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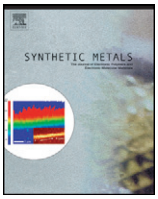

Electrodeposition of polyaniline nanostructures: A lamellar structure

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ABSTRACT

The growth process of polyaniline (PANI) nanofibers during the electrochemical polymerization was investigated in detail. The nano-fibrillar morphology appears to be intrinsic to PANI, and the unique character is attributable to a combined effect of electrophilic substitution reaction mainly taking place at the para-position of aniline or its oligomers and aniline oligomers with one-dimensional (1D) structure. Interestingly, the PANI film formed on the electrode exhibits a lamellar structure with compact two-dimensional (2D), micro-granular, nanorod-shaped, and nano-fibrillar PANI layers from bottom to top. In addition, the possible formation mechanism of the lamellar structure of PANI film is discussed.

1. Introduction

Inherently electrical conducting polymers have been intensively studied over the last three decades due to their potential applications in sensor and actuator, supercapacitor, electromagnetic shielding, corrosion protection, as well as in electronic, electroluminescence, and electrochromic devices [1–6]. In particular, polyaniline (PANI) has been studied in great detail because of its ease of synthesis, simple nonredox doping/dedoping chemistry based on acid/base reactions, and high environmental stability. Development of reliable and scalable synthetic methods for one-dimensional (1D) PANI nanostructures, including nanofibers, nanowires, nanorods, and nanotubes, has attracted much attention across scientific and engineering disciplines due to their superior properties compared to their bulk counterparts in turn on/off time, strength, and conductivity [7,8].

Although PANI nanofiber may be prepared by physical process [9], PANI nanofibers are often synthesized chemically by adding oxidants or electrochemically by applying potentials to the aimed electrodes. Chemical polymerization methods include “hard and soft” template [10,11], nanofibers seeding [12], oligomer-assisted [13], dilute solution [14], interfacial [15], and rapid mixing [16] polymerization. Chemical polymerization should be the preferred methods to prepare nanofibers in bulk quantities. However, removal of templates is tedious, and PANI might be destroyed in this process. In addition, the remaining oxidants may contaminate PANI samples and affect their properties. Compared with chemical polymerization, electrochemical polymerization is a more environmentally friendly method used to produce PANI nanofibers. The specific advantages of electrochemical polymerization are as follows: (1) discharged liquid can be easily treated because no oxidant or surfactant is needed in this process; (2) polymerization media can be used repeatedly; (3) polymerization rate can be controlled easily by varying oxidation potential. So, electrochemical polymerization should be one of the most favored methods for fabricating PANI nanofibers, and there has been a great deal of interest in the past decades in fabricating PANI nanofibers electrochemically.

The electrochemical polymerization of aniline mainly occurs on the surface of conducting substrate and forms dense nanostructured PANI film on the electrode. Many methods, including the potentiostatic [17], galvanostatic [18], pulse galvanostatic [19], pulse potentiostatic [20–22], and stepwise galvanostatic [23] polymerizations, have been described in literatures discussing the synthesis of PANI nanofibers without any template. It is important to note that: (1) the PANI nanofibers obtained had similar morphologies in spite of the diversity in the synthetic approaches, that is; they generally formed dense films consisted of nanofibers with 50–150 nm diameters on the electrodes; (2) the applied potentials or current densities were relatively low. We speculate that the two points mentioned above indicate a common underlying

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mechanism about the formation of PANI nanofibers. In the previous literatures [15,16,24], Huang has demonstrated that PANI is prone to fibrillar growth in the chemical polymerization process using interfacial and rapid mixing polymerization. However, unfortunately, despite the general directive significance for nanofiber formation in the electrochemical polymerization of aniline, there are few pieces of literature focused on the reason why PANI forms such extended, elongated fibrillar nanostructures in the electrochemical polymerization [25]. Furthermore, there is no detailed report on the deposition process and the evolution of PANI morphology at the electrode surface. The uppermost nano-fibrillar PANI layer will give an illusion that the formed PANI films are entirely composed of pure nanofibers. However, this is not the case.

In this study, the growth process of PANI during electrochemical polymerization was investigated in detail, and the formation mechanism of PANI nanofibers is proposed. The formation of PANI nanofibers is attributed to a combined effect of electrophilic substitution reaction mainly taking place at the para-position (*p*-position) of aniline or its oligomers and aniline oligomers with 1D structure. Moreover, we discovered that the PANI film formed on the electrode exhibited a lamellar structure. Firstly, a thin compact two-dimensional (2D) PANI layer was formed during the initial stage of electrodeposition. Subsequently, the micro-granular, nanorod-shaped, and nano-fibrillar PANI layers were formed from bottom to top, respectively. Although the uppermost layer of PANI film was composed of nanofibers, the compact 2D, micro-particles, and nano-rods layers would make the performance of the electrode worse than pure PANI nanofibers-modified electrode for applications ranging from sensors, energy storage and flash welding to digital nonvolatile memory which utilized the high surface area, porosity, and high conductivity of PANI nanofibers. It is therefore of both great technological and scientific importance to discover the lamellar structure, which might be beneficial to investigate how we can make nanostructured PANI devices perform better in those already established areas, and to ask if they can create new opportunities.

