Graphical Abstract

Investigation of the H₂S Poisoning Process for Sensing Composite Material Based on Carbon Nanotubes and Metal Oxides

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Abstract

The poisoning of H₂S sensing material based on the mixture of acid-treated carbon nanotubes, CuO and SnO₂ was investigated by exposing the material to high doses of H₂S (1% in volume) and following the changes spectroscopically. The presence of metal sulfides (CuS and SnS₂), sulfates and thiols was confirmed on the surface of this material as the result of H₂S poisoning. Further study revealed that leaving this material in air for extended period of time led to reoxidation of metal sulfides back to metal oxides. The formation of thiols and sulfates directly on carbon nanotubes is not reversible under these conditions; however, the extent of the overall surface reaction in this case is substantially lower than that for the composite material.

Keywords: carbon nanotubes, copper, tin dioxide, H₂S sensor, XPS.

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1. Introduction

H₂S is a well-known gaseous toxic material. It can affect the neural system in humans and could be lethal even when the concentration present is as low as 250 ppm [1, 2]. Hence, sensors with high sensitivity and fast response to H₂S are always in demand. One major category of H₂S sensors is based on semiconducting metal oxides [3-5], and the most commonly used materials are tin dioxide or zinc oxide [6, 7]. In addition to low cost, these sensors demonstrate high sensitivity and fast response [8]. However, oxygen is always required in order to recover and maintain the sensing ability of such materials [9-12]. The traditional semiconducting metal oxides sensors also usually require the optimum operation temperature above 350 °C. Although a number of studies suggest that metal oxides can be used at room temperature as reliable sensing materials, their sensitivity improves dramatically at elevated temperatures [13-16]. On the other hand, carbon nanotube-based gas sensors have the advantage of being able to operate reliably at room temperature [17]. In addition to outstanding chemical stability [18] and electrical properties [19], some carbon nanotube-based sensors have exhibited detection limit as low as 10 ppb (part per billion) [20] and shown a very high selectivity towards target gases [21]. For instance, singlewalled carbon nanotube (SWCNT) - based gas sensors were shown to detect target gases such as CO or NH₃ [22-24], and multiwalled carbon nanotube-based (MWCNT) sensors were used to successfully detect H₂S, CHCl₃, and ethanol [18, 25, 26].

High sensitivity and fast response time of metal oxide sensors and high stability as well as simplicity of CNT-based sensors naturally lead to combining these materials into a single composite sensing element [27-29]. In recent work it was found that a mixed

CuO/SnO₂ material performed even better than the pure tin dioxide for H₂S sensing and still retained chemical stability and high sensitivity at low cost [30-34]. It has been suggested [30, 31] that copper improves the sensor performance by increasing the concentration of surface active sites and decreasing the crystalline size of SnO₂; alternatively, the introduction of H₂S may destroy the p-n junction between CuO and SnO₂ by forming CuS, therefore improving the sensing ability [34, 35]. Moreover, oxygen is still needed to recover this material following H₂S exposure, meaning that this sensor can only operate in oxygen-rich conditions. At the same time, it has been suggested that oxygen may not be necessary to recover the sensing ability of acid-treated carbon nanotubes [22]. Specifically, the resistance change in carboxylic acid-modified carbon nanotubes could be due to the weak hydrogen bonds formed between carboxylic acid groups on the carbon nanotube surface and H₂S, which can change charge distribution of the carbon nanotubes. In this case, no oxygen is required to reverse this type of interaction. Thus, composite sensing materials based on metal oxides and acid-treated carbon nanotubes could possess all the prerequisites of an excellent sensor for H₂S [28, 36]. However, in order for this sensor to be practical and to fully understand the sensing mechanism, the chemical reactions and possible poisoning processes for such material need to be investigated first.

To address this challenge, the first part of this work describes the compositional and morphological changes of the composite sensing material and its main components following large exposures of H₂S and proposes a possible poisoning mechanism for the composite material consisting of the acid-treated singlewalled carbon nanotubes (SWCNT-COOH), CuO, and SnO₂. The second part compares key findings with the

sensor material based on the mixture of acid-treated multiwalled carbon nanotubes (MWCNT-COOH), CuO, and SnO₂. In this set of investigations, acid-treated carbon nanotubes were chosen for a number of reasons described above and for having better sensing response compared to non-functionalized carbon nanotubes, as reported previously [18, 22].

To understand the poisoning process, large doses of H₂S (1% by volume) were used throughout the experiments unless indicated otherwise. A T-shape chamber was utilized as the main reaction chamber and the samples were placed in this chamber with a fixed air or nitrogen flow to measure sensor response during H₂S exposure. X-ray photoelectron spectroscopy (XPS) was used to characterize the material before and after H₂S exposure and to follow its recovery in air. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were utilized to interrogate the changes in surface morphology and surface element distribution.

2. Experimental

2.1 Sensor testing setup

A T-shape chamber was used as the reaction chamber throughout all the experiments described in this work. The sensor material was placed inside the chamber and flexible tubing (Marprene, Watson Marlow Tubing) was used to connect the gas lines to the chamber to provide required air or N₂ (boil-off, purity 99.99%) flow. A flowmeter (Dwyer) was used to control the flow speed of the incoming air or N₂. The predetermined amount of H₂S (purity 99.5%+, Sigma Aldrich) was injected into the chamber via a

syringe, providing a spike of the target gas with a calibrated concentration. DC power supply (SCI/Speco, model: psv-5, 0.3 V voltage) and galvanometer (Keithley 485) were connected to the surface of the sensor via small tantalum clips to provide good electrical contact. The k-type thermocouple was attached independently to the sensor surface to measure its temperature directly. The sensor surface was heated and kept at 473 K throughout the experiments to be consistent with previously reported conditions [37-39]. Dry air was used as a carrier gas unless indicated otherwise.

