

# Extreme-Low Power NaOCl Sensor Using EG-CNTs as Sensing Element

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**Abstract** — This paper presents a chemical sensor employing Electronic-Grade Carbon Nanotubes (EG-CNTs) as the active sensing element for sodium hypochlorite (NaOCl) detection. EG-CNTs are aligned between the microelectrodes with a gap distance of 2 $\mu$ m by using AC dielectrophoretic (DEP) technique on a glass substrate. 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 demonstrated the electrical responses of the sensor to NaOCl solution with different concentrations at room temperature. To fully study the properties of the sensor when used to detect NaOCl, different configurations of flow rate and total volume injected into the channel are carried out as well.

## I. INTRODUCTION

With the rapid progress and improvement of nanotechnology, sensors fabricated by using carbon nanotubes (CNTs) as the sensing element were reported to give electrical response to various kinds of gas such as NO<sub>2</sub>, NH<sub>3</sub>, CO and O<sub>3</sub> [1, 2]. CNTs sensors provide high sensitivity, low power and portable tools for in-situ chemical analysis. The CNT based sensing platform can also be extended to detect liquid as well by using microfluidic systems. Most sensors demonstrated thus far have used single-wall nanotubes (SWNTs) as sensing element for detecting these molecules and the sensor responded to NO<sub>2</sub> via an increase of conductance while the same sensor responded to NH<sub>3</sub> via a decrease of conductance. The phenomenon was elaborated by J. Kong et al. in 2000 [3]. NO<sub>2</sub> molecules, as an oxidant, withdraw electrons from CNT and leave holes on it, as a result the electrical properties are changed. In 2001, R. Chen et al. [4] presented that SWNTs appear hole doped in air as a result of donating electrons to oxygen molecules. The responses to every kind of gas molecules are different due to the difference of binding energy and charge transfer from the molecule to the CNT.

Sodium hypochlorite, as a high production volume chemical, is widely used for household bleach, disinfection of municipal water, sewage, swimming pool and food industry, chemical synthesis as well as pulp and paper industry. 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 industry and jeopardizes both environment and workers' health, and it could be equally harmful especially if the end is human consumption or the production of foodstuffs. 25 cases of product tampering involving bleach had been investigated between the years from 1992 to 2004 by the Forensic Chemistry Center (FCC) at the U.S. Food and Drug Administration for bleach being

adulterated into beverage. David Jackson et al. presented an indirect method for detecting sodium hypochlorite component within beverages [5]. 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 were given for the assessment of disinfection efficiency [6] as well as the electrochemical method for monitoring hypochlorite in drinking water [7, 8].

Our group has been studying the properties of electronic grade carbon nanotubes (EG-CNTs) as the sensing elements integrated in microfluidic systems for fabricating shear stress sensors [9] as well as the sensors used to detect alcohol [10]. 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 the sodium hypochlorite sensor based on EG-CNTs which are formed by DEP force on glass substrate by using microfluidic system. Sensor performance towards constant-current configuration will be evaluated, and different configurations will also be introduced to test the response to NaOCl under different situations.

## II. EXPERIMENTAL DETAILS

### A. Formation of EG-CNT Sensors Using DEP Force

Dielectrophoresis (DEP) is a phenomenon where neutral particles undergo mechanical motion inside a nonuniform ac electric field [11]. All particles exhibit dielectrophoretic activity in the electric fields but the strength of the force depends on the particles' electrical properties and their shapes, as well as the frequency of the electric field. By applying a given frequency of the electric field, the particular particles can be manipulated selectively.

The methodology is simple and has been proven to form CNTs sensors between two electrodes effectively. First of all, gold electrodes on a substrate is prepared using standard photolithographic method, and the separation between two electrodes must be small enough to ensure that DEP force is generated and can align the CNT bundles. Secondly, bundles of CNTs in powder form should be ultrasonically dispersed in ethanol solution. After putting a droplet of the CNTs solution between two electrodes, AC biased voltage is applied to the electrodes and DEP force is generated. After a few minutes, the ethanol solution is evaporated and the CNT bundles are formed and aligned between the electrodes, and one CNT based sensor is fabricated. However, the sensor needs to be treated by heating it to 60°C-80°C for several hours before usage. Figure

