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Polyaniline Nanofiber−Metal Salt Composite Materials for Arsine Detection

Shabnam Virji,[†,§] Robert Kojima,[‡,§] Jesse D. Fowler,[†] Richard B. Kaner,[‡] and
Bruce H. Weiller*[,†]

[†]*Materials Processing and Evaluation Department, Physical Sciences Laboratory, The Aerospace Corporation, P.O. Box 92957/M2-248, Los Angeles, California 90009, and* [‡]*Department of Chemistry & Biochemistry and California NanoSystems Institute, University of California, Los Angeles, California 90095-1569.* [§]*These authors contributed equally to this work*

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We report the use of polyaniline nanofiber−metal salt composites for the detection of arsine gas (AsH_3) using the resistance change of the materials. Aqueous dispersions of polyaniline nanofibers facilitate the preparation of metal salt/polyaniline nanofiber composites with the use of water-soluble inorganics. Various composites were tested including $CuCl_2$, $CuBr_2$, CuF_2, $Cu(O_2CCH_3)_2$, $Cu(NO_3)_2$, $EuCl_2$, $NiCl_2$, $FeCl_3$, and $CoCl_2$. The copper(II)bromide/polyaniline nanofiber composite yields the best response with greater than an order of magnitude change in resistance upon exposure to arsine. The response is dependent on the metal and the counterion of the metal salt, as well as environmental conditions such as temperature and humidity. A mechanism that involves redox chemistry of the metal ion, polyaniline and AsH_3 is proposed and discussed.

Introduction

The conductivity (σ) of polyaniline (PANi) can be changed by more than 10 orders of magnitude simply by adding chemical dopants. Dopants such as acids protonate the insulating emeraldine base form of polyaniline ($\sigma < 1 \times 10^{-10}$ S/cm) converting it to the conducting ($\sigma > 1$ S/cm) emeraldine salt form.[1] Exposure to a strong base reverses this process.[2] This large conductivity change and sensitivity to acidic and basic gases can be exploited to create conductometric sensors. The use of high-surface-area, nanostructured polyaniline can enhance sensor response both in the magnitude of resistance change and response time.[3]

We have developed two approaches to synthesize polyaniline nanofibers, interfacial polymerization[4] and rapid mixing.[5] Both methods produce uniform polyaniline nanofibers with diameters ranging from 30 − 120 nm. These synthetic methods are also template-free and produce stable nanofiber suspensions in water.

Polyaniline nanofibers can be complexed with many species to create composite materials that are sensitive to certain chemical agents. For example, we have previously shown[6] that polyaniline nanofibers modified with $CuCl_2$ can detect hydrogen sulfide with 4 orders of magnitude change in resistance, whereas unmodified polyaniline exhibits essentially no response. In this case, the metal salt additive in the polyaniline nanofibers reacts with hydrogen sulfide to form an acid (HCl) that dopes the polyaniline nanofibers. This reaction scheme, in which the additive reacts with the analyte gas, can be used to detect other specific analyte gases such as phosgene using organic amine additives[7] and now arsine (AsH_3) using metal salts.

AsH_3 is a very toxic gas used in the semiconductor industry with a permissible exposure level (PEL) of 50 ppb.[8] This low detection threshold determines the need for a highly sensitive detector for AsH_3. Several methods have been reported for detection of AsH_3 including electrochemical,[9] chemiluminescence,[10] and a colorimetric method using paper tapes.[11] Each of these methods requires bulky devices that are fairly expensive, fragile, include many steps for analysis and in some cases involve toxic chemicals. Metal oxide sensors have been used to detect arsine, but require relatively high operating temperatures.[12] In this paper we present the use of metal salt-polyaniline nanofiber composite materials for the

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*Corresponding author. E-mail: bruce.h.weiller@aero.org.

