UV-Illumination Induced Desorption of CNT Sensors

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Abstract- **This paper presents a chemical sensor employing Electronic-Grade CNTs (EG-CNTs) as the active sensing element for sodium hypochlorite (NaOCl) detection and the-desorption phenomenon of the sensing element by applying UV illumination. By using AC dielectrophoretic (DEP) technique, EG-CNTs are aligned between the microelectrodes fabricated on a glass substrate with a gap distance of 2µm. A microfluidic chamber is created by bonding a PDMS microchannel of 1mm width onto the glass substrate on which pairs of microelectrodes are fabricated. This microfluidic chamber encloses the EG-CNTs sensing elements and ensures that they are submerged in a chemical solution of certain volume during experimental tests. We demonstrate the electrical response of the sensor to NaOCl solution of different concentrations at room temperature as well as to other chemical reagents for comparison. After the measurement the response, UV illumination with 3 UV light tubes of 15W each is applied to the sensor for desorption of NaOCl molecules. Preliminary experiments show that the response of CNT sensor to NaOCl is intense and varies with concentration of the solution. UV illumination significantly shortens the otherwise long recovery period, thus improves reversibility and repeatability of the CNT-based chemical sensors.**

I. Introduction

Recently, with the rapid progress of nanotechnology, sensors fabricated by using carbon nanotubes (CNTs) as the sensing element have been reported to give electrical response to such gases as NO_2, NH_3, CO, H_2 and O_3 [1, 2]. CNT sensors will provide potentially high sensitivity, low power and portable devices for in-situ chemical analysis. The CNT sensing platform can also be extended to detect liquid other than gas. Many sensors have been built using single-wall nanotubes (SWNTs) as sensing element for detecting molecules, and the sensors could have selective response to different molecures. For example, a SWNT sensor could respond to NO_2 via an increase of conductance while the same sensor could respond to NH_3 via a decrease of conductance. This phenomenon was elaborated by J. Kong et al. in 2000 [3]. Basically, NO_2 molecules, as an oxidizer, withdraw electrons from CNTs and leave holes on them, and as a result the electrical properties are changed. Similarly in 2001, R. Chen et al. [4] also discussed that SWNTs appeared to be hole-doped in air as a result of them donating electrons to oxygen molecules. We note here that oxygen photodesorption could also cause a reduction of the hole carriers in the SWNTs under UV illumination, thus the conductance of the SWNT could be lowered [5, 6].

This paper focuses on the response of CNTs to NaOCl solution medium, i.e., we investigated the oxidation of CNTs in liquid NaOCl. Although the oxidation of carbon nanofibers with various oxidizing agents was reported [7], the responses of CNT sensors to NaOCl molecules, a common oxidizer, are rarely studied.

Sodium hypochlorite (NaOCl), as a high production volume chemical, is widely used as household bleach, disinfection of municipal water, sewage, and swimming pool, and in the food, pulp, and paper industries. NaOCl is a strong oxidizer, which shows causticity, and the solution is hazardous since it could burn skin or damage eyes on contact. The leakage of NaOCl is reported occasionally in industries and could jeopardize both the environment and workers' health. It could also be fatally harmful if excessive amounts are used in the production of foodstuffs. D. Jackson et al. presented an indirect method for detecting sodium hypochlorite component within beverages [8]. The detection of hypochlorite is not only applied in the health or food industries, but also in the area of drinking water quality control. Methods to determine the chlorine residuals in municipal wastewaters have been given for the assessment of disinfection efficiency [9] as well as the electrochemical method for monitoring hypochlorite in drinking water [10, 11].

Our group has been studying the properties of EG-CNTs as shear stress sensing elements integrated in microfluidic systems [12] as well as using them to detect alcohol [13]. EG-CNTs show not only remarkable sensibility but also excellent repeatability, which is quite important for sensors. In this study, we will present our recent progress on developing sodium hypochlorite sensors based on EG-CNTs. Firstly, the sensor performance towards constant-current configuration will be evaluated, and then different configurations will also be introduced to test the EG-CNTs response to NaOCl. Secondly, photodesorption of the EG-CNTs induced by UV illumination will be demonstrated and further discussions of this phenomenon influences the CNT recovery process will be addressed.

