



Optimization routes for high electrical conductivity of polypyrrole nanotubes prepared in presence of methyl orange

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ABSTRACT

The synthesis of polypyrrole nanotubes using methyl orange as a structure guiding agent is a popular method for obtaining electrically conductive material of nanostructured morphology. This work presents certain route of chemical synthesis, where the experimental conditions were optimized in order to obtain a material with high conductivity (up to 91.6 S cm^{-1}) and specific surface area (up to $67.6 \text{ m}^2 \text{ g}^{-1}$) via modification of two parameters: a) the methyl orange concentration (from 0.5 mM to 25 mM) and b) the polymerization temperature (from -5°C to 35°C). The synthesized material was then characterized by scanning electron microscopy, energy X-ray dispersive spectroscopy, nitrogen physisorption, Fourier-transform infrared and Raman spectroscopies and measurement of electrical conductivity. It was found, that the concentration of methyl orange in polymerization solution strongly influences both the diameter (ranging from 60 to 900 nm) and the shape (circular or rectangular cross-section) of synthesized polypyrrole nanotubes. Moreover, while at low concentrations of methyl orange in the native liquor the resulting nanotubes are accompanied by globular form of polypyrrole, at higher concentrations the composite of polypyrrole nanotubes with acidic form of methyl orange is produced. The detailed mechanism of methyl orange role during the polymerization process was explained in terms of behaviour of planar aromatic sulfonic acids. As for the polymerization temperature, it has stronger influence on the morphology than on the chemical composition of resulting polypyrrole nanotubes. Finally, we report a universal relation – a power law describing dependency of electrical conductivity on nanotube diameter for this class of materials.

1. Introduction

Polypyrrole nanotubes (PPy-NTs), prepared using methyl orange (MO) as a structure guiding agent, have recently attracted considerable attention by properties superior to their granular counterpart (PPy-G) [1]. This particular synthesis excels due to its simplicity, effectivity and possibility to tune the outer diameter of nanotubes in nano- or micro-metric scale. Since the first experiments made by Yang et al. [2] in 2005, these PPy-NTs were successfully tested in a variety of applications: as a material for sensors, [3,4] supercapacitors and batteries [5–9], aerogels [10], synthetic absorbents [11], antioxidants [12,13], reducing agents [14], catalysts [15], photocatalysts [16], or conducting fabrics [17].

The synthesis of PPy-NTs using MO usually proceeds by chemical

way, but analogous, electrochemical synthesis by anodic oxidation of pyrrole monomer was also reported [18]. In a typical chemical synthesis, an oxidant is mixed with MO water solution resulting in formation of fibrous flocculant. Subsequently, the pyrrole monomer is added dropwise. Iron(III) chloride (FeCl_3) is a first choice oxidant for this kind of polymerization, but ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) [19], iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3$) [3,20], silver nitrate (AgNO_3) [20], or iron(III) sulphate ($\text{Fe}_2(\text{SO}_4)_3$) [21] can be also used.

According to generally accepted theory, the fibrous flocculant is created by the complex of MO-iron(III) chloride and serves as a self-degraded reactive template during the polymer synthesis [2,22]. Nevertheless, the detailed survey of the polymerization process [23] has shown that the reverse synthesis procedure, where MO is mixed with pyrrole followed by slow addition of oxidant also leads to PPy-

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NTs, although the flocculant intermediate is not created during the reaction. Therefore, the seeding mechanism of PPy-NTs formation, which emphasizes the role of MO aggregates (dimers or oligomers) formed in an aqueous solution [24], has been also proposed [23]. The hypothesis of the seeding mechanism is supported by the fact that using the pyrrole dimer, *i.e.* 2,2-bipyrrole (which serves as a homogeneous polymerization site instead of MO dimers) leads also to the similar PPy nanostructures, although no flocculant is created during the polymerization [25,26].

It is worth to note that MO as a structure-guiding agent also stimulates formation of nanotubes of other conductive polymers – polyaniline and polythiophene [22,27].

The supramolecular nature of PPy-NTs provides new or more pronounced material features among whose the most valuable are the increased electrical conductivity and large specific surface area. The increased electrical conductivity and large specific surface are desirable in many applications like in supercapacitors [6], sensors [4] or in cryogels substituting for instance polyaniline which has been mainly employed so far [28]. From this perspective, it is essential to reveal the influence of various synthesis conditions on both properties. In the previous studies it was found that the template-to-monomer ratio [23] and the type of oxidant [21] affects the final diameter and the conductivity of nanotubes. In the present study we focus on the structure-property relationship and optimization of synthesis and processing conditions in order to increase the electrical conductivity and the specific surface area of PPy-NTs. For this purpose, we selected a wide range of two experimental parameters: MO concentrations ranging from 0.5 to 25 mM and polymerization temperatures ranging from -5 to 35 °C.

2. Material and characterization

2.1. Synthesis

Pyrrole (Sigma-Aldrich), iron(III) chloride hexahydrate (Sigma-Aldrich), methyl orange *i.e.* (4-[4-(Dimethylamino)phenylazo]benzenesulfonic acid sodium salt; Fluka, Switzerland), ethanol (Penta, Czech Republic), acetone (Penta, Czech Republic) were used as received. PPy-NTs were prepared by the oxidation of the pyrrole monomer with iron (III) chloride in the presence of MO as a structure-guiding agent, according to the previously published procedure [23].