(1) Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 314–315.
(2) Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. *Chem.*—*Eur. J.* **2004**, *10*, 1314–1319.
(3) Virji, S.; Huang, J.; Kaner, R. B.; Weiller, B. H. *Nano Lett.* **2004**, *4*, 491–496.
(4) Huang, J.; Kaner, R. B. *J. Am. Chem. Soc.* **2004**, *126*, 851–855.
(5) Huang, J.; Kaner, R. B. *Agnew. Chem.* **2004**, *116*, 5941–5945.
(6) Virji, S.; Fowler, J. D.; Baker, C. O.; Huang, J.; Kaner, R. B.; Weiller, B. H. *Small* **2005**, *1*, 624–627.
(7) Virji, S.; Kojima, R.; Fowler, J. D.; Villanueva, J. G.; Kaner, R. B.; Weiller, B. H. *Nano Res.* **2009**, *2*(2), 135–142.
(8) National Institutes of Occupational Safety; http://www.cdc.gov/niosh/npg/.
(9) Funazaki, N.; Kume, S.; Hemmi, A.; Ito, S.; Azano, Y.; Yamashita, S. *Sens. Actuators, B* **1993**, *13*−*14*, 466–469.
(10) Idowu, A. D.; Dasgupta, P. K. *Anal. Chem.* **2007**, *79*, 9197–9204.
(11) Kroll, D. *J. Process Anal. Chem.* **2002**, *7*, 132–135.
(12) Varfolomeev, A. E.; Volkov, A. I.; Eryshkin, A. V.; Malyshev, V. V.; Rasumov, A. S.; Yakimov, S. S. *Sens. Actuators, B* **1992**, *7*, 727–729.

detection of AsH_3. Several metal salts are screened using a multisensor array to find the best candidates. Concentration and environmental effects are examined for several of the most promising composites and a mechanism for sensor response is proposed.

Experimental Section

All reagents were purchased from Aldrich, except for NaOH and ammonium peroxydisulfate (APS), which were purchased from Fisher Scientific. All chemicals were of ACS grade and used as received except for aniline which was distilled prior to use.

Polyaniline nanofibers were synthesized using a rapidly mixed method.[5] The general synthesis consists of combining a 1.0 M(aq) camphorsulfonic acid (CSA) solution of aniline with a 1.0 M(aq) CSA solution of APS. The combined solution is then rapidly mixed and allowed to react overnight. The resulting emeraldine salt polyaniline nanofibers are then dedoped with an equal volume of 1 M NaOH(aq) and then purified by centrifugation. The resulting nanofiber suspension in water was diluted to obtain a final concentration of 2 g/L.

Because the nanofibers synthesized by this method are suspended in water, they can be easily combined with any water-soluble metal salt to create a composite. In a typical synthesis, 10 mM aqueous metal salt was added to 2.0 g/L polyaniline nanofiber aqueous suspension in a 1:4 volume ratio. The resulting composite was drop-cast on sensor array substrates using a disposable microliter pipet and then dried in air. The metal salts that were used to make the composite materials include copper(II) bromide, copper(II) chloride, copper(II) fluoride, copper(II) acetate, copper(II) nitrate, cobalt(II) chloride, iron(III) chloride, nickel(II) chloride, and europium(II) chloride.

The array sensor consists of nine separate interdigitated electrodes fabricated on one substrate using standard photolithographic methods. Two sensor arrays (18 sensor elements) were mounted in 24-pin dual in-line packages and connections made with wire bonds with a common ground (Figure 1). Two of these packaged sensors were mounted in the cell for a total of 36 separate sensors and materials that can be characterized per run. Each sensor contains 35 pairs of fingers with 20 μm electrode gaps and a length of 1600 μm.

Electrical resistances were measured with a programmable electrometer (Keithley 2002). A scanner card and switch system (Keithley 7011S/7001) were used to multiplex measurements over 36 sensors. All instruments were controlled and read by computer using a GPIB interface and Labview software.

A certified gas mixture of 12 ppm arsine in nitrogen (Scott Specialty Gases) was diluted with nitrogen for gas exposures. Mass-flow controllers were used to meter separate flows of nitrogen buffer gas and the calibrated gas mixture. Gas exposures were carried out at various concentrations by varying the relative gas flows and AsH_3 concentrations were measured using Dräger tubes. Humidity was generated using a water bubbler and measured directly with a humidity sensor (Vaisala). The temperature was varied with a temperature-controlled enclosure using a recirculating bath (Neslab RTE-7) and a heat exchanger. The cell temperature was monitored with a thermocouple.

X-ray photoelectron spectroscopy (XPS) experiments were carried out by drop-casting copper(II) bromide/polyaniline nanofiber ($CuBr_2$/PANi) composite material onto a silicon wafer and drying it for 1 day in air. Samples were then continually exposed to 6 ppm arsine at 50% relative humidity for 12 h. An Omicrometer Nanotechnology XPS/UPS system was used with a base pressure of 2×10^{-10} torr and a Mg Kα radiation source ($h\nu$ = 1253.6 eV). The energy dispersive X-ray spectroscopy (EDS) measurements were performed on a JEOL model JSM-6460LV scanning electron microscope.

