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Diameter-Controlled Synthesis of Polyaniline Nanofibers

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Summary

Various diameters of polyaniline (PANI) nanofibers were easily made by varying the sweep rate in the electrochemical polymerization of the aniline monomer. At a sweep rate of 5 mV/s, the PANI nanofibers have an average diameter of 450 nm with a median of 440 nm. The fibers are short, on the order of a few microns in length, and exhibit a branched geometry. Increasing the sweep rate to 50 mV/s produced longer nanofibers with a smaller average diameter of 200 nm. Nanofibers synthesized at 100 mV/s were noted to be smaller with an average and median diameter of 100 nm. These results illustrate the ease in which the morphology of nanostructured PANI can be altered and indicate that the method has the potential to create multi-diameter fibers or mixed-morphology materials.

Introduction

In this communication we report a simple and facile method for synthesizing the conducting polymer, polyaniline (PANI) as a dense mat of nanofibers in diameters ranging from 75 to 550 nm. The synthesis relies on a potentiodynamic, electrochemical technique where the potential of the working electrode is linearly swept at a constant rate. By changing the sweep rate, this novel method allows one to simply "dial-in" a desired nanofiber diameter. PANI nanofibers synthesized in this fashion have potential applications in the areas of microelectronics, nanoscale devices, and chemical sensors for environmental contaminants.

Nanostructured materials, such as carbon nanotubes,[1,2] semiconductor nanowires, [3] or fullerenes,[4] have novel properties that are derived, in part, from their nanoscale morphology. Nanostructured materials have found applications in many areas including molecular electronics,[5,6] nanocomposites, [7] and chemical sensing.[8,9] They often exhibit enhanced performance compared to their amorphous analogs, as demonstrated by the increased acid-sensing ability of PANI nanofibers over granular forms.[9,10,11] Despite these advances, rational control over the morphology of nanostructured materials, in particular organic polymers, remains a challenge.

Several solution-based techniques for creating nanostructured materials have been developed including the use of templates,[12,13,14,15] self-assembly, [16,17] electrospinning, [18] or template-free syntheses.[10,19,20,21] A major drawback to these approaches is they can be time-consuming, multi-step processes. Electrochemical methods for synthesizing nanostructured PANI have also been developed. In general, electrochemically synthesized PANI requires little to no processing or purification. In the case of chemical sensors, PANI films can be electrochemically synthesized directly onto interdigitated electrodes, eliminating several steps from the analogous solution-based approach. Potentiometric [22] and galvanic [23] electrochemical modes have been used with Au [22, 24] or Pt [25,26] working electrodes to synthesize nanostructured and amorphous PANI thin-films.

Experimental

Micropatterned Au Electrode – The synthesis was carried out electrochemically using a micropatterned Au working electrode. Glass substrates were sputtered with 500 Å of titanium followed by 1,500 Å of Au. Photolithographic techniques were then used to micropattern an array of parallel lines that were approximately 13 microns wide. The Au lines were separated by a gap of approximately 13 microns consisting of exposed glass substrate. Except when noted, the electrodes were pre-treated with 4-aminothiophenol (4-ATP; Aldrich Chemical) to form a self-assembled monolayer (SAM). The micropatterned electrodes were cleaned with piranha solution [27] prior to soaking in an ethanolic solution of 4-ATP (previously recrystallized) for 4-6 hours. The electrodes were then rinsed with 200 proof ethanol and stored under N_2.

Electrosynthesis – PANI nanofibers were synthesized electrochemically using a standard three-electrode configuration with a PAR, model 263A potentiostat. The micropatterned electrodes described above were used as the working electrode. Both the Pt wire auxiliary electrode (Aldrich Chemical) and the Ag/AgCl reference electrode (Bioanalytical Systems) was placed in a glass tube fitted with a Vycor tip. The electrochemical solution contained 0.5 M 1*R*-(–)10-camphorsulfonic acid (electrolyte and dopant) and 0.03 M aniline which was previously vacuum distilled over zinc powder. The potential at the working electrode was linearly swept from 0 V to 1.2 V and then reversed to –0.01 V before returning to the starting point. This cycle was repeated until an appreciable amount of (PANI) had formed on the electrode. The electrodes were dip-rinsed with water and then air dried.

SEM Images – SEM micrographs were recorded with a JEOL model JSM-6460LV scanning electron microscope (SEM).

Results and discussion

The template-free synthetic method described herein relies on standard electrochemical techniques and does not require post-synthetic processing or purification. PANI nanofibers were synthesized directly onto micropatterned Au electrodes as described in the experimental section. The pattern was chosen to mimic a two-contact, interdigitated electrode that is typical of substrates used to create sensors from polymer thin films[9]. 4-ATP and similar thiols have been used to covalently bond PANI to Au substrates [28,29] and have been shown to increase thin-film density [24].

