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Direct Electrical Measurement of the Conversion of Metal Acetates to Metal Sulfides by Hydrogen Sulfide

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Copper acetate and related metal salt films react directly with hydrogen sulfide at room temperature to form metal sulfides, resulting in conductivity changes as large as 10^8. The observed changes in conductivity are related to the solubility product constant (K_{sp}) and the difference in conductivity between the metal salt and the resulting metal sulfide. A smaller K_{sp} indicates a more stable metal sulfide and, therefore, greater metal salt reactivity. Polyaniline nanofiber/metal salt composites were also examined and show metal sulfide conversion with changes in resistance up to 10^6. The direct electrical measurement of the conversion of metal salt to metal sulfide has the potential to be the basis of a new type of sensitive, thin-film chemical sensor.

Introduction

Hydrogen sulfide is a toxic, dense gas that has a pungent odor and can be fatal at high concentrations (>100 ppm). It has a permissible exposure limit (PEL) of 20 ppm, but the human odor threshold is as low as 0.5 ppb.[1] Odor alone cannot be used as an indicator of exposure because the sense of smell is lost upon continuous exposure to hydrogen sulfide. As a result, sensitive and reliable hydrogen sulfide sensors are needed with low detection thresholds.

Existing sensors for the detection of hydrogen sulfide include conductive metal oxides, such as tin oxide[2] and tungsten oxide,[3,4] but these generally require high temperatures for operation. Their limit of detection is on the low ppb level. Paper tapes[5] are also useful, but their main drawback is the need for a relatively bulky reader with large power requirements.

Here, we demonstrate the direct, electrical detection of metal sulfide formation by monitoring the electrical conductivity of metal salt films as they react with hydrogen sulfide to form conductive metal sulfides at room temperature. In particular, we show that copper acetate gives a remarkable conductivity change of over 8 orders of magnitude as it is converted into copper sulfide. These changes are induced by only parts-per-million concentrations of hydrogen sulfide. The conductivity change is related to the conductivity of the resulting metal sulfide and to the extent of reaction. The extent of reaction correlates with the solubility product constant (K_{sp}) of the resulting metal sulfide. Smaller solubility product constants indicate a more stable metal sulfide and lead to a greater extent of conversion from metal salt to metal sulfide. To create films with lower initial resistances, metal salts were incorporated into a polyaniline nanofiber matrix. The resulting films are also capable of converting metal salts to metal sulfides, with an up to 6 orders of magnitude change in resistance. These data demonstrate the possibility of fabricating small, sensitive chemical sensors for hydrogen sulfide based on simple electrical measurements at room temperature.

Experimental Section

Copper acetate and copper chloride solutions were made by dissolving the metal salt in water to yield a final concentration of 0.1 M. For use as a host matrix, polyaniline nanofibers were

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synthesized using an aqueous interfacial[6] or rapid mixing process[7,8] and purified by filtration. The nanofibers were dried and subsequently redispersed in water to form a final concentration of 1 g/L. Polyaniline nanofibers were modified with different transition metal salts in solution, deposited on sensor array substrates, and dried in air to produce films with thicknesses of ~0.4 μm. The final concentration of metal salt in the polyaniline nanofiber dispersion that gave the optimum response was 0.0075 M. Metal salt films were deposited on the electrodes by simple drop casting from the above solutions and dried under ambient conditions overnight.

The experimental techniques have been described previously.[9] Briefly, the sensor arrays consist of six separate interdigitated electrode sensors fabricated on one substrate using standard photolithographic methods. The electrode geometry is comprised of 50 pairs of digits, with each digit having dimensions of 10 μm $\times$ 3200 μm $\times$ 0.18 μm (width $\times$ length $\times$ height) and a 10 μm gap between digits.

A certified gas mixture of 200 ppm of hydrogen sulfide in nitrogen (Scott Specialty Gases) was diluted with humidified nitrogen for gas exposures. All gas exposures were carried out with a concentration of 10 ppm of hydrogen sulfide. Mass flow controllers were used to meter separate flows of nitrogen buffer gas and the calibrated gas mixture. All the gas flow experiments were performed using 45% relative humidity in the nitrogen gas flow. The humidity was generated using a bubbler and measured in the nitrogen flow with a humidity sensor (Vaisala). The final humidity levels were calculated from the flow ratios. Typically, only one relative humidity value (45%) was used throughout these experiments. Upon varying the humidity, we observed that the resistance of copper acetate remained constant in the range of 0−80% relative humidity. At greater humidity levels, the resistance decreases by falling about 1 order of magnitude at 100% relative humidity. This may be due to enhanced ionic conductivity with higher water loading in the films.