2.2 Preparation of SWCNT-COOH and MWCNT-COOH

The acid-treated singlewalled carbon nanotubes (SWCNT-COOH, purity 95%+, Nanostructure & Amorphous Material Inc.) were used as purchased without additional treatment. In order to functionalize the multiwalled carbon nanotubes (MWCNT, purity 95%+, Nanostructure & Amorphous Material Inc.) with carboxylic acid groups, the carbon nanotubes were treated with a mixture of 8 M nitric (Fisher, 15.8 normality) and 8 M sulfuric acid (Fisher, 98% purity). The slurry was then placed into an ultrasonic bath for 2 hours at 60 °C. Following this step, carbon nanotubes were separated from the acid by centrifugation at 4500 rpm and washed 5 times with deionized water [40, 41].

2.3 Preparation of pure SnO₂, MWCNT-COOH/CuO/SnO₂ and SWCNT-COOH/CuO/SnO₂ composite materials

For the test material made of pure SnO₂, SnO₂ nanopowder (Aldrich, <100nm particle size) was used directly without further treatment. The nanopowder was dispersed

in deionized water and deposited onto a silicon wafer (Virginia Semiconductor, >0.1 Ohm-cm resistance, 500 μm thickness) by drop-casting. The sample was then dried in the oven at 80 °C to allow the solvent to evaporate. To prepare a sensing material based on MWCNT-COOH, CuO, and SnO₂, 1.5 mg of MWCNT-COOH was mixed with 25 mg CuO/SnO₂ nanopowder (Cu powder, 99.5% purity, Alfa Aesar; Sn powder, 99% purity, Aldrich) prepared as described previously [42] with an atomic concentration (by weight) of copper approximately 2% confirmed by EDS. The MWCNT-COOH/CuO/SnO₂ mixture was then dispersed in deionized water and sonicated for 20 min, and deposited onto a silicon wafer by drop-casting. The wafer was then placed into an oven at 80 °C to allow the solvent to evaporate. The SWCNT-COOH/CuO/SnO₂ material was prepared following the same procedure.

2.4 Characterization methods

The Zeiss Auriga 60 FIB/SEM at the W. M. Keck Electron Microscopy facility at the University of Delaware was used to perform all the scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) experiments for all the samples. In-lens detector with an accelerating energy of 20 keV and a working distance of 5.00 mm was used.

The X-ray photoelectron spectroscopy (XPS) spectra were collected on a PHI 5600 X-ray photoelectron spectrometer. Al K α X-ray source ($h\nu = 1486.6$ eV) was used in all experiments at a 45° takeoff angle. All the measurements were conducted in a vacuum chamber with a base pressure of 1.0×10^{-9} Torr. To calibrate the resulting spectra,

C 1s at 284.6 eV was used. CasaXPS 2.3.17 version software was utilized to process all the XPS data.

3. Results and discussion

Since the main target of this work is to understand the chemical processes leading to sensor poisoning rather than to optimize the sensor performance, large doses of H₂S, substantially higher than in realistic conditions, were used. Nominally, the concentration of H₂S reached approximately 1% by volume for all of the experiments unless indicated otherwise. The sensor responses to these large doses were measured as:

$$\text{Response} = \frac{|R_g - R_o|}{R_o},$$

where R_g is the resistance of the sensor in the presence of H₂S and R_o is the resistance of the sensor without H₂S (in air or in nitrogen, as indicated below).

3.1 SWCNT-COOH/CuO/SnO₂ response to H₂S

SWCNT-COOH/CuO/SnO₂ was chosen as the main target of the present investigation due to the relatively simple physical and chemical structure of SWCNT-COOH. MWCNT-COOH/CuO/SnO₂ mixture was largely explored to supplement the findings of the SWCNT-COOH/CuO/SnO₂ study. For SWCNT-COOH/CuO/SnO₂, XPS characterization was performed following each H₂S dose to interrogate the compositional changes of the system as a function of H₂S exposure and recovery process. In order to visualize the topographical changes and to interrogate elemental distribution on the surface of the material, SEM and EDS were also performed.

Figure 1. XPS of Cu 2p spectral region for SWCNT-COOH/CuO/SnO₂ sensing material (A) and the corresponding zoom-in image (indicated by arrows) that illustrates the binding energy shift of copper (B): a) is the spectrum taken before exposure to H₂S; b) is the spectrum taken immediately after the first exposure to H₂S; c) is the spectrum taken immediately after the second exposure to H₂S; d) is the spectrum taken 2 days (kept in air at room temperature) following the third exposure to H₂S; e) is the spectrum taken 7 days (kept in air at room temperature) following the third exposure and f) is the spectrum taken following re-exposure of the sample in (e) to H₂S. Dashed lines show the binding energies corresponding to CuO and CuS, as indicated by the labels.

Figure 1 summarizes the XPS studies of Cu 2p spectral region (A) before and after exposing the SWCNT-COOH/CuO/SnO₂ sensing material to H₂S, with a zoom-in of the relevant spectral features given in Figure 1B (as indicated by arrows). Spectrum (a) in Figure 1A indicates that before exposure to H₂S the sample surface mostly consists of

CuO and Cu(OH)₂, since the 2p_{3/2} feature can be fitted with two peaks at 933.3 eV and 935.3 eV, respectively [43, 44]. The presence of Cu(OH)₂ can be explained by moisture present in ambient [35]. Based on the changes within this spectral region as a function of H₂S exposure and recovery in air, two major conclusions can be inferred. First, in Figure 1A, following consecutive H₂S exposures, the spectral changes from (a) to (c) indicate that the Cu(II) from CuO and Cu(OH)₂ is consumed during the process, as the shake-up satellite peaks between 940 eV and 945 eV disappear and the main Cu 2p_{3/2} peak at 933.4 eV shifts to 932.5 eV. Thus, CuO and Cu(OH)₂ interact with H₂S and transform chemically [43]. Figure 1B shows the zoom-in of the relevant spectral region from the corresponding Figure 1A spectra (indicated by the black arrows) to further illustrate the difference in binding energy for copper. Second, according to the changes recorded for spectral features of the “poisoned” sensing material recovered in air, this step is effectively leading to reoxidation of copper. Starting from the next poisoning cycle, as illustrated in Figure 1A spectrum (f), it again leads to chemical changes in copper species and the formation of sulfides. It is worth noting for XPS identification purposes that CuS does not have the satellite peak around 940 eV as CuO does [35, 45-47]. It is also very difficult to distinguish Cu₂S from CuS by examining Cu 2p spectral region or even in the Cu LMM region. The only practical way to distinguish them in this complex system is by examining S 2p spectral signature, as described below.

