High-performance H2S detection by redox reactions in semiconducting carbon nanotube-based devices†

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Here we report the highly effective detection of hydrogen sulfide (H2S) gas by redox reactions based on single-walled carbon nanotubes (SWCNTs) functionalized with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a catalyst and we also discuss the important role of water vapor in the electrical conductivity of SWCNTs during the sensing of H2S molecules. To explore the H2S sensing mechanism, we investigate the adsorption properties of H2S on carbon nanotubes (CNTs) and the effects of the TEMPO functionalization using first-principles density functional theory (DFT) and we summarize current changes of devices resulting from the redox reactions in the presence of H2S. The semiconducting-SWCNT (s-SWCNT) device functionalized with TEMPO shows a very high sensitivity of 420% at 60% humidity, which is 17 times higher than a bare s-SWCNT device under dry conditions. Our results offer promising prospects for personal safety and real-time monitoring of H2S gases with the highest sensitivity and low power consumption and potentially at a low cost.

Introduction

Hydrogen sulfide (H2S) is a deadly gas which causes asphyxiation, lung damage, and teratogenic effects when exposed to it.1,2 Thus the monitoring and elimination of H2S is very important for safety because this gas is found widely in industry such as in natural gas, petroleum and mines, and is given off as a by-product in the manufacture of rayon, synthetic rubber, dyestuffs and the tanning of leather.3,4 So far wide varieties of inorganic and organic materials such as tungsten oxide, tin oxide and carbon have been proposed as electrical sensors that can detect the H2S gas.5–8 Although there are several successful devices available commercially, drawbacks of existing H2S monitors include high power consumption, high operating temperatures, short lifetime, interference from other gases and high cost.9

Recently there has been significant interest in using carbon based nanomaterials as chemical sensors due to several advantages of nanostructured carbon such as light weight, high electrical conductivity, electrochemical surface area and superior sensing performance. Particularly, carbon nanotubes (CNTs) are in growing demand due to their high electron mobility and large current capability,10,11 which, on one hand, can potentially help in reducing the power consumption of the sensor whereas, on the other hand, high temperature stability and chemical inertness of CNTs may provide a stable and robust platform to detect specific gas.12–24 Since pristine CNT based chemical sensors utilize their intrinsic electrochemical properties to overcome their limitations in selectivity and sensitivity, the most promising approach is to functionalize CNTs with covalent or non-covalent materials.24–33 However owing to their one-dimensional nanostructure, CNTs are highly sensitive to environments such as humidity and temperature,34,35 in practice the effect of the relative humidity (RH) on CNT based chemical sensors must be investigated further because the humidity varies greatly depending on the season, region and weather.

Here, we report molecular doping of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a catalyst on the surface of single-walled carbon nanotubes (SWCNTs) and the effective detection of H2S gas by a redox reaction at room temperature. We also discuss the important role of water vapor in the electrical conductivity of SWCNTs during the sensing of H2S molecules.

Experimental

Fabrication of SWCNT arrays on a substrate

First, a plasma treatment is used to enhance the hydrophilic nature of the SiO2 surface. To improve the contact between the SWCNT-deionized water solution and substrate, the substrate was pretreated using an Inductively-Coupled Plasma (ICP) with...
mixed gas flow of O₂ (20 sccm), SF₆ (20 sccm), and Ar (5 sccm). Second, 600 nm thick PMMA photoresist patterns are constructed using electron-beam lithography (EBL) to build nanoscale channels which form templates for building the interconnect architectures. Next, these templated substrates are dip-coated in a SWCNT-DI water solution (purchased from Brewer Sci. Inc. and used as is) at a constant pulling rate of 0.1 mm min⁻¹, which resulted in organized and aligned SWCNT networks having well-defined shapes at micro- and nano-scale and were defined by the geometry of PMMA patterns on the substrate.³⁶,³⁷ After the SWCNT assembly, contact pads or electrodes were deposited. Initially a 5 nm Ti layer was deposited followed by a 150 nm Au layer. Au contacts were then wire bonded. Here, SWCNTs serve as an active channel layer because of their ultra-high surface area to volume ratio and no chemical interaction with H₂S or other gases that may interfere.

