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One-step synthesis of oriented polyaniline nanorods through electrochemical deposition

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Summary

Large-scale of oriented Polyaniline nanorods have been synthesized by one-step electrochemical deposition on aluminium electrode without the aid of any templates. The diameters and lengths of polyaniline nanorods are in the range of 50－60 nm and 150－250 nm, respectively. The morphologies and molecular structures of the film are characterized by field-emission scanning electron microscopy (FE-SEM), Ultraviolet-Visual (UV-vis) and Fourier transform infared (FTIR). The effects of synthetic parameters, such as the concentration of aniline and electric current intensity, on the morphologies of polyaniline films are investigated.

Introduction

Recently, the rapid development in nanoscience and nanotechnology has stimulated an increasing effort in studying one-dimensional nanostructures, including nanowires, nanofibers, nanotubes and nanorods. Since these one-dimensional nanostructures are among the smallest entities through which electrons could be transported, they are important “building blocks” for the construction of nanodevices [1]. Polyaniline is one of the important classes of conjugated polymers due to its interesting electrochemical and optical properties and environmental stability. It readily reacts with chemical species at room temperature. After it reacted with oxidizing or agents, electrical and optical properties of polyaniline were changed, meanwhile, polyaniline can transfer from an initial insulating state to an electrically conducting state. This transition can be used in such applications as optical sensors, chemical sensors, and biosensors [2,3,4,5,6]. Oriented nanostructures have high surface area and high porosity for allowing fast diffusion of molecules into the structures, so oriented polyaniline as sensors have higher sensitivity and faster response than misoriented nanostructures.

Different nanostructures of polyaniline, such as hollow microspheres, dendrites, fibers and rods, have been obtained through diverse methods, which generally include physical and chemical routes. Physical methods, including mechanical stretching and electrospining, had also been used to make polyaniline [7,8]. Chemical polymerization of aniline monomer is a facile approach to preparation of polyaniline nanofibers and nanowires [9,10]. But it usually needs aid of either a “hard” or a “soft” template in order to synthesize oriented nanofibers or nanorods. Hard templates include anodized alumina, track-etched polycarbonate and zeolite channels [11,12]. Soft templates include surfactants, micelles, liquid crystals, and polyacids [13,14,15]. Nanofibers of tens of nanometers in diameter appear to be an intrinsic morphology of polyaniline and they can be made without any template [16] Electrochemical deposition of aniline monomer may be a suitable method to preparation oriented polyaniline nanostructures, as the course of polyaniline synthesis does not need above templates and it is easier to prepare oriented polymer nanostructures on complicated surfaces [17]. Liu and his co-workers prepared large-scale of oriented polyaniline nanowires on some substrates through three-step electrochemical deposition without using a supporting template [18,19]. In this paper, we present one-step electrochemical deposition to synthesize large-scale of oriented polyaniline nanorods on aluminium plates without aid of any templates. These aligned polyaniline nanorods have uniform diameter ranging from 50－60 nm and its lengths ranged from 150－250 nm.

Experimental

Pretreatment of electrodes

All chemicals were of analytical grade and used as received. The aniline monomer was doubly distilled before use. The polyaniline films were synthesized by electrochemical method on aluminium plates. In order to carry out the successful electropolymerization of polyaniline, the substrates (electrodes) needed to be pretreated. In this paper, we adopted the method of mechanical surface treatment to deal with the electrodes. The aluminium plates and stainless steel plates were machined flat and polished to a final smoothness of around 0.1 μm on successively finer grades of alumina powder lubricated with distilled water. Then, they were cleaned ultrasonically and rinsed with ethanol.