Figure 2. XPS of S 2p spectral region for SWCNT-COOH/CuO/SnO₂ sensing material: a) is the spectrum taken before exposure to H₂S; b) is the spectrum recorded immediately following the first exposure to H₂S; c) is the spectrum recorded immediately following the second exposure to H₂S; d) is the spectrum taken 2 days (kept in air at room temperature) after the third exposure; e) is the spectrum taken 7 days (kept in air at room temperature) after the third exposure and f) is the spectrum taken following re-exposure of sample in (e) to H₂S. Only the peaks in spectrum (f) are fitted with corresponding fitting curves, as described in the text.

Figure 2 shows the XPS studies of the S 2p spectral region as a function of sensor exposure to H₂S and recovery in air. From (a) to (c), the increasing intensity of the peaks around 162.5 eV and 169.4 eV indicates the accumulation of S²⁻ and (SO₄)²⁻ surface species, respectively [43, 48-50]. The presence of substantial amounts of HS species or chemisorbed H₂S can be ruled out since the binding energy of S 2p peaks for those

species is expected to be between 163.5 eV and 165 eV [51, 52]. This statement will be further elaborated below by analysis of H₂S interaction with CNT material. As mentioned above, the only feasible way to differentiate CuS from Cu₂S is from the S 2p XPS investigation. Specifically, spectral features corresponding to these two copper sulfides exhibit approximately 0.7 eV binding energy difference. A series of previous XPS investigations at relatively low resolution reported the positions of unresolved S 2p features for Cu₂S as 161.8 eV, and for CuS this energy is 162.5 eV [43, 48, 49]. Hence, the peaks at 162.0 eV and 163.2 eV (S 2p_{3/2} and S 2p_{1/2} in spectrum (f) labeled as S1) with the average position of S 2p feature close to that reported for CuS can be assigned to CuS rather than Cu₂S. Other studies also reported the formation of CuS from CuO following the introduction of H₂S with the temperature varying from room temperature to 453 K [53, 54]. However, given the fact that tin from SnO₂ may also interact with H₂S to form SnS₂ at temperature as low as 523 K, S1 could be a combination of the two species, which will be discussed in more detail later [55]. Moreover, in Figure 1A from (d) to (e), the spectra indicate that following exposure of the poisoned sensing material to air, the copper is reacted again to form CuO as well as Cu(OH)₂ since the shake-up satellite peaks show up again between 940 eV and 945 eV and the FWHM of the main Cu 2p_{3/2} peak increases. At the same time, in Figure 2 from (d) to (e), it is obvious that the peaks corresponding to sulfides around 162.5 eV decrease dramatically following exposure of the “poisoned” sensing material to air while the peaks for sulfates around 169.4 eV still exhibit the same intensity. Considering the fact that (d) and (e) were taken 2 days and 7 days after the exposure, respectively, it is reasonable to conclude that after being exposed to air, CuS can form CuO [35, 54, 56] and Cu(OH)₂ again in ambient. The peaks around

169.4 eV (S 2p_{3/2} and S 2p_{1/2} in spectrum (f) labeled as S3) can be assigned to Sn(SO₄)₂ since the same feature is observed after exposing SnO₂ nanopowder to H₂S, as discussed below. The complex product containing C-O-S that derives from the interaction between H₂S and SWCNT-COOH may also contribute to the formation of the peak around 169.4 eV, which will also be discussed later. The reason the feature at 169.4 eV in Figure 2 cannot be assigned to CuSO₄ is that despite the existence of the peaks at 169.4 eV, there is no corresponding shake-up satellite peaks observed between 940 eV and 945 eV which would indicate the presence of CuSO₄ as recorded in spectra (c) and (f) in Figure 1A [43, 50, 57]. This statement is also supported by the previous studies of CuO reaction with H₂S to form CuSO₄ at temperature of nearly 1273 K, which is much higher compared to the experimental temperature used in the present study (473 K) [58].

In order to further examine chemical changes in the composite material following its recovery in air, an additional re-exposure of H₂S is performed to interrogate the surface species formed. As shown in spectra (f) in Figures 1A and 2, after this re-exposure, Cu peaks shift to the lower binding energy again and the shake-up satellite peaks between 940 eV and 945 eV disappear similarly to the results presented in spectrum (c) in Figure 1A following an initial set of H₂S exposures. The peak around 162.5 eV appears again to indicate the formation of sulfides, shown in Figure 2f. It is again worth noting that S1 species may correspond to a combination of sulfides of copper and tin in the mixture. Meanwhile, S2 species indicated by a fit at 163.8 eV and 165.0 eV represents S 2p_{3/2} and S 2p_{1/2} for thiol functional group [59]. Although the binding energy (S 2p) of elemental sulfur or S₈ is within the same range, around 164.0 eV [60], the high experimental temperature (473 K) helps rule out their existence in these studies [33]. S3

species with spectral signatures at 169.0 eV and 170.2 eV likely originate from a combination of S 2p_{3/2} and S 2p_{1/2} features of Sn(SO₄)₂ and C-O-S as mentioned before. This result can serve as a strong evidence for the reactions between H₂S and all the components of the SWCNT-COOH/CuO/SnO₂ sensing material. The same peaks are also observed for the mixture MWCNT-COOH/CuO/SnO₂, implying a similar reaction mechanism for both types of materials (Figure S1 in Supporting Information section).

Figure 3. XPS of Sn 3d spectral region for SWCNT-COOH/CuO/SnO₂ sensing material: a) is the spectrum taken before exposure to H₂S; b) is the spectrum recorded immediately after the first exposure to H₂S; c) is the spectrum recorded after the second exposure to H₂S; d) is the spectrum taken 2 days (kept in air) following the third exposure; e) is the spectrum taken 7 days (kept in air) following the third exposure.

