Polyaniline Nanofibers and Composite Materials for Chemical Detection

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ABSTRACT

Recently we developed a simple, template-free chemical synthesis for polyaniline nanofibers that is selective for nanofibers, can be readily scaled to make large quantities and can be controlled to selectively produce nanofibers with narrow size distributions. Chemical sensors fabricated from polyaniline nanofibers have significantly better performance than conventional material in both sensitivity and time response. The high surface area, small diameter, and porous nature of the nanofiber films allow for facile diffusion of vapors, which is responsible for the enhanced performance. Most recently we have shown that composites with polyaniline are useful to detect analytes that do not give a significant response with unmodified polyaniline. These include fluoroalcohol additives for hydrazine detection and inorganics for hydrogen sulfide detection. Polyaniline nanofibers are superior materials that have excellent potential for many chemical detection applications.

Keywords: chemical sensors, polyaniline, nanofiber, conducting polymer.

INTRODUCTION

Conducting polymers hold much potential to accomplish the chemical detection tasks required for chemical agents, toxic industrial chemicals or explosives. Conducting polymers are unique because they show very large electrical property changes when they are chemically treated with oxidizing or reducing agents. After chemical treatment with protonating, deprotonating, or reducing agents, these polymers can change from an initially electrically insulating state to a conducting state [1] with a change in conductivity that can approach ten orders of magnitude. This transition can be used to perform very sensitive chemical sensing [2,3] or biosensing [4,5,6]. Other vapor interactions with the polymer also cause smaller conductivity changes; these include vapor induced swelling or conformational changes that affect the interchain conduction.

Of the conducting polymers, polyaniline is one of the most promising from an applications standpoint since it is very stable in air and undergoes doping and dedoping by simple acids and bases. Other conducting polymers require stronger oxidizing or reducing agents to be converted between conducting and insulating forms. However, conventional films of polyaniline have not found much use as chemical sensors due to relatively low sensitivity or time response.

Recently, we have successfully developed a chemical synthesis to make polyaniline nanofibers in bulk quantities [7,8]. Instead of using the traditional homogeneous aqueous solution of aniline, acid, and oxidant, the polymerization is performed in an immiscible organic/aqueous biphasic system. The products are polyaniline nanofibers with nearly uniform diameters between 30 and 50 nm with lengths varying from 500 nm to several micrometers. Gram-scale products can be synthesized that contain almost exclusively nanofibers. The nanofibers can be modified by a variety of dopants and dedoping doesn't appear to affect their morphology. This novel, yet simple synthetic method makes polyaniline nanofibers readily available for development of inexpensive chemical sensors. Because the nanofibers can be isolated, purified and chemically modified, they can be tailored to provide response to new classes of chemicals as needed for homeland security and other applications.

EXPERIMENTAL

The emeraldine base form of polyaniline was chemically synthesized from aniline by oxidative polymerization using ammonium peroxydisulfate in an acidic media. The polyaniline nanofibers were synthesized in an aqueous-organic two-phase system and purified by dialysis. Polyaniline solutions were made by either dissolving polyaniline in hexafluoroisopropanol (HFIP, 2 mg/mL) or by dissolving polyaniline in N-methylpyrrolidinone (NMP, 1 mg/mL). Filtered solutions were then used to cast films onto substrates by dropping the desired amount of solution from a disposable microliter pipette. The films were air dried (HFIP) or dried in a 60°C oven overnight (NMP). The nanofiber suspensions

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obtained after synthesis and dialysis were diluted with water and drop-cast onto the substrates. Film thicknesses were controlled by dilution of the original synthesized suspensions using a constant volume for casting.

Interdigitated electrode sensor substrates were fabricated using standard photolithographic methods at The Aerospace Corporation. The electrode geometry consists of 50 pairs of fingers, each finger having dimensions of 20 μm x 4970 μm x 0.18 μm and a 10 μm gap. Film thicknesses were measured with a profilometer (DekTak II). Electron microscope images were obtained using field-emission scanning electron microscope (JEOL JSM-6401F). Electrical resistances (DC) were measured with a programmable electrometer. Instruments were controlled and read by computer using a GPIB interface and Labview software.

