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An all cis-polyaniline nanotube film: Facile synthesis and applications

Zhongde Wang[a], Yanhong Wang[a], Xiaogang Hao[a,*], Shibin Liu[a], Guoqing Guan[b,**], Abuliti Abudula[b]

[a] Department of Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China
[b] North Japan Research Institute for Sustainable Energy (NJRISE), Hirosaki University, 2-1-3, Matsubara, Aomori 030-0813, Japan

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ABSTRACT

An all cis-polyaniline nanotube film was successfully prepared using a novel unipolar pulse electropolymerization method and its formation mechanism was analyzed and discussed. Due to its unique chemical molecular conformation, many excellent performances such as low charge transfer resistance, good water wettability, high apparent diffusion coefficient, large redox site capacity and super-stability were identified. When it was applied for the supercapacitor electrode, a high specific capacitance of 1007.7 F g^{-1} with a dramatic retention life of 99% after 2000 charge/discharge cycles was obtained. The ascorbic acid sensor fabricated by this film showed a large linear range for the detection of ascorbic acid between 1.0×10^{-6} and 1×10^{-2} M with a high sensitivity of 182 mA M^{-1} cm^{-1}.

1. Introduction

Polyaniline (PANI)-based conducting polymers have been investigated extensively due to their excellent electrical, magnetic and optical properties similar to a metal with good mechanical property and processability, unique redox tunability, low-cost, ease of synthesis and their potential for applications in multidisciplinary areas such as sensors, actuators, energy conversion and storage, microelectronics, and optoelectronic devices [1–6]. PANI and its derivatives are generally synthesized by chemical or electrochemical oxidative polymerization method, and studies focusing on their synthesis, characterizations, and applications have been widely reported [7–10]. It is believed that some special physical and chemical properties differing from those of the bulk material of PANI can be achieved and applied for new purposes by the creation of nanostructured PANI-based conducting polymers. Template and non-template synthesis methods and a combination of the two are main approaches for the production of one-dimensional nanostructured PANI, including micro- or nanoscaled fibers and tubes, and have been reported by several groups [11–15]. The synthesis of bulk PANI, either by chemical polymerization [16,17] or electrochemical polymerization [18,19] can also be adopted for the production of nanostructured PANI. However, compared to chemical methods, electrochemical routes for preparing micro-nanostructures of conducting polymers are more facile and more easily controlled. Recently, a novel unipolar pulse electropolymerization (UPEP) method was successfully developed by our group for the controllable preparation of PANI-based films [20–23]. In general, PANI obtained from polymerization of aniline monomer can be found in one of three different oxidation states, i.e., the completely reduced 'leucoemeraldine', the completely oxidized 'pernigraniline' and the mixed 'emeraldine', or physical mixtures of these components. On the other hand, three different types of isomers, i.e., *positional, cis/trans, and rotational isomers*, which can play extraordinarily important roles in determining the electronic, magnetic, optical, structural and mechanical properties of PANI, are in principle possible for the PANI prepared [24–26]. The presence of different amounts of the multitudinous possible isomeric forms of PANI in the materials obtained can lead to completely different results. However, to date, little attention has been paid to these potentially important species on which the chemical and physical properties of PANI are based. Only a few scattered reports can be found in the literature with respect to the molecular conformation of PANI and the effects of possible isomeric forms on the intrinsic properties of PANI [24–26]. That may be why some conflicting results were reported by some research groups. Accordingly, in order to understand the performance mechanism of PANI and to determine the intrinsic properties of PANI, it would be very interesting if we can synthesize PANI preferably in one isomeric form or as a mixture containing fewer numbers of different isomers [26].

In the present study, an all cis-PANI nanotube film grown on a platinum substrate via a facile UPEP method was developed, and

* Corresponding author. Tel.: +86 351 6018193; fax: +86 351 6018554.
** Corresponding author. Tel.: +81 17 762 7756; fax: +81 17 735 5411.
E-mail addresses: zdwangtyut@hotmail.com (Z. Wang), xghao@tyut.edu.cn (X. Hao), guan@cc.hirosaki-u.ac.jp (G. Guan).

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the film obtained exhibited much more excellent performances when used as supercapacitors and sensors than mixed-PANI films. In addition, the mechanism for the formation of the all cis-PANI nanotube is discussed.

2. Experimental

2.1. Materials

Aniline, H_2SO_4 (98%) and ascorbic acid were purchased from Shanghai Chemical Reagent Co. Aniline was distilled under reduced pressure and other reagents were used as received without further treatment.

2.2. Synthesis of an all cis-polyaniline nanotube film

The aniline monomer (10 mL, 0.4 M) was dissolved in H_2SO_4 (10 mL, 1 M) solution and stirred magnetically at room temperature for 0.5 h to a uniform solution at first. The electrochemical synthesis of the all cis-PANI nanotube film was carried out in a three-electrode system (platinum sheet as working electrode, platinum wire as counter electrode, and saturated calomel electrode as reference electrode) with VMP3 electrochemical workstation (Princeton, USA). Each Pt substrate (effective surface area, 0.5 cm^2) was prepared by first polishing it to a mirror finish with fine-grade aqueous alumina slurry (grain size, 5–0.5 μm) on a piece of cloth, followed by rinsing with deionized water and finally drying in a vacuum oven. Following the similar strategy used in our previous study [22], the typical UPEP process for the preparation of the all cis-isomeric PANI nanotube film was performed in a freshly prepared solution composed of 0.5 mol L^{-1} of H_2SO_4 and 0.2 mol L^{-1} of aniline. Each pulse consisted of an on-time t_{on} when a certain potential was applied to generate a current and an off-time t_{off} when no current was allowed to flow. In particular, the potential V_{on} applied during the on-time (simply termed as the pulse potential) ranged from 0.85 to 1.1 V. The on-time period was 0.4 s while the duty cycle was 50%. The number of pulse cycles to generate the film was 300, and as such, it took only 4 min to complete the preparation of film. In order to obtain good nanotube film, the operation condition was optimized. For comparison, PANI films were also fabricated by the commonly used CV method in the same solution by cycling the potential from −0.2 to 1.0 V at 0.1 V s^{-1} for 25 cycles. After PANI films were formed, the samples were immersed in a 0.5 M H_2SO_4 solution and its electrode potential were maintained at 0.8 V for 10 min, followed by rinsing with deionized water and finally drying in a vacuum oven.

