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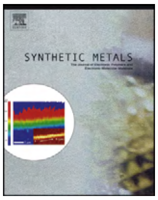

Nanostructured polyaniline synthesized using interface polymerization and its redox activity in a wide pH range☆

Shaolin Mu

Department of Chemistry, Yangzhou University, Si Wang Ting Road, 180, Yangzhou 225002, Jiangsu Province, China

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Purely nanostructured polyaniline with the conductivity of 7.2 S cm^{-1} was synthesized via the quick addition of the oxidant of the solid ammonium peroxydisulfate into a cooled solution containing aniline and hydrochloric acid without any templates. The morphology of polyaniline is constructed of interwoven fibers with an average diameter of about 50 nm with lengths varying from 250 nm to 370 nm. In general, the conventional polyaniline completely lost its electric activity including conductivity and redox activity at pH 6; however, the polyaniline reported here shows two pairs of redox peaks on its cyclic voltammogram in 1.0 M NaCl solution with pH 7.0, which is similar to that of the conventional polyaniline in the more acidic solutions; and it still holds the redox activity until pH 9.0. The pH dependence of conductivity of polyaniline is also improved compared to that of the conventional polyaniline. The ESR measurements show that the deprotonated polyaniline still holds rather high unpaired spin densities. The ^{1}H NMR spectra of polyaniline synthesized using interface polymerization are different those of the conventional polyaniline. The electrochemical behavior and spectra of polyaniline synthesized via the quick addition of an oxidant solution into a solution of aniline were reported and discussed.

1. Introduction

The revolutionary discovery of the electric conductance of polyacetylene created a new type of conducting material and opened a new research field of conjugated polymers for chemists and physicists [1]. The key strategy for this discovery is that the doping method was first used to introduce charge carriers into the insulating polymer, which made it a conducting polymer. Among conducting polymers, polyaniline has received more attention than most other conducting polymers due to relatively high conductivity, redox reversibility with different redox states and good environmental stability. These properties provide the basic conditions for its applications in rechargeable batteries [2,3], electrochromic devices [4], sensors [5,6], corrosion prevention [7], and super capacitors [8]. These applications are related to the electric properties of polyaniline including its conductivity and redox activity, which however are strongly dependent on pH value. Diaz and Logan reported that the electrochemical behavior of polyaniline at pH > 3 is different from that of polyaniline in 0.10 M H_2SO_4, based on the result of cyclic voltammograms [9]. MacDiarmid and co-workers reported that two pairs of redox peaks occurred on the cyclic voltammograms of chemically synthesized polyaniline at pH ≤ 2, and however did not occur on the cyclic voltammograms at pH > 4 [10]. Therefore, they made a conclusion that polyaniline is essentially electrochemically inactive at pH 6 [10]. Focke et al. reported that the conductivity of electrochemically synthesized polyaniline vanished at pH 6 [11]. Therefore, researchers generally considered that polyaniline becomes electrochemically inactive at pH > 4 [12]. Our experimental result also demonstrated that electrochemically synthesized polyaniline using cyclic voltammetry between −0.2 V and 1.0 V almost completely lost its redox activity at pH > 5, evidence is no redox peaks on its cyclic voltammograms [13]. The vanishing of the redox activity and conductivity of polyaniline makes the above-mentioned applications become impossible. Furthermore, the applications of polyaniline in biochemical and environmental science fields are also limited because the neutral solutions are needed for these systems. An effective way of improving the pH dependence of polyaniline reactivity was carried out by using the sulfonation of polyaniline with fuming sulfuric acid (i.e. self-doped polyaniline) [14] or copolymerization of aniline and aniline derivatives with a pH functional group, such as $-SO_3H$ [12], −OH [13], and −COOH [15,16]. The conductivity of the self-doped polyaniline is independent of pH in the aqueous acid solution of pH ≤ 7 [14]. The aniline copolymers with one pH functional group of −OH [17–19] or two pH functional groups of −OH and $-SO_3H$ [20] or $-NH_2$ [21] have redox activity from pH < 1 to 10 or 11. Therefore, these aniline copolymers can be used to catalyze the oxidation of biomolecules [22] and to treat contaminated water in the neutral aqueous solutions [23].

☆ Dedicated to my supervisor, professor Alan G. MacDiarmid of University of Pennsylvania, on his great contributions to conducting polymers.

E-mail address: slmu@yzu.edu.cn.

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Research on polyaniline is also closely related to the rapid development in its nanostructures that have aroused considerable interest in their unique properties [24,25], and potential applications [26,27]. The nanostructured polyaniline can be prepared by using chemical, electrochemical, and physical methods, which have been widely reviewed and discussed elsewhere [28]. Among these methods, the chemical oxidative polymerization of aniline with and without templates has received growing interest in recent years because this method can readily and rapidly prepare bulk quantities of nanostructured polyaniline [29–33], compared to the electrochemical method. In addition, rapidly mixed reaction of the oxidant solution and the aniline solution has been used for making pure nanofibers by suppressing the secondary growth of polyaniline in the absence of any templates [34].

Recently, we found that polyaniline has a distinct redox activity at $pH > 6$ during investigating the chemical synthesis of the nanostructured polyaniline. Even though many papers about the synthesis and electric properties of polyaniline have been published, to our knowledge, no paper reported the redox activity of polyaniline at $pH > 6$. Therefore, the above experimental phenomenon strongly attracts us to approach electric properties of polyaniline again. In this work, we report synthesis of purely nanostructured polyaniline in the absence of any templates, discuss the relationship between the electric properties and structure of polyaniline and confirm the pH dependence of polyaniline synthesized via the quick addition of an oxidant solution into aniline solution.

