. 1 shows that the morphology of PPy-NSA is significantly affected by changes in the working electrode. For an ITO electrode, round grains with different diameters (up to 3.0 µm) were observed (Fig. 1a). However, irregular grains containing a few "rods" 1–2 µm in diameter and 5–20 µm in length were obtained when HOPG was used as the working electrode (Fig. 1b). In particular, fibrous PPy-NSA 0.7–2.0 µm in diameter and about 15 µm in length was observed when a non-corrosive steel plate was used as the working electrode (Fig. 1c). TEM images proved that those fibers were hollow as shown in Fig. 2. Obviously, the above results showed that PPy-NSA microtubules could only be synthesized by electrochemical template-free polymerization using a non-corrosive steel plate as the working electrode. Non-corrosive steel as the working electrode is essential for synthesizing PPy-NSA microtubules by this new method. As mentioned in the Experimental, the solution containing pyrrole monomer and β-NSA dopant looked like an emulsion due to the surfactant characteristics of the β-NSA dopant. It is reasonable to assume that these micelles play a template-like role in controlling the morphology of the resulting PPy-NSA.[32] In addition, the morphology of the absorbed micelles on the surface of the electrode is affected by the surface state of the working electrode and the interaction between micelles and working electrode. Thus, it is expected that the morphology of PPy-NSA formed on the surface of the working electrode should be affected by the working electrode used. As a result, the following results and discussion were based on using non-corrosive steel as the working electrode.

In order to study the influence of the surface state of the electrode (*e.g.* surface smoothness) on the tubular morphology of PPy-NSA, the non-corrosive steel was polished by metallographic emery papers along the length direction of the electrode, then it was washed with acetone and deionized water several times. It was found that the order of the PPy-NSA microtubules strongly depended on the surface smoothness of the electrode. For a non-polished electrode, for example, uniform and randomly distributed microtubules 0.8–1.0 µm in

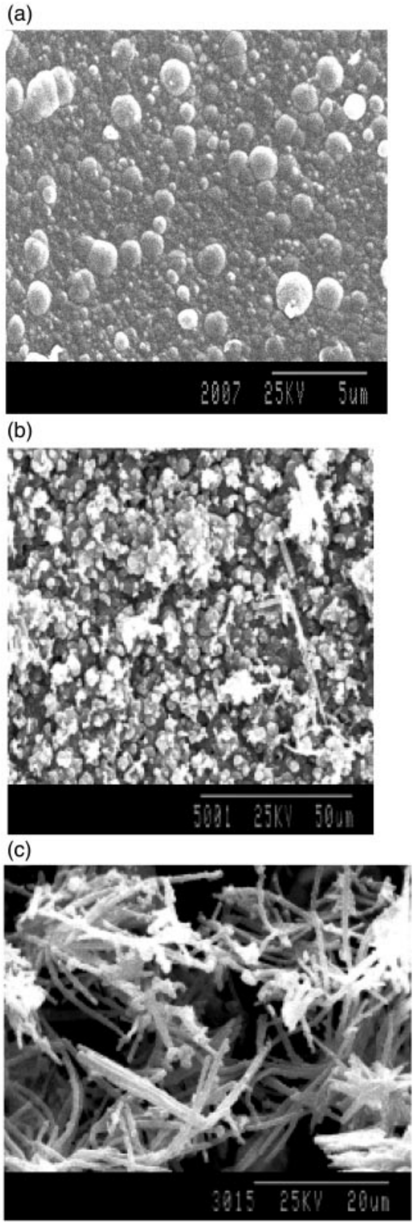

Fig. 1 SEM images of PPy-NSA synthesized by the electrochemical template-free method with (a) ITO, (b) HOPG, (c) non-corrosive steel as the working electrode. Pyrrole: 0.53 mol L^{-1}, β-NSA: 0.57 mol L^{-1}, $j = 0.36$ mA cm^{-2}, polymerization time: 5 minutes.