Figure 3 shows the XPS spectra of Sn 3d spectral region before and after the H₂S exposure and recovery in air. All the spectra show nearly the same binding energy for Sn 3d_{5/2}, which matches up with the binding energy for SnO₂ at 487.3 eV [61-63]. The

binding energy of Sn 3d_{5/2} for SnS₂ is reported to be 486.5 eV [64, 65], which indicates a noticeable difference from the observed value but it is possible that a very minor feature corresponding to SnS₂ is hidden under the peak corresponding to SnO₂. However, the presence of SnS can be ruled out because the binding energy of Sn 3d_{5/2} for this compound is 486.0 eV [64], which is more than 1 eV lower than that for the main peak corresponding to Sn 3d_{5/2} in SnO₂.

Figure 4. XPS of S 2p (Panel A) and Sn 3d (Panel B) spectral regions for pure SnO_2 before and after H_2S exposure: a) spectra taken before exposure to H_2S , b) spectra taken immediately following exposure to H_2S , and c) are the spectra taken 2 days (kept in air at room temperature) following the exposure to H_2S .

To further elaborate on the possibility of a reaction between SnO_2 and H_2S and to contrast it with the formation of CuS confirmed above, reaction of H_2S directly with SnO_2 material in conditions identical to those reported above for a composite material have been performed. Figure 4 compares the S 2p and Sn 3d spectral regions for samples of nanoparticulate SnO_2 before H_2S exposure, following this step, and after recovery in air for 2 days. Overall, these spectra are very similar to those recorded for a composite material and reported in Figure 2 (2c and 2d). In particular, the peak at 169.3 eV for S 2p in Figure 4a coincides with the sulfate peak observed in Figure 2 with a binding energy of 169.4 eV. This implies that this feature in Figure 2 should indeed be assigned to $\text{Sn}(\text{SO}_4)_2$, as was proposed above. In addition, the binding energy of tin in the 3d region does not change noticeably following exposure to H_2S , as summarized in Panel B of Figure 4 (487.2 eV for spectrum (a) and (b), 487.3 eV for spectrum (c)). Thus, the presence of Sn(IV) and not Sn(II) is confirmed on the surface of both pure tin oxide and the same material incorporated into a composite network with CuO and carbon nanotubes throughout all the experiments [65]. Thus, all these observations suggest that SnO_2 has reacted with H_2S and the formation of $\text{Sn}(\text{SO}_4)_2$ in this system is irreversible under the conditions studied. At the same time, the sulfide formed on the surface appears to be SnS_2 since the presence of surface -SH species can be ruled out as mentioned earlier [51, 52, 55] and the formation of this sulfide can be reversed by exposing the material to ambient air.

To better understand the morphology as well as the surface element distribution, SEM and EDS were performed following the second introduction of the H_2S . The SEM image in Figure 5a shows the nanoparticles as a part of the composite material studied.

The bright area in the center corresponds to the mixture of CuO and SnO₂ and the dark area around it is SWCNT-COOH. This is also confirmed by the elemental mapping using EDS in Figure 5b. Figures 5c and 5d show that the locations for copper and sulfur coincide within this material following its exposure to H₂S, which suggests that a compound of copper and sulfur is formed efficiently and it dominates the surface. This is fully consistent with the XPS results described above. This statement is further supported by the observation that the formation of a compound containing both copper and sulfur is recorded within the area that is depleted of tin, and even oxygen concentration is decreased. It must be emphasized that since the composite material used here is a mixture of CuO and SnO₂ within the carbon nanotube matrix, the distribution of the elements within the material is not expected to be uniform. What appears to be a protrusion in Figure 5e for tin concentration actually corresponds to the presence of CuO particles reacted with H₂S.

Figure 5. SEM and EDS images of the surface following the 2nd introduction of H₂S. a) SEM image of the surface showing SnO₂ and CuO (bright area) mixed with SWCNT-COOH (dark area). b) EDS elemental mapping of oxygen (light blue), carbon (green), copper (dark blue), sulfur (orange) and tin (red) on the surface. c) EDS elemental mapping of copper on the surface. d) EDS elemental mapping of sulfur on the surface. e) EDS elemental mapping of tin on the surface. f) EDS elemental mapping of oxygen on the surface.

One last part of chemical characterization of the composite material should address the possibility of chemical interaction between the SWCNT-COOH and H₂S. Hence, another set of experiments were performed by using pure SWCNT-COOH to

better understand the interactions between H_2S and SWCNT-COOH. All the experimental parameters were kept the same as for testing the composite material described above. Figure 6 follows the S 2p spectral region in XPS measurements before (Figure 6a) and after (Figure 6b) exposure to H_2S . These results are compared to the investigation of the samples recovered in air for 2 and 7 days (Figures 6c and d, respectively).

Figure 6. XPS spectra of pure SWCNT-COOH showing S 2p spectral region: a) spectrum recorded before exposure to H_2S ; b) spectrum recorded immediately following the exposure to H_2S ; c) spectrum taken 2 days (kept in air at room temperature) following the exposure, and d) spectrum taken 7 days (kept in air at room temperature) following the exposure.

It is obvious that following the exposure to H_2S , a sulfide or a thiol compound forms as the product with a spectral signature of S $2p_{3/2}$ at 163.8 eV and S $2p_{1/2}$ at 165.0 eV. This spectral feature is a perfect fit with the feature labeled as S2 in spectrum (f) of Figure 2 above for the composite material studied. Pure unfunctionalized SWCNT

material is also examined and found to have the same peak at the same binding energy (Figure S2 in Supporting Information section). According to the data presented in spectra (c) and (d) in Figure 6, these features, once formed, do not show any noticeable changes even if the resulting samples are kept in air at room temperature for 7 days. This observation explains the presence of a minor species in spectra (d) and (e) in Figure 2 with the same spectral signature. In other words, for the SWCNT-COOH/CuO/SnO₂ material, the peak around 162.5 eV consists of copper/tin sulfides (species labeled S1 in spectrum (f) in Figure 2) as well as thiols formed on the surface of carbon nanotubes (S2 in spectrum (f) in Figure 2) [59, 66]. Since the formation of copper/tin sulfides can mostly be reversed after exposure to air (as discussed in the previous sections), the intensity of the overall complex feature decreases following sample exposure to air for extended period of time; however, thiols formed on carbon nanotube do not appear to react, so the spectral feature corresponding to thiol formation on the carbon nanotube component of the composite sensing material remains unchanged. Overall, this remaining spectral signature corresponds to a minor component of the composite material, as SWCNT-COOH is only present there at approximately 6% by weight. Besides the sulfide peaks, spectra (b) - (d) in Figure 6 also show minor peak around 168.6 eV (also labeled as S3 in spectrum (f) in Figure 2), suggesting the formation of minor amounts of sulfate species directly on the surface of carbon nanotubes following their exposure to H₂S [43]. Combination of the XPS results from Figures 2 and 6 can serve as a strong evidence that chemical reactions between SWCNT-COOH and H₂S occur during the exposure process and surface thiols and sulfates form as products and that the formation of these products is not affected by the subsequent exposure to air.