2. Experimental

The chemicals used were of analytical regent grade. Aniline was distilled under reduced pressure before use. Doubly distilled water was used to prepare solutions. The electrolytic cell for cyclic voltammetry consisted of a platinum foil counter electrode, a polyaniline working electrode and a saturated calomel reference electrode (SCE). The electrochemical experiments were performed on a CHI 407 electrochemical workstation.

The polymerization rate of aniline was controlled by the feeding rate of the solid ammonium peroxydisulfate. One is that a given amount of the solid oxidant was very quickly added into a solution containing 0.20 M aniline and 1.0 M HCl within 20 s. Ammonium peroxydisulfate was completely solved in the aniline solution within 4 min. The polymer synthesized in this way is labeled polyaniline-A; the other is that the solid oxidant was stepwise added into the aniline solution within 30 min. The polymer synthesized using this method is labeled polyaniline-B. The resulting solution approximately consisted of 0.20 M aniline, 0.25 M $(NH_4)_2S_2O_8$ and 1.0 M HCl. Before the reaction, the aniline solution was cooled with an ice bath and stirred with a stirring magnetic bar; and a platinum foil ($1\ cm^2$) was immersed into the aniline solution and then the solid oxidant was added into the stirred aniline solution. After the addition of the solid oxidant, the polymerization of aniline started to take place at the surface of the solid oxidant particles. For simplicity, this reaction is called the interface polymerization. As the chemical polymerization proceeded, aniline was polymerized on a platinum foil to form a polyaniline electrode, which was used for the electrochemical experiments. The reaction time was controlled in 2 h. After ending polymerization, most of the product precipitated in the bottom of a beaker was washed with 0.05 M HCl solution until the filtrate was colorless, dried at 104 °C. The product was used to measure the spectra of ESR and ^1H NMR, and conductivity.

The SEM images of polyaniline films polymerized chemically on platinum foils were measured on an S-4800 II FESEM instrument. The proton NMR spectra of polyaniline were conducted on a 600 MHz Bruker spectrometer at 303.1 K in dimethyl sulfoxide-d_6 (DMSO-d_6) in a 5-mm diameter NMR tube. The deprotonated polyaniline samples used for the determination of conductivity and the measurements of ESR and ^1H NMR spectra were prepared via the deprotonation of the nanostructured emeraldine salt, which was immersed in 0.4 M NH_4OH solution for 24 h, then washed with distilled water and dried. The ESR measurements were carried out using a Bruker A300 spectrometer operating in *X*-band (9.862 GHz). The microwave power for the measurement of polyaniline in the solid state was set 2×10^{-3} mW in order to avoid saturating ESR signals; the modulation amplitude was set at 1.0 G. The Bruker Company provided a *g*-factor marker of $S^{3/2}$; and its *g*-value is 1.9800 ± 0.0006. To determine the unpaired spin densities of polyaniline samples, each sample and 2,2-diphenyl-1-picrylhydrazine (DPPH) were weighed. DPPH with known unpaired spin density was used as a reference standard. The polyaniline samples for ESR measurements were sealed in a thin glass tube by heating. The conductivity of polyaniline was measured on a pressed pellet using a four-probe technique.

3. Results and discussion

3.1. Morphology of polyaniline samples

Fig. 1A shows the SEM image of polyaniline-A, which reveals the fact that the morphology is constructed of interwoven fibers with different diameters and lengths. The fibers in Fig. 1A have an average diameter of about 50 nm with lengths varying from 250 nm to 370 nm. It is clear that the size of the fiber diameter of polyaniline falls into the nanometer range. The formation of the nanofibers in this manner is caused by both the polymerization of aniline at the surface of solid oxidant particles and the rapid polymerization rate of aniline due to the quick addition of the solid oxidant into the stirred aniline solution. Polyaniline formed at the solid surface quickly went away from it by stirring the solution; and the rapid polymerization is very helpful to form a large amount of polyaniline nuclei in the short-duration experiment, which caused the reactants to be exhausted quickly. Hence both the interface polymerization and the rapid polymerization rate suppressed the growth of polyaniline nuclei. The above result indicates that this method provides a simple way to synthesize bulk quantities of purely nanostructured polyaniline in the absence of any templates.

Fig. 1B shows the SEM image of polyaniline-B. Its morphology is similar to that shown in Fig. 1A. The fibers in Fig. 1B have an average diameter of about 70 nm with lengths varying from 350 nm to 600 nm, whose sizes are a little larger than those shown in Fig. 1A. This difference is expected because the polymerization rate of aniline under the stepwise addition of the solid oxidant into aniline solution is slower than that of aniline under the quick addition of the solid oxidant into aniline solution due to the feeding time of the former lasting as long as 30 min.

3.2. Electrochemical behavior and conductivity of polyaniline synthesized using interface polymerization

The electrochemical behavior of chemically synthesized polyaniline was determined using cyclic voltammetry that was carried out in 0.20 M HCl solution and 1.0 M NaCl solutions with different pH values, respectively. The experiments of cyclic voltammetry were continuously performed from the low pH to the high pH using a same electrode. The scan rate was controlled at $60\ mV\ s^{-1}$. Fig. 2A shows the cyclic voltammograms of a polyaniline-A electrode in 0.20 M HCl. There are two pairs of redox peaks in Fig. 2A. This electrochemical behavior is the same as that of the conventional polyaniline in 1 M HCl [10]. Except curve 1 for the first