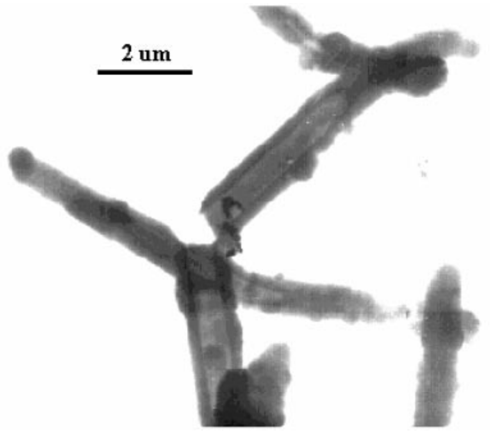

Fig. 2 TEM image of PPy-NSA microtubules. Pyrrole: 0.53 mol L^{-1}, β-NSA: 0.57 mol L^{-1}, $j = 0.36$ mA cm^{-2}, polymerization time: 5 minutes.

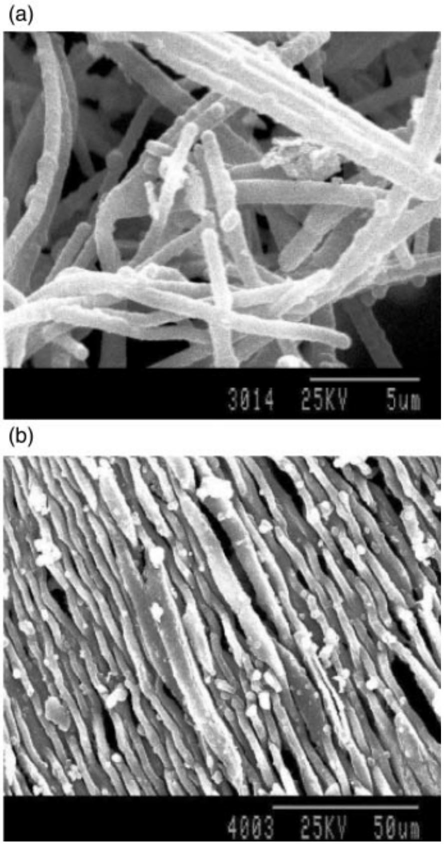

Fig. 3 Influence of polish treatment of the working electrode on the morphology of the PPy-NSA. (a) Non-polished. (b) Polished. β-NSA: 0.57 mol L^{-1}, pyrrole: 0.53 mol L^{-1}, $j = 0.36$ mA cm^{-2}, polymerization time: 5 minutes.

diameter and up to 20 μm in length were formed (Fig. 3a). For a polished electrode, on the other hand, orderly, rough and rope-like fibers were obtained (Fig. 3b). Such orderly fibers may be a result of the scratched traces produced by the polish treatment. In other words, the PPy-NSA "nucleus" was first formed along the scratched traces, then it had grown to form orderly PPy-NSA tubules. It should be noted that the influence of the distance between two electrodes on the tubular morphology of PPy-NSA microtubules was negligible when the distance changed from 5 mm to 15 mm.

With respect to the current density, uniform microtubules were formed when the current density varied from 0.05 mA cm^{-2} to 0.75 mA cm^{-2} as shown in Fig. 4. PPy-NSA microtubules 0.8–2 μm in diameter and about 15 μm in length, for example, were obtained when the current density was lower than 0.75 mA cm^{-2}, indicating that the influence of current density on the morphology and the size of tubular PPy-NSA was negligible. However, irregular PPy-NSA tubules were observed when the current density was greater than 1.0 mA cm^{-2} as a result of the high polymerization rate, which forms large amounts of PPy-NSA within a short time. In contrast, the morphology of PPy-NSA depended strongly on the concentration of β-NSA and pyrrole monomer used. As Fig. 5 shows, an increase in the concentration of β-NSA favors the formation of tubular PPy-NSA except for a concentration of 0.05 mol L^{-1}. The diameter and length of the PPy-NSA increased with increasing concentration of β-NSA as shown in Table 1. However, the optimal concentration of β-NSA for forming PPy-NSA microtubules was found to be about 0.57 mol L^{-1}. At this concentration, uniform PPy-NSA microtubules 0.8–1.0 μm in diameter and about 15 μm in length were obtained. This value (*i.e.* 0.57 mol L^{-1}) was consistent with the results obtained by chemical template-free method.[24] For a given molar ratio of pyrrole to NSA (*e.g.* 1 : 1), the diameter of the PPy-NSA became larger when the concentration of pyrrole monomer was higher. As shown in Table 2, the diameter increased from 1–2 μm to 4–5 μm, when the concentration of pyrrole varied from 0.25 mol L^{-1} to 1.0 mol L^{-1}. On the other hand, thin and flexible PPy-NSA microtubules were obtained when the concentration of pyrrole was lower.

