

Using Carbon Nanotubes to Absorb Low-Concentration Hydrogen Sulfide in Fluid

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Abstract—Hydrogen sulfide is a colorless and flammable gas under room temperature. Usually hydrogen sulfide is considered to be toxic; however, the recent research revealed that hydrogen sulfide in the cardiovascular system plays the role of a vascular dilator. The physiological role of hydrogen sulfide depends on its *in vivo* level. As such, the measurement of hydrogen sulfide with nano-quantity resolution becomes an important subject. Existing methods generally require bulky samples and are invasive and offline. It will be significantly helpful to measure hydrogen sulfide with a small amount of tissue in a noninvasive method. The first attempt was to take a blood or serum sample with a trace amount to examine the interaction between hydrogen sulfide and carbon nanotube. The carbon nanotube is chosen because of a known fact that hydrogen sulfide can be adsorbed by activated carbon. The carbon nanotube is an excellent activated carbon in this regard. Fluorescence intensity of the carbon nanotube with and without immersion of it in a hydrogen sulfide medium was examined in the study. It was found that the intensities increase as the concentrations of hydrogen sulfide increase. Furthermore, the concentration of 10 μM hydrogen sulfide in water was successfully measured.

Index Terms—Carbon nanotubes, hydrogen sulfide, measurement.

I. INTRODUCTION

IN ANIMALS and humans, H_2S can be found in the blood, brain, lung, heart, liver, spleen, and kidney [1], [2]. Hydrogen sulfide in the animal body mainly comes from three sources. The first is bacteria when it interacts with various body tissues and cells. The second source is the cysteine protein when it is in a reaction catalyzed by cystathionine b-synthase (CBS) and/or cystathionine g-lyase (CSE). In some tissues CBS and CSE are both needed for the generation of H_2S gas,

while in other tissues one enzyme suffices. The third source is the process of the nonenzymatic reduction of elementary sulfur to H_2S . It is noted that the second and third sources are called endogenous sources. Oxidation is the primary metabolic pathway for H_2S [3].

Although limited results have been obtained by direct studies on humans, these results indicate that exposure to H_2S (at high concentrations) has profound effects on the respiratory system leading to, sometimes, death. It is suggested that H_2S is absorbed rapidly through the lung [4]–[7]. Exposure to H_2S can also increase cardiovascular-related deaths [8]. However, recent research has found that hydrogen sulfide gas naturally produced by the body is not simply a toxic gas, but can be a vascular dilator. In its function as a vascular dilator, the gas acts as a biological switch, relaxing contracted blood vessels and reducing blood pressures [9], [10].

The physiological importance of hydrogen sulfide depends on its *in vivo* level. As such, the measurement of hydrogen sulfide becomes an important issue. Unfortunately, a limited number of analytical techniques have been used for measuring hydrogen sulfide in the breath (expired air), biological tissues, and fluids, including blood and saliva. Current methods for measurement of hydrogen sulfide include chromatography [2], [11]–[17], spectrophotometry [18], and the sulfide ion-specific electrode [9]. These methods were originally derived from the determination of sulfide in a polluted air and water samples and were applied to biological samples.

Each of these methods appears to have a complex generic procedure: 1) tissues are taken out of mammalian bodies and homogenized; 2) the homogenized tissues are reacted with the L-cysteine to generate hydrogen sulfide as the active CBS or CSE which exists in the homogenization; and 3) the generated hydrogen sulfide is then quantified into the H_2S concentrations depending on what method is used (three methods in this case, as mentioned before) [19], [20].

Furthermore these methods generally require bulky samples and are invasive and offline. A new paradigm of measurement of hydrogen sulfide is to have a nanomechanical implant into substances of animal bodies and observe the change in the mechanical behavior of the implant to infer the low concentration of hydrogen sulfide [19]. Another less exciting paradigm is to take a small amount of tissue, such as blood, to measure hydrogen sulfide. To make these new paradigms work, the first attempt was to take a hydrogen sulfide water solution sample with a trace amount and to examine the interaction between hydrogen sulfide and carbon nanotube. The carbon nanotube is chosen because of a known fact that hydrogen sulfide can be adsorbed by activated carbon. The carbon nanotube has a large specific surface area

Manuscript received August 11, 2005; revised May 6, 2006. This work was supported in part by the Gasotransmitter REsearch And Training (GREAT) program of CIHR/HSF. *Asterisk indicates corresponding author.*

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Digital Object Identifier 10.1109/TNB.2006.880843