Acid and base gas exposures used certified gas mixtures of HCl, NH_3 or H_2S in nitrogen. For hydrazine exposures, a permeation tube of hydrazine was used with a certified emission rate. Mass flow controllers were used to meter separate flows of nitrogen buffer gas and the gas mixture.

RESULTS AND DISCUSSION

Figure 1a shows a typical TEM image of the polyaniline nanofibers after dialysis. The lengths of the fibers range from 500 nm up to several microns. The nanofibers tend to agglomerate into interconnected nanofiber networks, rather than bundles. A closer look at the nanofibers reveals that many of them are twisted, as shown in the inset. The sample uniformity and narrow diameter distribution are also confirmed by field emission SEM images. Figure 1b shows a typical SEM secondary electron image of a nanofiber thin film cast on an electrode substrate from dialyzed suspension. Dedoping has no noticeable effect on the fiber morphology.
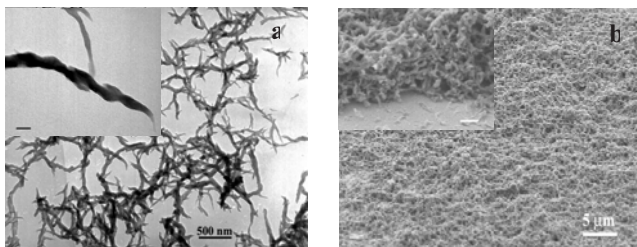

Figure 1. a) TEM images of polyaniline nanofibers cast from suspension. The inset shows a twisted fiber (scale bar = 50 nm), b) SEM secondary electron images of a thin film deposited on sensor substrates. The inset shows a cross-sectional view of the film on the glass substrate (scale bar = 200 nm).

Figure 2 shows the resistance changes of a dedoped film upon exposure to 100 ppm of HCl (left) and a fully HCl doped film exposed to 100 ppm of NH_3 (right). The nanofiber thin film responds much faster than a conventional film to both acid doping and base dedoping even though it is more than twice as thick. This is likely due to the small diameters of the nanofibers that gives rise to a high surface area within the film that can be accessed by the gas vapors. With the small diameter of the fibers, it takes the gas molecules a much shorter time to diffuse in and out of the fibers. This also leads to a much greater extent of doping or dedoping over short times for the nanofiber films. The nanofiber films have better performance in both sensitivity and time response compared to conventional films. In addition, the nanofiber films show no thickness dependence to their sensitivity or time response whereas the conventional films show a strong dependence on the thickness. We have not tested the lower detection limit for HCl but reasonable assumptions indicate detection levels in the ppt range are feasible. Many of the toxic industrial chemicals of concern are strong acids or hydrolyze to form strong acids. Therefore polyaniline nanofibers should be useful to detect many of them.
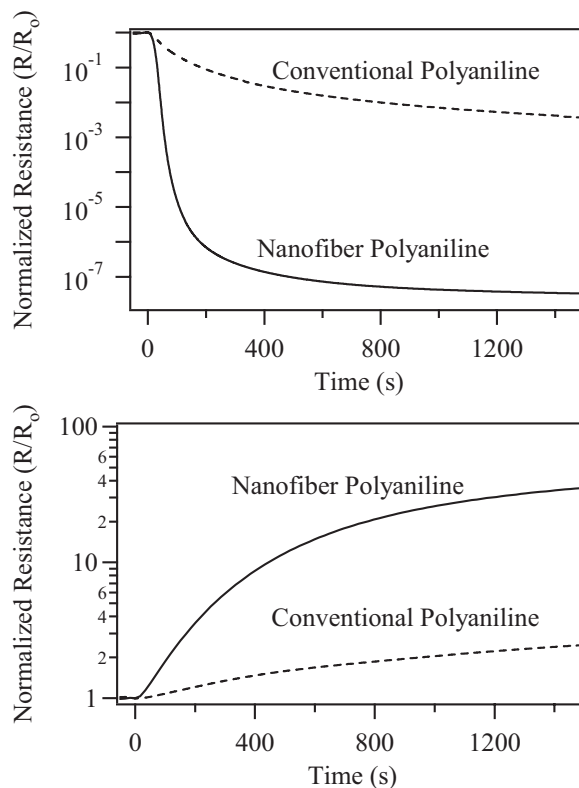

Figure 2. Resistance changes of a nanofiber emeraldine base thin film (solid line) and conventional (dotted line) emeraldine thin film upon exposure to (top) 100 ppm HCl vapor and (bottom) 100 ppm NH_3 vapor. R/R_0 is the resistance (R) normalized to the initial resistance (R_0) prior to gas exposure.