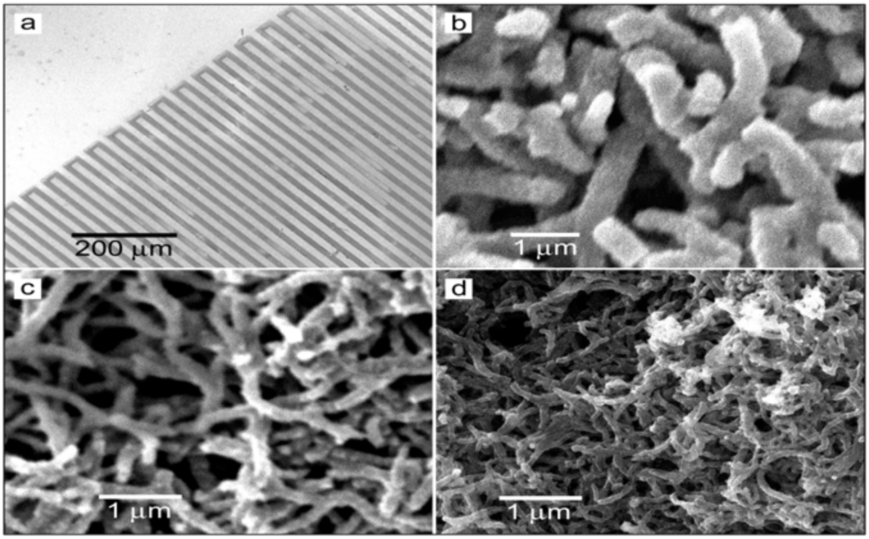

Figure 1. (a) SEM image of a micropatterned Au electrode (dark areas are glass). SEM images of electrochemically synthesized PANI at sweep rates of (b) 5 mV/s, (c) 50 mV/s, and (d) 100 mV/s.

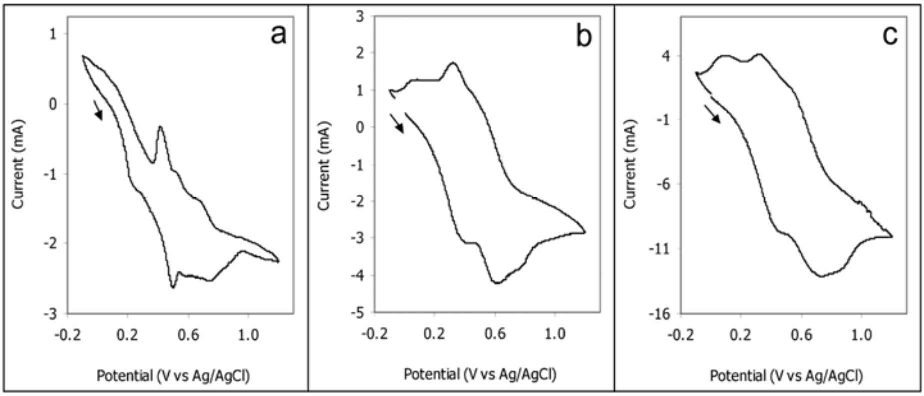

Figure 2. Cyclic voltammograms taken from the synthesis of PANI nanofibers at (a) 5 mV/s, (b) 50 mV/s, (c) 100 mV/s. The traces were taken after a thick layer of PANI nanofibers had formed.

PANI nanofibers synthesized with this method have different diameters [30] depending on the sweep rate (Figure 1). At 5 mV/s, the PANI nanofibers have an average diameter of 450 nm with a median of 440 nm. The fibers are short, on the order of a few microns in length, and exhibit a branched geometry. Increasing the sweep rate to 50 mV/s produced longer nanofibers with a smaller average diameter of 200 nm. Nanofibers synthesized at 100 mV/s were smaller still, with an average and median diameter of 100 nm. These results illustrate the ease in which the morphology of nanostructured PANI can be altered and indicate that the method has the potential to create multi-diameter fibers or mixed-morphology materials. This reduction in diameter as a function of reaction time is consistent with the observations made by Huang and Kaner [31] in their interfacial polymerization route: rapid mixing (analogous to faster electrochemical sweep rates) limit secondary growth of the polyaniline nanofibers by quickly consuming the reactants during the initial polymerization. It is proposed that faster sweep rates in the electrochemical approach suppresses additional growth (similar to the chemical interfacial method) and thus yields smaller diameter fibers. While the exact mechanism of formation of these nano- and microstructures is not completely understood, the right combination of dopant concentration [32], sweep rate [33], oxidant concentration [34] and oxidant redox potential [35] appears to facilitate their formation.

To synthesize the nanofibers pictured in Figure 1, the potential was cycled 20-200 times until a thick layer of nanofibers had formed. The dissimilar shapes of the cyclic voltammograms (CV), taken from the last cycle of the syntheses (Figure 2), cannot be explained solely by scan rate effects and suggest morphology-induced differences in electroactivity exist. Similar behavior was observed for PANI electrosynthesized on Pt electrodes [36]. The CVs may also reflect the multi-layered structures (Figure 3) that are produced with this method. PANI initially forms surface-bound ribbon structures that increase in ribbon density with sweep rate. Dense mats of nanofibers are then formed, potentially using the ribbons as initiation sites.