2. Formation mechanism of microtubules

The important results described above are summarized as follows. 1. Non-corrosive steel as the working electrode was essential for forming PPy-NSA microtubules by the new method. 2. The diameter and length of the microtubules were affected by the current density and especially the concentration of β-NSA and pyrrole monomer, however, their tubular morphology was not affected. In order to further investigate the growth processes of these tubules, SEM images of the PPy-NSA as-synthesized for different polymerization times were measured and the obtained results are shown in Fig. 6. It was found that the size of the PPy-NSA microtubules increased with prolonged polymerization time. The diameter of the microtubules increased from 0.8–2 μm to 3–5 μm, and its length extended from 15 μm to 20 μm when the polymerization time was prolonged from 5 minutes to 60 minutes. However, the tubular morphology did not change when the polymerization time increased; this indicates that the tubular morphology has been formed at the initial polymerization stage. These results suggest that the electrochemical formation of PPy-NSA microtubules is a fast process which occurs within less than 1 minute. This is quite different from the formation process of PPy-NSA microtubules synthesized by the chemical template-free method. In the latter case, a growth process of grain–short tube–long tube took place and the growth process is a slow and self-assembled process.[33] In fact, β-NSA acts as a hydrotrope, and anionic surfactant, which increases the solubility of organic compounds in water.[34] Therefore, pyrrole could be dissolved in β-NSA solution, and β-NSA tended to form micelles in a high concentration. These micelles could be considered as "template-like" in forming the PPy-NSA tubules.[33] Thus, it is expected that the absorbed micelles on the working electrode (*e.g.* non-corrosive steel plate) play a template-like role and form PPy-NSA microtubules on the electrode *via* electrochemical polymerization. This is why the growth process of PPy-NSA microtubules is a fast process when the electrochemical template-free method was used, and the size of tubules was only affected by the polymerization conditions (*e.g.* the concentration of β-NSA and pyrrole monomer, current density and polymerization time).

3. Structural characterization and electrical properties

Fig. 7 shows the FTIR spectra of PPy-NSA tubules, and the assignment of typical characteristic bands is given in Table 3. The spectra show that the polymer chains of the PPy-NSA microtubules are similar to the PPy-NSA synthesized by other chemical or electrochemical methods.[35-37] Two peaks at 1648 cm^{-1} and 1036 cm^{-1} corresponding to the naphthalene ring and $-SO_3^-$ group were observed. This indicates that PPy is doped by β-NSA, which is consistent with a conductivity of these tubules at room temperature measured by a four-probe method of about 5.0 S cm^{-1}. However, a difference in the FTIR spectra between granular and tubular PPy-NSA was observed. The peak at 3349 cm^{-1} corresponding to the N–H bond of PPy-NSA microtubules was very weak, for example, while that of PPy-NSA grains at 3424 cm^{-1} was strong. The peaks at 470 cm^{-1}, 558 cm^{-1}, 616 cm^{-1}, 856 cm^{-1}, moreover, were slightly blue-shifted compared with those of PPy-NSA grains. This may suggest that the condensed state in PPy-NSA microtubules is different from that of the PPy-NSA grains. The