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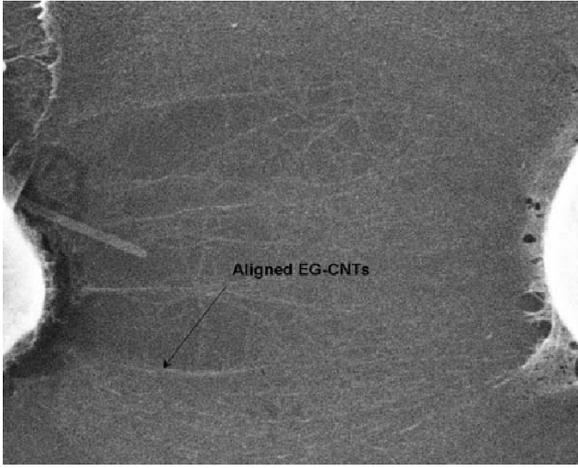


Fig. 1. The SEM image of the EG-CNTs between two microelectrodes after fabrication by DEP force.

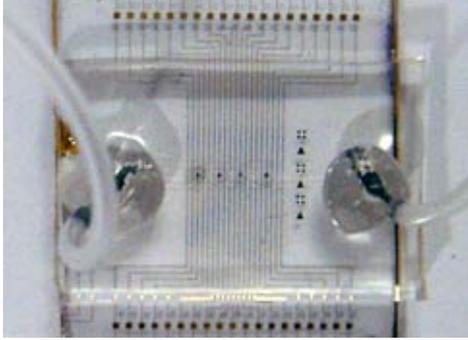


Fig. 2. Photograph of the EG-CNTs sensor which is used to detect chemical agents with a microchannel (L x W x T = 21mm x 1mm x 40 $\mu$ m) to contain the static liquid.

1 shows an SEM image of the EG-CNTs between two microelectrodes after fabrication by DEP force.

### B. Sensor Fabrication

Dielectrophoresis (DEP) manipulation was applied for sensor formation by aligning the EG-CNTs between a pair of Au microelectrodes fabricated on glass substrate. The pattern of microelectrodes, as shown in Figure 2, was etched by wet chemical etching process after the photolithography procedure onto the Au layer with the thickness of  $\sim 3000\text{\AA}$ . There is also a layer of  $\sim 1000\text{\AA}$  chromium (Cr) between the Au layer and glass substrate. AC bias voltage with frequency of 1MHz and amplitude of 8V was applied to excite the droplet of EG-CNTs solution on the two  $5\mu\text{m}$  width microelectrodes. The distance between the two electrodes was  $2\mu\text{m}$ . After the solvent including the EG-CNTs solution was evaporated, a linkage with EG-CNTs as sensing element was left between the electrodes with resistance ranged from several hundred ohms to tens of thousands ohms at room temperature according to the concentration and volume of the solution of EG-CNTs. Then, a PDMS (SYLGARD 184 Silicone Elastomer Kit, Dow Corning Co., USA) shaped by a mold was bonded onto the glass surface to form the microchannel in which the reagent could be confined. The length of the microchannel was 21mm and the area of the cross section was  $1\text{mm}\times 40\mu\text{m}$ . Because of the fixed microchannel, the volume of the reagent was kept constantly,

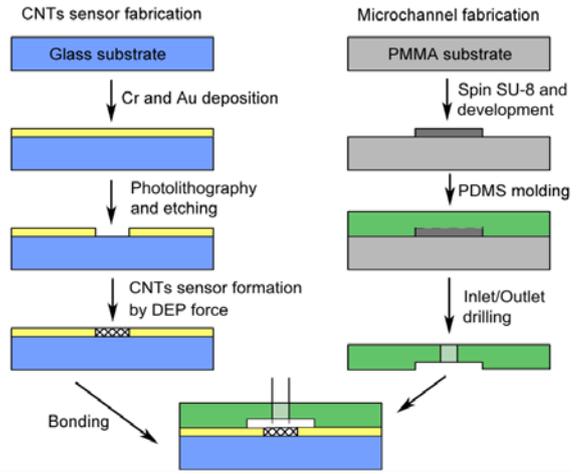


Fig. 3. Fabrication process of the EG-CNTs sensor.

which enhances the repeatability when conducting experiments with the device.

The whole fabrication process is shown as Figure 3.