Electrical resistances (dc) were measured with a programmable electrometer (Keithley 617) with a resistance measurement range from 2 $\times$ 10^{11} to 0.1 Ω. A low-current scanner card and switch system (Keithley 7158 and 7001) were used to multiplex measurements over 10 sensors from two sensor arrays. All instruments were controlled and read by a computer using a GPIB interface and LabView software.

Results and Discussion

The exposure of copper acetate to hydrogen sulfide is shown in Figure 1. As can be seen from Figure 1, a film of copper acetate changes resistance by over 8 orders of magnitude upon exposure to 10 ppm of hydrogen sulfide at room temperature. Note that other hydrogen sulfide sensors often require high operating temperatures.[2,3] The change observed here is rapid with a time response of about τ_{90} = 3.8 s (τ_{90} is the response to 90% of full scale). At 100 ppb of hydrogen sulfide, copper acetate responds with an over 5 orders of magnitude decrease in resistance and a time response of less than 1 min. This large change can be attributed to the direct conversion of a very insulating copper acetate starting material (high initial resistance) to a highly conductive copper sulfide product (low final resistance). Analysis of the copper acetate films before and after exposure to hydrogen sulfide using energy-dispersive X-ray analysis (EDX) and X-ray diffraction (XRD) clearly shows the formation of copper sulfide (CuS).

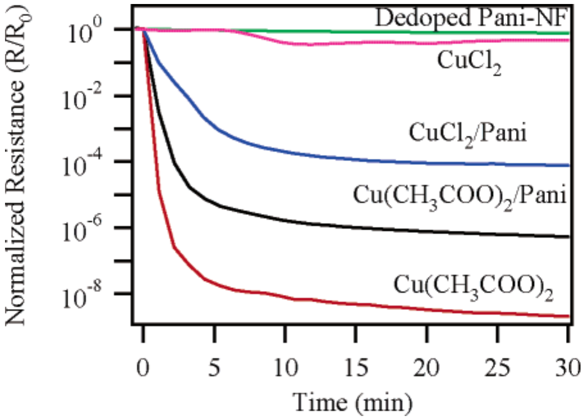

Figure 1. Electrical response of dedoped polyaniline nanofibers (dedoped Pani-NF, green), copper chloride ($CuCl_2$, magenta), copper chloride/polyaniline ($CuCl_2$/Pani, dark blue) nanofibers, copper acetate/polyaniline ($Cu(CH_3COO)_2$/Pani, black) nanofibers, and copper acetate ($Cu(CH_3COO)_2$, red) films exposed to 10 ppm of hydrogen sulfide.

Copper acetate and related salts are known to react with hydrogen sulfide both in solution and in the solid state. Copper acetate has been reported to react with hydrogen sulfide in water to produce an insoluble black copper sulfide precipitate[10] or, more recently, in organic solutions to produce organosols.[11] Copper sulfide films have been deposited using atomic layer deposition from the surface reaction of a copper β-diketonate and hydrogen sulfide.[12] Copper acetate films have also been shown to react directly with hydrogen sulfide to form copper sulfide,[13] but this conversion has yet to be examined electrically. Copper acetate films are highly insulating, and the ability to measure such high resistances has been a limitation in the past. The use of an electrometer with a very large dynamic range and interdigitated electrodes allows us to monitor the resistance change associated with the conversion of copper acetate to copper sulfide, a small band gap semiconductor with a conductivity of 10 S/cm.[14]

Copper acetate has a much larger change in conductivity than neat copper chloride or composites of copper acetate or copper chloride with polyaniline nanofibers (Figure 1). This is likely due to the high reactivity of copper acetate films with hydrogen sulfide and their very high initial resistance. Also, acetate ligands are labile enough to dissociate from the metal center more freely upon interaction with hydrogen sulfide. Copper chloride films, on the other hand, do not react with hydrogen sulfide to produce any

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significant change in resistance. Chloride ions are apparently much more tightly bound to the metal center than acetate ions, and as a result, metal chlorides show no direct electrical response to hydrogen sulfide.