As shown above, when protonated polyaniline interacts with base, it becomes de-protonated, reverses the effect of acid and loses its conductivity. In contrast to the high concentrations of ammonia shown in Figure 2, low

concentrations of n-butylamine (24 ppb) have also been detected with *unoptimized* nanofiber sensors. Once we optimize the nanofiber sensors, we believe it will be possible to detect very low levels of basic vapors such as many of the chemical agents of concern.

The response time of the films is a central issue to sensing applications. The acid doping response is expected to be very rapid since it involves the diffusion of protons into the film. The data shown in Figure 2 was taken at relatively low flow rates in a large volume cell hence the fastest data shown is flow rate limited. The data is also plotted over many orders of magnitude on a log scale which makes the time response data appear slow. Figure 3 shows that when the change in resistance of both the nanofiber and polyaniline films are plotted on linear scales, we find that the response time (90%) is ~2 sec for the nanofiber film and ~30 sec for the conventional film. However, the response time is still instrumentally limited. In addition, when very high flow rates are used, resistance changes of 10^7 occur in less than 4 seconds for the nanofiber films. This is consistent with the other data supporting that the nanofibers should and do respond very rapidly. The true response time of the nanofibers should be very fast; work in progress is geared toward an intrinsic time response measurement.
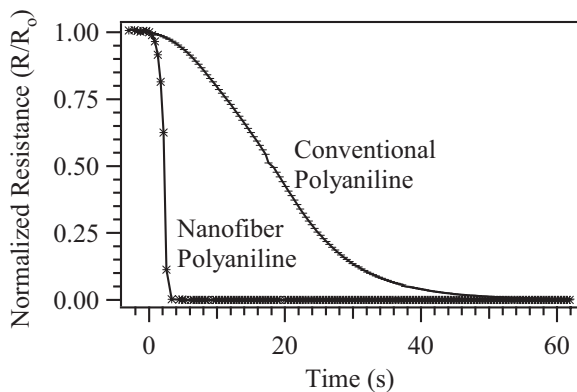

Figure 3. Response time of a nanofiber and conventional polyaniline sensor to 100 ppm HCl.

Hydrazine is a toxic industrial chemical that is used as a rocket fuel and is explosive. Figure 4 shows that polyaniline nanofibers respond to 3 ppm of hydrazine with about a 25-fold increase in resistance. Surprisingly the response of a conventional polyaniline film cast from N-methyl pyrrolidinone (NMP) is negligible ($R/R_0 \sim 1.25$) as shown [9]. We expect the minimum detection limit in the low ppb or even ppt level for hydrazine. Polyaniline is known to undergo a redox reaction with hydrazine. We believe that the nanometer morphology and large surface area of our sensors allows this reaction to occur very rapidly giving a large response in a relatively short time. We expect this type of mechanism to be useful for the detection of other toxic industrial chemicals that can undergo redox reactions with the polyaniline nanofibers.
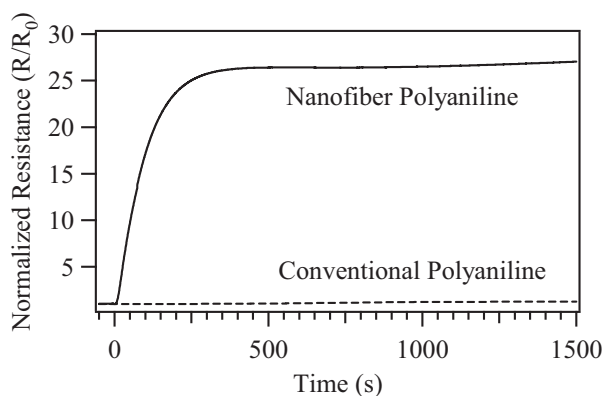

Figure 4. Response of polyaniline nanofibers and a conventional film to 3 ppm of hydrazine.