**Standard lab preparation of H₂S gas molecules**

For generation of H₂S gas, ferrous sulfide (FeS, purchased from Sigma-Aldrich) was reacted with sulfuric acid. FeS(s) + H₂SO₄(aq) → FeSO₄(s) + H₂S(g). Because H₂S gas is denser than air, it is more convenient to collect it in a glass vial by downward delivery. The gas produced in a chemical reaction is passed through a delivery tube into the glass vial, where it sinks and pushes the air out of the top. Calculated volumes of the H₂S were then introduced into 1 L of a gas sensing chamber using a microliter syringe.

**Gas detection using SWCNT (w/wo TEMPO) devices on finger electrodes**

In order to investigate the sensing mechanism and improve sensitivity, we compared sensor performances between semiconducting SWCNT (s-SWCNT) and metallic SWCNT (m-SWCNT) devices with and without TEMPO functionalization and studied the behavior of H₂S and H₂O molecules. Here, s-SWCNTs play a major role in gas detection due to their different redox properties.³⁸,³⁹ For this, we performed a controlled experiment where 99% purity 10 mL m-SWCNT and s-SWCNT nanotube solutions (purchased from Nanointegrins Inc.) were drop-cast on each inter-digitated finger electrodes (ESI Fig. S1†). The solution was allowed to dry and was rinsed with water to remove surfactants until maximum current was recorded. After this step, the devices were exposed to TEMPO vapors for 15 min. The devices were then cooled down at room temperature and allowed to equilibrate for an additional 30 min. For gas sensing, each device was carefully outgassed by joule heating under 10⁻³ torr for 1 h in a sensing chamber followed by a flow of dry N₂ gas. The gas chamber was then closed and a pre-calculated amount of H₂S gas was introduced in it. The applied bias voltage was kept constant for every measurement and changes in current were monitored as a function of time for different gas concentrations. To understand the effects of concentration of H₂S gas, the sensor devices were exposed to H₂S gas of 5, 10, 50, 100, and 200 ppm, respectively, in the chamber with dry N₂. To investigate the effect of H₂O on sensing of H₂S molecules, 100 ppm H₂S gas was introduced in the presence of 20, 40 and 60% RH. Changes in current were observed until it reached saturation. Once the current saturated, the chamber was exposed to dry N₂ for the sensor recovery. In graphs of the real-time current changes, a sharp decrease in current indicates the sensor response to H₂S gas when a certain amount of H₂S gas is injected into the closed chamber. The current increases when the sensor is allowed to recover in N₂ gas.

**Computational methods**

To explore the chemical reaction of H₂S, O₂, and TEMPO molecules, we performed the first-principles calculations based on density functional theory (DFT) implemented in the DMol³ package.⁴⁰ We used the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional⁴¹ to describe the exchange-correlation (XC) functional. A double numerical polarized basis set was chosen with a real-space cutoff of 4.0 Å to expand the electronic wave functions. The octupole scheme for the multipolar fitting procedure and a fine grid scheme for the numerical integration were employed for an accurate evaluation of the charge density. To search for a three-dimensional trajectory for the reaction path between reactants and products during the chemical reaction, the linear synchronous transit and quadratic synchronous transit (LST/QST) calculations⁴²,⁴³ were carried out with conjugate gradient minimization.⁴⁴