Figure 7. Response of the sensor under air flow at 473 K (SWCNT-COOH/CuO/SnO₂) before (A) and after (B) several large doses of H₂S (when sulfide and sulfate peaks are observed as shown in Figure 2c). Response under N₂ is shown in plot (C) with an arrow indicating the time of the introduction of air. All the doses in 7A are 600 ppm. The first dose in 7B is 600 ppm and 2 subsequent doses are 120 ppm. Only one dose of 600 ppm is recorded in 7C.

One of the most important questions to be answered is how the chemistry described above affects the performance of the sensing material. It is indeed important to quantify how the chemical changes affecting each material component (CuO, SnO₂ and CNTs) affect the sensor performance. The sensitivity study is outside the scope of this work; however, it is important to follow the consistency of the sensor response and also to determine if this material could operate without oxygen present. In other words, is the poisoning process described above irreversible in terms of sensor performance? Figure 7 summarizes the sensor response investigation for the target material, SWCNT-COOH/CuO/SnO₂ at the key points summarized above, specifically before and after surface sulfides and sulfates are formed, and also following sensor material recovery in air. The initial sensor response for relatively large doses of 600 ppm concentration of H₂S in air is presented in Figure 7A, which suggests consistent changes and recovery even for such a large dose. If the sensor is effectively “poisoned” by much higher exposures of H₂S but is constantly recovered in air flow, XPS results suggest that surface sulfides and sulfates are formed but surface sulfides (mostly CuS) are reoxidized.

The overall expected general mechanism for metal oxide components poisoning by H₂S can be put together based on previous investigations. In particular, reactions (1), (2) and (3) occur when H₂S is introduced into the system to form CuS, SnS₂ and Sn(SO₄)₂ on the surface [33, 34]. It is reported that the formation of CuS is the main cause of the resistance change of the material [35]. On the other hand, reactions (4) and (5) are proposed to take place when the recovery process starts [33]. Hence, when only N₂ is available to the system, the sulfides cannot be reoxidized back to the original state, which leads to the effective “poisoning” of the material.

In agreement with the above reactions, Figure 7B shows that following such steps, the response is still largely unaffected and reproducible, as long as the sensor material is constantly “bathed” in air. However, as suggested by the studies shown in Figure 7C, if the same steps are repeated in N₂ flow instead of air, the sensor does not recover and is effectively “poisoned” by the formation of surface species discussed above. It is only following the recovery in air that the sensor response can be recorded again. It is worth noting that the recovery time of the sensor shown in Figure 7 is substantially shorter (several minutes) compared to the sample used for the XPS studies (spectra in Figure 1 and Figure 2). Two factors may contribute to this difference: Firstly, all the response tests are recorded at 473 K in Figure 7, while the sample used in XPS measurement was kept in air at room temperature for days to recover and perform the spectroscopic investigation. High temperature (473 K) will definitely accelerate the recovery process. Secondly, much larger dosage (1%) is applied to the sample in order to have reliable signal of the target elements in the XPS spectra while 120 ppm and 600 ppm are used to test the sensor response. This will lead to much shorter time of recovery for the latter one. Figure S3 in the Supporting Information section also shows the response curve for a sensor designed based on a pure SnO₂ material.

3.2 MWCNT-COOH/CuO/SnO₂ response to H₂S

Figure 8. SEM images of sensing material based on MWCNT-COOH/CuO/SnO₂ taken before (a) and after (b) exposure to H₂S under the same conditions as those described in detail above for SWCNT-COOH/CuO/SnO₂. The arrows in 8b indicate the “island” structures formed on the surface after the exposure.

To generalize the findings presented above, a material constructed by the same procedure as for SWCNT-COOH/CuO/SnO₂ but based on MWCNT-COOH was prepared. The XPS studies for this mixture confirm the formation of very similar surface products as reported above for SWCNT-COOH/CuO/SnO₂, i.e., the formation of sulfides and sulfates on the surface (Figure S1 in the Supporting Information section). However, if the morphologies of the materials based on SWCNT-COOH and on MWCNT-COOH are compared before and after the exposure to large doses of H₂S, as summarized in Figure 8, there are some important differences. Figure 8a shows a representative image for a MWCNT-COOH/CuO/SnO₂ material recorded before exposure to H₂S. Image in Figure 8b is recorded after several large doses of H₂S (1% in volume). Compared to Figure 8a, there are clearly a number of “island” structures newly formed on the surface in Figure 8b, several of which are indicated in the figure by arrows. From the XPS survey, it is shown that the apparent surface sulfur to copper ratio of the MWCNT-COOH/CuO/SnO₂ material is nearly 3:1 while that of the SWCNT-COOH/CuO/SnO₂ is approximately 1:1. This may suggest that the amount of sulfur trapped on a surface depends on the specific chemical arrangement of the components of the sensing materials, which could lead to the formation of the “islands”. However, due to the size of the “island” structures (around 10 nm in diameter) and the limitation of the instrument used, the quantitative investigation of the elemental composition of these structures is difficult and will be the subject of additional further investigations.

4. Conclusions

This work examines the poisoning process for a promising H₂S sensing material, based on carbon nanotubes, copper oxide and tin dioxide. The mixture of SWCNT-COOH/CuO/SnO₂ is investigated in detail spectroscopically as a function of large exposures to H₂S and following its recovery in air. A combination of XPS and electron microscopy investigations reveals the details of the chemical reactions that occur on the surface of the composite material during these steps: when H₂S is initially introduced, each component of the composite material, CuO/Cu(OH)₂, SWCNT-COOH and SnO₂, reacts with this gas to form sulfides, sulfates, and thiols. The formation of surface copper and tin sulfides can be reversed in air either after several days at room temperature or after several minutes at 473 K while the formation of sulfates and thiols cannot be reversed under these conditions. For the mixture of MWCNT-COOH/CuO/SnO₂, with the help of SEM and XPS, similar chemistry is also confirmed. However, in the case of a material based on MWCNT, the formation of small islands is also recorded following the exposure of the material to large doses of H₂S. Interestingly, recovery in air allows for continuous operation of the sensors based on these materials; however, if the air flow is replaced by nitrogen, the poisoning process is irreversible.