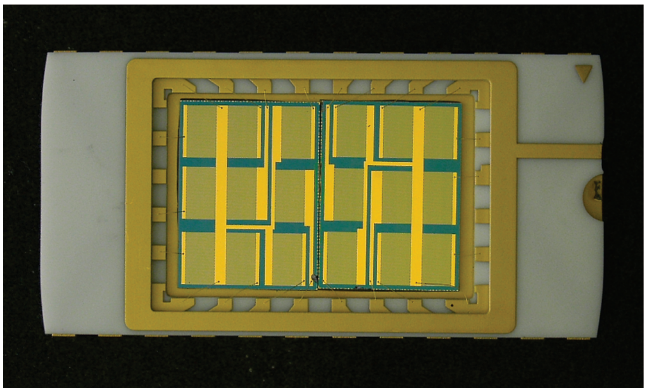

Figure 1. Photograph of the chemical sensor array. There are 18 sensor elements, each with 20 μm electrodes and gaps.

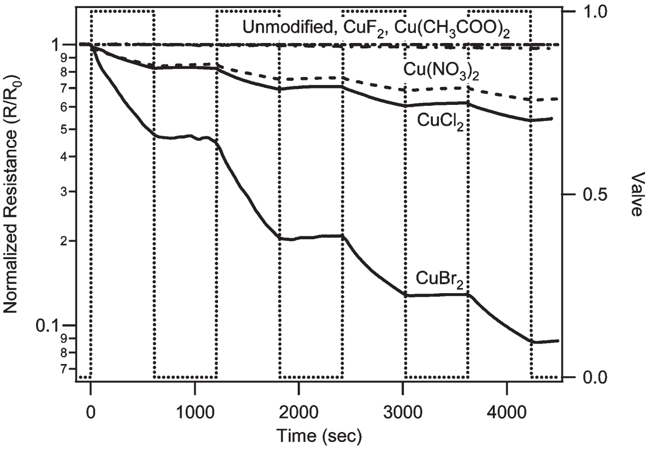

Figure 2. Unmodified and metal-salt-modified polyaniline nanofiber films exposed to 500 ppb AsH_3 at room temperature with 50% relative humidity. The valve state (dotted line) is shown on the right axis.

Results and Discussion

Arsine (AsH_3) reacts with a number of metal salts to form adducts and these reactions have been used to develop colorimetric detectors. For example, Dräger tubes that detect AsH_3 employ a gold salt that undergoes redox chemistry in the presence of arsine resulting in a progressive color change that determines the arsine concentration.[13] This redox chemistry between the metal center and arsine is also used for paper tape detection methods in which $HgBr_2$ is impregnated into the paper. Arsine reacts with $HgBr_2$ in a step-by-step reaction until a color change is observed.[14] Here, we utilize the redox chemistry of AsH_3 with different metal salts to design conductometric sensors, whose resistance changes upon interaction of AsH_3 with the metal salt–polyaniline nanofiber composites. The advantages of our AsH_3 sensors are a large electrical response under low

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(13) Dräger tube information sheet, www.draeger.com.
(14) Kinniburgh, D. G.; Kosmus, W. *Talanta* **2002**, *58*, 165–180.

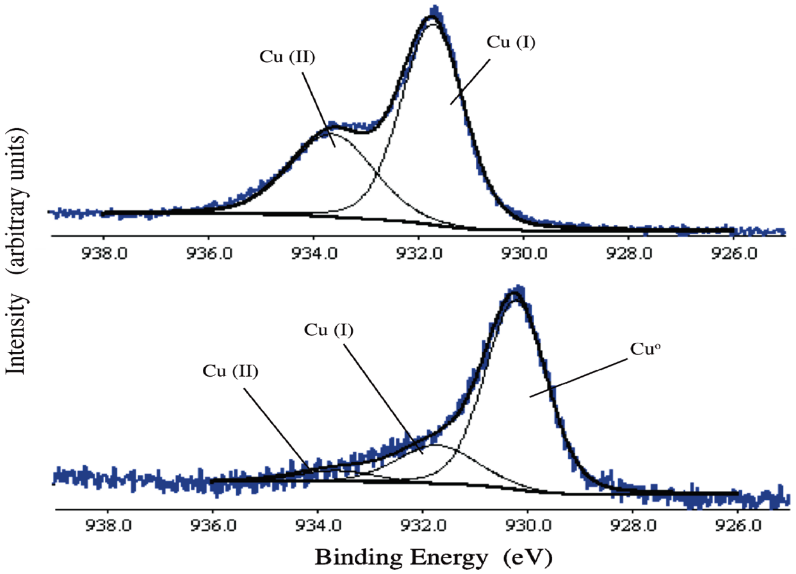

Figure 3. X-ray photoelectron spectra of copper(II) bromide−polyaniline nanofibers before (top) and after (bottom) exposure to AsH_3.

concentrations, the use of inexpensive and inert materials and a synthetic method that is easily scalable.