**Results and discussion**

**Experimental setup and H₂S gas detection**

Fig. 1a–d show the scanning electron microscope (SEM) images of the experimental setup for H₂S gas detection. We assembled SWCNT microarrays by a template guided fluidic assembly process in order to obtain uniform networks⁴⁶,⁴⁷ and then
electrodes were formed on top of them (see Experimental section for more details). Such a process allowed us to assemble SWCNT network arrays with very precise control over placement and density of SWCNTs over wafer scale (Fig. 1e). Fig. 1f shows the chemical structure of TEMPO molecules. SWCNTs serve as an active channel layer because of their ultra-high surface area to volume ratio and no chemical interaction with H2S or other gases that may interfere. Since TEMPO possesses a stable nitroxy group provided by the adjacent four methyl groups, it has widely been used as a radical trap, as a structural probe for biological systems, as a reagent in organic synthesis, and as a mediator in controlled free radical polymerization.\(^{45-48}\) Thus it is also capable of oxidizing the gaseous H2S and can be utilized as a sensory molecule for making a chemical sensor to detect H2S.

We exposed the non-covalently functionalized SWCNT devices to different concentrations of \(\text{H}_2\text{S}\) gas ranging from 10–100 ppm. The applied bias voltage was kept constant for every measurement and changes in current were monitored as a function of time for different gas concentrations. Fig. 1g shows the current vs. time plot for the functionalized SWCNT sensor when exposed to different concentrations of \(\text{H}_2\text{S}\) gases. The sharp decrease in current indicates the sensor response to \(\text{H}_2\text{S}\) gas when a certain amount of \(\text{H}_2\text{S}\) gas is injected into the closed chamber. When the chamber is opened and the sensor is allowed to recover in open air, the current increases to approximately its previous level before exposure to \(\text{H}_2\text{S}\) gas. For each concentration of \(\text{H}_2\text{S}\), we evaluated sensitivity \(S\) defined by \(S = \frac{(R_{\text{gas}} - R_i)/R_i}{(I_i - I_{\text{gas}})/I_{\text{gas}}} \times 100 = \frac{(I_i - I_{\text{gas}})}{I_{\text{gas}}} \times 100\), where \(I_i\) is the initial current and \(I_{\text{gas}}\) is the changed current after injection of \(\text{H}_2\text{S}\) gas. The sensitivity of the functionalized SWCNT arrays shows a 4.7% change at 10 ppm and 13.7% at 100 ppm.

**Sensing of \(\text{H}_2\text{S}\) molecules by redox reactions**

In order to investigate the sensing mechanism and improve sensitivity, we compared sensor performances between semiconducting SWCNT (s-SWCNT) and metallic SWCNT (m-SWCNT) devices with and without TEMPO functionalization and studied the behavior of \(\text{H}_2\text{S}\) and \(\text{H}_2\text{O}\) molecules. Here, s-SWCNTs play a major role in gas detection due to their different redox properties.\(^{49,50}\) For this, we performed a controlled experiment where 99% purity m-SWCNT and s-SWCNT nanotube solutions (purchased from Nanointegris Inc.) were drop-cast on each inter-digitated finger electrode (ESI Fig. S1†). Then we functionalized the SWCNT based devices with TEMPO using a vaporization method to achieve uniform and thin coating for the functionalization of SWCNTs, which was then carefully outgassed by joule heating under \(10^{-3}\) torr for 1 h followed by injection of dry \(\text{N}_2\) gas in a sensing chamber. Non-covalently functionalized SWCNT devices were exposed to \(\text{H}_2\text{S}\) gas under dry \(\text{N}_2\) or controlled water vapor. Clearly, in all the above-mentioned detections, the sensing materials come in contact with either \(\text{H}_2\text{O}\) or \(\text{H}_2\text{S}\) or a mixture of these two.