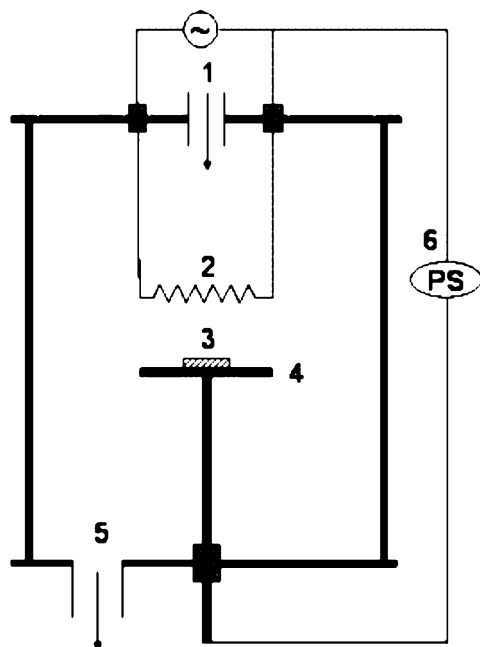


Fig. 1. Hot filament chemical vapor deposition system [62]. 1: gas inlet 2: filament. 3: substrate. 4: substrate holder. 5: pumping port. (6) DC power supply, ± 600 V.

and a nanoscale structure, and this provides a plenty of sites at which H_2S can react. The carbon nanotube therefore shows a very good adsorption property that leads to many applications. It is widely known that carbon nanotube can “store” hydrogen [21]. These properties give the carbon nanotube the potential of being material to use in sensors, scanning probes [22], and nano-electronic devices [23]. In the literature, there are many studies on hydrogen adsorption with carbon nanotubes [24]–[27]. To the best of our knowledge, there is no study reported on the hydrogen sulfide adsorption with carbon nanotubes, especially hydrogen sulfide in a water solution.

In this paper, we report a study using the carbon nanotube to adsorb hydrogen sulfide in a water solution. Both Raman and laser scanning microscopies are used to observe the adsorption. Therefore, the hypothesis underlying this study was that hydrogen sulfide can be effectively adsorbed with the carbon nanotube in a certain form, and the adsorption can be examined with the Raman or laser scanning microscope.

II. MATERIALS AND METHODS

A. Carbon Nanotube Preparation

There are two types of nanotubes, single-wall nanotubes (SWNTs) and multiwall nanotubes (MWNTs). A single-wall carbon nanotube is a nanoscale tube of a monolayer graphene sheet rolled up into a long seamless cylinder, while multiwall nanotubes have many layers. Generally, there are three types of methods to make carbon nanotubes: 1) the carbon arc-discharge technique [28]–[37]; 2) the laser-ablation technique [38]–[40]; and 3) the chemical vapor deposition technique [41]–[51].

In this experiment, the carbon nanotubes in powder form were prepared by using a microwave plasma-enhanced chemical vapor deposition (MPECVD) reactor in a gas mixture of hydrogen and methane, as shown in Fig. 1. The substrate stage consisted of an inconel 600 plate and a stainless steel substrate

TABLE I
CARBON NANOTUBE GROWTH CONDITION

Growth parameters	Typical value
Microwave power (W) at 2.45 Hz	1000
Substrate temperature ($^{\circ}C$)	350
Methane concentration (vol.%)	1
Bias voltage (V)	-100 V
Gas flow rate (sccm)	100
Deposition pressure (Torr)	30
Substrate	inconel
Gas mixture	$H_2 + CH_4$

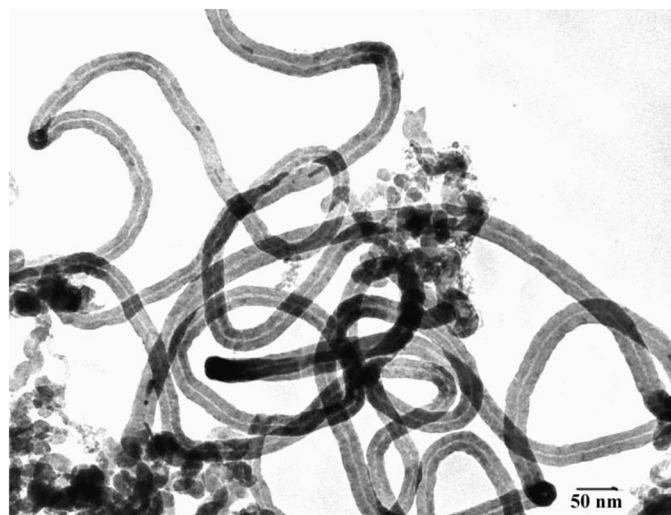


Fig. 2. TEM image of carbon nanotubes.

