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Current correlation functions for chemical sensors based on DNA decorated carbon nanotube

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ABSTRACT

The current characteristics of DNA decorated carbon nanotubes for different gas odors are studied. A simple model of charge transfer between the Gas–DNA–base complex and single wall carbon nanotube (SWCN) is proposed to explain the current response for different odors. The autocorrelation and two-point correlation functions are calculated for the current sensitivity curves. These correlation functions together with the current characteristics form finger-prints for detection of the odor and DNA sequence.

1. Introduction

The discovery of carbon nanotubes (CNTs) [1] has generated a tremendous amount of interest and activity in basic research and applied technologies. The unique properties of CNTs make them a potentially ideal material for molecular sensing. The simplest nanotube is a single layer of graphite rolled into a seamless cylinder and is called the single wall carbon nanotube (SWCN) having diameters ranging from 1 to 2 nm [2]. This unique structure results in electronic and chemical properties that are ideal for the direct electronic detection of chemical vapors [3]. The electronic properties of CNTs can be altered by modifying their parent structure [4] and this can be done by doping them with certain molecules or polymers [5–15]. It is found that the conductance of SWCNs changes in response to exposure to certain molecules that undergo charge transfer upon adsorption [5–15]. In particular, CNTs can be functionalized with single stranded deoxyribonucleic acid (ss-DNA) or DNA nucleoside [4,16–20]. Functionalization of CNTs with DNA offers interesting prospects in different fields including detection of chemical vapors, solubilization in aqueous media, and nucleic acid sensing [4,17–20].

This work presents a theoretical understanding of the current characteristics of gas flow over DNA decorated CNTs [17]. The article [17] studies the nanoscale chemical sensors, with ss-DNA for chemical recognition and single walled carbon nanotube field effect transistors (SWCN-FETs) for electronic readout. The composites, SWCNs coated with ss-DNA, respond to various gas odors that do not respond or cause a detectable conductivity change in the bare devices (without DNA). As a result of functionalization of SWCNs with DNA a change in the current is observed for each gas odor.

These findings motivated us to analyze the ss-DNA–Gas/SWCN complex system and to understand the reason for the observed change in the current. Our analysis gives two main results: the first is the proposal of a simple phenomenological model based on charge transfer between the Gas–DNA–base complex and the SWCN, and the second is the calculation of the correlation functions for the current characteristic curves of Ref. [17]. We find that the current fluctuations (correlation functions) together with the current characteristics form finger-prints for detection of the odor. More importantly the characteristic pattern of the DNA sequence is captured in these current correlation functions. Hence these gas flow sensors may also be used as sequence detectors for DNA where the pattern of correlation functions may be used as a benchmark for the particular chemical signal encoded in a DNA sequence.

2. Experimental details

SWCNs were synthesized by catalytic chemical vapor deposition (CVD) of methane (2.50 sLm[1]) at 900 °C on a SiO_2/Si substrate using

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[1] Standard liters per minute.

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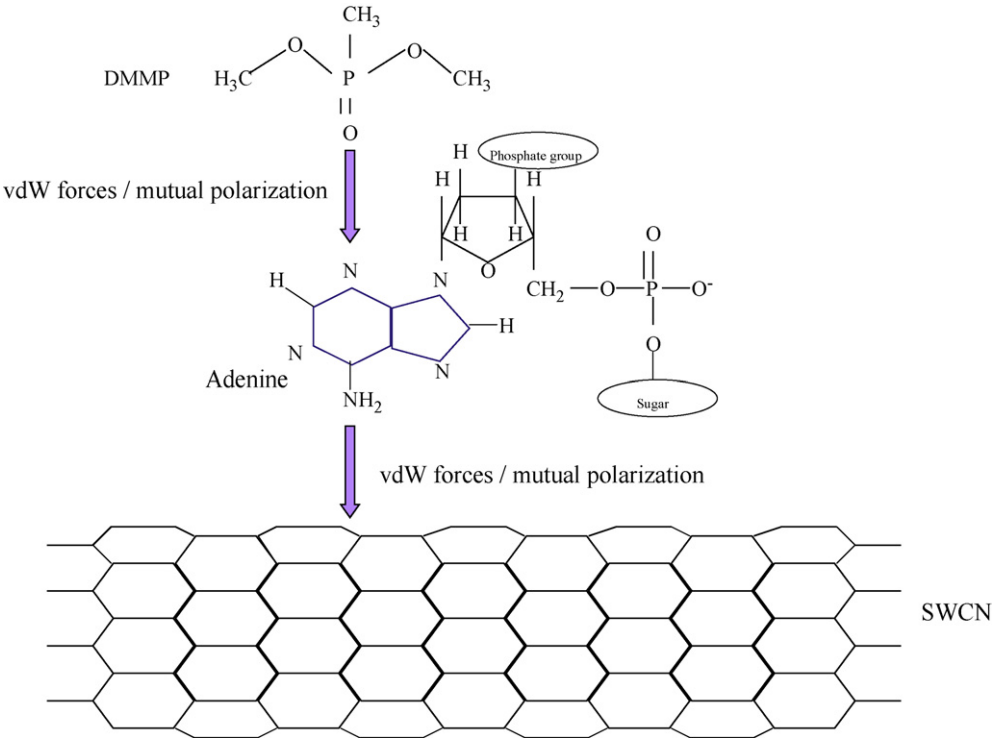

