



Influence of synthetic conditions on the structure and electrical properties of nanofibrous polyanilines and their nanofibrous carbonized forms



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ABSTRACT

Nanofibrous polyanilines (PANIs) were synthesized by several oxidative polymerization pathways that have in common the presence of excess oxidant(s) (ammonium peroxydisulfate and its mixture with hydrogen peroxide), the absence of added acid, and the absence of external template (self-assembly process). Conducting forms of the synthesized PANI nanofibers (re)doped with various acids were further used as precursors for carbonization process to obtain nanofibrous carbonaceous materials (Carb-PANIs). Morphology, molecular structure, surface properties and electrical characteristics of PANI nanofibrous precursors and their carbonized counterparts were studied by scanning electron microscopy, Raman spectroscopy, by measurements of ζ -potential and determination of isoelectric points, as well as by measurements of electrical conductivity.

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1. Introduction

Due to a number of favorable features, such as simple synthesis, high thermal and environmental stability, low cost, high conductivity, good reversibility of redox- and doping/dedoping processes as well as broad applications field, polyaniline (PANI) is one of the mostly studied conducting polymers [1]. High electrical conductivity of PANI is observed only for its half-oxidized, protonated and doped form—green emeraldine salt (ES). Granular PANI-ES powders possess electrical conductivity in the range $1\text{--}10\text{ S cm}^{-1}$ [2–4] while free-standing PANI-ES films exhibit conductivity up to 10^3 S cm^{-1} [5]. Half-oxidized blue emeraldine base $((\text{--B--N=Q=N})_n(\text{--B--NH--})_{2n})$, fully oxidized violet pernigraniline base $((\text{--B--N=Q=N})_n)$, and fully reduced colorless/transparent leucoemeraldine base of PANI $((\text{--B--NH--})_n)$ are insulating [1,3].

The structure and physical properties of PANI depend on synthetic procedure. The synthesis of bulk quantities of highly conducting PANI is usually performed as a chemical oxidation of

aniline by ammonium peroxydisulfate (APS) in the solution of strong acid at $\text{pH} < 2$. The molar ratio of $[\text{APS}]/[\text{aniline}]$ is usually 1.25 which is the theoretical stoichiometric ratio needed for the formation of PANI-ES [3,4]. During the polymerization reaction the hydrogen atoms are released, this leads to decrease of pH value of the reaction mixture. For the case when the difference between the starting and final pH values is significant (e.g. starting $\text{pH} \sim 5\text{--}7$, and final $\text{pH} \sim 1.5$), this process is known as “falling-pH method”, this is one of the simplest template-free, self-assembly methods to produce 1-D nanostructured PANI structures composed of nanotubes, nanorods and/or nanofibers [1,6–13]. Properties of such synthesized PANIs are mainly affected by initial acidity of the polymerization solution and initial molar ratio $[\text{APS}]/[\text{aniline}]$. The simplest ‘falling-pH method’ provides synthesis of 1-D PANI nanostructures in water without any added acid, therefore it is a ‘dopant-free template-free method’ [6,7,14]. It is also commonly performed at $[\text{APS}]/[\text{aniline}] = 1.25$. Besides nanotubes and nanorods, the products contain some amount of nanosheets and nanogranules. More uniform and much longer PANI nanofibers/nanotubes were produced by modified dopant-free template-free synthetic route in which an excess of oxidant (APS) is used [15].

During the last two decades an extensive research has been devoted to the development of new carbon-based (nano)

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materials for various applications. Introduction of heteroatoms (such as nitrogen, boron and phosphorus) into the structure of carbon (nano) materials (heteroatom doping) has received especial attention because of its influence on electronic, chemical and mechanical properties. The interest for preparation, characterization and processing of one-dimensional (1-D) N-containing carbon nanotubes, nanofibers, nanorods and nanowires has rapidly increased in recent years due to their versatile applicability as materials for energy conversion and storage (hydrogen storage, electrocatalysts for fuel cells, supercapacitors), analytical applications (gas sensors, electrochemical (bio) sensors), catalysis, nanoelectronics or adsorbents [16]. During the past few years, the carbonization of N-containing nanostructured polymers, such as PANI, has emerged as an efficient route to produce new N-containing nanostructured carbon materials, whose morphology is mainly determined by the morphology of the polymeric precursor [16–21]. For example, carbonization of nanotubular PANIs leads to materials similar to N-containing carbon nanotubes (NCNTs). It has been reported that 1-D nanostructured carbonized PANIs exhibit high performance as materials for supercapacitors [22,23], electrocatalysts of oxygen reduction [23,24] and electrochemical production of hydrogen peroxide (H_2O_2) [20], or sensing of nitrite ions and ascorbic acid [25]. Besides its simplicity, carbonization of polymers is advantageous in the absence of metallic impurities in final N-containing carbon materials. Also, the properties of N-containing carbons can be tuned by modification structure or properties of its polymeric precursor as well as by the choice of carbonization method, temperature, duration, and gas atmosphere [16,21].

In the present work, nanofibrous PANIs were synthesized by several oxidative polymerization pathways that all have in common the *usage of the oxidant in excess* (APS and H_2O_2), the *absence of added acid* at the beginning of aniline polymerization, and the *absence of external template*. Carbonization of PANI nanofibers resulted in nanofibrous N-containing carbon materials. The morphology, molecular structure and electrical characteristics of PANI nanofibrous precursors and their carbonaceous counterparts produced by carbonization (Carb-PANI) were studied by scanning electron microscopy (SEM), Raman spectroscopy, measurements of ζ -potential and electrical conductivity.