II. Experimental Details

A. Fabrication and Experimental Setup

Dielectrophoresis (DEP) manipulation was applied for sensor formation by aligning the EG-CNTs between pairs of Au microelectrodes fabricated on glass substrate. The pattern of microelectrodes, as shown in figure 1(a), was microlithographically defined and etched by wet chemical etching process. An Au layer of ~3000Å thickness with an

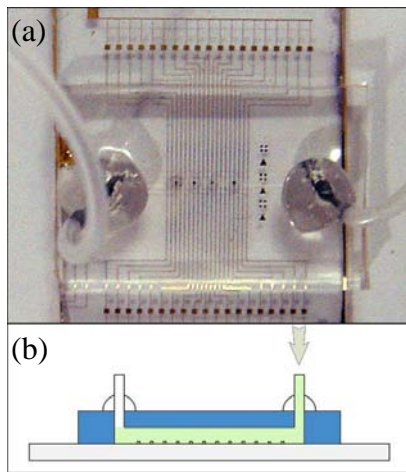Fig. 1. (a) Photograph of the EG-CNT sensor which is used to detect chemical agents with a microchannel (L x W x T = 21mm x 1mm x 40μm) to contain the static liquid; (b) Illumination of the cross-section of the sensor.

Fig. 2. I-V characteristics of a typical EG-CNTs sensing element.

adhesion layer of ~1000Å chromium (Cr) beneath it was used to form the microelectrodes. AC bias voltage with frequency of 1MHz and amplitude of 8V was applied to excite the droplet of EG-CNTs solution between two microelectrode pairs. The distance between each electrode pair was ~2μm and the width of each electrode was 5μm. After the EG-CNTs solution was evaporated, a linkage with EG-CNTs as sensing element remained between the electrodes with resistance ranged from several hundred Ohms to tens of thousands Ohms at room temperature, i.e., the resistance depended on the concentration and volume of the solution of EG-CNTs used. Then, a PDMS microchannel mold, fabricated by using SU-8 on PMMA substrate, was bonded onto the glass surface to form the microchannel in which the reagent could be confined as shown in figure 1(b). The length of the microchannel was 21mm and the area of the cross section was 1mm×40μm. Because of the fixed microchannel dimension, the volume of the reagent was kept constantly, which enhances the repeatability of a device's response.

During the experiments, the solution of reagent was injected from the inlet on the PDMS by a syringe and kept static in the microchannel during the reaction. For constant-current configuration, a commercial source meter (Keithley 2400 Source Meter) was used to generate current to activate the sensors and their response were recorded by a computer. When tests for the desorption of NaOCl molecules were carried out, a retailed UV exposure unit (KVB-30D) including three UV light tubes of 15W each was used to generate UV light emission with wide wavelength range from 350nm to 420nm.

B. I-V characteristics

During the experiments, temperature is fixed at 24°C and humidity is controlled at 50%. The I-V characteristic of a typical EG-CNT sensor is shown in figure 2. Compared to the Ohm's law expectation, the results show linear I-V relationship before 50μA, while the self-heating effect causes the non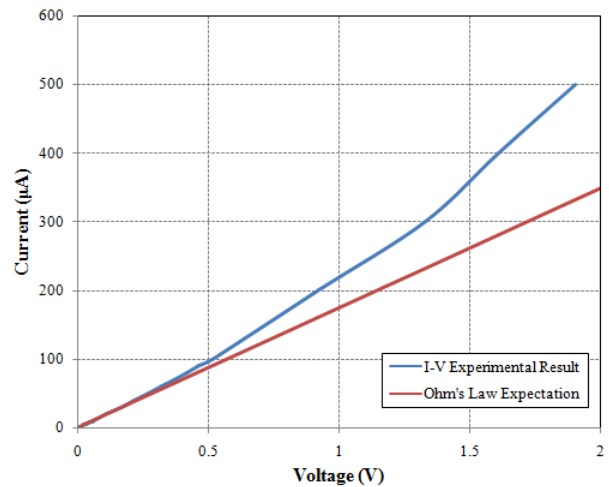linearity beyond 50μA. To avoid the self-heating effect, the operating current in our experiments was controlled at 10μA. Although the temperature coefficient of resistance (TCR) can be measured and plays an important role for other detection schemes [14], it is not necessary to evaluate the TCR for the sensors based on EG-CNTs to detect NaOCl. The reasons will be elaborated later.

C. Experimental Results of Responses

As a chemical solution, which can be obtained readily, sodium hypochlorite contains different byproducts in its solution, which are normally sodium chloride (NaCl) and sodium hydroxide (NaOH). Therefore, responses to these ingredients were tested to eliminate the influences of the byproducts by the same EG-CNTs sensor. A sensor with initial resistance of ~7kΩ was used for this test. A constant current of 10μA was applied and the concentration of each reagent was 90ppm. Figure 3 shows the sensor responses to NaOCl, NaOH, NaCl and deionized water (DI water). Note here that the sensor response is defined by conductance change (ΔG) over the initial value of conductance (G_i). During the test, the solution was injected into the microchannel at the one minute mark, before that the sensor was kept intact to measure static air response. Then, after the injection of a solution, the response was measured for another three minutes. It is clearly shown that the response of the EG-CNTs sensor to NaOCl solution is very clear. Compared to the relatively insignificant responses to NaCl and DI water, the response to NaOH is noticeable but with the trend of conductance change opposite to that of NaOCl, which implies that the response to NaOCl is mainly induced by OCl⁻ instead of the byproducts.