### C. Experimental Setup

During the experiments, the solution of reagent was injected from the inlet on the PDMS by a pneumatic pump. A Versapump 6 (Kloehn Ltd., USA) syringe pump was used to control the flow rate and inject the liquid into the CNT sensor chip with a certain volume. With the resolution down to about  $5.2\cdot 10^{-5}\text{mL}$  per step, the total volume injected into the microchannel and flow rate could be controlled accurately and consistently during each experiment. After injecting the reagent from the inlet, the solution is 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 sensor and its response was recorded by a computer. The setup is shown in Figure 4.

### D. Noise and Accuracy

To measure the signal-to-noise ratio (SNR) of an EG-CNTs sensor in air environment, constant current was applied and the voltage between the two electrodes was recorded. With 500 data of voltages in a sequence, the SNR was calculated by Equation (1):

$$SNR = 20\log_{10} \frac{|\bar{x}|}{\sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \bar{x})^2}} \quad (1)$$

Where  $\bar{x}$  stands for the average value of all data, and N means the total number of data. Here N is equal to 500.

The SNR was tested under different conditions of power consumption by adjusting the current before each test. The result is shown as in Figure 5. For smaller power values, the SNR levels were better than the ones with higher power. However, all the SNR values were acceptable for sensing the NaOCl solution concentration as explained in the following section.

### E. I-V Characteristics

During all experiments, environmental temperature was fixed to 24C and humidity was controlled to 50%. The I-V

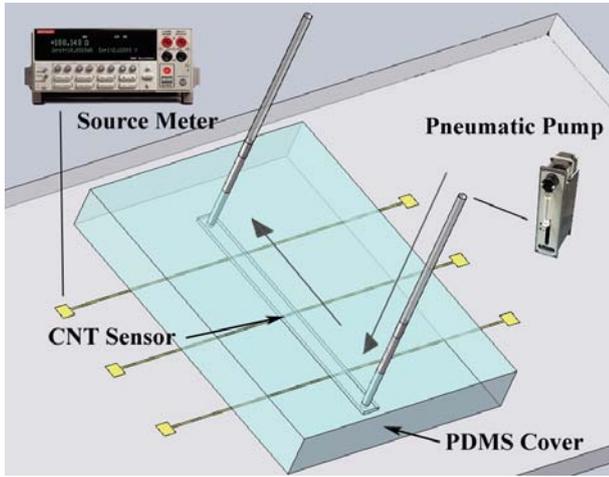


Fig. 4. The experimental setup when testing the response of the CNT sensor to the injected solution.

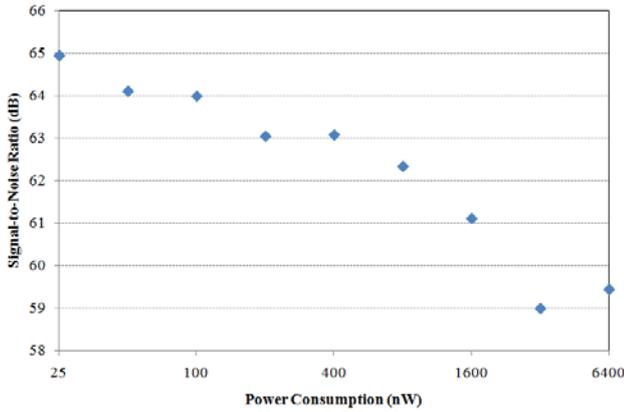


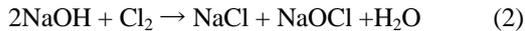
Fig. 5. Signal-to-Noise Ratio as a function of power.

characteristic of a typical EG-CNTs sensor showed linear relationship before  $50\mu\text{A}$  while the self-heating effect caused the nonlinearity beyond  $50\mu\text{A}$ . The resistance of the sensor fell as temperature rose because CNTs are known to have negative TCRs. To avoid the self-heating effect, the operating current in our experiments was controlled to no larger than  $10\mu\text{A}$  (with power not larger than  $500\text{nW}$ ). Although the temperature coefficient of resistance (TCR) can be measured and plays an important role for other detection applications [12], it is not necessary to evaluate the TCR for the NaOCl sensors since the responses are assumed to be induced by chemical adsorption.