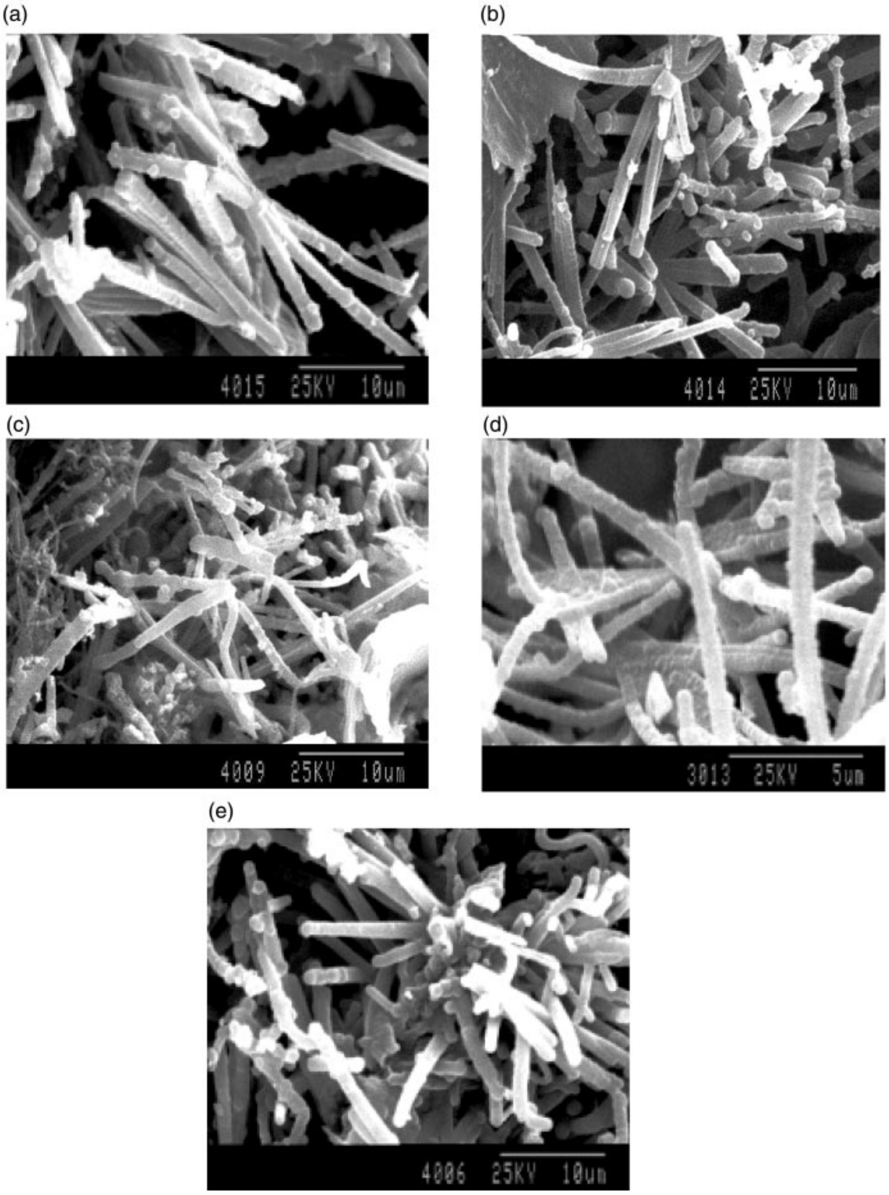

Fig. 4 SEM images of the PPy-NSA synthesized at different current density (a) 0.05 mA cm^{-2}; (b) 0.15 mA cm^{-2}; (c) 0.25 mA cm^{-2}; (d) 0.36 mA cm^{-2}; (e) 0.75 mA cm^{-2}. Pyrrole: 0.53 mol L^{-1}, β-NSA: 0.57 mol L^{-1}, polymerization time: 5 minutes.

X-ray scattering pattern of the PPy-NSA showed that these PPy-NSA microtubules are amorphous, which was consistent with results obtained from chemical template-free method.[23]

The conductivity of the PPy-NSA microtubules at room temperature was estimated by the four-probe method to be *ca.* 5.0 S cm^{-1}. This is not only consistent with that of PPy-NSA grains (6.3 S cm^{-1}), but also in agreement with that of PPy-NSA synthesized by chemical template-free method (10.0 S cm^{-1}).[23] Temperature dependence of conductivity of these PPy-NSA microtubules showed a semiconductor behavior, and followed two dimensional Variable Range Hopping (2 D-VRH) model proposed by Mott[38] (Fig. 8), which can be expressed as shown in eqn. (1).

$$\sigma(T) = \sigma_o \exp\left(-(T_o/T)^{1/3}\right) \qquad (1)$$

Where σ_o is a constant, T_o the hopping barrier, and T the Kelvin temperature. T_o was calculated to be about 1.43×10^5 K. For tubular PPy-NSA synthesized by chemical template-free method the temperature dependence of conductivity was best fit to a 3 D-VRH model with a T_o value of 1.54×10^5 K.[23] These differences may be due to their different condensed states caused by different polymerization methods. Moreover, it should be noted that the $\ln(\delta T)$–$T^{-1/3}$ curve measured by following temperature increase was slightly different from that measured by cooling down temperature, indicating these PPy-NSA microtubules are thermally irreversible.