holder plate separated by a 5.3-cm-long quartz tube. High-purity diamond thin films were deposited on Si substrates located on the substrate holder (the upper part of the substrate stage). Carbon nanotubes were deposited on the inconel substrate located at the low part of the substrate stage. In this process, the temperature is approximately $550^{\circ}C$ for the Si substrate and $350^{\circ}C$ for the inconel substrate. The deposition conditions are summarized in Table I

The powder-form carbon nanotubes were obtained from the carbon nanotubes which grew from the substitute. The powder-form carbon nanotubes were observed by Philips CM-10 transmission electron microscope (TEM); see Fig. 2. The diameter of the carbon nanotube shown in Fig. 2 is about 25 nm and its inner diameter is approximately 5 nm. From Fig. 2, it can be found that the carbon nanotubes are curved, long tubes with length up to submillimeter scale; furthermore they do not appear to be pure carbon nanotubes but consist of other allotropes of carbon. The high-resolution TEM observation further reveals the multiwall structures of the nanotubes.

There was another supply of carbon nanotubes for this experimental study, particularly from Saskatchewan Structure Sciences Center (SSSC) of the University of Saskatchewan. Unfortunately the specification of this carbon nanotube was unknown at the point of time of this experimental study except that the carbon nanotube was in the powder sheet form.

In the following discussion, the carbon nanotube made by the first approach (i.e., the one shown in Fig. 2) is called sample A; while the carbon nanotube supplied by SSSC is called sample B.

B. Hydrogen Sulfide Preparation

Hydrogen sulfide gas-saturated solution (90 mM at 30 °C), was made by bubbling pure hydrogen sulfide gas (Praxair, Mississauga, ON, Canada) into 40 ml distilled water at 30 °C and 10 lbf/in², or pounds-force per square inch (1 atm = 760 mmHg = 14.7 lbf/in²). Fresh 0.1 M (mole/liter) for 40 min. NaOH solution (300 ml) was used to trap the extra hydrogen sulfide gas. The equipment was tightly sealed.

Direct measurement of hydrogen sulfide concentration was using a sulphide sensitive electrode (Model 9616, Orion Research, Beverly, MA) on a Fisher Accumet AR50 pH meter (Fisher Scientific, Pittsburgh, PA) following the manufacturer's instructions. Standards are prepared from Na₂S stock solution, which is freshly prepared on the day of the measurement. The exact concentration of the stock solution is determined by titrating 10 ml of the standard with 0.1 M lead perchlorate. The linear rang of the sulphide sensitive electrode is greater than 0.32 parts per million (ppm) (1 ppm = 31.12 μmol/L S²⁻) or 10⁻⁵ M (mol/L) S²⁻.

Lower concentrations (μM level) hydrogen sulfide solutions were diluted from 90 mM hydrogen sulfide solution. Specially, their concentrations are, respectively, 10, 20, 30, 40, 50, and 100 μM.

C. Data Acquisition

A laser scanning microscope (ZEISS LSM 510 META) was used to measure the fluorescence of the powder-form carbon nanotubes. The selected excitation wavelength is 514 nm with 10% transmitting and collected emission wavelengths from 539 to 753 nm; 515-nm filters were used in collection. The pinhole was set at 332 nm and gain was 726. The lens we used is a 25× water immersed lens. In order to get the intensity versus time curve, we used time series. The collection was done every 1 min.

A Raman microscope (Renishaw system 2000) was used to measure illuminates of the samples. In these measurements, a 514-nm wavelength was used and emissions were collected from 518- to 800-nm wavelengths.

D. Procedure

For sample A, different powder-form carbon nanotubes were immersed in sufficient distilled water, 10, 20, 30, 40, 50, and 100 μM hydrogen sulfide solutions, respectively, for 2 min, and the resulting carbon nanotubes were dried at room temperature for laser scanning microscope measurement. It is noted that for each of these concentrations, a different powder form of carbon nanotube was used.

For sample B, carbon nanotubes in the sheet form were cut into small pieces for Raman microscope measurement. Different pieces of the carbon nanotube with the size of 2–3 mm were immersed into sufficient distilled water, 50 and 100 μM hydrogen sulfide water solutions, respectively, for 2 min, and the resulting carbon nanotubes were dried at room temperature for Raman microscope measurement.