Preparation of polyaniline films

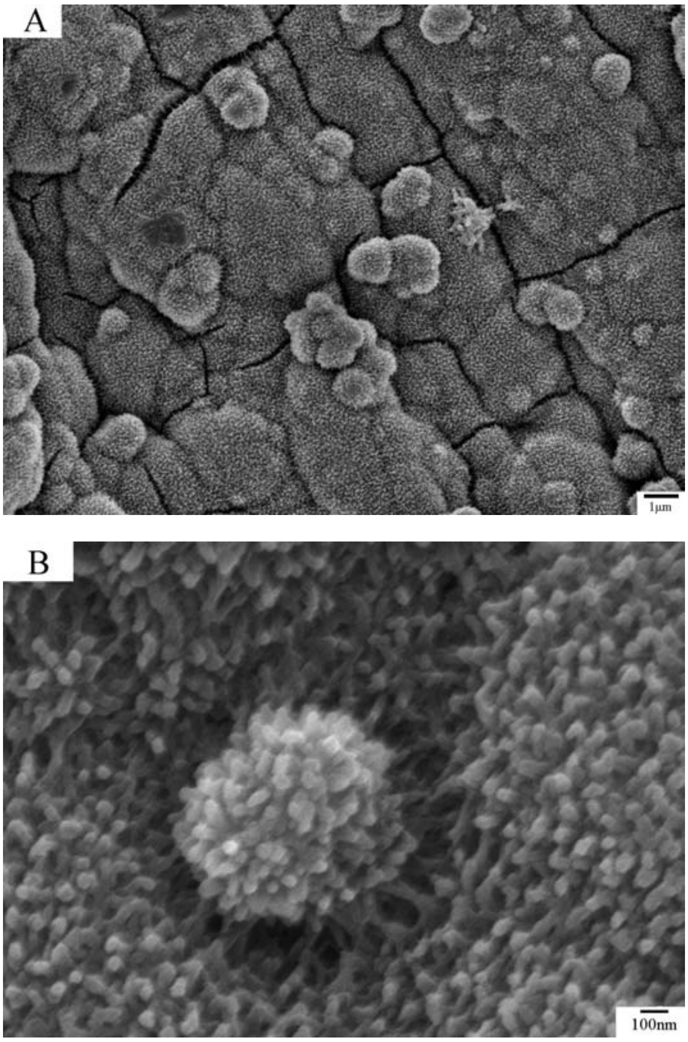
Electrochemical polymerization experiments were carried out at constant galvanostat using HY1792-5(S) Model Potentiostat-Galvanostat. (Beijing Hangyu Sci. and Tech. Co.Ltd) The electrolysis cell used for the experiments was H-shaped. It only consisted of working electrodes and counter electrodes without reference electrodes. The aluminium plates and stainless steel plates were used as the working electrodes and counter electrodes respectively. Their dimensions were the same 4.6 cm × 4.1 cm × 0.2 cm (with a surface area of 41.2 cm^2) Nitrogen gas was purged with solutions of 0.125 $mol \cdot L^{-1}$ aniline concentration and 0.50 $mol \cdot L^{-1}$ oxalic acid concentrations for 30 minutes. The pH of the electrolytic solution was 1.5. The current intensity was set 0.1 A all the time. After about 5 minutes, the dark green substances appeared on the aluminium plate. This showed polyaniline had been synthesized. The quantity of polyaniline became more and more with the proceeding of the reacting. The polymers that coated the working electrode were washed using bidistilled water. They were then dried at 60°C in a vacuum oven for 24 hours.

Characterization of polyaniline films

The morphologies of resultant polyaniline nanorods on aluminium plates were characterized by field-emission scanning electron microscopy (FE-SEM). SEM measurements were conducted on a JSM-6700F field-emission scanning microscope at an acceleration voltage of 16.0 KV. Before SEM imaging, the samples were sputtered with thin layer of gold. The molecular structures of rodlike polyaniline nanoparticles were measured by Fourier-transform infrared FT-IR) spectroscopy and UV-vis spectroscopy. A little of polyaniline peeled out of the film on the aluminium were used as samples for the FT-IR. FT-IR spectra were determined on a Nicolet Magna IR-750 spectrophotometer using KBr pressed discs. Samples for UV-vis spectroscopy were prepared as above. UV-vis spectra were measured on a Cary 5000 UV-vis-NIR spectrophotometer.