Figure 2 shows the response of $CuBr_2$/PANi, $CuCl_2$/PANi, CuF_2/PANi, $Cu(O_2CCH_3)_2$/PANi, and $Cu(NO_3)_2$/PANi composites and unmodified polyaniline nanofibers exposed to 500 ppb arsine under 50% relative humidity. The left axis of the graph is the normalized resistance, i.e., the time-dependent resistance divided by the initial resistance and the right axis is the analyte valve state, with the valve closed at 0 and open at 1. As can be seen from the figure, the unmodified polyaniline nanofibers show no response to AsH_3, while several of the different copper salt composites show dosimeter type responses. The composites with $Cu(O_2CCH_3)_2$ or CuF_2 do not show a response. For the composites showing a response, the polyaniline nanofiber composite film becomes more conducting upon exposure to AsH_3. The magnitude of the increase in conductivity suggests the generation of an acid with a subsequent doping of polyaniline.

The redox chemistry of the arsine and copper salts were examined using X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS). XPS analysis of the Cu $2p_{3/2}$ line in the copper (II) bromide-polyaniline nanofiber composite material prior to exposure to arsine indicates mixed valences for copper; Cu(I) at 931.7 eV, and Cu(II) at 934.5 eV (Figure 3).[15,16] Polyaniline is a redox active material and has clearly reduced some of the Cu(II) to Cu(I) upon interaction with the polymer which is consistent with previous reports in the literature.[17,18] After extended exposure to arsine, both the Cu(I) and Cu(II) peaks are replaced with a new signal near 930.3 eV, indicating the reduction of both copper species to copper(0) (Figure 3). EDS analysis of the composite film after arsine exposure shows generation of a new arsenic peak that was not present before exposure (Figure 4).

From the data in Figures 2−4, we propose the following mechanism for the detection of AsH_3 by our metal salt/polyaniline nanofiber composites (Scheme 1). XPS data of $CuBr_2$/PANi before exposure to AsH_3 clearly indicate that polyaniline reduces a large portion of copper(II) to copper(I) upon formation of the composite (Scheme 1, eq 1). Although there is an excess of reducing imine nitrogens in PANi to copper ions in the composite (4.4:1), the conversion of all copper(II) to copper(I) may not occur since the reduction potential of the polymer changes as more copper ions are reduced. Therefore upon exposure to AsH_3, which is well-known as a strong reducing agent,[19] the remaining copper(II) in the composite would be reduced to copper(0) (Scheme 1, eq 2). Dorfman et al. have shown that AsH_3 reduces copper(II) to copper(I) and that the presence of copper(I) greatly enhances this reaction.[20] Note that the polyaniline serves not only as a conducting backbone for the conductometric sensor but also as a reducing agent that is able to stabilize and make copper(I) available for the enhancement of this reaction.

As shown above, the acid byproduct of the redox reaction dopes the polyaniline (Scheme 1, eq 3) resulting in a decrease in resistance as seen upon exposure to AsH_3 in Figure 2. The acid that is generated from Scheme 1 is dependent on the counterion of the metal salt in the composite and therefore has correspondingly different acid strengths. Previous work has shown that the magnitude of the response of polyaniline nanofibers to various

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(15) Brand, P.; Freiser, H. *Anal. Chem.* **1974**, *46*, 1147.

(16) Van Der Laan, G.; Westra, C.; Haas, C.; Sawatzky, G. A. *Phys. Rev. B* **1981**, *23*, 4369.

(17) Lim, S. L.; Tan, K. L. *Langumir* **1998**, *14*, 5305.

(18) Klein, J. C.; Proctor, A.; Hercules, D. M.; Black, J. F. *Anal. Chem.* **1983**, *55*, 2055.

(19) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. Advanced Inorganic Chemistry, 6th ed.; John Wiley & Sons: New York, 1999.

(20) Dorfman, Y. A.; Yukht, I. M.; Levina, L. V.; Polimbetova, G. S.; Petrova, T. V.; Emel'yanova, V. S. *Russ. Chem. Rev.* **1991**, *60*, 1190–1228.