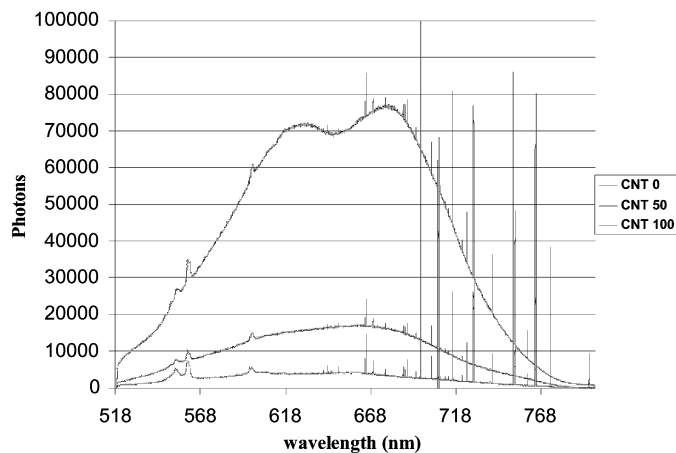


Fig. 3. Fluorescence of different concentration of hydrogen sulfide in a carbon nanotube by Raman. CNT 0, CNT 50, and CNT 100 means distilled water, 50 μM hydrogen sulfide water solution, and 100 μM hydrogen sulfide water solution.

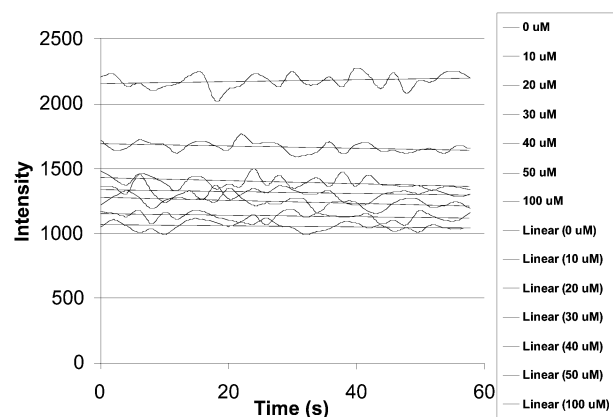


Fig. 4. Intensity versus time and the corresponding linear tendency of different concentrations of hydrogen sulfide by laser scanning microscope.

III. RESULTS AND DISCUSSION

The result of sample B with the Raman microscope is shown in Fig. 3, where CNT 0 was the nanotubes treated by distilled water, CNT 50 was the nanotubes treated by 50 μM hydrogen sulfide water solution, and CNT 100 was the nanotube treated by 100 μM hydrogen sulfide water solution. The fluorescence of the nanotubes increased with the increase of the immersed hydrogen sulfide concentration. In the figure, the *y* axis represents the photons received by the Raman and the *x* axis is the wavelengths from 518 to 800 nm. We collected 6342 points between these wavelengths and the two peaks appearing at 552 and 559 nm were carbon peaks.

The result of sample A with laser scanning microscope is shown in Fig. 4. In this figure, the emitted fluorescence intensity from the carbon nanotubes increases with the increase of concentration of hydrogen sulfide in the water solution. Also in Fig. 4, the solid lines represent the linear tendency of the corresponding curves. It can be seen from this figure that the intensity versus time keeps stable during the data collecting period, which further implies that the measurement is highly reliable.

Fig. 5 shows the emitted fluorescence intensity versus different concentrations of hydrogen sulfide from laser scanning microscope for sample A. The intensity versus the concentration

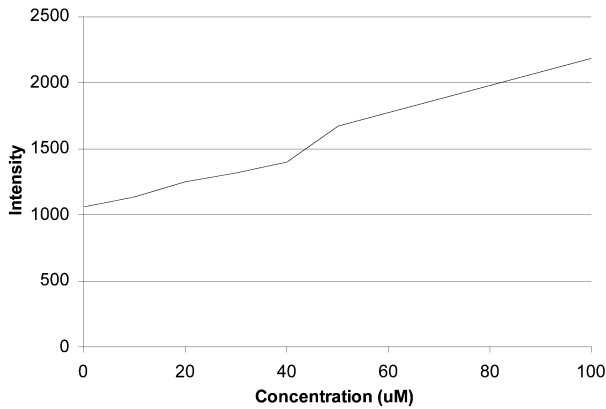


Fig. 5. The intensity versus concentration of hydrogen sulfide by laser scanning microscope.