Results and Discussion

Typical SEM images of polyaniline films obtained with 0.125 mol L^{-1} aniline in 0.5 mol · L^{-1} oxalic acid were shown in Figure 1. At the low magnification [Figure 1 (A)],



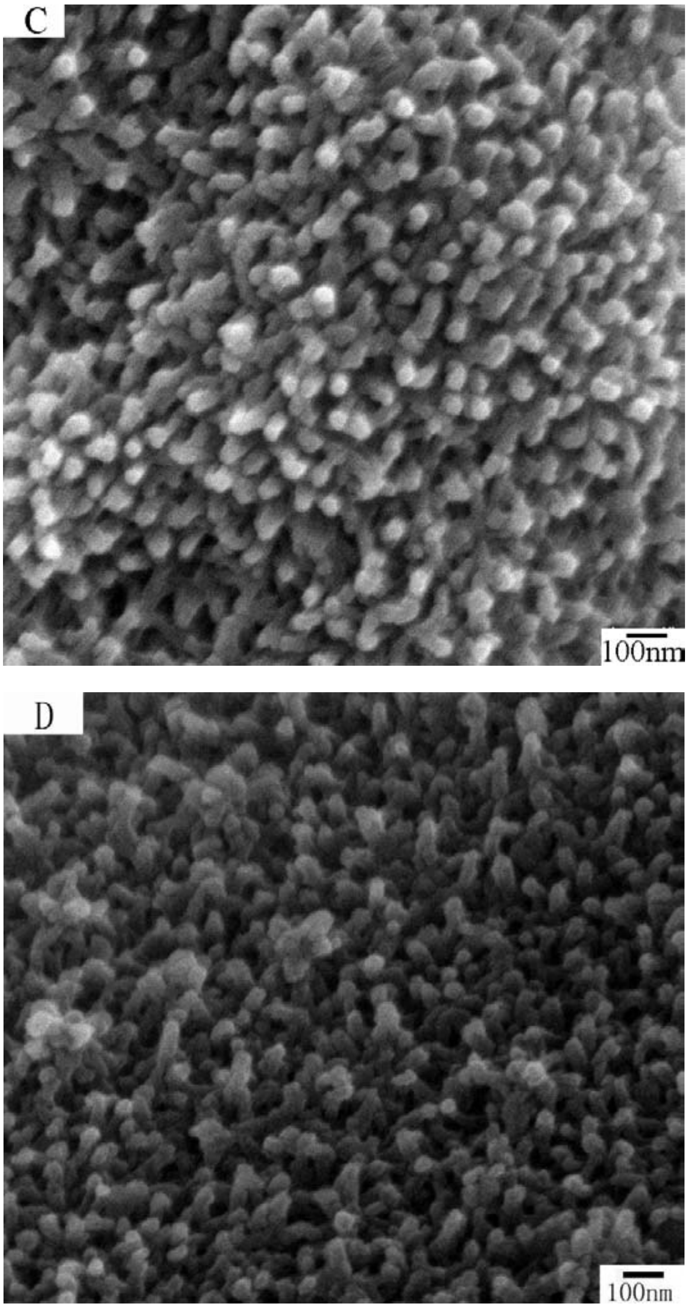


Figure 1 SEM images of oriented polyaniline nanorods synthesized on aluminium plates with 0.125 mol · L^{-1} aniline (current intensity is 0.1 A). [A] Top view, low magnification; [B] and [C] High magnification; [D] Tilted view, high magnification

we can see that the film present a quantity of something villous and mastoid region, which consisted of innumerable white points. In high magnification SEM image [Figure 1 (B)], the nanostructures of the mastoid region were observed clearly. In high magnification SEM image [Figure 1 (C)], we viewed large-scale of oriented polyaniline nanorods that were perpendicular to the aluminium plates. Judging from the SEM view with about 40°tilting [Figure 1 (D)], they have uniform diameters of the ranging from 50－60 nm, and their lengths are 150－250 nm. This indicates that we prepared large-scale oriented polyaniline nanorods through one-step electrochemical deposition.

The effects of synthetic parameters, such as the concentration of aniline and electric current intensity, on the morphologies of polyaniline films are investigated.

We also prepared oriented polyaniline nanorods in higher concentration of aniline (0.20 mol · L^{-1} aniline) under the same current intensity. Figure 2 (A) shows the oriented polyaniline nanorods had lower aspect ratio compared with the concentration of 0.125 mol · L^{-1} aniline. As the monomer concentration increased up to 0.350 mol · L^{-1}, Figure 2 (B) reveals that it did not have oriented nanorods deposited on aluminium plate. In addition, if the concentration of the monomer was too low, there did not generate any substances. Through many groups of experiments , we concluded that in order to electrochemically synthesized oriented polyaniline nanorods on aluminium plate, the appropriate value should be kept between 0.05 and 0.25 mol L^{-1}.