Thus, this paper discussed the chemical changes of each active component (CuO, SnO₂ and CNTs) following introduction of H₂S. These results provide a chemical insight into the poisoning process for the H₂S sensors that contain copper/tin and carbon nanotubes as sensing elements and can serve as a starting point for adapting some of these materials for further sensing applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at [http: xxx.xxx.xxx](http://xxx.xxx.xxx)

References

- [1] J. Chen, K. Wang, L. Hartman, W. Zhou, H₂S detection by vertically aligned CuO nanowire array sensors, *J. Phys. Chem. C* 112 (2008) 16017-16021.
- [2] W.H. Tao, C.H. Tsai, H₂S sensing properties of noble metal doped WO₃ thin film sensor fabricated by micromachining, *Sens. Actuators, B* 81 (2002) 237-247.
- [3] S.D. Bakrania, M.S. Wooldridge, The effects of the location of Au additives on combustion-generated SnO₂ nanopowders for CO gas sensing, *Sensors* 10 (2010) 7002-7017.

- [4] Y. Zhou, Y. Huang, D. Li, W. He, Three-dimensional sea-urchin-like hierarchical TiO₂ microspheres synthesized by a one-pot hydrothermal method and their enhanced photocatalytic activity, *Mater. Res. Bull.* 48 (2013) 2420-2425.
- [5] G. Sberveglieri, I. Concina, E. Comini, M. Falasconi, M. Ferroni, V. Sberveglieri, Synthesis and integration of tin oxide nanowires into an electronic nose, *Vacuum* 86 (2012) 532-535.
- [6] K. Wetchakun, T. Samerjai, N. Tamaekong, C. Liewhiran, C. Siri Wong, V. Kruefu, A. Wisitsoraat, A. Tuantranont, S. Phanichphant, Semiconducting metal oxides as sensors for environmentally hazardous gases, *Sens. Actuators, B* 160 (2011) 580-591.
- [7] H.-J. Kim, J.-H. Lee, Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview, *Sens. Actuators, B* 192 (2014) 607-627.
- [8] J.-K. Choi, I.-S. Hwang, S.-J. Kim, J.-S. Park, S.-S. Park, U. Jeong, Y.C. Kang, J.-H. Lee, Design of selective gas sensors using electrospun Pd-doped SnO₂ hollow nanofibers, *Sens. Actuators, B* 150 (2010) 191-199.
- [9] S.R. Wang, Y.Q. Zhao, J. Huang, Y. Wang, S.H. Wu, S.M. Zhang, W.P. Huang, Low-temperature carbon monoxide gas sensors based gold/tin dioxide, *Solid-State Electron.* 50 (2006) 1728-1731.
- [10] M. Vrnata, V. Myslik, F. Vyslouzil, M. Jelinek, J. Lancok, J. Zemek, The response of tin acetylacetonate and tin dioxide-based gas sensors to hydrogen and alcohol vapours, *Sens. Actuators, B* 71 (2000) 24-30.
- [11] R.K. Sharma, P.C.H. Chan, Z.A. Tang, G. Yan, I.M. Hsing, J.K.O. Sin, Sensitive, selective and stable tin dioxide thin-films for carbon monoxide and hydrogen

- sensing in integrated gas sensor array applications, *Sens. Actuators, B* 72 (2001) 160-166.
- [12] J.M. Lee, J.E. Park, S. Kim, S. Kim, E. Lee, S.J. Kim, W. Lee, Ultra-sensitive hydrogen gas sensors based on Pd-decorated tin dioxide nanostructures: Room temperature operating sensors, *Int. J. Hydrogen Energy* 35 (2010) 12568-12573.
- [13] X. Xue, L. Xing, Y. Chen, S. Shi, Y. Wang, T. Wang, Synthesis and H₂S sensing properties of CuO-SnO₂ core/shell PN-junction nanorods, *J. Phys. Chem. C* 112 (2008) 12157-12160.
- [14] C.H. Wang, X.F. Chu, M.W. Wu, Detection of H₂S down to ppb levels at room temperature using sensors based on ZnO nanorods, *Sens. Actuators, B* 113 (2006) 320-323.
- [15] J.L. Solis, S. Saukko, L. Kish, C.G. Granqvist, V. Lantto, Semiconductor gas sensors based on nanostructured tungsten oxide, *Thin Solid Films* 391 (2001) 255-260.
- [16] L.A. Patil, D.R. Patil, Heterocontact type CuO-modified SnO₂ sensor for the detection of a ppm level H₂S gas at room temperature, *Sens. Actuators, B* 120 (2006) 316-323.
- [17] J. Li, Y.J. Lu, Q. Ye, M. Cinke, J. Han, M. Meyyappan, Carbon nanotube sensors for gas and organic vapor detection, *Nano Lett.* 3 (2003) 929-933.
- [18] P. Kar, A. Choudhury, Carboxylic acid functionalized multi-walled carbon nanotube doped polyaniline for chloroform sensors, *Sens. Actuators, B* 183 (2013) 25-33.
- [19] A. Baykal, M. Senel, B. Unal, E. Karaoglu, H. Sozeri, M.S. Toprak, Acid functionalized multiwall carbon nanotube/magnetite (MWCNT)-COOH/Fe₃O₄

hybrid: synthesis, characterization and conductivity evaluation, *J. Inorg. Organomet. Polym.* 23 (2013) 726-735.

