Synthetic Metals 192 (2014) 56–65

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Dopant-free interfacial oxidative polymerization of aniline

Aleksandra A. Rakić[a], Snežana Trifunović[b], Gordana Ćirić-Marjanović[a,*]

[a] *Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12–16, 11158 Belgrade, Serbia*
[b] *Faculty of Chemistry, University of Belgrade, Studentski Trg 12–16, 11158 Belgrade, Serbia*

ARTICLE INFO

Article history:
Received 2 December 2013
Received in revised form 15 February 2014
Accepted 11 March 2014
Available online 4 April 2014

Keywords:
Polyaniline
Interfacial polymerization
Dopant-free method
Nanogranules

ABSTRACT

Polyaniline (PANI) was synthesized by the oxidation of aniline with ammonium peroxydisulfate (APS) as an oxidant in an immiscible organic/aqueous biphasic system, without added acid. An organic phase contained aniline dissolved in chloroform, while the oxidant was dissolved in water. The produced PANIs have conductivities in the range 0.008–0.1 S cm^{-1}. Their nanogranular morphology was confirmed by scanning electron microscopy (SEM). Molecular structure of synthesized PANIs was investigated by FTIR, Raman, and UV–Vis spectroscopies, and elemental analysis. The influence of mechanical stirring and reaction time on the yield of polymerization, structure, and properties of synthesized PANIs was studied. The differences in the molecular structure, morphology, and conductivity between PANI prepared by dopant-free interfacial polymerization and PANI prepared by corresponding polymerization in monophasic aqueous system are discussed. The results are also compared with the literature data on the interfacial polymerizations of aniline with APS in the presence of acids.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Polyaniline (PANI) has been studied extensively due to its simple low-cost synthesis, good environmental stability, and tunable redox activity, electroactivity, electrochromism, sensing and catalytic ability, charge/discharge, capacitive, optical and magnetic properties, and electrical conductivity from metallic (10^3 S cm^{-1}) to insulator ($\leq 10^{-10}$ S cm^{-1}) level through reversible acid/base and/or redox doping/dedoping chemistry [1]. This unique set of physico-chemical properties make PANI applicable in the industry of rechargeable batteries, sensors, actuators, catalysts, electromagnetic shielding materials, antistatic and anticorrosive coatings, separation membranes, electrooptic and electrochromic devices, supercapacitors, fuel and solar cells [1].

Molecular structure, morphology and properties of PANI strongly depend on the applied synthetic methods and polymerization conditions. Classical syntheses of the PANI powders and films, accomplished by the chemical or electrochemical oxidative polymerization of aniline in an acidic aqueous solution (pH < 2), usually lead to the granular PANI materials [2]. During the past two decades, many methods have been developed for production of nanostructured PANIs, e.g., PANI nanofibers (PANI-NFs), nanotubes (PANI-NTs), etc., which have considerably improved properties and better performance in numerous applications in comparison with ordinary PANI [1,3]. Physical methods such as electrospinning and ultrasonication were successfully employed only for the fabrication of some PANI nanostructures such as PANI-NFs [3], while electrochemical methods, e.g., voltammetric, potentiostatic, and galvanostatic methods, produced nanostructured PANI only at small scales. Chemical oxidative polymerizations of aniline in the presence of hard templates (nanoporous membranes and nanostructured templates such as nanofibers and nanotubes of various insoluble inorganic and organic materials) and soft templates (soluble/colloidal fibrillar oligomers and polymers, micelles built up from surfactants and/or amphiphilic acids, etc.), produce regularly shaped nanostructures of PANI, but demanding post-synthetic template removal and purification could damage such obtained PANI nanostructures [3]. Kaner's group [4] first showed that PANI has the intrinsic nanofibrilar morphology, formed by primary growth in the early stages of aniline polymerization under acidic conditions, which undergoes the severe secondary overgrowth/agglomeration as classical synthesis proceeds. Nanosheets/nanoribbons and nanogranules may also be added to the list of intrinsic PANI morphologies formed by primary PANI growth at different pH [5]. Since commercial applications of nanostructured PANI demand low cost, simple and efficient synthetic procedures that will produce high-quality PANI nanostructures in bulk quantities without use of any template, it was not surprising that the development of template free methods has led to the synthesis of PANI nanostructures by means of suppressing the secondary growth in various ways,