Conclusion

PPy-NSA microtubules with 0.8–2 μm diameter and 15–30 μm length were synthesized by an electrochemical template-free method in the presence of β-NSA as the dopant for the first time. Influence of the polymerization conditions (*e.g.* electrode materials, concentration of β-NSA and pyrrole monomer as well as polymerization time) on the morphologies of the PPy-NSA was investigated. The use of non-corrosive steel as the working electrode is important in forming PPy-NSA tubules by the new method, while other parameters only change the size of the tubules. The formation of PPy-NSA tubules synthesized by the new method is a fast-growth process, in particular, it is mainly completed at initial polymerization stage, and absorbed micelles of β-NSA on the working electrode act as templates in forming PPy-NSA tubules due to the surfactant characteristic

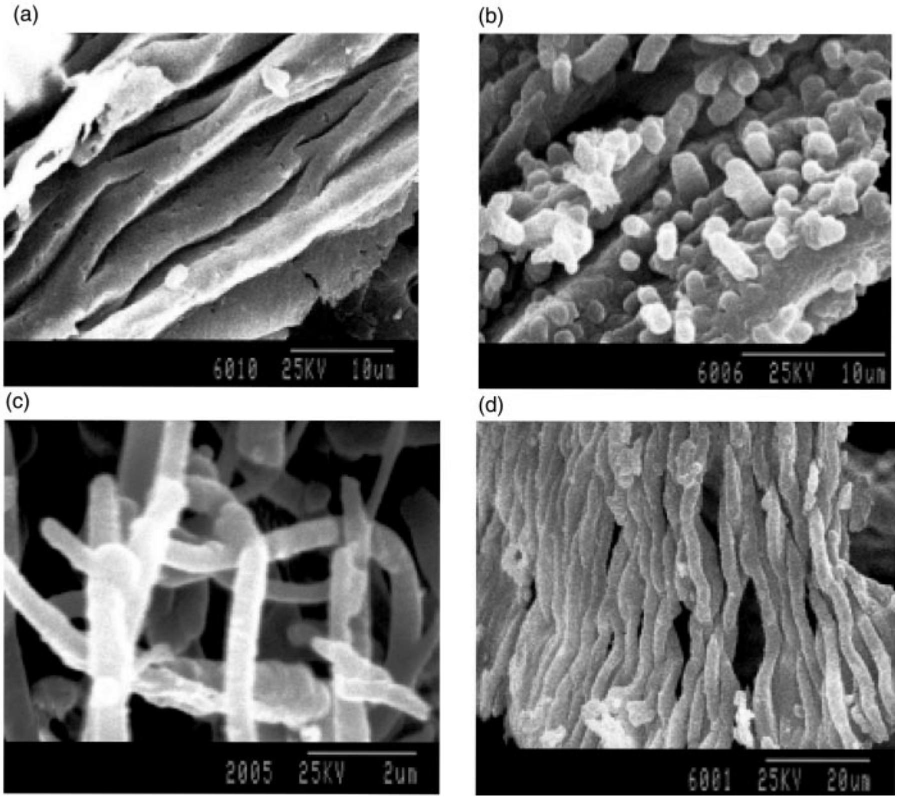

Fig. 5 SEM images of the PPy-NSA synthesized at different concentrations of β-NSA (a) 0.05 mol L^{-1}, (b) 0.1 mol L^{-1}, (c) 0.57 mol L^{-1}, and (d) 1.0 mol L^{-1}. Pyrrole: 0.53 mol L^{-1}, $j = 0.36$ mA cm^{-2}, polymerization time: 5 minutes.

Table 1 The size of PPy-NSA microtubules synthesized in solutions with different concentrations of β-NSA

The concentration of NSA/mol L^{-1}	0.05	0.1	0.57	1.0
Diameter/μm	—	0.8–1	0.8–1	1–2
Length/μm	—	5	15	30

Table 2 The size of PPy-NSA microtubules synthesized in solutions with different concentrations of pyrrole monomer

The concentration of pyrrole monomer/mol L^{-1}	1.0	0.53	0.25
Diameter/μm	4–5	1–2	1–2
Length/μm	30	30	30

of β-NSA dopant. Some differences in the growth process of the tubules between chemical and electrochemical template-free method were observed. The electrical properties of PPy-NSA tubules synthesized by the new method are slightly different from those of the PPy-NSA tubules synthesized by chemical template-free method due to their different condensed states.