Possible explanation of the phenomenon that EG-CNTs sensors show response to NaOCl molecules can be led by studying the response of single-wall nanotubes to gas molecules as discussed by other researchers. When CNTs sensors are used to detect gas [15], molecules such as NH_3 and NO_2 will either transfer electrons to or withdraw electrons from carbon nanotubes, leaving charge carriers or holes in the CNTs [16, 17]. As a result, the conductance of the CNTs is
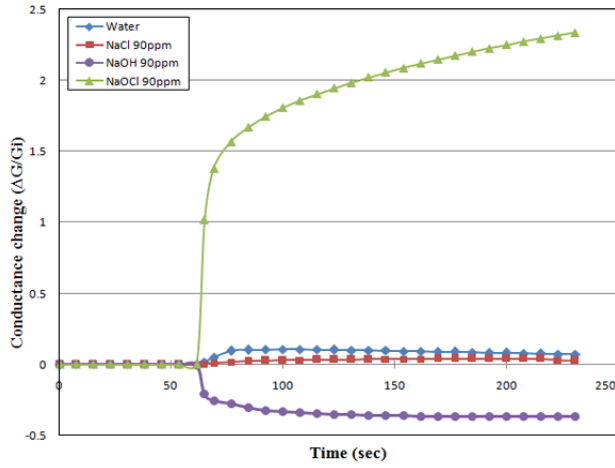
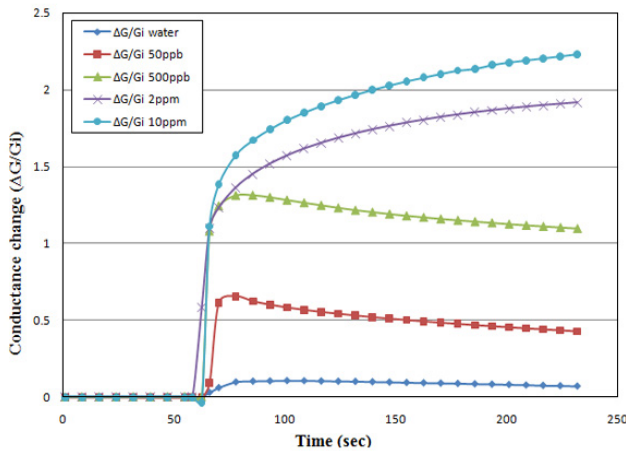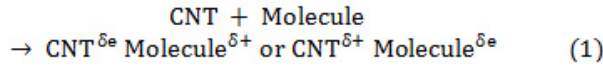Fig. 3. The response of an EG-CNTs sensor to different reagents.

Fig. 4. The response of an EG-CNTs sensor to NaOCl of different concentrations.
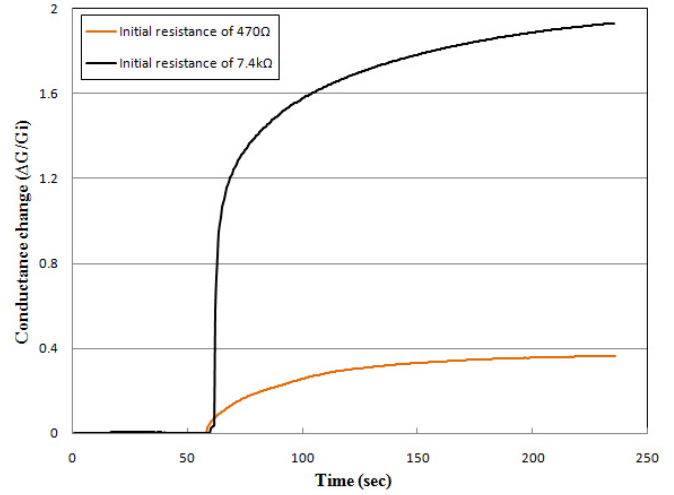

Fig. 5. The response to 2ppm NaOCl solution of two different sensors.

Figure 5 shows the responses to NaOCl solution of 2ppm with different EG-CNTs sensors and the same current is applied within the linear region of each sensor. This implies that the EG-CNTs sensors with distinct resistance would give dissimilar performance.

III. PHOTODESORPTION INDUCED BY UV ILLUMINATION

When there is a strong response, due to the strong bonds and more partial electron transfer between nanotubes and molecules, the resistance of the CNTs sensor is difficult to recover back to the initial value of resistance, i.e., this long recovery time has been reported previously [3]. In order to enhance the repeatability and allow the sensor be reusable within a short period of time, UV illumination is induced to test the recovery process. Figure 6 shows the conductance change of an EG-CNTs sensor during cycles of NaOCl adsorption and UV induced desorption at room temperature in air. Firstly, the sensor gave response to the solution for 6 minutes, with different concentrations of each cycle, then the solution was extracted out of the microchannel and the UV exposure was applied immediately. The recovery procedure under UV illumination is shown within the grey region in the Figure 6, and the illumination was ceased after the conductance came back to the original baseline. The inset figure presents the recovery spell in 6 hours after the response to the NaOCl solution of 100ppm, without any kind of illumination. During the recovery, the solution was extracted and the sensor was kept intact to measure static air.