- [20] L. Valentini, I. Armentano, J.M. Kenny, C. Cantalini, L. Lozzi, S. Santucci, Sensors for sub-ppm NO₂ gas detection based on carbon nanotube thin films, *Appl. Phys. Lett.* 82 (2003) 961-963.
- [21] S. Chopra, K. McGuire, N. Gothard, A.M. Rao, A. Pham, Selective gas detection using a carbon nanotube sensor, *Appl. Phys. Lett.* 83 (2003) 2280-2282.
- [22] K.Y. Dong, J. Choi, Y.D. Lee, B.H. Kang, Y.Y. Yu, H.H. Choi, B.K. Ju, Detection of a CO and NH₃ gas mixture using carboxylic acid-functionalized single-walled carbon nanotubes, *Nanoscale Res. Lett.* 8 (2013).
- [23] D.L. Fu, H.L. Lim, Y.M. Shi, X.C. Dong, S.G. Mhaisalkar, Y. Chen, S. Moochhala, L.J. Li, Differentiation of gas molecules using flexible and all-carbon nanotube devices, *J. Phys. Chem. C* 112 (2008) 650-653.
- [24] J. Kong, N.R. Franklin, C.W. Zhou, M.G. Chapline, S. Peng, K.J. Cho, H.J. Dai, Nanotube molecular wires as chemical sensors, *Science* 287 (2000) 622-625.
- [25] D.Z. Zhang, K. Wang, J. Tong, B.K. Xia, Characterization of layer-by-layer nano self-assembled carbon nanotube/polymer film sensor for ethanol gas sensing properties, *Microsyst. Technol.* 20 (2014) 379-385.
- [26] N. Izadi, A.M. Rashidi, S. Golzardi, Z. Talaei, A.R. Mahjoub, M.H. Aghili, Hydrogen sulfide sensing properties of multi walled carbon nanotubes, *Ceram. Int.* 38 (2012) 65-75.

- [27] B.Y. Wei, M.C. Hsu, P.G. Su, H.M. Lin, R.J. Wu, H.J. Lai, A novel SnO₂ gas sensor doped with carbon nanotubes operating at room temperature, *Sens. Actuators, B* 101 (2004) 81-89.
- [28] F. Mendoza, D.M. Hernandez, V. Makarov, E. Febus, B.R. Weiner, G. Morell, Room temperature gas sensor based on tin dioxide-carbon nanotubes composite films, *Sens. Actuators, B* 190 (2014) 227-233.
- [29] M.-G. Willinger, G. Neri, A. Bonavita, G. Micali, E. Rauwel, T. Herntrich, N. Pinna, The controlled deposition of metal oxides onto carbon nanotubes by atomic layer deposition: examples and a case study on the application of V₂O₄ coated nanotubes in gas sensing, *Phys. Chem. Chem. Phys.* 11 (2009) 3615-3622.
- [30] R.K. Mishra, A. Kushwaha, P.P. Sahay, Influence of Cu doping on the structural, photoluminescence and formaldehyde sensing properties of SnO₂ nanoparticles, *RSC Adv.* 4 (2014) 3904-3912.
- [31] W.X. Jin, S.Y. Ma, Z.Z. Tie, J.J. Wei, J. Luo, X.H. Jiang, T.T. Wang, W.Q. Li, L. Cheng, Y.Z. Mao, One-step synthesis and highly gas-sensing properties of hierarchical Cu-doped SnO₂ nanoflowers, *Sens. Actuators, B* 213 (2015) 171-180.
- [32] G. Korotcenkov, Metal oxides for solid-state gas sensors: What determines our choice?, *Mater. Sci. Eng., B* 139 (2007) 1-23.
- [33] G.-J. Sun, S.-W. Choi, A. Katoch, P. Wu, S.S. Kim, Bi-functional mechanism of H₂S detection using CuO-SnO₂ nanowires, *J. Mater. Chem. C* 1 (2013) 5454-5462.
- [34] J.H. Liu, X.J. Huang, G. Ye, W. Liu, Z. Jiao, W.L. Chao, Z.B. Zhou, Z.L. Yu, H₂S detection sensing characteristic of CuO/SnO₂ sensor, *Sensors* 3 (2003) 110-118.

- [35] V.R. Katti, A.K. Debnath, K.P. Muthe, M. Kaur, A.K. Dua, S.C. Gadkari, S.K. Gupta, V.C. Sahni, Mechanism of drifts in H₂S sensing properties of SnO₂ : CuO composite thin film sensors prepared by thermal evaporation, *Sens. Actuators, B* 96 (2003) 245-252.
- [36] H. Dai, P. Xiao, Q. Lou, Application of SnO₂/MWCNTs nanocomposite for SF₆ decomposition gas sensor, *Phys. Status Solidi A* 208 (2011) 1714-1717.
- [37] C. Wongchoosuk, A. Wisitsoraat, A. Tuantranont, T. Kerdcharoen, Portable electronic nose based on carbon nanotube-SnO₂ gas sensors and its application for detection of methanol contamination in whiskeys, *Sens. Actuators, B* 147 (2010) 392-399.
- [38] H. Huang, Y.C. Lee, O.K. Tan, W. Zhou, N. Peng, Q. Zhang, High sensitivity SnO₂ single-nanorod sensors for the detection of H₂ gas at low temperature, *Nanotechnology* 20 (2009).
- [39] J.K. Srivastava, P. Pandey, V.N. Mishra, R. Dwivedi, Sensing mechanism of Pd-doped SnO₂ sensor for LPG detection, *Solid State Sci.* 11 (2009) 1602-1605.
- [40] Y. Xing, L. Li, C.C. Chusuei, R.V. Hull, Sonochemical oxidation of multiwalled carbon nanotubes, *Langmuir* 21 (2005) 4185-4190.
- [41] Y. Xing, Synthesis and electrochemical characterization of uniformly-dispersed high Loading Pt nanoparticles on sonochemically-treated carbon nanotubes, *J. Phys. Chem. B* 108 (2004) 19255-19259.
- [42] V. Kumar, S. Sen, K.P. Muthe, N.K. Gaur, S.K. Gupta, J.V. Yakhmi, Copper doped SnO₂ nanowires as highly sensitive H₂S gas sensor, *Sens. Actuators, B* 138 (2009) 587-590.