---

* Corresponding author. Tel.: +381 113336633/+381 113336623; fax: +381 112187133.
E-mail address: gordana@ffh.bg.ac.rs (G. Ćirić-Marjanović).

http://dx.doi.org/10.1016/j.synthmet.2014.03.010
0379-6779/© 2014 Elsevier B.V. All rights reserved.

e.g., interfacial, not-shaken-not-stirred, rapid-mixing, and dilute polymerization [3].

Typical interfacial polymerization [6] is conducted at the interface of two immiscible phases without stirring, at pH < 2 and ambient temperature, giving nanofibrillar PANI. Reactants and products are mainly separated: aniline and low-molecular-weight aniline oligomers are dissolved in non-polar or low-polarity organic solvents (benzene, hexane, toluene, carbon tetrachloride, chloroform, methylene chloride, diethyl ether, carbon disulfide) rather than in water, while an oxidant and PANI are prevalent in highly acidic aqueous solution. After protonation, PANI-NFs diffuse from the interface into the aqueous phase avoiding secondary growth. Introduction of polar organic phase [7,8], addition of different dopants [9–11] and surfactants [11–13], stirring [14–16], use of various oxidants [17], and changes of temperature [18], aniline concentration [19,20], aniline/oxidant molar ratio [21], and reaction time [22] in the interfacial polymerization setup, lead to the PANI-NFs with changed dimensions and uniformity.

The most frequently used template-free technique for the synthesis of PANI-NTs is based on the oxidation of aniline with ammonium peroxydisulfate (APS) in water under pH-falling conditions, i.e., the oxidation of aniline with APS starting in alkaline, neutral or slightly acidic conditions, in the presence of various acids (strong, week, inorganic, organic, etc.) at aniline/acid molar ratio ≥ 1, and finishing at pH < 2 [3]. The simplest template-free pH-falling method of the synthesis of PANI-NTs that uses only monomer (aniline), oxidant (APS) and solvent (water) is known as a dopant-free template-free method [3]. It should be noted that the term “dopant-free” means the absence of external dopant acid, since the sulfuric acid, formed in situ by peroxydisulfate reduction to sulfate accompanied with the proton release during the aniline oligomerization/polymerization, acts as an internal dopant. It is also important to note that the term “template-free” means the absence of external template, since the oligoanilines and their aggregates act as internal templates. A main practical problem accompanied with this synthetic technique was the formation of the various nanostructures besides PANI-NTs in a single sample: nanorods, nanosheets, and nanospheres frequently in agglomerated form [23,24]. Various oxidants (cupric chloride, ferric chloride, ferric sulfate, cerium (IV) sulfate, hydrogen peroxide) were also used instead of APS in dopant-free template-free synthesis of PANI nanostructures [25]. It was observed that the diameter of the 1D PANI nanostructures significantly decreases with decreasing redox potential of the used oxidants [25]. The effect of the liquid–vapour interface property, i.e., the relative humidity of air on the morphology of the PANI nanostructures synthesized by the oxidation of aniline with APS in water without added acid was studied by Wan’s group [26]. Dopant-free template-free method of the synthesis of nanostructured PANI was also performed at different APS/aniline molar ratios [27,28] and aniline concentrations [29–31], as well as in the presence of methanol [32], 1-propanol [33], 2-propanol [34], 1,6-hexanediol [35], ethyleneglycol [36], glycerol [36], zeolite [37], colloidal SiO_2 [38], TiO_2 nanoparticles [39–41] and nanotubes [42].

In the present study, we investigated molecular structure, morphology, and properties of PANI synthesized by using the combination of dopant-free template-free and interfacial polymerization method under stirring as well as under not-stirred conditions. Elemental composition, molecular structure, morphology and properties of synthesized PANI were explored by elemental microanalysis, FTIR, Raman and UV–Vis spectroscopies, scanning electron microscopy (SEM), and conductivity measurements. The main issue is to find out whether the two combined methods, which were regularly used during the past decade for the template-free synthesis of 1D PANI nanostructures, would produce exclusively PANI-NFs or PANI-NTs, combination of these 1D nanostructures, or disordered aggregates of PANI particles.

