1256 *Chem. Mater.* **2005,** *17,* 1256−1260

Hydrazine Detection by Polyaniline Using Fluorinated Alcohol Additives

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Received September 14, 2004

A new sensor for hydrazine detection is reported using conventional polyaniline thin films processed from hexafluoroisopropanol. This and other fluorinated alcohols are shown to react with hydrazine to produce a strong acid. The hydrofluoric acid (HF) protonates the emeraldine base form of polyaniline leading to large increases in conductivity—greater than 4 orders of magnitude. In contrast, conventional polyaniline films processed from other organic solvents and polyaniline nanofiber films processed from water become more insulating upon exposure to hydrazine. In these cases, hydrazine acts as a strong reducing agent, converting the emeraldine form of polyaniline to its leucoemeraldine oxidation state. The concept of using additives to enhance the sensing ability of polyaniline films could prove useful for other analytes as well as for other conducting polymers.

Introduction

Polyaniline is one of the most widely studied conducting polymers because of its environmental stability and straightforward synthesis. In its undoped, insulating emeraldine oxidation state, polyaniline is an interesting material for chemical sensors because its conductivity can increase by over 10 orders of magnitude on exposure to doping acids. This process can be reversed by dedoping in the presence of bases. Polyaniline sensors have been used to detect a number of different chemical species including hydrochloric acid,[1] ammonia,[2] organic vapors,[3] and strong reducing agents such as hydrazine.[1]

Detection of hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine is important because they are used as rocket fuels and have low threshold limit values (TLV) of 10 ppb.[4] Hydrazine has also been implicated in terrorist incidents.[5] Previous work on conducting-polymer-based hydrazine sensors includes using both polypyrrole and polythiophene as the detecting material. Polythiophene sensors can measure very low concentrations of hydrazine, on the parts-per-billion level, but polythiophene is air sensitive and subject to degradation if stored at room temperature.[6] Polypyrrole sensors are air stable but have unreasonably high detection limits of ∼1%.[7]

Hydrazine is a strong reducing agent and is known to reduce both doped and dedoped polyaniline from its half oxidized emeraldine oxidation state to its fully reduced leucoemeraldine oxidation state (Scheme 1).[8] Since leucoemeraldine is electrically insulating, the decrease in conductivity associated with this change can be used to develop polyaniline hydrazine sensors. Our previous work has demonstrated that doped polyaniline nanofibers respond to hydrazine with an increase in resistance and a corresponding change in structure from emeraldine salt to leucoemeraldine.[1] The same type of change occurs for conventional polyaniline processed from *N*-methylpyrrolidinone, but the increase in resistance is much smaller. This shows that direct detection of hydrazine with polyaniline is possible but the response is relatively small.

A potential method to make more sensitive hydrazine sensors is to incorporate an additive into the polyaniline that would increase the response of polyaniline to hydrazine. Additives have been widely used in biosensors to increase the sensitivity of polymers to analytes such as glucose,[9] urea,[10] oxygen,[11] and chloride.[12] Here we demonstrate that when dedoped polyaniline containing small amounts of the

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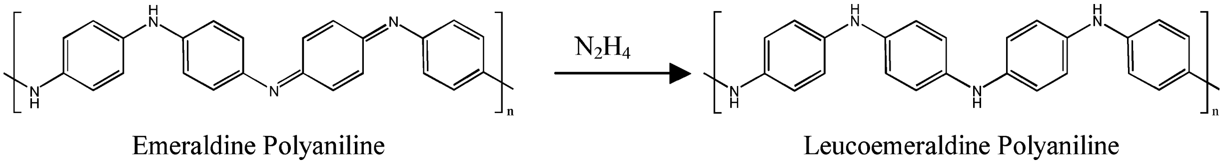
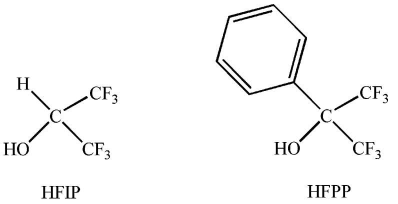
10.1021/cm0484091 CCC: $30.25

Scheme 1. Conversion of Emeraldine Polyaniline to Leucoemeraldine Polyaniline with Hydrazine



Scheme 2. Structures of Hexafluoroisopropanol (HFIP) and Hexafluoro-2-phenylisopropanol (HFPP)



additive hexafluoroisopropanol (HFIP) is exposed to hydrazine, its resistance decreases dramatically.