### III. EXPERIMENTAL RESULTS

#### A. Byproducts Responses

The NaOCl solution is typically prepared by absorbing chlorine gas in cold sodium hydroxide solution as shown in Equation (2):



During the reaction, the sodium hypochlorite and water will yield Hypochlorous acid (HOCl) which is a stronger oxidant than chlorine with poor stability and it will further yield oxygen which help bleach or disinfect, as the equation (3) and (4):

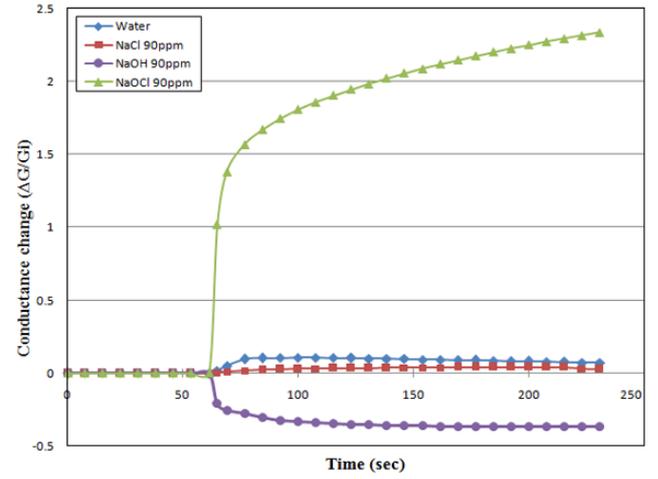
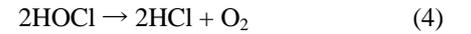
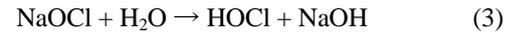


Fig. 6. The response of an EG-CNTs sensor to different reagents, including two major byproducts NaCl and NaOH of the same concentration with NaOCl.



The household bleach includes normally from 4% to 6% NaOCl as its effective ingredient and around 0.2% sodium hydroxide (NaOH) as its major byproduct in the solution. NaOH is used to maintain a pH-dependent equilibrium between hypochlorite and chlorine. 0.5% to 1.5% Sodium Chloride (NaCl) exists within the NaOCl solution as well. Hence, there are two byproducts in a stable NaOCl solution, which is a commercial product being used widely. Therefore, responses to these ingredients were tested to eliminate the influences of the byproducts by the same EG-CNTs sensor. A sensor with initial conductance of  $\sim 0.14\text{mS}$  was used for this test. A constant current of  $10\mu\text{A}$  was applied and the concentration of each reagent was 90ppm. Figure 6 shows the sensor responses to NaOCl, NaOH, NaCl and deionized (DI) water.

During the experiment, the solution was injected into the microchannel after one minute of static air response measurement. After the solution was injected from the inlet, the response between EG-CNTs sensor and the reagent was measured continuously for another three minutes. The results clearly showed that the response of the EG-CNTs sensor to NaOCl solution was much more intense. Compared to the relatively insignificant responses to NaCl and DI water, the response to NaOH was noticeable but with the trend of conductance change opposite to that of NaOCl, which implies that the response to NaOCl is mainly induced by  $\text{OCl}^-$  instead of its byproducts.

Possible explanation to the phenomenon that EG-CNTs sensors show response to NaOCl molecules can be provided by studying the response of single-wall nanotubes to gas molecules such as  $\text{NH}_3$  and  $\text{NO}_2$ . When charge transfer occurs between the CNTs sensor and particular molecules, there will be holes or carriers left onto the CNTs. As a result, the conductance of the CNTs is increased or decreased. Typical electrochemical interaction may be denoted as Equation (5):

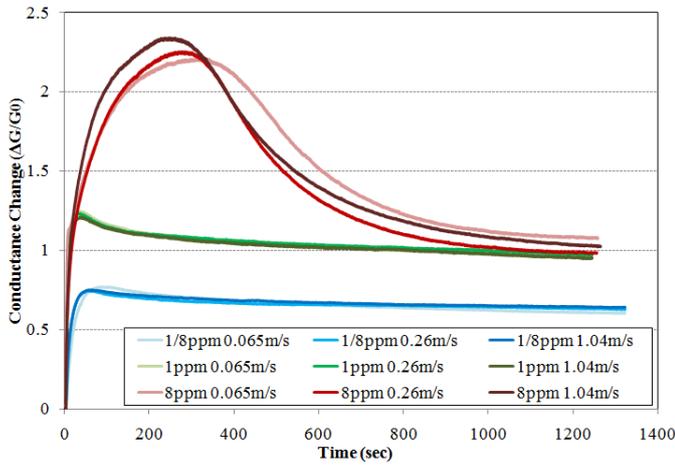
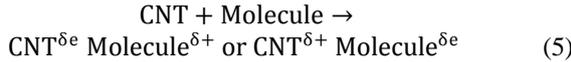


Fig. 7. The flow rate test by the responses to the solution with identical volume value but different concentrations of 3 groups.