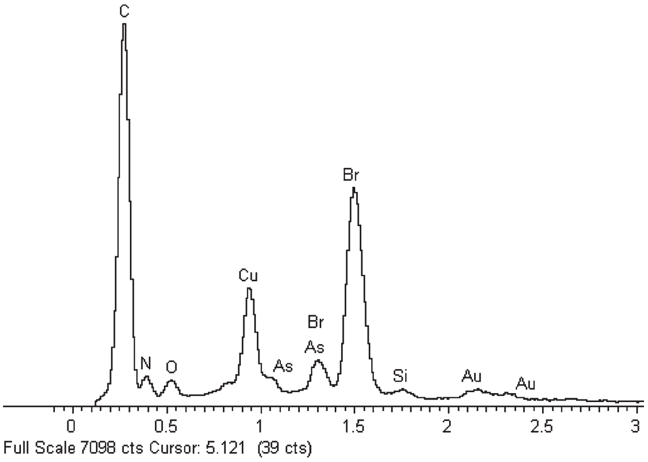
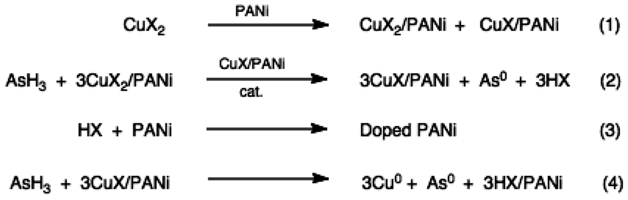


Figure 4. Energy-dispersive X-ray spectra of a copper(II) bromide–polyaniline nanofiber film after exposure to AsH_3. The *x*-axis is in keV and the full scale *y*-axis is 7098 counts.

Scheme 1. Proposed Mechanism of Interaction of Metal Salt–Polyaniline Nanofiber Composite Material with Arsine Gas



$$CuX_2 \xrightarrow{PANi} CuX_2/PANi + CuX/PANi \quad (1)$$

$$AsH_3 + 3CuX_2/PANi \xrightarrow[cat.]{CuX/PANi} 3CuX/PANi + As^0 + 3HX \quad (2)$$

$$HX + PANi \longrightarrow Doped\ PANi \quad (3)$$

$$AsH_3 + 3CuX/PANi \longrightarrow 3Cu^0 + As^0 + 3HX/PANi \quad (4)$$

acids corresponds with acid strength.[21] For the copper salts used in Figure 2, the acids that would be generated are acetic acid (CH_3CO_2H), hydrofluoric acid (HF), nitric acid (HNO_3), hydrochloric acid (HCl) and hydrobromic acid (HBr). The composite materials that produce the strong acids HNO_3 ($pK_a = -1.3$), HCl ($pK_a = -8.0$), and HBr ($pK_a = -9.0$) exhibit increasingly strong responses to AsH_3, in agreement with their acidic strengths. The markedly enhanced response demonstrated by the $CuBr_2$/PANi could be in part due to the possible accelerating effect of bromide ions in the reduction of copper(II) by AsH_3.[22] Not surprisingly, there was no response from $Cu(O_2CCH_3)_2$/PANi, because acetic acid is only known to dope polyaniline at high concentrations.[23] However, CuF_2/PANi also showed no response even though HF is known to dope polyaniline.[24] We suspect that the low concentration of HF formed in concert with its nature as a relatively weak acid ($pK_a = +3.17$) results in a lack of an observable response under these conditions. In the final step (Scheme 1, eq 4), XPS data show the eventual conversion of almost all copper ions to copper(0). The known reduction of copper(II) to copper(I) by AsH_3 is also shown to completely reduce copper(I) to copper(0) in this system.

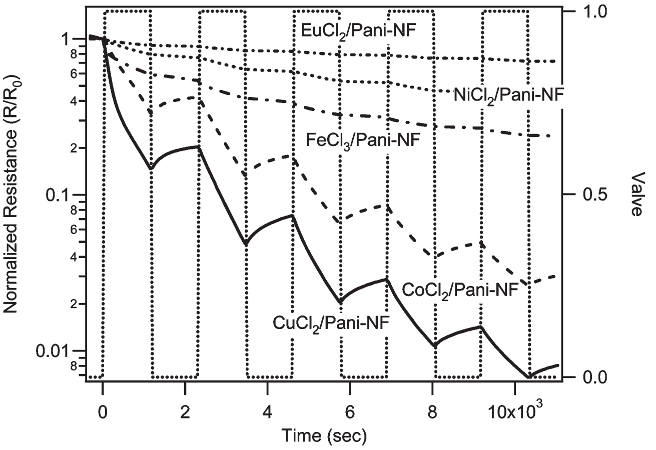


Figure 5. Different metal-salt-modified polyaniline nanofiber films exposed to 1 ppm AsH_3 at room temperature with 50% relative humidity. The valve state (dotted line) is shown on the right axis.

