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Layer-by-layer assembly of polyaniline nanofibers/poly(acrylic acid) multilayer film and electrochemical sensing

Zhichao Hu, Jingjing Xu, Yuan Tian, Ru Peng, Yuezhong Xian*, Qin Ran, Litong Jin*

Department of Chemistry, East China Normal University, Shanghai 20062, China

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ABSTRACT

Polyaniline (PANI) nanofibers are synthesized by dilute polymerization and subsequently used for layer-by-layer assembly with poly(acrylic acid) (PAA). The chemical synthesized PANI nanofibers are characterized by SEM and TEM. In addition, the LBL assembly process is characterized by SEM, UV–vis spectrometry and electrochemical methods. PAA inside the multilayer film can dope nanostructured PANI effectively and shift its electroactivity to a neutral pH environment. Compared with PANI/PAA film co-deposited on the electrode by electropolymerization, the redox behavior of PANI/PAA multilayer via LBL assembly is more reversible, indicating the enhancement of electron transfer. The obtained nanostructured PANI/PAA multilayer films are very stable and show high electrocatalytic ability toward H_2O_2, which makes it an ideal substrate for H_2O_2 detection and offers great promise for biosensing.

1. Introduction

In the past decades, a great deal of effort has been made in the field of nanoscaled conductive polymers because the nanostructures often behave significantly difference from those of the same material in the bulk in the aspect of physical and chemical properties [1–4]. Among all the conducting polymers, polyaniline (PANI) is regarded as one of the most popular and promising conducting polymers because of its unique stability and interesting electrical and optical properties [5–10]. It has been being wildly used in lightweight batteries [11,12], microelectronics [13–15], organic light emitting diodes [16,17] and chemical sensors [18–20]. As for sensor applications, the manipulation of conducting polymers is of important as it provides an opportunity to fabricate ultrathin films of these materials with thicknesses, composition and architecture that are controllable on a nanometer scale. Within nanofabrication, the electrostatic layer-by-layer (LBL) assembly technique affords molecular-level control to fabricate ultrathin film by precise control of polymer assembly and to create an ideal tool for tailoring the properties of electroactive polymer films on the nanometer scale by electrostatic deposition of polycation and polyanion [21]. Therefore, LBL assembly provides a versatile method for ultrathin PANI film preparation as for sensor application. An apparent disadvantage of PANI is that the emeraldine form of PANI is usually deprotonated and non-conducting at neutral pH, and it is redox-active only at acidic conditions, normally at $pH < 4$ [22–25]. This greatly restricts its further application in bioelectrochemistry, which requires a neutral pH environment. Recent reports, however, have demonstrated that by introducing acidic groups (such as –COOH, –SO_3H, etc.) into the PANI chain and forming the “self-doped” PANI [25,26], or by doping PANI with negatively charged polyelectrolytes (such as poly(acrylic acid) (PAA), poly(vinyl sulfonate) (PVS), poly(styrene sulfonate) (PSS), or sulfonated PANI (SPANI), etc.), this drawback can be well overcame [27–30].

In our previous work, ordered PANI/PAA nanoelectrode ensembles (NEEs) were obtained via electrochemical polymerization of aniline in presence of PAA using porous sol–gel film as template [31]. In this article, LBL assembly, a simple and easy control strategy, was proposed to prepare nanostructured PANI/PAA film without the aid of template. PANI nanofibers were prepared via dilute polymerization. Then, a well-defined PANI/PAA nanocomposite film was obtained by alternative depositing nanostructured PANI and PAA via LBL self-assembly technique. We find that the alternately dipping glassy carbon (GC) or indium-tin-oxide (ITO) electrode between PANI nanofibers and PAA solution results in linear film growth with the ultimate thickness being controlled by the number of bilayers deposited. The assembling process and the electrochemical behavior of PANI/PAA multilayer films have been studied in detail. The obtained nanostructured PANI/PAA multilayer films are very stable and the redox activity of PANI can be shifted to neutral condition because of the assembling of PAA. Moreover, the PANI/PAA multilayer films show excellent electrocatalytic ability

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* Corresponding authors.
E-mail addresses: yzxian@chem.ecnu.edu.cn (Y. Xian), ltjin@chem.ecnu.edu.cn (L. Jin).

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toward H_2O_2, which makes it an ideal substrate for H_2O_2 detection and offers great promise for biosensing.

2. Experiment

2.1. Chemicals and reagents

Aniline (99.5%, Shanghai Reagent Factory) was distilled under vacuum before use. Ammonium persulfate (APS, 99.99%, Sinopharm Chemical Reagent Company) and PAA (Mw = 450,000) were purchased from Aldrich. Other chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared with deionized water.

2.2. Instruments

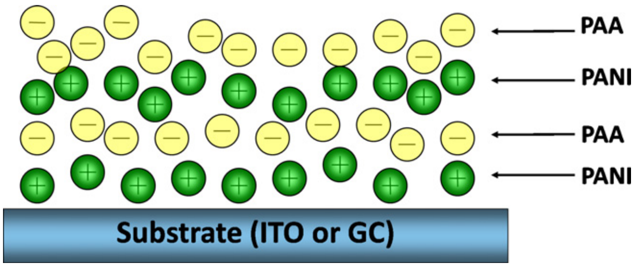
UV–vis spectra were recorded on a Cary 50 UV–vis spectrophotometer (Varian, Australia). The morphologies of the samples were observed by an S-4800 cold field emission scanning electron microscope (SEM) (Hitach, Japan) and a JEM-2100 transmission electron microscopy (TEM) (JEOL, Japan). Electrochemical experiments were performed on a CHI-660C electrochemical workstation.