Previously we have shown that polyaniline nanofiber/metal salt composite films respond to hydrogen sulfide with orders of magnitude resistance changes in under 1 min.[15] For those measurements, polyaniline nanofiber composites with metal chlorides and unmodified polyaniline nanofibers were used. Unmodified polyaniline nanofibers show essentially no response to hydrogen sulfide since it is a weak acid and cannot dope polyaniline at these concentrations. A copper chloride/polyaniline nanofiber composite film exposed to 10 ppm of hydrogen sulfide responds to hydrogen sulfide by exhibiting a greater than 4 orders of magnitude decrease in resistance (Figure 1). Once the metal salt is incorporated into a polyaniline matrix, it is proposed that the metal cation weakly coordinates to the imine and amine nitrogens of the polyaniline backbone.[16,17] The polyaniline backbone appears to act like a weak ligand, so that the metal cation can easily react with hydrogen sulfide to form a metal sulfide and an acid byproduct that dopes the polyaniline. This hypothesis is consistent with the observed reactivity of copper salts with large ligands that are weakly bound to a metal center, such as copper acetate.

Copper acetate films are insulating, and their resistance is difficult to measure. However, copper acetate can be incorporated into a conductive matrix to give a material with lower initial resistance. An example of a useful conducting matrix is a film of polyaniline nanofibers. A composite film was formed from copper acetate and polyaniline nanofibers, and its response to hydrogen sulfide is shown in Figure 1. The copper acetate/polyaniline nanofiber composite is less responsive than the copper acetate alone, largely because the initial resistance is different for the two films: $>2 \times 10^{11}$ Ω for the copper acetate film and 1×10^{9} Ω for the composite film. The response for the copper acetate/polyaniline nanofiber composite film is greater than that for the copper chloride/polyaniline nanofiber composite film. This is consistent with the fact that copper acetate reacts much more readily with hydrogen sulfide than copper chloride.

Figure 2 shows dosimeter response curves for copper acetate and copper acetate/polyaniline nanofiber films exposed to hydrogen sulfide and acetic acid. The response of the copper acetate/polyaniline nanofiber film exposed to acetic acid (1%) is fully reversible and is unlike the response to hydrogen sulfide, which is irreversible. One percent acetic acid is a weak acid with a pK_a of 4.75 that cannot dope polyaniline to a highly conducting state as a strong acid can.[18]

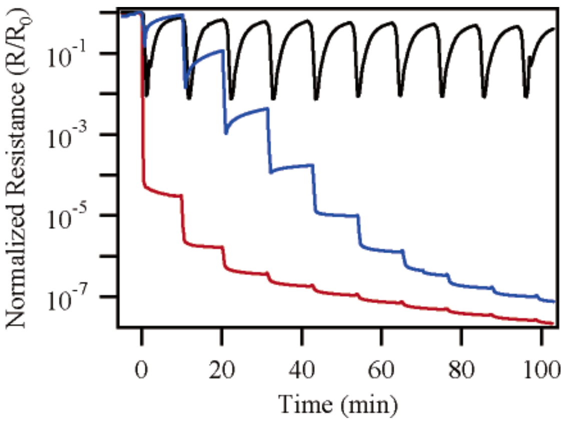

Figure 2. Dosimeter response curves for a copper acetate film (red) and a copper acetate/polyaniline nanofiber composite film exposed to 10 ppm of hydrogen sulfide (dark blue). For comparison, the copper acetate/polyaniline nanofiber composite film was also exposed to 1% acetic acid (black). All exposure times were for 1.4 min with 10.0 min between exposures. The traces are not exactly aligned due to a slight variation in cycle time between experiments.