Figure 3 with Figure 1 are SEM images of polyaniline synthesis under the circumstance of same concentration of monomer and different current intensity. It is indicate that the electric current intensity plays an important role in controlling the morphologies of the products through the contrast. When the electric current intensity increased from 0.1 A (current density $j=2mA \cdot cm^{-2}$) to 0.25A (current density $j=5mA \cdot cm^{-2}$), the microstructures of polyaniline became irregular, the scale of particles reached hundreds of nanometer.

The electrochemical preparation of oriented polyaniline nanorods follows a specific mechanism. The formation of the polyaniline nanorods involves two process nucleation and growth events [18,19]. In order to prepare large arrays of oriented polyaniline, we designed appropriate experiment parameters to control the nucleation and growth courses. Nucleation is favored on the substrate rather than in the solution. There will generate large number of nuclei of polyaniline on the aluminium plates when the monomer concentration and current intensity are appropriate. The oriented polyaniline nanorods grow from the nucleation sites with the development of electrochemical reaction.

A typical Fourier transform infared (FTIR) spectrum of the polyaniline film obtained with 0.5 mol · L^{-1} oxalic acid and 0.125 mol · L^{-1} aniline was shown in Figure 4, The adsorption peak at 1294 cm^{-1} corresponds to the C-N stretching modes of the leucoemeraldine component [20]. The peak at 1130 cm^{-1} was due to the C-H in-plane bending mode of permigraniline and that at 1244 cm^{-1} was related to the protonated C-N group [21]. The characteristic peaks at 1491 cm^{-1} and 1578 cm^{-1} were assigned to the C=C stretching modes of the benzenoid ring and the quinoid ring, respectively. There indicating that the state of the polyaniline is emeraldine rather than solely the leucoemeraling or permigraniline forms [22,23].

As shown in Figure 5 (dotted line), the UV-vis spectrum of the polyaniline film on aluminium plate shows two adsorption peaks 315 nm and 646 nm indicating it was polyaniline in conducting state. The peak observed at 315 nm was attributed to π-π^* transition in transition in benzenoid units and the peak at 646 nm was attributed to