Experimental Section

All chemicals were of analytical grade and used as received from Fisher except hexafluoroispropanol (99+%) which was obtained from Aldrich and hexafluoro-2-phenylisopropanol (97%) which was obtained from Synquest Fluorochemicals.

The emeraldine salt (doped) form of polyaniline was chemically synthesized from aniline by oxidative polymerization using ammonium peroxydisulfate in an acidic medium.[13] The dedoped form was produced by treatment with ammonium hydroxide (1 M). Polyaniline solutions were made by dispersing polyaniline in hexafluoroisopropanol (2 mg/mL) or in *N*-methylpyrrolidinone (1 mg/mL). The solutions were filtered with an Acrodisc PTFE syringe filter (Aldrich) with 0.2-μm pores. The filtered solutions were then used to cast films onto the bare substrate by dropping the desired amount of solution from a disposable microliter pipet (Drummond Scientific). Film thicknesses were controlled by the amount of solution dropped onto the substrate. This deposition method gives smooth and uniform films. The films were then dried in air for polyaniline/HFIP films or in an oven at 60 °C for ~2 h for polyaniline/NMP films to produce 0.3-μm thick films.

Solutions of conventional polyaniline dispersed in NMP with different amounts of fluorinated alcohols were prepared. The fluorinated alcohols used were hexafluoroisopropanol (HFIP) and hexafluoro-2-phenylisopropanol (HFPP) as shown in Scheme 2. Solutions of the mixed solvents at molar ratios of 0.2 or 0.1 fluorinated alcohol to NMP were prepared. The solutions were cast onto substrates by dropping the desired amount of solution from a disposable microliter pipet. The resulting films were then dried at 60 °C for ~2 h.

The polyaniline nanofibers were synthesized in an aqueous–organic two-phase system and purified by dialysis.[14] The interfacial reaction is typically performed in a 20-mL vial, where the organic layer consists of 3.2 mmol of aniline dissolved in 10 mL of an organic solvent such as benzene, toluene, or xylene. The aqueous layer consists of 0.8 mmol of ammonium peroxydisulfate dissolved in 10 mL of a 1 M acid, such as H_2SO_4 or HCl. The product is purified through dialysis using tubing with a 12 000–14 000 MW cutoff (Fisher Scientific) against water or 0.1–1 M NH_4OH to obtain suspensions of doped or dedoped nanofibers, respectively. The nanofiber suspensions were drop-cast onto the bare sensor substrate using a disposable microliter pipet. Film thicknesses were controlled by the amount of dilution of the original synthesized suspensions.

Interdigitated gold electrode substrates were fabricated at The Aerospace Corporation as previously described.[1] The DC electrical resistances of the polymer films were measured with a programmable electrometer (Keithley 617). All measurement parameters were controlled and acquired with a computer (PC) by means of an IEEE interface and Labview program software. All FTIR spectra were obtained from reflectance measurements of the films on the sensor substrates. A Nicolet Magna 550-IR spectrometer with a Nic-Plan IR microscope and a mercury cadmium telluride detector was used to obtain the spectra. An MKS model 247C 4-channel readout was used with Mykrolis mass flow controllers to control the gas flows.

Doped polyaniline nanofiber and conventional polyaniline films processed from either hexafluoroisopropanol or *N*-methylpyrrolidinone were made by exposing dedoped films to a gas mixture of 100 ppm HCl in nitrogen (Scott Specialty Gases). Varying amounts of HCl were added to the films by controlling the exposure time. Longer exposure times led to higher doping levels and lower resistances. After the films were doped they were then exposed to hydrazine.

For hydrazine exposures, a certified permeation tube (KinTek) of hydrazine was used with a calibrated emission rate. The concentration could be adjusted by changing the flow rate across the tube and the temperature of the tube. Hydrazine concentration for all exposures was 3 ppm and was verified with a well-known colorimetric method using *p*-dimethylaminobenzaldehyde.[15] All gas exposures were carried out in dry gas mixtures without added humidity.