2.3. Characterization

The morphologies of the prepared films were investigated by scanning electron microscopy (SEM, JEOL JSM-6700F) as well as transmission electron microscopy (TEM, JEOL JEM-2010). Fourier transform infrared (FTIR) spectroscopic measurements of the samples were taken on a Japanese SHIMADZU FTIR-8400 workstation.

All electrochemical experiments were conducted with a VMP3 electrochemical workstation (Princeton, USA) using a conventional three-electrode system. Before electrochemical experiments, the prepared PANI films were immersed in a 0.5 M H_2SO_4 and its electrode potential cycled 150 times from −0.2 to 0.55 V at 0.1 V s^{-1}, followed by rinsing with deionized water and finally drying in a vacuum oven. The CV curve obtained during the final cycle was used to characterize electroactivity of the sample. Electrochemical impedance spectroscopy (EIS) measurement was made in the frequency range from 10^5 Hz down to 10^{-2} Hz, using an AC amplitude of 10 mV at open circuit potentials (OCP) in a 0.5 M H_2SO_4 solution. The number of frequencies per frequency decade was

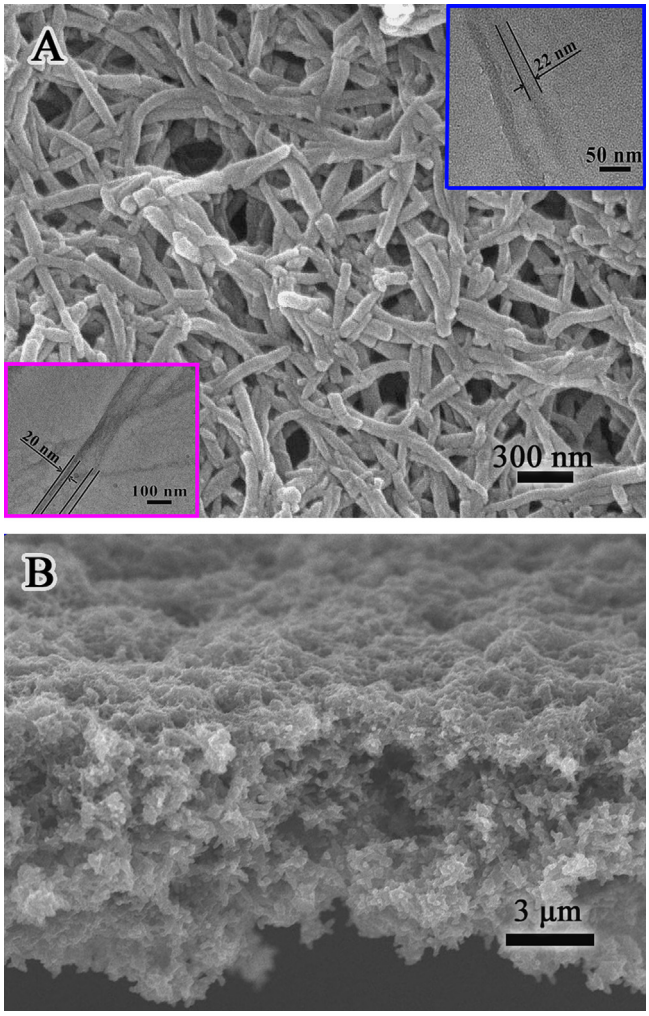

Fig. 1. (A) Plane SEM images of the all cis-PANI film; Inset: TEM images of the all cis-PANI film (different fiber). (B) SEM images of vertical cross section of the all cis-PANI film.

10. The cycle stability of each film was assessed by carrying out 2000 repetitively voltammetric cycles in 0.5 M H_2SO_4 at a scan rate of 0.1 V s^{-1}. Pseudo-capacitive properties of the polymer films were studied using chronopotentiometry through constant current charge/discharge experiments in 0.5 M H_2SO_4 solution between 0 and 0.75 V, at a defined current density of 2 mA cm^{-2}. Linear sweep voltammetry for the all cis-PANI film recorded in 0.1 M H_2SO_4 solution in the presence of 1×10^{-5} M ascorbic acid at 5 mV s^{-1}. Amperometric responses of the cis-PANI nanotube film electrode at 0.3 V to various concentrations of ascorbic acid by successive injection of ascorbic acid into a conventional three-electrode electrochemical cell (40 mL) containing electrolytes with stirring were measured. Before the successive addition of ascorbic acid, electrodes were first polarized at the operating potential until the background current became stable.

3. Results and discussion

3.1. Characterizations of the all cis-PANI and mixed PANI films

As shown in Fig. 1, PANI film composed of homogeneous nanotubes with diameters much less than 100 nm and average wall thicknesses of approximately 20 nm were obtained by using the present electrochemical method.