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Synthesis and formation mechanism study of rectangular-sectioned polypyrrole micro/nanotubules

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Abstract

Aligned polypyrrole (PPy) micro/nanotubules were synthesized via a self-assembly method using $FeCl_3$ as oxidant and Acid Red 1 (C.I. 18050, 5-(acetylamino)-4-hydroxy-3-(phenylazo)-2,7-naphthalenedisulfonic acid) as dopant. PPy has a typical length of 530 μm and a unique rectangular-sectioned morphology. Its general morphology could be manipulated by varying synthetic conditions including polymerization time, monomer concentration, oxidant species, and stirring. The synthesized PPy and reaction intermediates were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and solubility tests in methanol and water. Our observation and results suggest a plausible formation mechanism of rectangular-sectioned PPy micro/nanotubules. AR1–Fe(II) complex formed from the complexation of Acid Red 1 and Fe^{2+}(reduced from Fe^{3+}), which precipitated in the aqueous solution, might have functioned as 'template' during the polymerization of pyrrole monomers. The conductivity of PPy with different morphologies was also measured and compared.

Keywords: Polypyrrole; Rectangular; Micro/nanotubules

1. Introduction

Intrinsically conducting polymers have gained wide attentions for their unique electroactive properties and potential applications in molecular electronics [1,2], electrical displays [3,4], chemical and biomedical sensors [5–7], and drug delivery [8]. Particularly, conducting polymer micro/nanotubular structures are of great interests for their metal-like conductivity. They are excellent templates or 'micro/nanoreactors' to manufacture molecular wires or rings which are elements of molecular devices [9]. On the other hand, among the conductive polymers, polypyrrole (PPy) is one of the most extensively studied conducting polymers for its high conductivity and long-term environmental stability [10–12].

Previous studies have used template-synthesis method to prepare PPy micro/nanostructures [13–16]. A typical template-synthesis process uses a microporous or nanoporous membrane as a template to control the PPy structure during the polymerization, which also needs to be removed after the synthesis. Wan's group [9,17–20] developed a self-assembly method and prepared PPy and polyaniline (PANI) micro/nanotubules. Because of not using external template, the self-assembly method has been considered a convenient way to prepare conducting polymer micro/nanotubules [21–23].

Despite of its simplicity, self-assembly method has not been widely applied because the morphology of PPy tubules fabricated by self-assembly method is generally unsatisfactory comparing to those obtained by template-synthesis. The self-assembly method has the advantage of simplicity and potentially lower cost, but it also has the difficulty in manipulating the morphology of product due to the absence of template during the synthesis. Previously synthesized PPy and PANI tubules using self-assembly method [9,17–23] were exclusively cylindrical, with a typical length less than 100 μm [19,20,22]. Synthesis of PPy micro/nanotubules with rectangular sections or longer length has not been achieved so far via the self-assembly method. However, long conducting polymer

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tubules are preferred as long tubules can be easily tailored for various applications but insufficient length will limit their applications. In addition, PPy micro/nanotubules with rectangular sections may be highly desirable for some uses because the remarkable rectangular-sectioned micro/nanotubules may exhibit exceptional optical and mechanical properties that are not achievable in circular PPy micro/nanotubules [24].

To our best knowledge, the synthesis of rectangular PPy tubules has not been reported yet except in our previous study [25]. In this paper, we synthesized PPy with different morphologies, i.e. granular, cylindrical, and rectangular-sectioned micro/nanotubules, by controlling synthetic conditions in a self-assembly process. The formation mechanism of rectangular-sectioned PPy micro/nanotubules was studied by characterizing resultant PPy and reaction intermediates sampled at various conditions. The conductivity of PPy rectangular-sectioned micro/nanotubules, cylindrical micro/nanotubules, and granule was also measured and discussed.