Fig. 2 shows sensing of \(\text{H}_2\text{S}\) molecules with SWCNT devices and the effect of relative humidity. In order to investigate the exact sensing mechanism and interactions between SWCNT-TEMPO-\(\text{H}_2\text{S}-\text{H}_2\text{O}\), we compared sensor performances in the absence or presence of water between s-SWCNT and m-SWCNT devices which are either functionalized by TEMPO or not. First, to understand the effects of \(\text{H}_2\text{S}\) gas on a bare SWCNT, SWCNT-based sensor devices without TEMPO functionalization were exposed to \(\text{H}_2\text{S}\) gas of 5, 10, 50, 100, and 200 ppm, respectively in the chamber with dry \(\text{N}_2\). Fig. 2a shows the sensitivity of the bare s-SWCNT device with \(\text{H}_2\text{S}\) concentration in dry \(\text{N}_2\) (ESI Fig. S2† for real time current change). The sensitivity at 200 ppm of \(\text{H}_2\text{S}\) shows 38% change. However, the bare m-SWCNT device shows less than 5% sensitivity (ESI Fig. S2†) on detecting \(\text{H}_2\text{S}\) gases. This result is consistent with previous reports,\(^4\) indicating more redox properties of the s-SWCNTs.

To investigate the effect of \(\text{H}_2\text{O}\) on sensing of \(\text{H}_2\text{S}\) molecules, we used only 100 ppm concentration of \(\text{H}_2\text{S}\) since it is known that, above this concentration, the human olfactory nerve can be paralyzed in a few inhalations. Then sensing of \(\text{H}_2\text{S}\) gas was performed at different RH. Fig. 2b shows the real-time current changes in a bare s-SWCNT device when 100 ppm \(\text{H}_2\text{S}\) gases were exposed at an RH of 0, 20, 40 and 60% (ESI Fig. S4† for more details and ESI Fig. S5† for the bare m-SWCNT device). First, we observed that the current in the s-SWCNT device decreased when exposed to water vapor. Then a further substantial reduction in conductance was observed when \(\text{H}_2\text{S}\) gas was introduced in the presence of predetermined RH. After each sensing test at a given RH, the chamber was exposed to dry \(\text{N}_2\) for the sensor recovery for sensing of \(\text{H}_2\text{S}\) in increased RH. The real-time current measurements clearly demonstrate that redox properties do change in the presence of \(\text{H}_2\text{S}\) and water vapor. The sensitivity of bare s-SWCNT devices was increased significantly at 150% at 60% RH (Fig. 2d).

\(\text{H}_2\text{O}\) molecules can be adsorbed on the surface of SWCNTs and act as electron donors in a p-type semiconductor reducing...
the hole density in s-SWCNTs resulting in the current decreases. To explain the increased H$_2$S sensitivity of s-SWCNTs, the interaction of H$_2$S and H$_2$O molecules is a possible subset. Because the moisture concentration of 60% RH at 20 °C is about 0.01 g in 1 L of the chamber, the amount of water molecules will decide the sensing reaction. Therefore, the conductance after injection of H$_2$S gas can be changed significantly by more water molecules at higher RH. Moreover, the redox reactions with TEMPO can additionally generate more water molecules as shown in Fig. 3a. This indicates that moisture is one of the important factors in practical applications and sensitivity of the chemical sensors.

To maximize sensitivity based on the above facts, TEMPO was used as a homogeneous catalyst for redox reaction of H$_2$S and H$_2$O. As shown in Fig. 2c and d (ESI Fig. S7† for more details), s-SWCNT devices functionalized with TEMPO showed 420% sensitivity at 60% RH, which is about 3 times higher than that of the bare s-SWCNT sensor at the same RH, and 17 times higher than that of the bare s-SWCNT device under dry N$_2$ conditions.

Redox reactions and sensing mechanism

To understand the underlying sensing mechanism, we paid close attention to the redox reactions of various molecules existing near active CNT channels (see ESI Table S1†), which exhibit p-type characteristics under ambient conditions. This is attributed to the fact that the CNT is p-doped due to the oxygen adsorption, where each O$_2$ molecule takes an electron away from or donates a hole to the CNT. These adsorbed O$_2$ molecules exist in the form of O$_2^-$ and will participate in our proposed redox reaction by donating electrons back to the CNTs resulting in less p-doped CNT channels.