Figure 5 shows the effect of using a fluorinated alcohol additive on the response of a conventional polyaniline film. When hexafluoroisopropanol (HFIP) is used as a solvent to cast films of polyaniline, we observed a very different response to hydrazine. Instead of reduction of the polyaniline to a nonconducting form, we find a response consistent with doping of the polyaniline. When most of the HFIP is removed from the film by oven drying, we see a reduced response of the sensor. Furthermore, studies using HFIP diluted in NMP shown a similar effect. Similar results were obtained using a chemical analog of HFIP, hexafluoro-2-phenylpropanol (HFPP) [10].
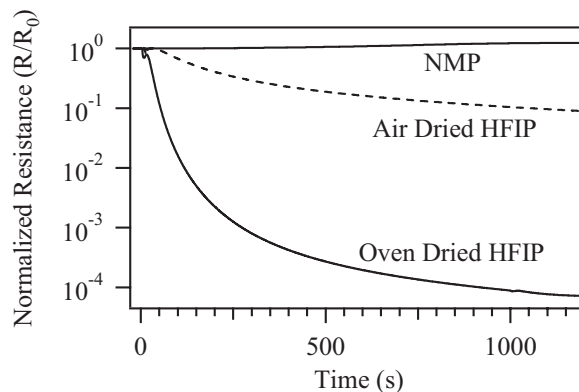

Figure 5. Response of conventional dedoped polyaniline films with added HFIP and NMP upon exposure to hydrazine.

All of these results strongly suggest that the hydrazine is reacting with the HFIP or HFPP to create a strong acid that dopes the polyaniline. The most likely product of this reaction is HF however, literature searches found no reports of such a reaction. Separate experiments show that aqueous hydrazine reacts strongly with HFIP with a drop in the pH of the solution consistent with this proposal. Furthermore, anhydrous hydrazine can be used to defluorinate fluorinated carbon nanotubes with proposed formation of HF [11].

We have also shown that new inorganic composites with polyaniline nanofibers are useful for the detection of hydrogen sulfide [12]. Figure 6 shows that untreated nanofibers give only a small response to hydrogen sulfide. This is due to the weak acidity of H_2S and the lack of direct doping of the polyanilne. When a composite material is formed between polyaniline nanofibers and inorganic complexes (ML_n), this new material shows a dramatic response to H_2S, $R/R_0 < 10^{-4}$. As before the inorganic material reacts with H_2S to create a strong acid that dopes the polyaniline. The approach takes advantage of the tremendous conductivity change of polyaniline and holds great promise for the detection of many different chemicals.
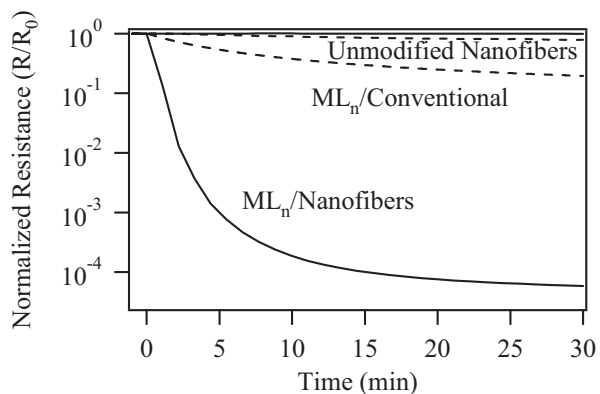

Figure 6. Resistance changes of the polyaniline films upon exposure to hydrogen sulfide; doped polyaniline nanofibers (—), dedoped polyaniline nanofibers (---), and conventional polyaniline containing metal ligand complex (ML_n) (---) and polyaniline nanofibers containing ML_n (—). The H_2S concentration was 10 ppm with 45% relative humidity, all film thicknesses were 0.25 μm.

CONCLUSIONS

In conclusion, when the nanofibers are compared to conventional polyaniline films, they give significantly better performance in both sensitivity and time response for all sensor detection applications examined. We believe this is due to the high surface area, small nanofiber diameter, and porous nature of the nanofiber films. Recent results indicate that composites with polyaniline are useful to detect analytes that do not give a significant response with unmodified polyaniline. These include fluoroalcohol additives for hydrazine detection and inorganics for hydrogen sulfide detection. Therefore polyaniline nanofibers appear to be a superior chemical sensor material for many analytes and have excellent potential for many chemical detection applications including homeland security.

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