Results and Discussion

Polyaniline is difficult to process from solution and much effort has been directed toward the improvement of its solubility. Solvents that have been used to process polyaniline include *N*-methylpyrrolidinone (NMP),[16] *m*-cresol,[17] formic acid,[18] and hexafluoroisopropanol (HFIP).[19] The conductivity of doped polyaniline films formed from each of these solvents differs due to differences in polymer chain–solvent interactions. In NMP, polyaniline tends to form a compact coil and as a result is not particularly soluble in this solvent.[16]

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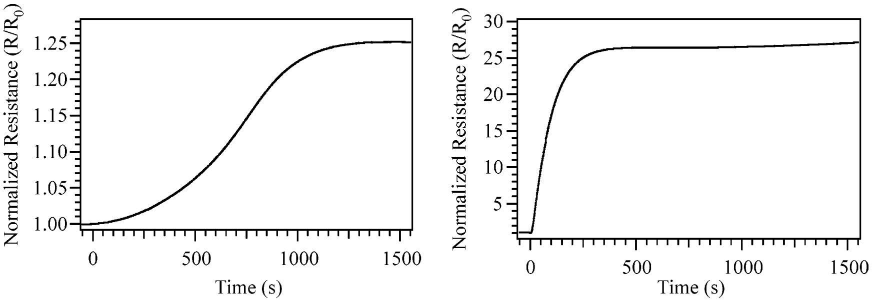

Figure 1. Response of a conventional polyaniline/NMP film (left) and a polyaniline nanofiber film (right) to hydrazine.

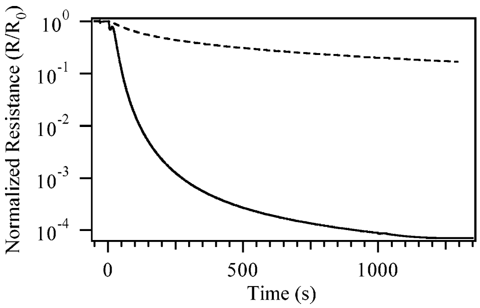

Figure 2. Response of conventional dedoped polyaniline/HFIP films to hydrazine: air-dried (—), and oven-dried (- - -).

On the other hand, in *m*-cresol and HFIP polyaniline adopts an expanded coil conformation leading to films with enhanced conductivities reaching 400 S/cm.[17,19] Among these solvents, HFIP is favored for processing polyaniline because it has a low boiling point (59 °C) and can be used to disperse both the emeraldine salt and emeraldine base forms of polyaniline.[19] In this study of polyaniline as a hydrazine sensor, polyaniline processed from HFIP exhibits unique interactions with hydrazine that lead to dramatic changes in resistance upon hydrazine exposure.

The response of a conventional partially doped polyaniline film processed from NMP to 3 ppm of hydrazine is shown in Figure 1. The *y*-axis is the normalized resistance (R/R_0), where R_0 is the initial resistance of the doped film before exposure to the test gas at $t = 0$ and R is the time-dependent resistance of the film exposed to the test gas. In this case the resistance increases by a relatively small factor (1.25 times) over the starting resistance. Contrast this with the response of a doped polyaniline nanofiber film to the same concentration of hydrazine (Figure 1). Again an increase in resistance is observed, however, there is a much larger change, ~25 times that of the starting resistance. The response of both films is consistent with reduction of the polyaniline from its emeraldine oxidation state to its leucoemeraldine state. The greatly enhanced response of the nanofiber films can be attributed to the much greater surface area of the nanofibers.[1]

The responses of conventional dedoped polyaniline films processed from HFIP to 3 ppm hydrazine are shown in Figure 2. In this case, polyaniline responds to hydrazine gas with a resistance decrease greater than 4 orders of magnitude. After removing some of the HFIP by drying in an oven at 60 °C, the response of the film to hydrazine decreases significantly. This observation suggests that hydrazine may be reacting with residual HFIP to give a product that dopes the polyaniline.

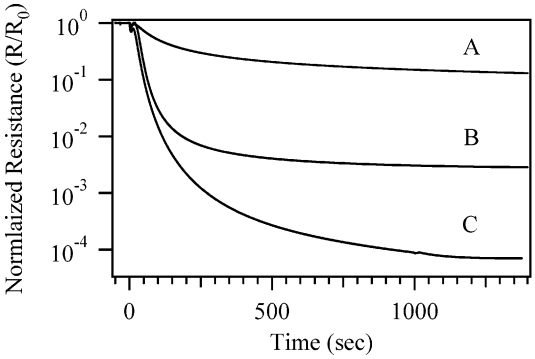

Figure 3. Response of conventional polyaniline/HFIP films exposed to hydrazine as a function of doping level: (A) doped; (B) partially doped; and (C) dedoped.