2. Experimental

2.1. Materials

Pyrrole (98%, Sigma–Aldrich) monomers were distilled at reduced pressure. The treated pyrrole was refrigerated and stored in the dark under the protection of nitrogen. Acid Red 1 (5-(acetylamino)-4-hydroxy-3-(phenylazo)-2,7-naphthalenedisulfonic acid) was purchased from Aldrich and was used as dopant in the synthesis. The molecular structure of Acid Red 1 is shown in Fig. 1. The sulfonic groups provide the hydrophilicity of Acid Red 1, and the hydroxyl and azo groups adjacent to the naphthol ring are strong ligands which could form complexes with transitional metal ions [26]. The as-received Acid Red 1 was purified by repeated crystallization in methanol before use. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, ≥98%, Beijing Chemicals), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, 99%, Beijing Chemicals), methanol (anhydrous, 99.8%, Aldrich), and ammonium persulfate (APS, ≥98%, Fluka) were used as-received.

2.2. Preparation

The synthesis process of the rectangular-sectioned PPy micro/nanotubules was as follows: 1 mol L^{-1} $FeCl_3$ aqueous solution was prepared by dissolving ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in deionized water. The prepared $FeCl_3$ solution was used as the oxidant. Pyrrole monomer of 20 mmol (1.4 mL) and 4 mmol Acid Red 1 were dissolved in 30 mL deionized water with vigorous magnetic stirring for 30 min. A total amount of 33.4 mL of the prepared $FeCl_3$ solution was added dropwise into the solution for 2 h without stirring at 278 K. The resultant mixture was allowed to stand for 24 h. The precipitated PPy solids were filtered and washed with a large volume of deionized water until the filtrate became colorless. The PPy solids were further purified by a soxhlet extraction using methanol as the solvent until the extraction solution became colorless. The obtained PPy solids were dried in vacuum oven for 12 h at 298 K.

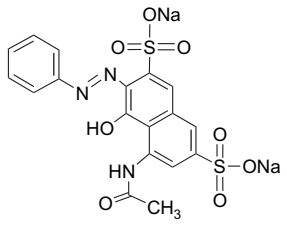

Fig. 1. The molecular structure of the dopant Acid Red 1.

Experimental conditions were varied to investigate their influences on the morphology of resultant PPy. The effect of polymerization time was investigated by allowing the reaction to stand for 2, 4, and 24 h respectively, and examining the morphology of resultant PPy. Other conditions were unchanged. The effect of pyrrole concentration was studied at two initial monomer concentrations (0.31 and 0.15 mol L^{-1}) with other conditions unchanged. The influence of oxidant was investigated by replacing the 33.4 mL of 1 mol L^{-1} $FeCl_3$ solution with 33.4 mL of 0.5 mol L^{-1} ammonium persulfate (APS) solution with other conditions unchanged.

To study the formation mechanism of rectangular-sectioned PPy micro/nanotubules, two Acid Red 1 solutions were prepared separately by dissolving 4 mmol Acid Red 1 into 30 mL deionized water; 33.4 mmol $FeCl_2 \cdot 4H_2O$ and 33.4 mmol $FeCl_3 \cdot 6H_2O$ were added into the Acid Red 1 solutions for 2 h with gentle stirring. The precipitated solids in two solutions, designated as AR1–Fe(II) and AR1–Fe(III), were filtered and washed with deionized water. The solubility of AR1–Fe(II) was tested in deionized water and methanol, respectively.

2.3. Characterization

Morphologies of PPy obtained at different experimental conditions were examined by transmission electron microscope (TEM, Hitachi JEM-200CX), scanning electron microscope (SEM, Hitachi-530), and field emission scanning electron microscope (FESEM, JEOL JSM-6700F). AR1–Fe(II) and AR1–Fe(III) solids were characterized by SEM. The synthesized rectangular-sectioned PPy micro/nanotubules (unwashed and methanol-washed), AR1–Fe(II), and AR1–Fe(III) solids were examined by powder X-ray diffraction (XRD) on a Rigaku D/Max-2400X X-ray diffractometer with Cu Kα radiation. The conductivity of PPy was measured by the four-probe method using a Keithley 196 SYSTEM DMM digital multimeter, and an ADVANTEST R6142 programmable DC voltage/current generator as the current source. All conductivity measurements were conducted at room temperature.

3. Results and discussion

3.1. Morphology

Fig. 2 shows the morphology of synthesized PPy micro/nanotubules. In Fig. 2(a) and (b), most PPy tubules have