Where  $\delta$  is a number that indicates the amount of charge transferred during the interaction [13]. “e” represents electron while “+” represents holes. As sodium hypochlorite is a kind of oxidant, it is expected to respond similarly or has alike trend with other oxidants or molecules which withdraw electrons from the CNT sensors.

### B. Flow Rate Response

The flow rate in our experiments was controlled by a pneumatic pump. Three groups of experiments were conducted, which were classified by the concentration of NaOCl solution: 1/8ppm, 1ppm and 8ppm. For each group, three values of volumetric flow rate were tested: 2.6 $\mu\text{L/s}$ , 10.4 $\mu\text{L/s}$  and 41.7 $\mu\text{L/s}$ . Since the area of the cross section of the microchannel was 0.04 $\text{mm}^2$  and the same channel was used to test all the responses, flow rate values for these three groups were converted to 0.065m/s, 0.26m/s and 1.04m/s correspondingly. Each response was tested for 20 minutes in total, and the results are shown as Figure 7.

During the experiment, the total volume injected into the channel was fixed to be 26.5 $\mu\text{L}$  (dictated by pump) for all nine responses, which was also controlled by the pump consistently. Constant current was applied to the sensor and the initial power consumption could be adjusted to about 100nW (constant current was set to 3.4 $\mu\text{A}$ ).

The results clearly show that the flow rate is not a major factor which affects the response of the EG-SNTs sensor to NaOCl solution within the range from 0.065m/s to 1.04m/s. And as a result, we conclude that the influence by the speed of injection can be eliminated when conducting experiments using EG-CNTs sensors in microfluidic systems.

### C. Volume Response

Here the volume is defined as the “total volume of the solution which has been injected to the microchannel”. The larger the value is, the more solution is reacted with the EG-CNTs sensor, and hence more electron transfer should have

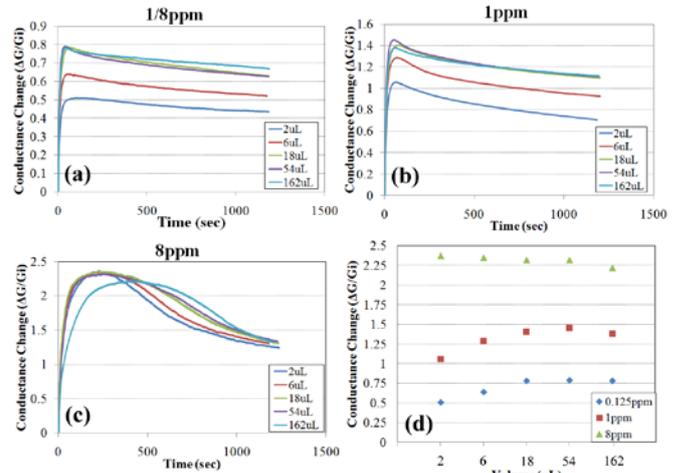


Fig. 8. The volume test demonstrated by 3 concentration groups of 0.125ppm, 1ppm and 8ppm, with the same flow rate of 1.56m/s.

occurred theoretically. To test the response to different volumes, the same EG-CNTs sensor was used (with the same input current of 3.4 $\mu\text{A}$ ). A flow rate of 1.56m/s was used in the following experiments.

Figure 8 shows 3 groups of responses to NaOCl solution with concentration of 0.125ppm, 1ppm and 8ppm. Five response tests were carried out for each concentration group by different volume configurations, i.e. 2 $\mu\text{L}$ , 6 $\mu\text{L}$ , 18 $\mu\text{L}$ , 54 $\mu\text{L}$  and 162 $\mu\text{L}$ . Figure 8(d) shows the maximum values of each conductance change as a function of concentration of the solution.