When the copper acetate/polyaniline nanofiber film is exposed to hydrogen sulfide (10 ppm), it first undergoes partial conversion to copper sulfide, releasing acetic acid, which is similar to the mechanism for the copper chloride/polyaniline nanofiber composite films.[15] However, there appear to be two components to the response early on: one reversible and the other irreversible. The reversible part is likely due to the formation of acetic acid, which reversibly dopes polyaniline. The irreversible part is likely due to the formation of conductive copper sulfide in the polyaniline matrix (as confirmed by EDX analysis). Upon further exposure to hydrogen sulfide, the copper acetate within the copper acetate/polyaniline nanofiber film is converted more fully to copper sulfide. At this stage, the conductivity is largely due to the copper sulfide formed, and the small amount of polyaniline doping by acetic acid plays an insignificant part in the overall film conductivity. At this point, the response looks very similar to the response of neat copper acetate films.

For the neat copper acetate films, there is a larger resistance change at earlier times because of the difference in the resistances of the starting and ending materials. The starting material is highly insulating with initial resistances on the order of 10^{11} Ω. This material is very reactive toward hydrogen sulfide, and just a small amount of reaction can reduce the resistance by several orders of magnitude. As the material is further converted, the change in resistance becomes smaller and smaller. As can be seen in Figure 2, the conversion of copper acetate to copper sulfide is irreversible; we have not found any conditions of temperature or acidity that cause this reaction to reverse.

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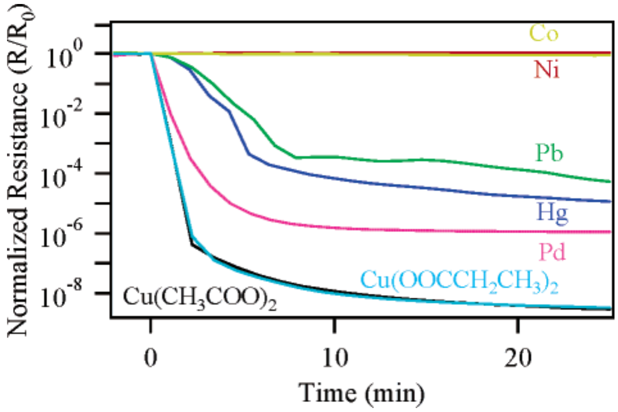

Figure 3. Resistance changes for different metal salts exposed to 10 ppm of hydrogen sulfide: cobalt acetate ($Co(CH_3COO)_2$, yellow), nickel acetate ($Ni(CH_3COO)_2$, red), lead acetate ($Pb(CH_3COO)_2$, green), mercury acetate ($Hg(CH_3COO)_2$, dark blue), palladium acetate ($Pd(CH_3COO)_2$, magenta), copper acetate ($Cu(CH_3COO)_2$, black), and copper propionate ($Cu(CH_3CH_2COO)_2$, light blue).

In any event, this reaction can be used as a dosimeter for hydrogen sulfide that measures total exposure to hydrogen sulfide. The PEL for hydrogen sulfide is 20 ppm for an 8 h workday, which equates to a dose of 9600 ppm/min. The detection levels demonstrated in Figure 2 are far below this: for copper acetate/polyaniline, the limit of detection is at least 14 ppm/min, and for neat copper acetate, it is several decades better.

Copper acetate is not the only copper salt that responds to hydrogen sulfide by conversion of the metal salt to a metal sulfide. We have tested various other copper salts with large ligands, including copper formate and copper butyrate, and found that salts with this type of ligand respond to hydrogen sulfide with resistance changes of several orders of magnitude. In particular, copper propionate responds similarly to copper acetate, as seen in Figure 3. Other metal acetates, such as palladium acetate, also respond to hydrogen sulfide (Figure 3) by forming palladium sulfide, as determined by EDX. In addition, silver, lead, and mercury acetates also show a decrease in resistance upon exposure to hydrogen sulfide. However, not all acetates respond to hydrogen sulfide. In particular, cobalt and nickel acetate show no response to hydrogen sulfide (Figure 3).

The differences in the response of various metal acetates can be attributed to the initial conductivities of the starting materials and the conductivities and solubility product constants of the resulting metal sulfides. Table 1 lists the conductivities and solubility product constants (K_{sp}) of the metal sulfides in the order of the observed responses of the metal acetates to hydrogen sulfide. The K_{sp} is a parameter that measures the aqueous solubility of a sparingly soluble salt. When a salt is dissolved in water, it dissociates into cations and anions and the solubility product constant is the product of the combined ion concentrations. A smaller solubility product constant indicates that a salt is less soluble and is, therefore, more stable. (In many cases, the K_{sp} values are calculated from the heats of formation of the salts and the ions.)