2. Experimental

2.1. Materials

Aniline (p.a. >99.5%, Centrohem, Serbia) was distilled under reduced pressure and stored under nitrogen prior to use. Ammonium peroxydisulfate, APS (p.a., Centrohem, Serbia) and chloroform (p.a., Centrohem, Serbia) were used as received.

2.2. Syntheses of PANI

In the performed dopant-free interfacial polymerization reactions, the organic phase (100 ml) was 0.2 M solution of aniline ($V_{aniline} = 1.83$ ml) in chloroform, while the aqueous phase (100 ml) was 0.25 M aqueous solution of APS ($m_{APS} = 5.705$ g). The solution of APS was carefully poured onto the solution of aniline to start the reaction. The reactions were performed with stirring, using magnetic stirrer (1000 rpm), and also without stirring. In both cases, two polymerization times (t_{pol}) of 4 and 24 h were used. The names of PANI samples synthesized with and without stirring contain suffix “S” or “NS”, respectively. The samples synthesized with stirring and with $t_{pol} = 4$ and 24 h are designated as PANI-S-4 and PANI-S-24, respectively. The samples synthesized without stirring and using $t_{pol} = 4$ and 24 h are denoted as PANI-NS-4 and PANI-NS-24, respectively. PANI-NS-24 and PANI-S-24 samples were synthesized in order to check whether the prolonged reaction time have any influence on the yield, structure, morphology and conductivity of polymerization products. The abbreviations PANI-NS and PANI-S are used to denote biphasic, non-stirred and stirred reaction systems, respectively. By visual inspection for both non-stirred and stirred systems, as well as by the temperature profile of the reaction for the stirred system, we have estimated that 4 h were enough to complete the interfacial polymerizations. The reference dopant-free oxidation of aniline was performed in water (monophasic starting system) by pouring the aqueous solution (100 ml) of 0.5 M APS ($m_{APS} = 11.410$ g) into the aqueous solution (100 ml) of 0.4 M aniline ($V_{aniline} = 3.65$ ml), with t_{pol} of $\approx$30 min (since the concentration of aniline in the starting reaction mixture was 0.2 M the sample thus produced is denoted as PANI-Water-0.2), as well as by the same procedure using starting solutions of 0.25 M APS ($m_{APS} = 5.705$ g) and 0.2 M aniline ($V_{aniline} = 1.83$ ml), with t_{pol} of $\approx$120 min (since the concentration of aniline in the starting reaction mixture was 0.1 M the sample thus produced is denoted as PANI-Water-0.1). Reaction times for the last two syntheses were chosen based on the recorded temperature profiles of the reactions so that the reactions pass the second exothermic phase. Upon adding APS solution over the aniline solution in the syntheses of the PANI-NS-4 and PANI-NS-24 samples, aniline and APS concentrations in two separated phases were similar, about 0.2 M and 0.25 M, respectively, to those used in the synthesis of PANI-Water-0.2 sample. However, the total content of aniline and APS in performed interfacial polymerizations was the same as in the synthesis of PANI-Water-0.1 sample. All reactions were performed at room temperature. The precipitated PANIs were collected on a filter, rinsed with aqueous solution of sulfuric acid (5×10^{-3} M) and dried in vacuum at 60 °C for 3 h. A portion of product was treated with an excess of 5% ammonium hydroxide for 2 h, to transform it to deprotonated form, PANI base. The resulting precipitate was collected on a filter, rinsed with 5% ammonium hydroxide, and dried in vacuum at 60 °C for 3 h.

2.3. Characterization

A scanning electron microscope JEOL JSM 6460 LV (JEOL Ltd., Japan) has been used to characterize the morphology of the samples. Powdered materials were deposited on adhesive tape fixed to specimen tabs and then coated by ion sputtered gold using a

Download English Version:

https://daneshyari.com/en/article/1441000

Download Persian Version:

https://daneshyari.com/article/1441000

Daneshyari.com