The doping level of polyaniline films processed from HFIP does not affect the response mechanism to hydrazine. However, the extent of resistance change does vary with doping level (Figure 3). Films of different doping levels were fabricated by varying the exposure times to gaseous HCl. These films were then exposed to hydrazine (3 ppm) and the results show that films with higher doping levels give smaller changes in resistance. All films in Figure 3 are approximately the same thickness so the initial resistance can be taken as a measure of the initial resistivity of the films. The initial resistances are 2.2×10^4, 3.9×10^6, and 2.3×10^9 ohms for films A, B, and C, respectively. Film C has the greatest response and film A has the smallest response. Despite the difference in the initial doping, each film shows that hydrazine reacts with residual HFIP in the films to further dope the film, making it more conducting. The extent of response is inversely related to the doping level and is associated with the reduced response expected for an already doped film. This implies that the doping level is not responsible for the difference in response mechanism between the NMP and HFIP films.

Hydrazine is a strong reducing agent and is known to reduce polyaniline from the emeraldine salt (conducting) form to the leucoemeraldine (insulating) form.[8] This transformation should lead to an increase in resistance as is observed for both the polyaniline nanofiber and conventional polyaniline/NMP films (Figure 1). Polyaniline/HFIP films, on the other hand, tend to become more conducting upon exposure to hydrazine, as verified by reflectance−IR measurements (Figure 4). After exposure to hydrazine, the

Scheme 3. Reaction of Fluorinated Alcohols with Hydrazine to Produce HF and Subsequent Doping of Polyaniline

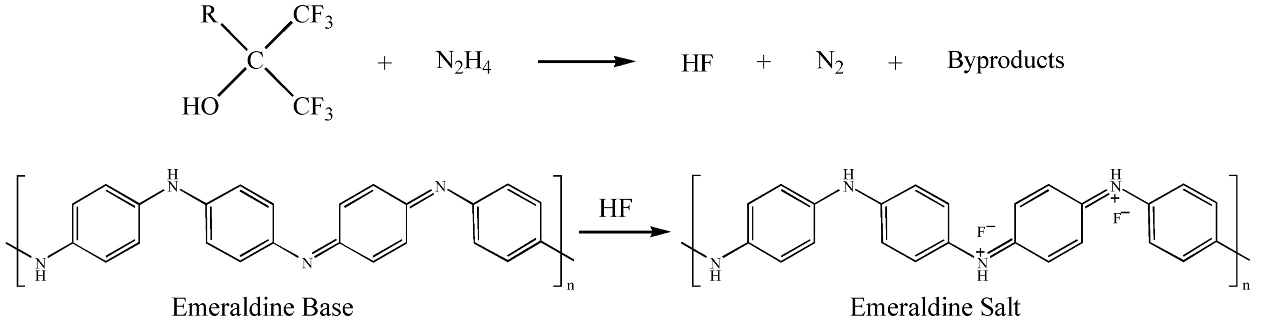

Table 1. Infrared Peak Frequencies[a] and Assignments for Polyaniline Films

peak assignments	emeraldine base polyaniline	polyaniline/HFIP exposed to hydrazine	emeraldine salt polyaniline	leucoemeraldine polyaniline
quinoid ring stretch	1586	1573	1576	1589
quinoid ring vibration	1496	1493	1506	1494
benzenoid ring C−N stretch	1319	1306	1303	1287
quinoid ring C−N stretch	1180	1133	1143	1165
quinoid ring C−H bend	850	839	835	811

[a] Frequencies are given in wavenumbers (cm^{-1}).