Table 1. Conductivities and Solubility Product Constants (K_{sp}) of Metal Sulfides

metal sulfide[a]	conductivity (S/cm)	K_{sp}[19]	observed response (R/R_0)
CoS[20]	5×10^{-8}	N/A	1
NiS[21]	1×10^{-7}	1.1	1
ZnS[22]	1×10^{-9}	2×10^{-4}	1
CdS[23]	1×10^{-10}	8×10^{-7}	1
PbS[21]	1×10^{-3}	3×10^{-7}	5×10^{-5}
Ag_2S[24]	7×10^{-3}	6×10^{-30}	3×10^{-5}
HgS[25]	6×10^{-3}	2×10^{-32}	1×10^{-5}
PdS[12]	1×10^{-3}	2×10^{-37}	1×10^{-6}
CuS[14]	10	6×10^{-16}	2×10^{-9}

[a] These are presented in order of observed resistance change upon reaction of the metal acetate with H_2S.

As can be seen from Table 1, palladium sulfide has the smallest solubility product constant, so it is the most stable metal sulfide but has a relatively low conductivity. Nickel sulfide has the largest solubility product constant and is the least stable metal sulfide. Table 1 also shows that copper sulfide is the most conducting metal sulfide on the list.

Figure 3 shows that the response to hydrogen sulfide is dependent on the solubility product constant and the conductivity of the resulting metal sulfide. Copper salts respond best because copper sulfide has a relatively small solubility product constant and a high conductivity. Palladium sulfide has a much smaller solubility product constant than copper sulfide, so it is expected that palladium acetate should react more than copper acetate. However, palladium sulfide has a much lower conductivity than copper sulfide, so the change in resistance for palladium acetate should be smaller. Palladium, lead, and mercury acetates have similar conductivities but different solubility product constants. As a result, their responses are related to their solubility product constants, with palladium having the largest response, mercury having the intermediate response, and lead having the smallest response. Cobalt and nickel sulfides have high solubility product constants but are insulating; this is consistent with the absence of a significant response to hydrogen sulfide by either of these two metal salts.

Other metal acetates that were examined and not shown in Figure 3 are presented in Table 1. As seen from the table, it is expected that cadmium and zinc acetate should not produce a metal sulfide because the sulfide conductivity is very low and the solubility product constant is high. This was confirmed experimentally; we see no reaction of cadmium or zinc acetate with 10 ppm of hydrogen sulfide by either conductivity measurements or EDX. Silver acetate also has a significant interaction with hydrogen sulfide, but the data were judged to be less reliable and, therefore, are not presented.

Conclusions

Copper acetate films respond with very large changes in resistance (up to or exceeding 8 orders of magnitude) through the formation of a conductive copper sulfide product upon exposure to hydrogen sulfide. The response times are on the order of a few seconds at room temperature. Other copper salts with large, weakly bound ligands also respond to hydrogen sulfide by forming metal sulfides. In particular, copper propionate responds similarly to copper acetate, giving essentially the same response time and magnitude. Other metal acetates also respond to hydrogen sulfide by forming metal sulfides; however, their responses are not as dramatic as that observed for copper acetate. It appears that the responses of all the metal salts studied are related to the solubility product constants and conductivities of the resulting metal sulfides. A smaller solubility product constant predicts a greater reaction with hydrogen sulfide, while the ability to detect a change is related to the conductivity of the resulting metal sulfide.

We have also demonstrated that copper acetate and other salts can be incorporated into a conductive matrix, such as polyaniline nanofibers, that provides a lower initial resistance and allows measurements to be made with simpler instrumentation. Copper acetate has a high initial resistance and requires complicated equipment for measurement, whereas a copper acetate/polyaniline nanofiber matrix has a much lower initial resistance. The lower initial resistance leads to a smaller response but still results in orders of magnitude changes in resistance. At early times, however, the effects of reversible doping of the polyaniline by the acetic acid byproduct are observed in addition to the formation of conductive metal sulfides. These data demonstrate the possibility of fabricating inexpensive chemical sensors based on simple electrical measurements of this gas−solid reaction at room temperature. We believe these observations can also be extended to other metal salt and analyte combinations, and we are currently working to develop such sensors.

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