At the beginning, the solution of MO in deionized water was prepared. The initial concentration of MO varied with each reaction so as to create ascending concentration series of 0.5; 1; 1.5; 2.5; 3.5; 5; 10; 25 mM. Totally five temperature series were created; the individual reaction solutions were tempered to -5 ; 5; 15; 25; 35 °C, respectively. In the next step, after tempering, the pyrrole monomer was added into the MO solution and mixed using a stirrer. After 15 min, a concentrated solution of the oxidizing agent, *i.e.* iron(III) chloride hexahydrate, was added dropwise into the solution. The monomer to oxidant molar ratio was 1: 1 (*see the note to the molar ratio selection in Supporting information*) and it was kept constant for all the syntheses. A black precipitate started to be formed immediately after the addition of oxidant, but the whole reaction mixture was kept tempered and under constant stirring for 24 h to ensure that all reactants have properly reacted (*see an example of the reaction in Supporting information*). Black precipitate of PPy-NTs was filtered after 24 h and purified by Soxhlet extraction using acetone. The purified black powder was dried in vacuum at 40 °C for several days.

2.2. Characterization

The morphology and chemical composition of samples were studied by scanning electron microscopy (SEM) using the Mira 3 LMH (Tescan) microscope at 3 kV of accelerating voltage and energy-dispersive X-ray spectroscopy (EDX) using Quantax 200 with XFlash 6|10 detector (Bruker) with the resolution of 127 eV and 15 kV of accelerating voltage, respectively.

The surface area of the PPy-NTs powders was evaluated by nitrogen physisorption using Quantachrome NOVA 2200e surface area analyser. The powders (50–200 mg per sample, depending on its morphology) were vacuum degassed at 140 °C at least 12 h and subsequently, adsorption-desorption isotherms (77 K) were measured. The specific surface area of the samples was calculated using Brunauer–Emmett–Teller (BET) theory.

Fourier-transform infrared (FTIR) spectra of powdered samples dispersed in potassium bromide and compressed into pellets were measured using Thermo Nicolet NEXUS 870 FTIR Spectrometer with DTGS TEC detector in 400–4000 cm^{-1} wavenumber region. Raman spectra were recorded with Renishaw InVia Reflex Raman microspectrometer using near infrared diode 785 nm laser excitation line. A research-grade Leica DM LM microscope was used to focus the laser beam. The scattered light was analysed with a spectrograph using holographic grating 1200 lines mm^{-1} . The Peltier-cooled CCD detector (576×384 pixels) registered the dispersed light.

Polypyrrole powders were compressed (at *ca.* 530 MPa) to the pellets of 13 mm in diameter and 0.5–1 mm thick. Their electrical conductivity was then measured by the four-point van der Pauw (VDP) method. The experimental set-up consisted of Keithley 220 programmable current source, Keithley 2010 multimeter as a voltmeter, and Keithley 705 scanner equipped with Keithley 7052 matrix card (*see Supporting information – the note to measuring current selection*).

The tensiometer Lauda TD1 was used for measurement of surface tension of MO solution at different concentration by Du Noüy ring method.

3. Results and discussion

Two synthesis conditions, *i.e.* a) concentration of MO and b) polymerization temperature, were varied in order to modify the PPy-NTs structure, diameter, specific surface area, chemical composition and electrical conductivity. Preliminary results from this area we reported in the recent paper [23]. To carry out more comprehensive research, we varied the concentration of MO in the native liquor from 0.5 to 25 mM and the temperature of synthesis from -5 to $+35$ °C. Hence a large set of data was obtained and subsequently, some generalized consequences among *synthesis conditions* \leftrightarrow *the PPy structure and chemical composition* \leftrightarrow *electrical conductivity of the polymer* could be formulated. Moreover, a universal relation between *electrical conductivity* and *nanotube diameter* of PPy-NTs has been proposed.

3.1. The effect of methyl orange concentration on properties of PPy-NTs

Firstly, we studied the effect of MO concentration (0.5–25 mM) on the above named properties of PPy. The partial results are summarized in Fig. 1 and in Fig. 2.

3.1.1. Structure and diameter of synthesized PPy nanotubes

Observation of the synthesized PPy-NT structure and evaluating the diameter of nanotubes by SEM have revealed some interesting facts.

Both the rectangular and the circular cross-sections of synthesized nanotubes are present (Fig. 1). Their diameter strongly depends on MO concentration. As can be seen from Fig. 2(i), in the interval of 0.5–3.5 mM the diameter of PPy-NTs decreases monotonously with rising concentration of MO in the reaction solution. For 5 mM and 10 mM concentration the diameter remains almost constant. The highest concentration, *i.e.* 25 mM of MO, was not included into Fig. 2(i), as the material produced under such conditions possesses rather compact, stone-like structure with barely visible contours of nanostructures.

The average diameter of the biggest tubes is in the range from 360 to 560 nm for 0.5 mM of MO, while the smallest tubes have the diameter between 65 and 85 nm for concentrations starting from 3.5 mM of MO. On the other side, the spatial density of created nanotubes

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