- [43] S.K. Chawla, N. Sankarraman, J.H. Payer, Diagnostic spectra for XPS analysis of Cu-O-S-H compounds, *J. Electron. Spectrosc. Relat. Phenom.* 61 (1992) 1-18.
- [44] N.S. McIntyre, S. Sunder, D.W. Shoesmith, F.W. Stanchell, Chemical information from XPS—applications to the analysis of electrode surfaces, *J. Vac. Sci. Technol.* 18 (1981) 714-721.
- [45] M. Romand, M. Roubin, J.P. Deloume, ESCA studies of some copper and silver selenides, *J. Electron. Spectrosc. Relat. Phenom.* 13 (1978) 229-242.
- [46] S.K. Chawla, B.I. Rickett, J.H. Payer, Formation of copper sulfide in moist air-sulfur dioxide, In *Corrosion of Electronic and Magnetic Materials*, ASTM STP 1148, P. J. Peterson, Ed., American Society for Testing and Materials, Pennsylvania (1992) pp. 21-35.
- [47] S. Bahadur, D. Gong, J.W. Anderegg, The investigation of the action of fillers by XPS studies of the transfer films of peek and its composites containing CuS and CuF₂, *Wear* 160 (1993) 131-138.
- [48] R. Scheer, H.J. Lewerenz, Photoemission study of evaporated CuInS₂ thin films. II. Electronic surface structure, *J. Vac. Sci. Technol., A* 12 (1994) 56-60.
- [49] V. Krylova, A. Andrulevicius, Optical, XPS and XRD studies of semiconducting copper sulfide layers on a polyamide film, *Int. J. Photoenergy* (2009) Article ID 304308.
- [50] C.D. Wagner, J.A. Taylor, Generation of XPS Auger lines by bremsstrahlung, *J. Electron. Spectrosc. Relat. Phenom.* 20 (1980) 83-93.

- [51] J.A. Rodriguez, S. Chaturvedi, M. Kuhn, J. van Ek, U. Diebold, P.S. Robbert, H. Geisler, C.A. Ventrice, H₂S adsorption on chromium, chromia, and gold/chromia surfaces: photoemission studies, *J. Chem. Phys.* 107 (1997) 9146-9156.
- [52] C.T. Campbell, B.E. Koel, H₂S/Cu(111): a model study of sulfur poisoning of water-gas shift catalysts, *Surf. Sci.* 183 (1987) 100-112.
- [53] S. Zhang, P. Zhang, Y. Wang, Y. Ma, J. Zhong, X. Sun, Facile fabrication of a well-ordered porous Cu-doped SnO₂ thin film for H₂S sensing, *ACS Appl. Mater. Interfaces* 6 (2014) 14975-14980.
- [54] N.S. Ramgir, S.K. Ganapathi, M. Kaur, N. Datta, K.P. Muthe, D.K. Aswal, S.K. Gupta, J.V. Yakhmi, Sub-ppm H₂S sensing at room temperature using CuO thin films, *Sens. Actuators, B* 151 (2010) 90-96.
- [55] M. Liu, J. Yang, Q. Qu, P. Zhu, W. Li, High-quality SnO₂@SnS₂ core-shell heterojunctions: designed construction, mechanism and photovoltaic applications, *J. Power Sources* 273 (2015) 848-856.
- [56] F. Shao, M.W.G. Hoffmann, J.D. Prades, R. Zamani, J. Arbiol, J.R. Morante, E. Varechkina, M. Rumyantseva, A. Gaskov, I. Giebelhaus, T. Fischer, S. Mathur, F. Hernandez-Ramirez, Heterostructured p-CuO (nanoparticle)/n-SnO₂ (nanowire) devices for selective H₂S detection, *Sens. Actuators, B* 181 (2013) 130-135.
- [57] R.P. Vasquez, CuSO₄ by XPS, *Surf. Sci. Spectra* 5 (1998) 279-284.
- [58] A. Chowdhuri, P. Sharma, V. Gupta, K. Sreenivas, K.V. Rao, H₂S gas sensing mechanism of SnO₂ films with ultrathin CuO dotted islands, *J. Appl. Phys.* 92 (2002) 2172-2180.

- [59] D.G. Castner, K. Hinds, D.W. Grainger, X-ray photoelectron spectroscopy sulfur 2p study of organic thiol and disulfide binding interactions with gold surfaces, *Langmuir* 12 (1996) 5083-5086.
- [60] Y.M. Shulga, V.I. Rubtsova, V.N. Vasilets, A.S. Lobach, N.G. Spitsyna, E.B. Yagubskii, EELS, XPS and IR study of C-60-center-dot-2s(8) compound, *Synth. Met.* 70 (1995) 1381-1382.
- [61] S. Suzer, T. Voscoboinikov, K.R. Hallam, G.C. Allen, Electron spectroscopic investigation of Sn coatings on glasses, *Fresen. J. Anal. Chem.* 355 (1996) 654-656.
- [62] J.K. Kwak, K.H. Park, D.Y. Yun, D.U. Lee, T.W. Kim, D.I. Son, J.H. Han, J.Y. Lee, Microstructural and optical properties of SnO₂ nanoparticles formed by using a solvothermal synthesis method, *J. Korean Phys. Soc.* 57 (2010) 1803-1806.
- [63] W.-S. Choi, The fabrication of tin oxide films by atomic layer deposition using tetrakis(ethylmethylamino) tin precursor, *Trans. Electr. Electron. Mater.* 10 (2009) 200-202.
- [64] M. Cruz, J. Morales, J.P. Espinos, J. Sanz, XRD, XPS and Sn-119 NMR study of tin sulfides obtained by using chemical vapor transport methods, *J. Solid State Chem.* 175 (2003) 359-365.
- [65] M.Y. Li, E.Z. Liu, H.L. Hu, S.X. Ouyang, H. Xu, D.F. Wang, Surfactant-free synthesis of single crystalline SnS₂ and effect of surface atomic structure on the photocatalytic property, *Int. J. Photoenergy* (2014) Article ID 394146.
- [66] P.E. Laibinis, G.M. Whitesides, D.L. Allara, Y.T. Tao, A.N. Parikh, R.G. Nuzzo, Comparison of the structures and wetting properties of self-assembled monolayers

of normal-alkanethiols on the coinage metal-surfaces, Cu, Ag, Au, J. Am. Chem. Soc. 113 (1991) 7152-7167.

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