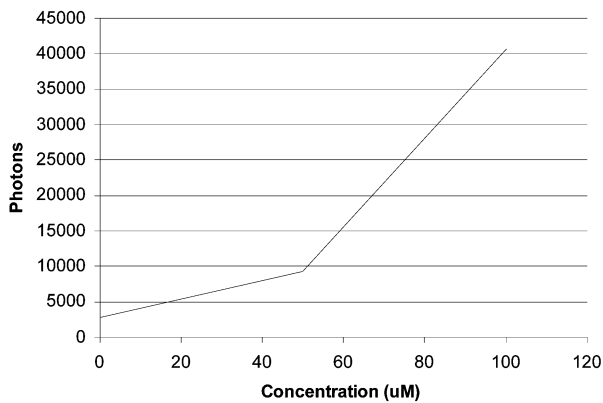


Fig. 6. Total photons versus concentration of hydrogen sulfide by Raman microscope.

of hydrogen sulfide in the water solution appears to be approximately linear. Fig. 6 shows that the total photons (corresponding to intensity) versus the concentration of hydrogen sulfide in the water solution from the Raman microscope measurement (for sample B). Only two concentrations plus the zero concentration were measured.

We also measured the concentration versus intensity by purified sample A carbon nanotube. There are many protocols for carbon nanotube purification. Different purification protocols apply to different carbon nanotube growing methods [52]–[60]. In our case, the nonpurification is caused by carbon. Therefore, a particular purification process we employed is to raise temperature of the nonpurified carbon nanotube more than 450 °C (at which the carbon is supposed to be eliminated) until there is no further weight loss with the carbon nanotube in the process. The result of using the purified powder-form carbon nanotube is shown in Fig. 7, which appears to be very similar to that of Fig. 5. From both Fig. 5 and Fig. 7, we can find that the relation of concentration versus intensity is almost linear. Further, using the Raman microscope, the nonlinearity of the curve shown in Fig. 6 may be due to the variation of different carbon nanotubes, which is relatively sensitive to the Raman microscope method. These preliminary results have demonstrated that carbon nanotubes can be used to measure H₂S within 10 μM difference and that the laser scanning microscope method appears to be more robust.

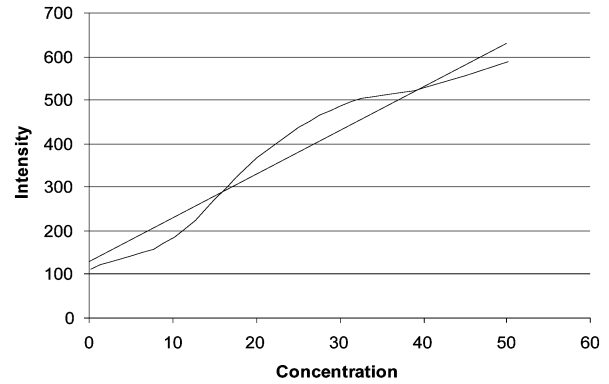


Fig. 7. The intensity increased with the increasing of the concentration of H₂S for purified carbon nanotubes.

IV. CONCLUSION AND FUTURE WORK

Hydrogen sulfide in a water solution can be adsorbed by carbon nanotubes in powder form without any chemical treatment. The minimum concentration of hydrogen sulfide in a water solution which can be measured is about 10 μM. The relationship between the concentration of hydrogen sulfide and the intensity (associated with laser scanning microscopes) appears to be linear. The laser scanning microscope appears to be better than the Raman microscope in detecting this adsorption. These results are promising towards the realization of the new paradigm of measurement of a trace amount of hydrogen sulfide.

Future work includes the following. First is further experimentation with the Raman microscope measurement to examine its nonlinearity behavior when it interacts with the CNT with hydrogen sulfide. Second, the effects of different CNT systems on their adsorption of hydrogen sulfide will be studied, which may result in an optimal design of CNT systems for the purpose of measuring a trace of hydrogen sulfide in fluid. Third, the effect of carbon nanotubes with a substitute or into a powder particle (e.g., quantum dot of carbon nanotube) is to be examined.

ACKNOWLEDGMENT

The authors would like to thank Dr. W. Yang for preparation of hydrogen sulfide fluids and Dr. A. K. Dalai for purification of the carbon nanotubes.

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Authors' photographs and biographies not available at the time of publication.