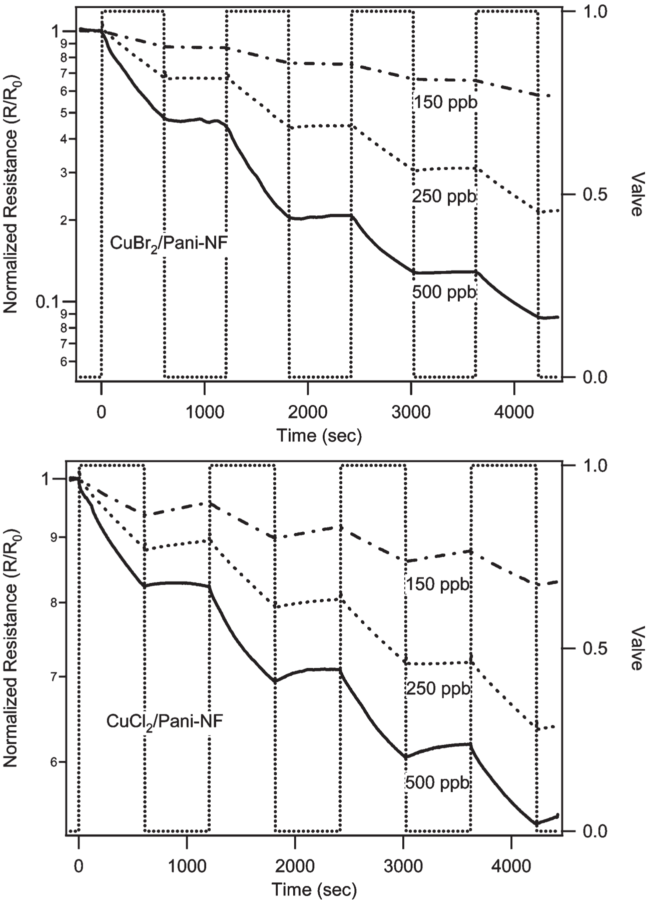


Figure 6. Concentration dependence of the response of $CuBr_2$ and $CuCl_2$ sensors to AsH_3. (top) $CuBr_2$-modified polyaniline nanofibers exposed to 150 (– · –), 250 (-----), and 500 (——) ppb arsine at room temperature with 50% relative humidity. (bottom) $CuCl_2$-modified polyaniline nanofibers exposed to 150 (– · –), 250 (-----), and 500 (——) ppb arsine at room temperature with 50% relative humidity. The valve state (dotted line) is shown on the right axis.

Figure 5 shows the response of other metal chlorides exposed to AsH_3. As seen from the figure, the other metal chloride composites do not respond as well as $CuCl_2$/PANi. This may be due to the reduced activity of the other metal salts in undergoing the redox conversion. Dorfman, et al. have shown that $FeCl_3$ has a much smaller rate

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(21) Hatchett, D. W.; Josowicz, M.; Janata, J. *J. Phys. Chem. B* **1999**, *103*, 10992–10998.

(22) Dorfman, Ya. A.; Kel'man, I. V. *Teor. Eksp. Khim.* **1991**, *27*, 653–658.

(23) Virji, S.; Kaner, R. B.; Weiller, B. *Inorg. Chem.* **2006**, *45*, 10467–10471.

(24) Virji, S.; Kaner, R. B.; Weiller, B. *Chem. Mater.* **2005**, *17*, 1256–1260.