2. Experimental

2.1. Materials

Aniline monomer (99% purity) was distilled under reduced pressure before use. Sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), hydrazine hydrate ($N_2H_4{\cdot}H_2O$) and ammonia solution (Tianjin Kewei Reagent Co.) were analytical grade and used without further purification. The water used in this work was de-ionized by passage through ion-exchange columns to yield 18 MΩ·cm quality water. Stainless steel (SS) (316; thickness, 2 mm) sheets were polished with $800^{\#}$ and then $2000^{\#}$ emery paper to turn the surface into a mirror, washed thoroughly with de-ionized water until free of emery particles and then dipped into an aqueous solution containing H_2O_2 (20%, wt) and H_2SO_4 (5%, wt) for 24 h. Other conducting substrates were uesd as-received; without further treatment.

2.2. Preparation and characterization of PANI nanofibers

Aniline polymerization was carried out in a one-compartment glass cell with a high purity nitrogen atmosphere using a PAR 273A potentiostat (Princeton Applied Research, Oak Ridge, TN) controlled by a computer. A saturated calomel electrode (SCE) and a SS sheet were used as reference and counter electrodes, respectively. An electrolyte containing H_2SO_4 and aniline was used for the electrodeposition of PANI nanofibers on the SS electrode (or other substrates). The deposition area was 1.5 cm × 1.5 cm. The morphology of PANI prepared by the previously mentioned methods was characterized under a field-emission scanning electron microscopy (FESEM, JSM-6700 F; JEOL, Tokyo, Japan).

3. Results and discussion

To fully understand the formation mechanism of PANI nanofibers, the growth process of PANI nanofibers on the electrode needs to be investigated clearly. The electrochemical polymerization of aniline mainly involved two stages [26]. In the initial stage, PANI grew on the bare electrode and represented a compact granular layer. In the advanced stage, PANI further grew on the surface of the compact PANI layer and finally formed a loosely bound open structure. Fig. 1 shows a typical chronoamperometric deposition curve for PANI nanofibers in a 1.00 M H_2SO_4 solution containing 0.25 M aniline on a SS electrode. Points A and B on the chronoamperometric curve represent the initial and advanced stage of aniline polymerization, respectively. From the curve, we can clearly see that the change of current density which reflects the different stages of aniline polymerization can be divided into three stages. The first stage (from 0 to 110 s) is the induction period of aniline polymerization. During this period, the current density has no obviously increase, and no PANI was found at the electrode. During the second stage (from 110 to 250 s), the current density increases more sharply than the first stage, but not as that of the third stage. At the end of this stage, only a transparent verdant PANI can be found. In fact, the first stage and the second stage are usually regarded as one stage called the initial stage of aniline polymerization (from 0 to 250 s). From the SEM image A inserted in Fig. 1, it can be seen that a compact 2D PANI layer was formed on the electrode surface after 250 s of electrodeposition. This phenomenon might be attributed to the fact that the lateral growth rate of PANI is much faster than the normal one during the initial stage. Such an effect could be explained by the oxidation of aniline on the bare electrode surface being favored in comparison with oxidation on the polymer chains [27]. At higher magnification (SEM image inserted in image A) we can clearly see that the compact 2D PANI layer was composed of a large array of PANI nodules. The third stage (250 s later), the current density increases sharply, and the sharp increase of current density suggests that the growth mechanism of PANI has changed (detailed explanation can be seen in the next paragraph.). As a result, these nodules grew upward to form PANI nanofibers in another 350 s (see SEM image B). The electrochemical experimental results show that the growth process of PANI nanofibers is similar to that of conventional PANI. However, several impor-

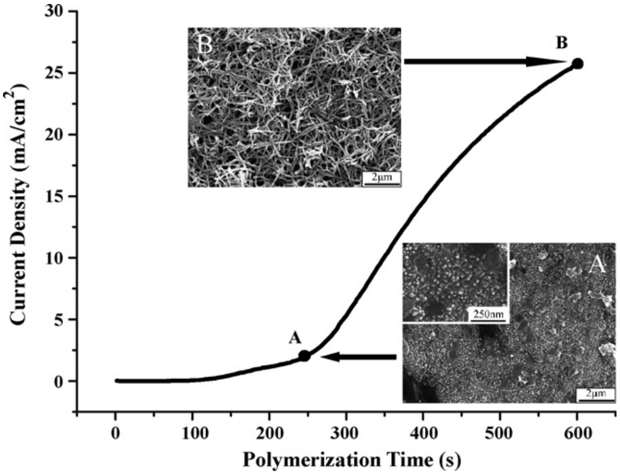

Fig. 1. Chronoamperometric curve of deposition of PANI on SS electrode at U = 0.75 V versus SCE in 1.00 M H_2SO_4 solution containing 0.25 M aniline.