2.3. Synthesis of PANI nanofibers

The chemical polymerization of aniline was carried out at room temperature as described previously [32]. Aniline was dissolved in a small portion of 1.0 mol/L HCl solution and carefully transferred to the solution of APS dissolved in 1.0 mol/L HCl solution in the beaker. The reaction lasted 24 h and the dark-green precipitate was collected after purifying by dialysis against deionized water. The initial concentration of aniline to the total volume of solution was maintained at 8.0 mmol/L, and the molar ratio of aniline to APS was kept at 2:1.

2.4. Preparation of PANI/PAA multilayer film

Nanocomposite film composed of alternating layers of PANI nanofibers and PAA was prepared on cleaned ITO substrates or GC electrode. The concentrations of the dipping solutions were 2.0 mg/mL for the PANI and 15.0 mg/mL for PAA. The pH of PANI and PAA solutions was 2.5 and 4, respectively. The LBL self-assembly process was presented in Scheme 1. First of all, the GC electrode was soaked in piranha solution (3:1 H_2SO_4/30% H_2O_2) for 3 min to make it covered with anions [33,34]. (Warning: Piranha solution is a strong oxidant and must be used with extreme caution.) Afterward, the substrate was rinsed with a large volume of deionized water. Then the GC electrode was exposed to the cationic PANI solution and anionic PAA solution, respectively. The deposition time for each layer was 15 min, followed by rinsing with deionized water (pH 2.5 for PANI and 4 for PAA, respectively) for 2 min and dried under a N_2 stream before proceeding to the subsequent layer. The cycle was repeated for the required number of layer pairs.



Scheme 1. Schematic representation of $(PANI/PAA)_n$ multilayer film deposited on ITO or GC electrode via LBL assembly.

2.5. Electrochemistry

All electrochemistry experiments were performed on a CHI-660C electrochemical workstation. A conventional three-electrode cell, with a modified GC electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a gold electrode as the auxiliary electrode, was used for electrochemical experiments. All potentials in this paper referred to the SCE reference electrode.

3. Results and discussions

3.1. Morphological analysis of PANI nanofibers

Dilute polymerization, proposed by Chiou and Epstein [32], was an easy, inexpensive, environmentally friendly, and scalable one-step method to produce highly pure, uniform PANI nanofibers with controllable diameters. This strategy was conducted in an aqueous solution with very low concentrations of aniline (8.0 mmol/L, in contrast with the relatively high concentrations (400 mmol/L) of aniline in the conventional polymerization) without the aid of specific templates. As long as polymerizations were performed using dilute aniline, nanofibers were formed. SEM and TEM were used to characterize the morphology of PANI via dilute polymerization. As shown in Fig. 1(a), the PANI shows similar ranges of lengths, up to several micrometer and the diameters of the nanofibers ranged from 50 to 100 nm. From the enlargement of SEM images (Fig. 1(b)), the PANI nanofiber shows interconnected and branched networks. The TEM image shown in Fig. 1(c) reveals that PANI is nanofiber instead of nanotube. Moreover, in contrast to the polymerization in a concentrated solution, the dilute polymerization results in loosely package of PANI nanofibers. According to the classical nucleation theory, the nanofibers formed initially may serve as nucleation sites for additional nanofibers. The small white spots on the PANI surface (as seen in Fig. 1(a)) may act as surface active sites for nucleation. When aniline is polymerized in the solution, there is a competition between a directional fiber-growth process and formation of additional nucleation centers. In a concentrated solution, a high density of nucleation centers is generated and a rapid precipitation occurs in a disordered manner, yielding irregular shapes. While in a dilute solution, less nucleation sites formed on the surface of the nanofibers, thus allowing PANI to grow only in a one-dimensional morphology [32].

3.2. Layer-by-layer assembly of PANI nanofibers/PAA multilayer film

The LBL assembly process of PANI nanofibers/PAA is characterized by SEM, UV–vis spectrometry and electrochemical methods. Fig. 2 shows the morphology studies of $(PANI/PAA)_n$ multilayers film prepared via LBL methods. As can be seen from Fig. 2(a), a highly porous network is formed after LBL assembly of three bilayers of PANI/PAA. The SEM micrograph of $(PANI/PAA)_6$ delineates clearly that PANI nanofibers are densely packed and merged with each other. In addition, the porosity of the film disappears because PANI nanofibers aggregate with PAA.

UV–vis spectroscopy is an important tool to investigate the LBL deposition process. The adsorption peak centered at 430 nm represents the presence of cation radicals (polarons) $-\pi^*$ electronic transition [35]. As reported previously, PANI has two absorption peaks at 324 and 639 nm, which are due to the $\pi-\pi^*$ transition of the benzenoid rings and the absorption of the quinoid rings, respectively [36,37]. In our experiment, however, only one absorbance