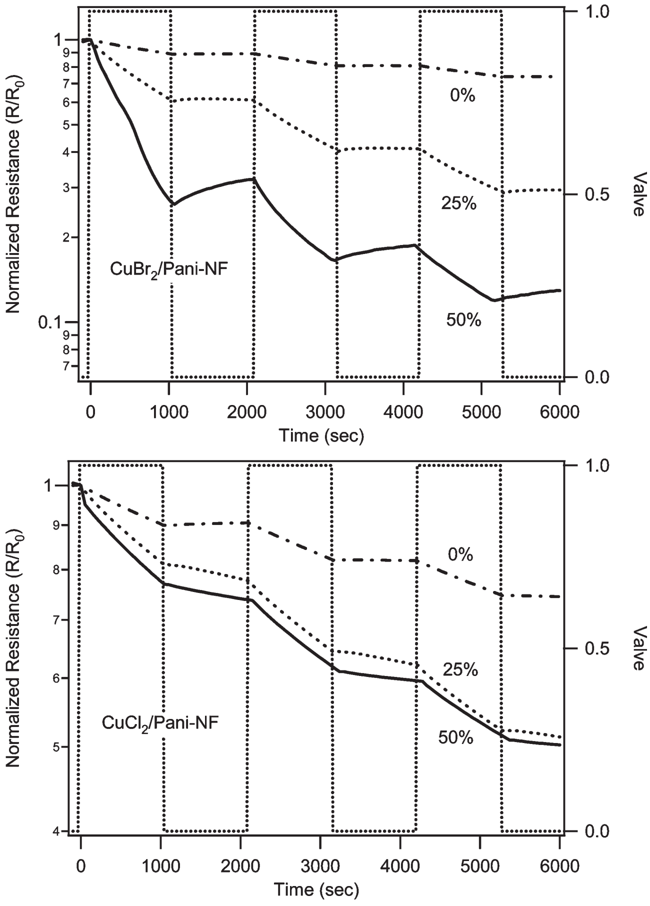

Figure 7. Humidity dependence of the response of CuBr$_2$ and CuCl$_2$ sensors. (top) CuBr$_2$-modified polyaniline nanofibers exposed to 500 ppb AsH$_3$ at room temperature under 0% (— · —), 25% (-----), and 50% (——) relative humidity. (bottom) CuCl$_2$-modified polyaniline nanofibers exposed to 500 ppb arsine at room temperature under 0% (— · —), 25% (-----), and 50% (——) relative humidity. The valve state (dotted line) is shown on the right axis.

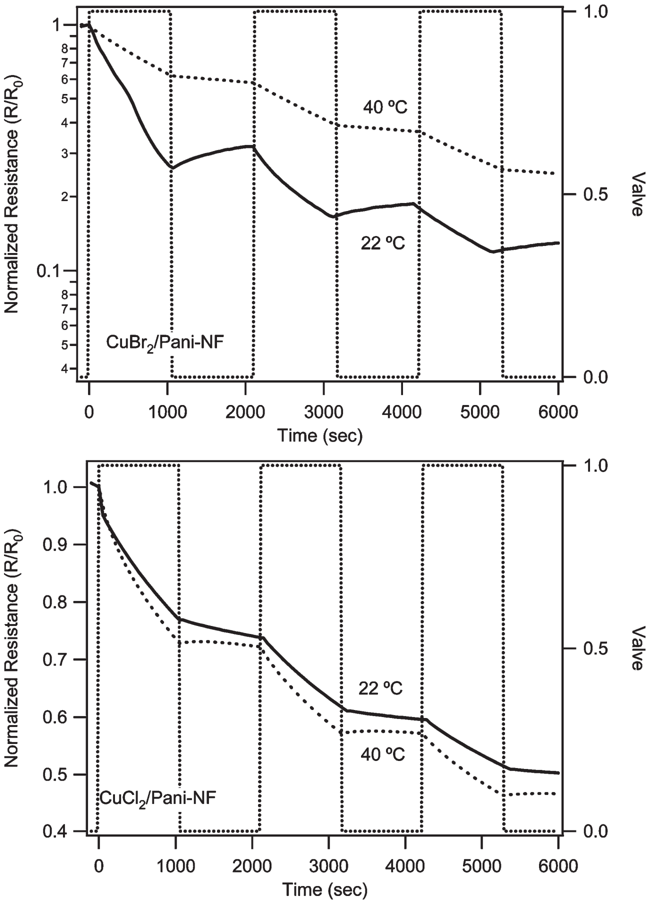

Figure 8. Temperature dependence of the response of CuBr$_2$ and CuCl$_2$ sensors. (top) CuBr$_2$-modified polyaniline nanofibers exposed to 500 ppb AsH$_3$ at 22 °C (——) and 40 °C (-----) under 50% relative humidity. (bottom) CuCl$_2$-modified polyaniline nanofibers exposed to 500 ppb arsine at 22 °C (——) and 40 °C (-----) under 50% relative humidity. The valve state (dotted line) is shown on the right axis.