For smaller concentration values such as 0.125ppm and 1ppm, the response to the solution ascended as the volume value increased until the volume value reached 18 $\mu\text{L}$ . The differences among 18 $\mu\text{L}$ , 54 $\mu\text{L}$  and 162 $\mu\text{L}$  were negligible. When the concentration of the solution was increased to 8ppm, all five responses showed similar overshoot amplitudes of conductance change. However the responses with larger volume values showed longer period of the overshoot, which is a different trend as compared to the responses to lower concentrations. Hence, as shown in Figure 8(d), the conductance change as a function of solution volume for 8ppm concentration is different from that of 0.125ppm and 1ppm. Although the reason behind this phenomenon remains unknown, the total volume injected into the channel was set to 18 $\mu\text{L}$  for all other experiments of chemical detection described henceforth. This is because, for this configuration, the amplitude of the response is expected to reach its maximum value for different concentration values.

### D. Concentration Responses

An EG-CNTs sensor with initial conductance of 2.9 $\mu\text{S}$  was used for the concentration response tests ranging from 1/32ppm to 8ppm. A constant current was used to activate the sensor with 30nW for each test. For every response to a particular concentration, flow rate and volume were fixed to 1.04m/s and 18 $\mu\text{L}$ , respectively. Therefore, the variation of each response was theoretically purely influenced by the amount of NaOCl molecules, or  $\text{OCl}^-$ , in the solution.

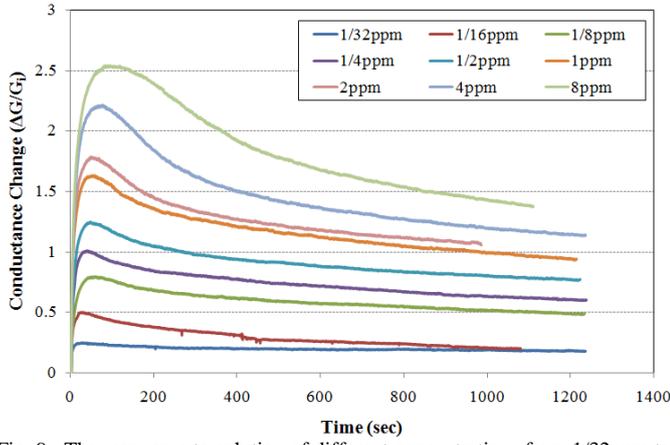


Fig. 9. The responses to solution of different concentrations from 1/32ppm to 8ppm.

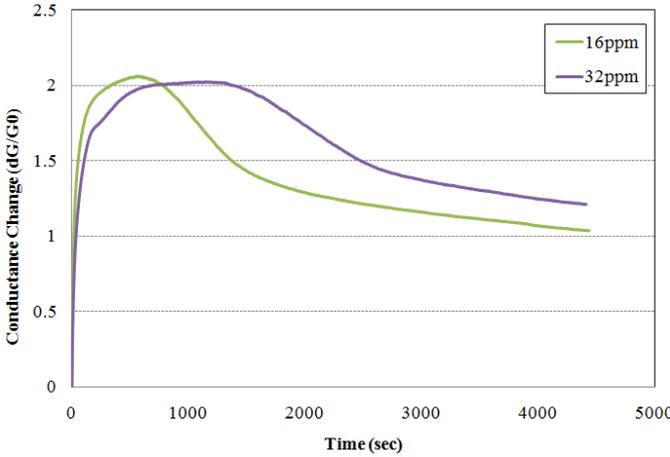


Fig. 10. The responses to solution of larger concentrations.

As shown in Figure 9, the response to solution concentration ascended consistently as the concentration increased from 1/32ppm. For all responses, an overshoot exists for each curve: the response reached the maximum value within a short period, and began to recover and gradually tended to some stable conductance value. The shapes of response curves were similar, with differences in amplitude and duration of overshoot period. As the concentration increased, the overshoot became much more obvious, and with higher peak amplitude. Also, the time constant required to reach the peak was prolonged.

Figure 10 shows the sensor response to larger concentrations such as 16ppm and 32ppm for over one hour period. The test was carried out using same configuration as the previous concentration tests described above. Compared to the response curves demonstrated previously, both amplitudes of overshoot were lower than the response to 8ppm solution, i.e. the periods of the overshoot were much longer. For the response to the 32ppm solution, the conductance response curve began to decline after 1300 seconds, whereas for the 16ppm solution, the decline starts at ~800 seconds. Also, the peaks for these 2 concentration response curves are lower than that of 4ppm and 8ppm responses. These results indicate that

Concentration	$y_0$	A	$\tau$
1/32	0.236	-0.22	2.536
1/16	0.487	-0.44	4.232
1/8	0.785	-0.7	9.256
1/4	0.999	-0.83	7.024
1/2	1.228	-1.08	8.121
1	1.618	-1.44	9.335
2	1.784	-1.57	9.585
4	2.189	-1.88	10.857
8	2.491	-2.12	13.63

Table 1. The fitted values of A,  $y_0$  and time constant  $\tau$  vs. concentration.