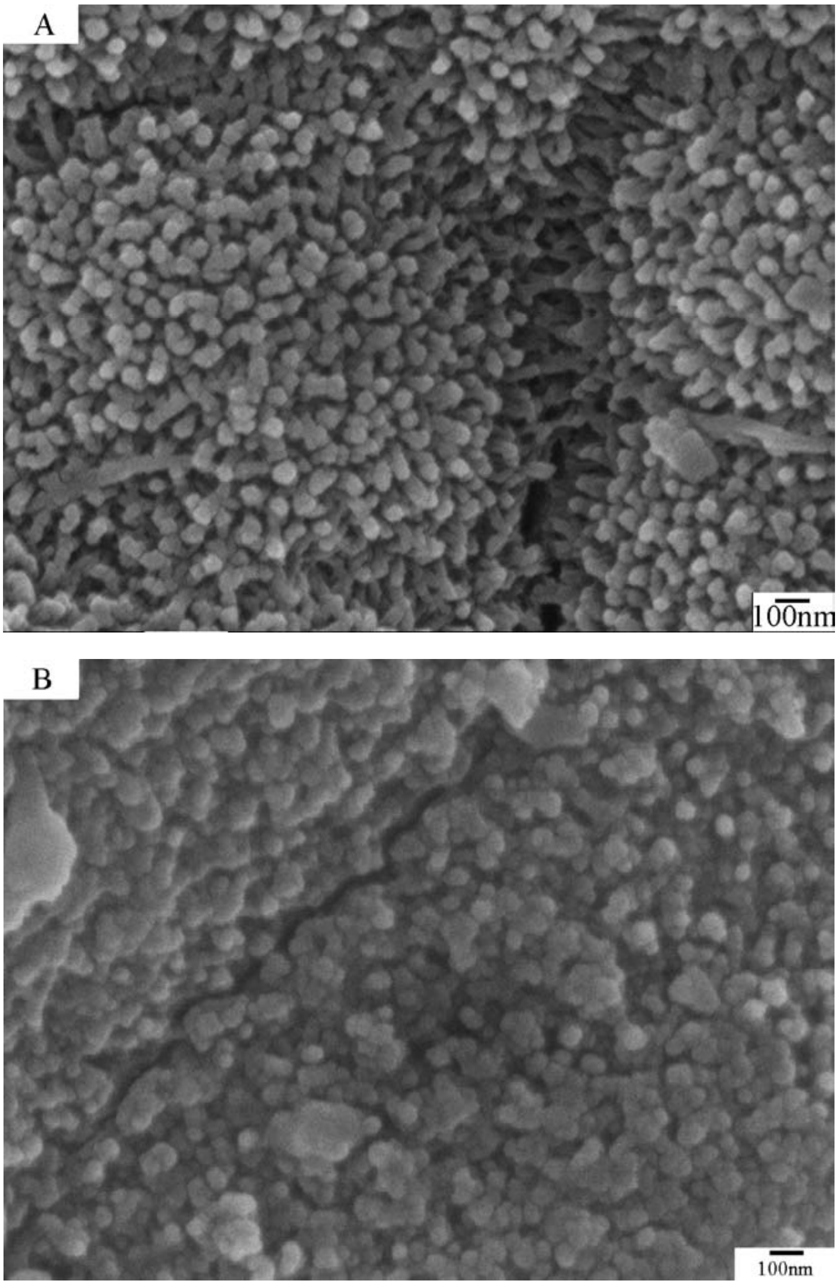


Figure 2 SEM images of polyaniline synthesized under the same current intensity of 0.1 A. [A] 0.2 mol · L-1 aniline; [B] 0.35 mol · L-1 aniline

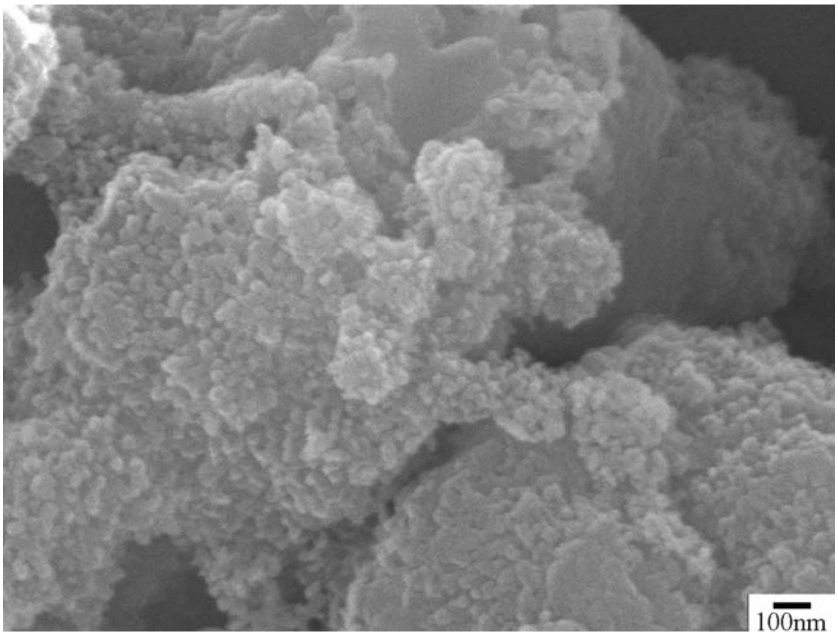


Figure 3 SEM image of polyaniline electrochemical deposition on aluminium plate at current intensity of 0.25 A (concentration of aniline monomer is 0.125 mol · L^{-1})