constant compared to CuCl$_2$ for the reduction of AsH$_3$.[25] In addition, other metal salts have been examined and show that the reactivity trend is dependent both on the metal center and the halogen counterion.[26] The redox reaction likely proceeds through the formation of transition state complexes involving the halide, AsH$_3$, and composite metal center. The inner-sphere interaction of AsH$_3$ with the halide (X$^-$) promotes redox decomposition of the intermediate, reduction of the composite metal ions.[27] As AsH$_3$ approaches the halide, a potential barrier emerges, which is used as an index of reactivity. The barrier value correlates with the activation and kinetic parameters and decreases upon the substitution of Cl$^-$ by Br$^-$ or I$^-$ and varies with metal center.[26]

The concentration dependence of the CuBr$_2$/PANi and CuCl$_2$/PANi composite films is shown in Figure 6. As can be seen from the figure, both the response time and magnitude decrease with lower concentration. These films are sensitive to AsH$_3$ at concentrations as low as 100 ppb.

Polyaniline has been used as a humidity sensor[28] because increasing amounts of water vapor increase the conductivity of polyaniline. The suggested cause is increased solvation by water of the charges along the polymer chain, that in turn helps increase charge transfer between chains resulting in increased conductivities.[29] Polyaniline sensing capabilities have also been shown to be affected by humidity.[30] Christie, et al. have demonstrated that there is an ideal humidity range that will not affect the sensor response of polyaniline films to ammonia.[31]

Figure 7 shows that the response of the polyaniline nanofiber composite materials decreases with decreasing humidity. The mechanism of the interaction between the composite material and AsH$_3$ suggests a doping of the polyaniline that results in an increase in conductivity. The doping process is enhanced in the presence of water and

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(25) Dorfman, Ya. A.; Polimbetova, G. S.; Doroshkevich, D. M. *Zh. Neorg. Khim.* **1995**, *40*, 1312–1319.

(26) Dorfman, Ya. A.; Polimbetova, G. S.; Doroshkevich, D. M. *Zh. Neorg. Khim.* **1996**, *41*, 658–666.

(27) Dorfman, Ya. A.; Polimbetova, G. S.; Emel'yanova, V. S.; Kel'man , I. V.; Abdreimova, R. R.; Doroshkevich, D. M. *Kinet. Catal* **1985**, *26*, 535–540.

(28) Jain, S.; Chakane, S.; Samui, A. B.; Krishnamurthy, V. N.; Bhoraskar, S. V. *Sens. Actuators, B* **2003**, *96*, 124–129.

(29) Angelopoulos, M.; Ray, A.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1987**, *21*, 21–30.

(30) Matsuguchi, M.; Okamoto, A.; Sakai, Y. *Sens. Actuators, B* **2003**, *94*, 46–52.

(31) Christie, S.; Scorsone, E.; Persaud, K.; Kvasnik, F. *Sens. Actuators, B* **2003**, *90*, 163–169.

may be due to the solvation of charges that results in a better charge transfer along the polymer chain increasing its conductivity path.[28] Water is also believed to affect the reaction mechanism because of the generation of protons that may be bonded directly to the transition state complex, producing a redistribution of electron density in the coordination sphere and promoting an increase in the reaction rate.[19]

In addition to humidity, temperature also affects the sensor performance. Figure 8 shows the dependence of the sensor response at room temperature and at 40 °C. As seen from the figure, the response of the $CuBr_2$/PANi nanofiber film to AsH_3 decreases at higher temperature; however, the response of the $CuCl_2$/PANi nanofiber film does not. We propose that increased temperature reduces the response because less water is available to interact with the film, decreasing the conduction pathway and creating a different transition state complex that decreases the reaction rate. The response of $CuBr_2$/PANi is affected much more by humidity than is $CuCl_2$/PANi. This is consistent with the smaller humidity dependence of the $CuCl_2$/PANi composite as shown in Figure 7.

In conclusion, metal salt−polyaniline nanofiber composite materials prove to be viable AsH_3 sensors, operating well at room temperature and utilizing inexpensive and inert materials. The reaction between AsH_3 and metal salt additive generates an acid, reduces the composite metal ion, and oxidizes AsH_3. The acid produced can then dope the polyaniline resulting in large changes in resistance. The composite metal center affects the magnitude of the response because of its ability to undergo redox chemistry. Differences in the catalytic activity of the counterion also affect the response and the resulting strength of the acid that is generated determines the composites ability to detect AsH_3 conductometrically. In this study, the copper(II) bromide−polyaniline nanofiber composite material is found to be the best sensor for AsH_3 resulting in greater response when compared to the other materials used. Polyaniline nanofiber composite materials such as these have proved useful in detecting toxic gases that unmodified polyaniline nanofibers are not able to detect.

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