Fig. 3a shows a schematic of a full cycle of the redox reactions that we propose to occur for H$_2$S detection near the CNT channel functionalized by TEMPO under humid conditions. In the first stage of the redox reactions, TEMPO is oxidized to be TEMPO$^+$ with positive charge, which is an important product for H$_2$S dissociation, while H$_2$O molecules with O$_2$ molecules from O$_2^-$ reduce. At the second stage of the redox reactions, the reduction reaction of TEMPO$^+$ to TEMPO–H is coupled to the dissociation process of H$_2$S to S$+2$H$^+$+2e$^-$. In the final stage of the redox reaction cycle, the sulfur atoms produced by the latter reaction in the second stage react with oxygen ions (O$_2^-$) responsible for the p-type characteristics of CNT devices and thus form various sulfuric oxides such as SO, SO$_2$ as the oxidation reaction during which the remaining electrons are back-donated to the CNT channels is less p-type. In the counter reduction reaction, TEMPO–H becomes back to TEMPO in the presence of other TEMPO molecules, and the detached H atoms may be involved in the formation of H$_2$SO$_4$ from the sulfuric oxides. Through such a complete reactions cycle, the TEMPO molecules together with water play a significant catalytic role in H$_2$S detection.

For further analysis, we investigated the chemical reaction barriers of H$_2$S, O$_2$, and TEMPO molecules functionalized on the CNT surface using first-principles density functional theory (DFT) (see Experimental section for computational methods). Fig. 3b shows a schematic diagram of the energy profile along the reaction coordinates exhibiting an activation barrier (E$_r$) in the chemical reactions between H$_2$S and O$_2$ molecules without/with TEMPO molecules. The reaction energies (E$_r$) are defined by the energy difference between the reactant and the product. We considered the initial geometries of H$_2$S and O$_2$ molecules without/with TEMPO molecules functionalizing the CNT surface and the optimized final structures of H$_2$SO$_4$ molecules. We obtained the interpolated pathway determined geometrically using linear synchronous transit (LST), and calculated E$_r$ and E$_f$ of the reaction. O$_2$ molecules on the CNT surface could interact with H$_2$S as well as H$_2$O molecules. The chemical reaction between H$_2$S and O$_2$ would eventually produce H$_2$SO$_4$. As a result, p-doped CNT surfaces by oxygen were deoxidized with reduction of the hole carrier density and thus the current in CNT devices. Although the schematic reaction diagram shown in Fig. 3b represents an oversimplified reaction path to produce H$_2$SO$_4$ from H$_2$S and thus cannot be matched with any reaction in the redox cycle, our calculations used for this diagram verifies an important catalytic behavior of TEMPO molecules. The activation barrier of 5.40 eV without TEMPO decreases by about 34% to be 3.56 eV with TEMPO implying that the presence of TEMPO may expedite the chemical reactions involving H$_2$S, O$_2$, H$_2$O, etc., leading to the improvement of sensitivity.

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promising prospects for real-time monitoring of H$_2$S gas not in devices making them less p-doped as discussed above, resulting the redox reactions cause the electron back donation to CNT as described in Fig. 3a. The H$_2$S sensitivity enhancement in the measurements is caused by the measured current decreases with the H$_2$S concentration from device functionalized with TEMPO highly responded to H$_2$S gas in water vapor. Its reactivity depends on the electronic properties of the active channel, especially s-SWCNTs showed a very high sensitivity of 420% at 60% humidity. Our sensors of typical semiconducting and metallic devices, respectively, in humid conditions with high RH can be elucidated by the fact the reaction of TEMPO to TEMPO$^-$ may increase with humidity.

Conclusions

In summary, to date, there has been a dearth of studies on the role of relative humidity in H$_2$S gas detection. The SWCNT device functionalized with TEMPO highly responded to H$_2$S gas in water vapor. Its reactivity depends on the electronic properties of the active channel, especially s-SWCNTs showed a very high sensitivity of 420% at 60% humidity. Our sensors offer promising prospects for real-time monitoring of H$_2$S gas not only with very high sensitivity and low power consumption, but potentially also at a low cost. The small size of the system will also allow future integration with low power microelectronics.

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Notes and references