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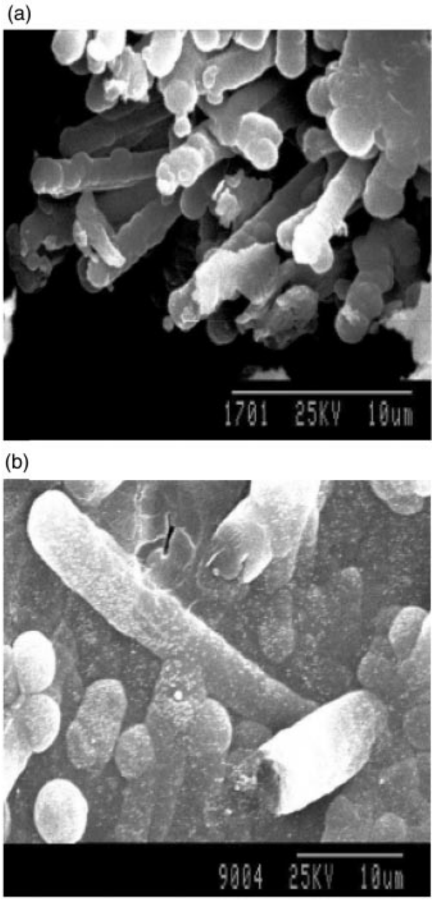

Fig. 6 SEM images of the PPy-NSA synthesized at different polymerization times (a) 1 minute, and (b) 60 minutes. β-NSA: 0.57 mol L^{-1}, pyrrole: 0.53 mol L^{-1}, $j = 0.36$ mA cm^{-2}.

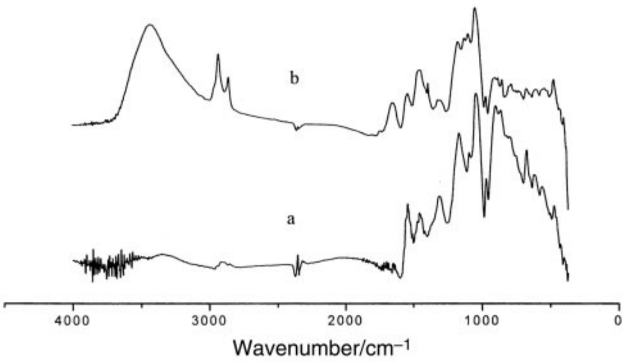

Fig. 7 FTIR spectra of the PPy-NSA (a) microtubules synthesized using non-corrosive steel and (b) grains synthesized using indium tin oxide ITO coated conducting glass as the working electrode. Pyrrole: 0.53 mol L^{-1}, β-NSA: 0.57 mol L^{-1}, $j = 0.36$ mA cm^{-2}, polymerization time: 5 minutes.

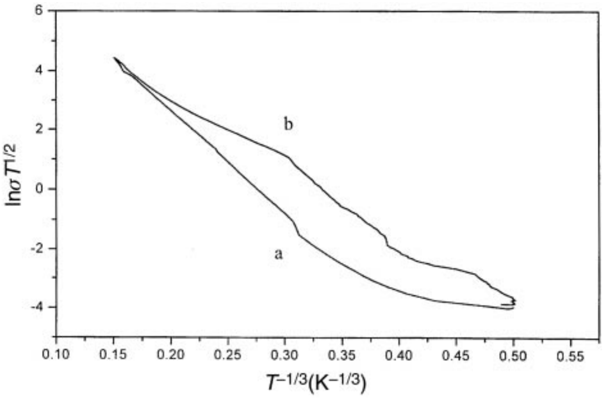

Fig. 8 Temperature dependence of conductivity of PPy-NSA microtubules. (a) Raising temperature, (b) Cooling down temperature. Pyrrole: 0.53 mol L^{-1}, β-NSA: 0.57 mol L^{-1}, $j = 0.36$ mA cm^{-2}, polymerization time: 5 minutes.

Table 3 FTIR absorption bands for PPy-NSA synthesized by electrochemical template-free method[a]

Band designation/cm^{-1}	A	B	C	D	E	F	G
	C=C & C–C str.	C–N str.	C–C & N–H def.	C–N str. & C–H def.	C–H def.	Ring def.	C–H wag.
PPy[b]	1551	1455	1307	1179	1042	933	796
Ppy-NSA grains	1534	1439	1314	1164	1036	965	779
Ppy-NSA microtubules	1538	1453	1307	1161	1036	965	793

[a] Abbreviations: str. = stretching; def. = deformation; wag. = waging. [b] Synthesized by other chemical or electrochemical methods.[10]

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