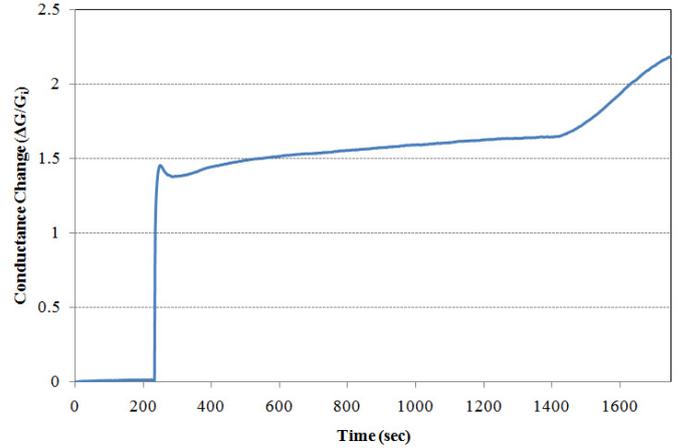


Fig. 11. The response to 8ppm NaOCl solution in a fluid flow environment.

the response of the CNT sensors could be saturated at a certain concentration level.

The ascending period for each response from 1/32ppm to 8ppm can be fitted by a first-order exponential function (6):

$$y = Ae^{-\frac{t}{\tau}} + y_0 \quad (6)$$

We have neglected the data from 16ppm and 32ppm response curve in the above curve fit because their responses were assumed to have saturated. Table 1 shows the fitted values of A, time constant  $\tau$ , and  $y_0$  as a function of concentration from 1/32ppm to 8ppm. The relationship between each variable and the concentration in log scale is linear, which indicates that the response of the EG-CNTs sensor to NaOCl solution is predictable by analyzing the ascending period of the response curve. As a result, currently our sensor is capable of testing solutions with concentrations ranging from 1/32ppm to 8ppm. Further study will be carried out to test the sensor response to lower concentrations in the future.

#### E. Response to Fluid Flow

Another test was also carried out by keeping injecting the solution into the sensor channel with a flow rate of 0.05m/s for a longer time. The result from this test is shown in Figure 11. The time period from when the solution was injected to the moment when the flow rate was stopped was about 20 minutes. The concentration of the solution was 8ppm and the constant current configuration was used with initial conductance of 0.14mS and initial power of 100nW. At the beginning, the response ascended with the same trend as with previous response test to 8ppm solution. However the value of conductance change declined a little, and then increased slowly

as the solution kept flowing into the channel. The maximum value of the overshoot (~1.5) was much lower than the previous test for 8ppm (~2.5). Only after the flow ceased could the response ascended higher. This result proved that the CNT sensors respond differently to dynamic and static-input situations. Since there are many unknown factors that may affect the response results when the solution is flowed into the sensing chamber, i.e. factors such as shear stress and heat transfer, chemical reaction tests using CNT sensors should be done in a static environment as much as possible.

#### IV. CONCLUSION

Chemical sensors, fabricated by using Electronic-Grade Carbon Nanotubes (EG-CNTs) as sensing element on glass substrate were developed and studied for the detection of sodium hypochlorite (NaOCl) solution concentration. 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 ascending period of the responses could be fitted by a first-order exponential function and all three variables show predictable linearity as a function of concentration in log scale. Therefore, we demonstrated the feasibility to use an EG-CNTs sensor for detecting static chemical liquid by integrating the sensor with a microchannel system. Different configurations of flow rate and total volume injected into the channel were tested. Flow rate had negligible influence on the sensor responses, while the volume of chemical did affect the result significantly. Saturation was shown when detecting solution of concentration higher than 8ppm. The comparison between the dynamic solution and static solution during the reaction was tested as well. Under different flow situations, the sensor reacted with different response curves. Although systematic explanations are difficult to list based on the current results, some test configurations which may lead to errors have been found, which should be avoided in future experiments.

#### ACKNOWLEDGMENT

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