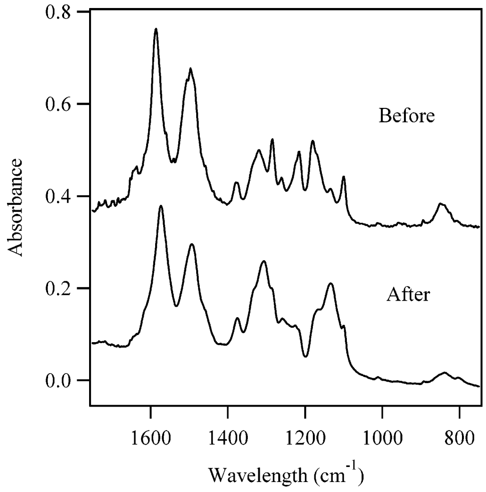

Figure 4. FTIR spectra of conventional dedoped polyaniline films processed from HFIP before (—) and after (···) exposure to hydrazine.

resistance decreases and the IR measurements show a change in conformation from the emeraldine base to the emeraldine salt form. Table 1 lists the peak assignments of the different oxidation states of polyaniline. As seen from this table the peak assignments of the polyaniline/HFIP film after exposure to hydrazine more closely match the peak assignments of the emeraldine salt form of polyaniline than the leucoemeraldine form of polyaniline. Also, the spectrum of the polyaniline/HFIP film after exposure to hydrazine does not look like a spectrum for the leucoemeraldine form of polyaniline.[20] The quinoid ring stretch and ring vibration have similar intensities for the emeraldine salt while the ring vibration is more than twice as intense for leucoemeraldine. Figure 4 shows the peak intensities of the quinoid ring stretch and vibration to be about equal in intensity and very similar to the spectrum of the emeraldine salt form of polyaniline.[20]

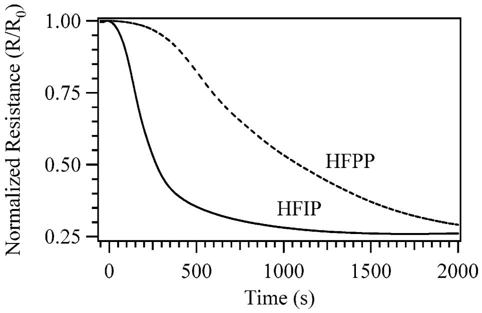

Figure 5. Response of polyaniline films processed using fluorinated alcohols diluted with NMP exposed to hydrazine: HFIP/NMP (—); and HFPP/NMP (- - -). The molar ratio is 1:4 in each case.

The responses of polyaniline films processed from dilute solutions of fluorinated alcohols in NMP on exposure to hydrazine are shown in Figure 5. Both HFIP and HFPP dilute solutions were made at a molar ratio of 0.2. In each case there is a decrease in resistance upon exposure to hydrazine supporting the idea of a reaction between the fluorinated alcohols, HFIP and HFPP, and hydrazine that produces an acid, which in turn dopes the polyaniline making it more conducting. The difference in response between the HFIP and HFPP films in Figure 5 may be due to steric interactions of the phenyl ring in HFPP that slow the reaction of hydrazine with HFPP (Scheme 2). The same experiment was performed using a molar ratio of 0.1 (flourinated alcohol/NMP). These films also gave similar decreases in resistance except the change in response was much smaller. This shows that varying the amount of fluorinated alcohol in the film can vary the response level of the film to hydrazine.

Another experiment was performed to verify the hypothesis of HF generation from the reaction of hydrazine with HFIP. When HFIP was carefully added to an aqueous solution of hydrazine (35 wt %), a strongly exothermic reaction was observed with a large concomitant decrease in pH (11 to 3). A possible mechanism for acid generation involves the exchange of fluorine atoms on the HFIP with hydrogen from the hydrazine to give HF and N_2. A literature

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search showed no prior report of this reaction. However, previous work on carbon nanotubes indicates that fluorinated single-walled carbon nanotubes can be defluorinated with anhydrous hydrazine with proposed products HF and N_2.[21]

In conclusion, polyaniline films with fluorinated alcohol additives are highly sensitive to hydrazine. A reaction between hydrazine and HFIP produces the strong acid HF which in turn dopes polyaniline as shown in Scheme 3. This causes the conductivity of the emeraldine base form of polyaniline to increase more than 4 orders of magnitude. The use of additives such as HFIP or HFPP to improve the sensing capabilities of polyaniline should prove to be a useful method to enhance the selectivity and sensitivity of conducting polymer sensors.

Acknowledgment. This work was supported by the National Science Foundation (NSF) through an Integrative Graduate Education Training (IGERT) fellowship (S.V.), the Microelectronics Advanced Research Corp. (R.B.K.), and The Aerospace Corporation's Independent Research and Development Program (B.H.W.). We thank Dr. Jiaxing Huang for helpful discussions.

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