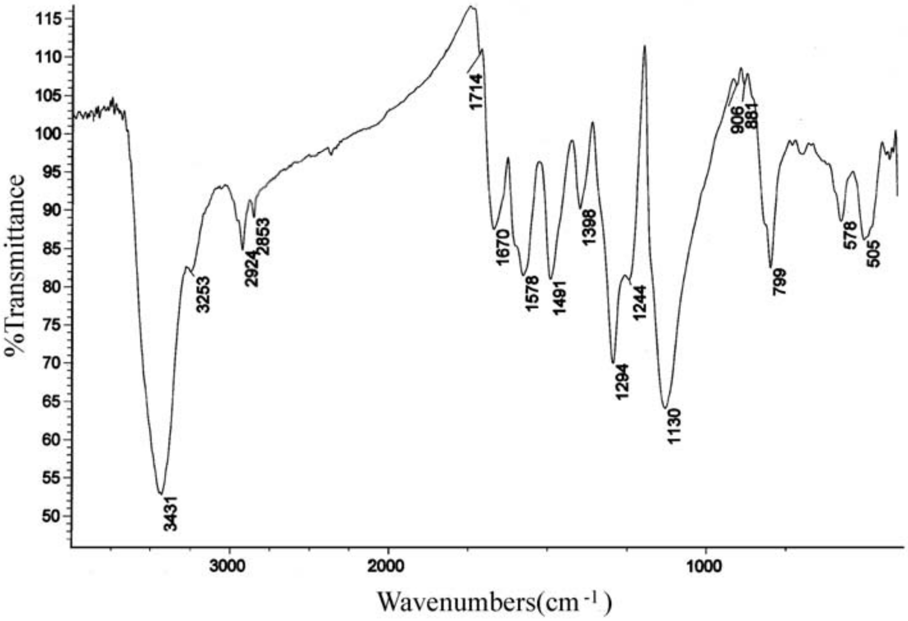


Figure 4 FTIR spectrum of polyaniline film electrochemical polymerized on aluminium plate with 0.5 mol · L^{-1} oxalic acid and 0.125 mol · L^{-1} aniline (Current intensity=0.1 A)

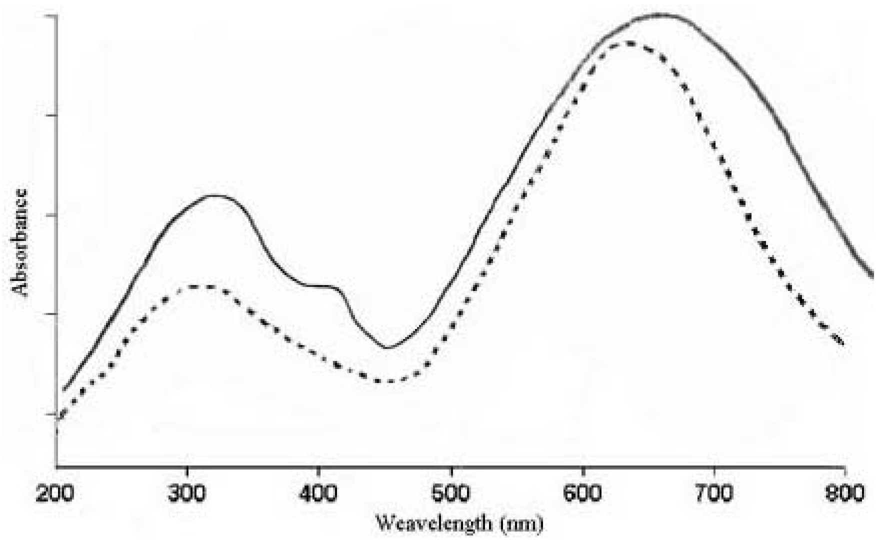


Figure 5 UV-vis spectrum of the polyaniline film before (dotted line) and after (solid line) doped HCl

exciton-like transition (the conducting form) in quinoid diimino units. The film can be re-doped by hydrogen chloride. The spectra of polyaniline film treated with 1 M HCl for 60 minutes is given in Figure 5 (solid line). An absorption peak at 415 nm can be assigned to the localized polarons which are the characteristic of the protonated polyaniline.

Conclusions

In summary, we used one-step electrochemical deposition to synthesize rapidly large area of oriented polyaniline nanorods on aluminium plate without the conventional templates. Oriented polyaniline nanorods have uniform diameters ranging from 50 nm to 60 nm and their lengths range from 150 nm to 250 nm. The concentration of monomer aniline and current intensity played an important role in the synthesis of oriented polyaniline films. This may establish basis for further study of polyaniline property and potential application.

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