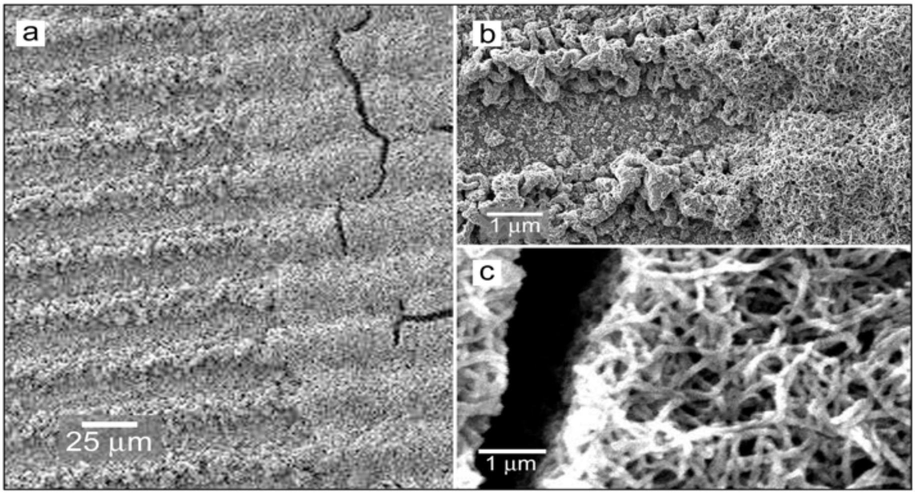

Figure 3. PANI nanofibers electrochemically synthesized at 50 mV/s. (a) SEM image of a micropatterned gold electrode containing both PANI ribbons and nanofibers. (b) Higher magnification image of the sample in Figure 3a showing the formation of nanofibers on top of the ribbon layer. (c) SEM image of a thick layer of nanofibers formed after repeated potential sweep cycles.

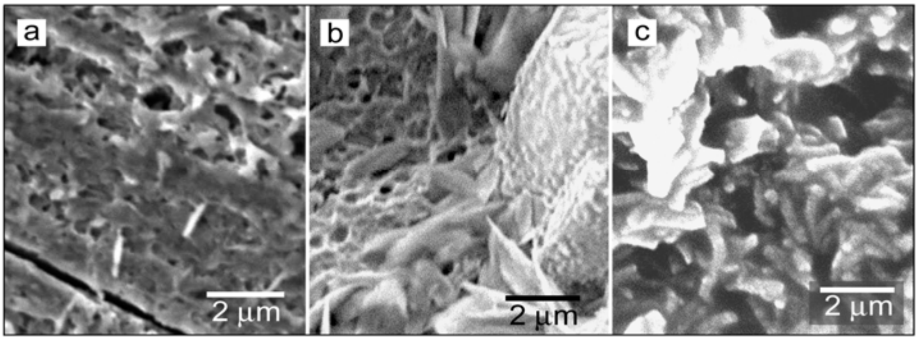

Figure 4. Changing any of the parameters of the PANI nanofibers results in unstructured films. SEM images of PANI electrosynthesized (a) on an unpatterned Au electrode treated with 4-ATP at 50 mV/s, (b) on a micropatterned electrode without 4-ATP at 50 mV/s, and (c) in potentiostatic mode at 1.2V vs. Ag/AgCl on a micropatterned electrode treated with 4-ATP.

While the mechanism for the formation of PANI nanofibers is not well understood, the combination of potential cycling, pretreatment with 4-ATP, and utilizing micropatterned Au electrodes appears to facilitate their formation. As illustrated in Figure 4, changing any of the parameters in the described electrochemical synthesis led to unstructured PANI. Substituting the working electrode with an unpatterned Au surface (Figure 4a) or omitting pre-treatment of the micropatterned electrode with 4-ATP (Figure 4b) produced irregular PANI morphologies. Changing the electrochemical mode to potentiostatic, by holding the potential of the micropatterned Au electrode fixed at 1.2V vs. Ag/AgCl, produced a fused mixture of fibers and unstructured material (Figure 4c). These results suggest that the non-uniform electric field generated by the micropatterned electrode is an important factor for forming nanofibers. In addition, the 4-ATP monolayer is necessary to form the ribbon structure that was a prerequisite for nanofiber formation.

Conclusions

The results presented in this report demonstrate a simple method for synthesizing PANI nanofibers. The complicated interplay between the lifetime of oxidized species, which is controlled by the sweep rate, and the transient electric field generated by the micropatterned electrode are key factors in controlling nanofiber diameter. This novel method has the potential to create a new class of polymeric materials in which structure-function relationships are dictated by molecular interactions rather than bulk phenomena.

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