Fig. 1. Schematic view of attachment of an adenine base of the ss-DNA sequence 2 and a DMMP molecule on the SWCN through vdW forces or mutual polarization.

iron salt catalyst ($Fe(NO_3)_3{\cdot}9H_2O$ dissolved in isopropyl alcohol) [17]. Hydrogen (0.320 sLm) and argon (0.600 sLm) are allowed to flow through the furnace throughout the heating and growth process. FETs were fabricated with Cr/Au source and drain electrodes using e-beam lithography and the degenerately doped Si substrate used as a backgate [17–19]. The resistance of the FETs was 100–500 k Ω [19] in the "ON" state.

The two ss-DNA sequences chosen in the experiment [17] are:

- Sequence 1: 5′-GAG TCT GTG GAG GAG GTA GTC- 3′
- Sequence 2: 5′-CTT CTG TCT TGA TGT TTG TCA AAC- 3′.

These oligonucleotides were diluted in distilled water to make a stock solution of 658 μg/ml (sequence 1) and 728 μg/ml (sequence 2). First the odor responses of bare devices were measured, and then the devices were functionalized with a particular ss-DNA sequence by applying a 500- μm diameter drop of the solution to the device for 45 min and then dried in a nitrogen stream [17–19].

The adsorption of ss-DNA on SWCNs was characterized by atomic force microscopy (AFM). The AFM images [17–19] of the same SWCN before and after the application of DNA show a clear increase in the tube diameter from 5.4 ± 0.1 nm to 7.2 ± 0.2 nm[2] indicating formation of a nanoscale layer of ss-DNA on the SWCN surface [17–19]. Functionalization of SWCNs with ss-DNA caused the threshold value of the gate voltage V_g to decrease by 3–4 V for measurable conduction and this corresponds to a decrease in the hole density [17–19].

The sensor response for five different odors methanol, propionic acid (PA), trimethylamine (TMA), 2, 6 dinitrotoluene (DNT) and dimethyl methylphosphonate (DMMP) was studied. Here the focus was on odor induced changes in the current measured with bias voltage $V_b = 100$ mV and $V_g = 0$ V [17]. In this experiment, gas and then air is alternately exposed to the device each for 50 s. The experiment is repeated for multiple odor exposures [17].

The bare and polymer-coated SWCNs respond to various gases [3,5–15] but some chemical species interact weakly or not at all with the bare SWCNs [17–19]. For molecular sensing, it is necessary that the chemical species get adsorbed on the device properly. When SWCNs are coated with DNA the bases bind to SWCNs through vdW forces and by forces due to their mutual polarization [16,20]. We propose that the chemical species get adsorbed on SWCNs through vdW forces and/or mutual polarization between the chemical species and DNA–SWCN complex (as in Refs. [16,20]), Fig. 1. Hence the DNA increases the binding affinity of the molecular species (odors) to the device. The model described below is a phenomenological model. The building of a microscopic (tight binding) model of CNTs is an important task and needs future work.

3. Model

Here we propose a model to explain the sensor response [17]. The model consists of a FET in which a p-type SWCN acts as an electronic wire between two metal electrodes with an ss-DNA sequence on it. For clarity of exposition the model illustrated in Fig. 2 has a simpler geometry than the experiment.

DMMP and 2,6 DNT: the current response of the bare device is less than the experimental sensitivity ($\triangle I/I \sim 1\%$; where I is the source–drain current) when exposed to DMMP with estimated concentration 25 ppm [17]. After coating the same device with ss-DNA sequence 2, exposure to DMMP gives a slight change (decrease) in the current, that is, the sensitivity of the device is $\triangle I/I = -7\%$ [17]. Due to the application of ss-DNA layer, the binding affinity of DMMP to the device increases through vdW forces and/or mutual polarization [20], this results in an increase in sensor response. The

[2] The mentioned diameter is most likely for a small bundle of nanotubes [19] as the CVD process used in Refs. [17–19] tends to produce nanotubes with a diameter from 1 nm to 2 nm.