It has been studied that for the individual SWNTs, the oxygen desorption can be fitted by (2):

$$G \cong e^{-\sigma Ft} \qquad (2)$$

Where σ is equal to $1.4 \times 10^{-17} cm^2$ and F is the photon flux. The equation provides clue for further studying the photodesorption of oxidizers such as NaOCl which shows similar trend with exponential changes.

increased or decreased. Typical electrochemical interaction may be denoted as (1):

$$CNT + Molecule$$
$$\rightarrow CNT^{\delta e} Molecule^{\delta +} \text{ or } CNT^{\delta +} Molecule^{\delta e} \qquad (1)$$

Where δ is a number that indicates the amount of charge transferred during the interaction [18].

NaOCl molecules, as an oxidizer which can increase the conductance of CNTs sensors, induce the charge transfer which takes place from the nanotubes to molecules, causing an enhancement of hole carriers in CNTs, thus the current is enlarged. Therefore the temperature coefficient of resistance plays minor role for sensing the reagent such as NaOCl since the response of interaction is due to chemical reaction such as molecule adsorption and desorption.

Same procedure was carried out for detecting the NaOCl solution with different concentration of 50ppb, 50ppb, 2ppm and 10ppm, as exhibited in Figure 4. While the responses to larger concentration show typical overdamped exponential curve of second order system, the responses to smaller concentration show critically damped exponential curve of second order system.
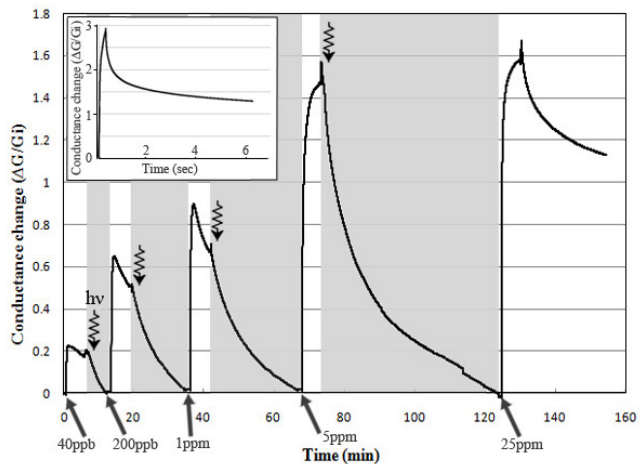
Fig. 6. The conductance change of an EG-CNTs sensor during cycles of NaOCl adsorption and UV induced desorption at room temperature in air with concentration of 40ppb, 200ppb, 1ppm, 5ppm and 25ppm, respectively. *Inset*: the recovery spell of resistance in 6 hours after the response to the NaOCl solution of 100ppm without illumination.

During the experiment, 3 UV light tubes of 15W each were used and the recovery time accelerated effectively. The UV exposure decreased the desorption energy barrier to ease the NaOCl molecules desorption. Since the hole carriers were reduced under UV illumination, the conductance of the EG-CNTs sensor here was lowered. It was reported that the photon with higher energy shows better performance on desorbing chemical molecules [19], and the exposure with wavelength of ~265nm has the best efficiency observed from the optical absorption spectrum of CNTs due to π plasmon, while there is nearly no effect when visible light is emitted with wavelength longer than 400nm in despite of the light intensity. The performance of the desorption should be improvable by changing the UV light tubes to give shorter wavelength light.

IV. CONCLUSION

Chemical sensors, fabricated by using electronic-grade carbon nanotubes as sensing element on glass substrate were developed and studied for the detection of sodium hypochlorite solution. We observed clear responses of EG-CNTs sensors to NaOCl solution compared to its byproducts, as well as the sensors' response to different NaOCl concentration using a constant-current sensor activation configuration. The responses of different sensors with various initial resistance were also explored. The conductance change of the EG-CNTs sensors under UV illumination by using three UV light tubes of wavelength from 350nm to 420nm was also carried out. The recovery characteristics of the sensors were studied and the principle of why this phenomenon exists was speculated. However, due to the limitation of available apparatus, the NaOCl molecules desorption process could not be carried out with shorter wavelength, which could possibly enhance the performance effectively. Additionally, for detecting NaOCl and other kinds of oxidizers, the selectivity of the EG-CNTs sensors was unclear, which need to be evaluated in the future.

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