ζ -potential is an important property for various applications of PANI and Carb-PANI (nano) materials, such as functionalization or immobilization of different compounds, sensors, electrocatalysis. There are only limited data on ζ -potentials of PANIs: for conventionally synthesized PANI [26], PANI synthesized in the presence of surfactant vesicles [27], PANI nanofibers produced by rapid mixing method [28], nanofibrous copolymers of aniline and substituted anilines [29]. ζ -potentials of carbon nanostructures, such as carbon nanotubes (CNTs) [30–35], carbon nanofibers [36–38], NCNTs [39,40] or N-doped graphene [40] are more often investigated. By our best knowledge, there is no data on ζ -potential measurements of Carb-PANI materials. That is why a special attention in the present work was paid to the measurements of ζ -potential, its dependence on pH and isoelectric point of dispersions of synthesized nanofibrous PANI and Carb-PANI materials.

2. Experimental

2.1. Syntheses of nanofibrous PANIs

Aniline (p.a., >99.5%, Centrohem, Serbia) was distilled under reduced pressure prior to use. APS (p.a., Centrohem, Serbia) has been used as received. PANI samples were synthesized by using three different procedures.

1) *Procedure I*: PANI hydrochloride, denoted hereafter as PANI1-HCl, was prepared by template-free procedure reported in [15]

with slight modification. Aqueous solution (100 mL) of oxidant (APS, 0.11 mol) was poured into the aqueous solution (100 mL) of aniline (2.73 mL, 0.03 mol) under intensive stirring at $\sim 22^\circ\text{C}$. The reaction mixture was stirred for 30 s, and then incubated without stirring. In 10 min the precipitated polymer was collected by filtering using Buchner funnel with a water aspirator, purified, and redoped with HCl. PANI was rinsed with 0.5 L distilled water, then with 0.5 L 1 M HCl (aq), 0.5 L ethanol, 100 mL 1 M HCl (aq), and finally with 100 mL ethanol. Obtained PANI hydrochloride was suspended in 100 mL ethanol. After 24 h the material was filtered, rinsed with 100 mL ethanol and dried in vacuum at room temperature for 6 h

- 2) *Procedure II*: PANI sulfate, denoted hereafter as PANI2- H_2SO_4 , was prepared using the modified template-free procedure reported in [15]. The modification related to *procedure I* refers to the acid used for post-synthetic redoping: aqueous solution (100 mL) of oxidant (APS, 0.11 mol) was poured into the aqueous solution (100 mL) of aniline (2.73 mL, 0.03 mol) under rapid mixing at $\sim 22^\circ\text{C}$ to start the reaction. The reaction mixture was stirred for 30 s, and then incubated without stirring. In 10 min the precipitated polymer was collected by filtering using Buchner funnel with a water aspirator, purified, and treated with 1 M H_2SO_4 . Precipitated PANI was rinsed with 0.5 L distilled water, with 0.5 L 1 M H_2SO_4 (aq), 0.5 L ethanol, 100 mL 1 M H_2SO_4 (aq), and finally with 100 mL ethanol. Obtained PANI- H_2SO_4 was suspended in 100 mL ethanol. After 24 h precipitated polymer was filtered, rinsed with 100 mL ethanol and then dried in vacuum at room temperature for 6 h
- 3) *Procedure III*: PANI sulfate samples denoted hereafter as PANI3a- H_2SO_4 and PANI3b- H_2SO_4 , were prepared by using a mixture of oxidants, APS and H_2O_2 . 100 mL of aqueous solution containing 6.85 g APS and 8.17 mL 30% H_2O_2 was poured into 100 mL of 0.3 M aniline (aq) at $\sim 22^\circ\text{C}$, stirred for 30 s, and then incubated without stirring for 50 min (PANI3a- H_2SO_4) or 70 min (PANI3b- H_2SO_4). The precipitated PANI sulfate was collected by filtering using Buchner funnel with a water aspirator, rinsed with 0.5 L distilled water, 0.5 L 1 M H_2SO_4 (aq), 0.5 L ethanol, 100 mL 1 M H_2SO_4 (aq), and 100 mL ethanol. Obtained PANI- H_2SO_4 was suspended in 100 mL ethanol. After 24 h the precipitated sample was filtered, rinsed with 100 mL ethanol and dried in vacuum at room temperature for 6 h.

2.2. Deprotonation and redoping of PANI samples

A part of the synthesized PANI samples (PANI1-HCl and PANI2- H_2SO_4) was deprotonated. 1 g of sample was suspended in 5% NH_4OH and incubated for 24 h. The formed PANI base was filtered, rinsed with 1 L of distilled water and dried. Deprotonated samples PANI1-HCl-dedop and PANI2- H_2SO_4 -dedop were treated (redoped) with H_3PO_4 and H_3BO_3 : 1 g of the deprotonated sample was suspended in 100 mL of 1 M H_3PO_4 (aq) or in 200 mL of 0.5 M H_3BO_3 (aq) and incubated for 24 h. Redoped sample was filtered and rinsed with 100 mL of aqueous solution of corresponding acid (1 M H_3PO_4 (aq) or 0.5 M H_3BO_3 (aq)) and 100 mL ethanol. Redoped samples derived from PANI1-HCl are denoted hereafter as PANI1- H_3PO_4 and PANI1- H_3BO_3 . Redoped samples derived from PANI2- H_2SO_4 are denoted hereafter as PANI2- H_3PO_4 and PANI2- H_3BO_3 .

2.3. Preparation of Carb-PANI samples by carbonization of PANI precursors

The prepared PANI precursors were carbonized in Ar atmosphere using horizontal electric furnace (Elektron, Banja Koviljača, Serbia) with a quartz tube. Gradual heating up to 800°C was performed with heating rate $10^\circ\text{C min}^{-1}$ for 15 min. After

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