

Electric-field assisted desorption of water molecules in DNA functionalized CNT network

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Abstract—This paper introduces the concept of electric field assisted desorption (EAD) of water molecules from the surface of DNA functionalized carbon nanotube (DFC) resistive network when a bias voltage V_{DS} is applied across it. EAD at a given V_{DS} is measured in terms of the characteristic life-time of desorption τ . The bias voltage produces an electric field E that aligns the molecular dipoles of water parallel to E . Mutually aligned neighboring dipole moments of water maximize the potential energy and drives them into a non-equilibrium state. The molecular dipoles return to the minimum potential energy state when water molecules escape from the surface of DFC. We find an exponential decrease in τ for $V_{DS} < V_{cr}$ which is attributed to EAD. Beyond V_{cr} we observe a linear increase in τ which is due to charge entrapment within ultrathin layer of water sandwiched between dielectric layers of DNA and air that prevents fast desorption of water molecules.

Index Terms— carbon nanotubes, desorption, dipoles, DNA, electric field

I. INTRODUCTION

Fast dynamic response of a sensor is essential for applications with real time monitoring of analytes. Carbon nanotube (CNT) based chemical sensors have shown promise as ultrafast detection system for sensing various gases and organic molecules [1-5]. However, dynamic response characteristics of CNT based sensors reveal that the output signal current is often not restored to its initial value on withdrawal of analyte exposure due to incomplete desorption from the nanotube surface[6]. Reduction in sensor recovery time (i.e., removal of the analyte through desorption) can be thermally assisted [7], UV assisted [8], by the application of gate voltage[9], or by hydrolysis to remove the moisture sensitive analytes from the walls of CNT [10].

The water molecules are bound to the surface of DNA functionalized carbon nanotube (DFC) through chemisorptions with a binding energy greater than 12 kcal/mol. In order to develop a DFC based humidity sensor with a low recovery

time, desorption of chemisorbed water molecules from the surface of DFC must be fast. When the RH stimulus is instantaneously withdrawn, the water molecules take sufficient time to overcome their binding energy with the DFC desorption from the sensor bed. The delay in recovery of the sensor is attributed to a large binding energy of chemisorbed water molecules and the entrapment of ionic charges on the surface of DFC.

It was shown in our previous work [11] that functionalization of CNT by ssDNA provides hydrophilic sites on the nanotube surface which increases the sensitivity of detection. But since humidity sensing is governed by the phenomenon of adsorption and desorption, the devices often suffer from delayed response and recovery times. Since the water molecules are chemisorbed on the DFC, sufficient energy must be expended to drive away the water molecules during desiccation.

In this paper we introduce the concept of electric field assisted desorption (EAD) of water molecules from the surface of DFC resistive network when a bias voltage V_{DS} is applied across it. EAD at a given V_{DS} is measured in terms of the characteristic time of desorption τ which is physically interpreted as the time required for the output current I flowing through the DFC network to decay by 63 % of the final value at steady state. The exponential decrease in τ for $V_{DS} < V_{cr}$ confirm that EAD is a non thermal and E driven phenomenon. Beyond V_{cr} we observe a linear increase in τ which is due to charge entrapment within ultrathin layer of water sandwiched between dielectric layers of DNA and air that prevents fast desorption of water molecules.

II. EXPERIMENTS AND RESULTS

The DFC solution was prepared as follows. First, the ssDNA solution was prepared by adding 0.1 mg of ssDNA in 5 ml tris buffer solution and allowing the ssDNA to dissolve overnight in the sample mixer (HulaMixer™ from Life Technologies-Invitrogen, USA). Following this, 0.2 mg SWNT was then added to the ssDNA solution, and subjected to 4 hours of alternate cycles of (i) low intensity sonication for 30 mins in an ice bath and (ii) mixing in sample mixer for 30 mins. The resultant solution was centrifuged at 2000 r/min to eliminate the large bundles of unmodified SWNT.

The supernatant solution was collected and drop cast between Au electrodes of gap length $L=25 \mu\text{m}$ by micro-cantilever based drop dispensing technique using Nano-eNabler system (Bioforce Nanoscience, USA). This drop

Manuscript received xxxxxxxx. This work was partially supported by DST-ITPAR program and partially by BARC, Dept. of Atomic Energy, Govt. of India.

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casting technique produces DFC film of maximum thickness 90 nm as characterized by Dektak surface profilometer. The steps of DFC synthesis and the process of device fabrication are discussed in detail in our earlier work [12]. The bias voltage V_{DS} builds an electric field $E(= \frac{V_{DS}}{L})$ in the order of $\sim 10^5$ V/m in the DFC film of average thickness 45 nm. The recovery of output signal current I as RH stimulus was reduced instantaneously from 80% to 40% was recorded for bias voltages in the range 1.3-4.0 V. The current I was found to decrease exponentially with time for given V_{DS} :

$$I = \alpha \exp(-\frac{t}{\tau}) + I_0, \quad (1)$$

The parameters α , τ and I_0 were determined through regression analysis of each curve in Figure 1 (inset a). The variation of τ with V_{DS} is shown in Figure 1. It is clear that the characteristic time of desorption τ decreases exponentially with $V_{DS} < V_{cr} = 3.2$ V which, importantly, is attributable to EAD:

$$\tau = A \exp(-\frac{V_{DS}}{\mathcal{G}}) - \tau_0, \quad V_{DS} < V_{cr} \quad (2)$$

where $A=85.10$, $\mathcal{G}=0.53$ V and $\tau_0=3.26$ s. The surface binding energy of an analyte chemisorbed on the surface of DFC is directly proportional to $e\mathcal{G}$, where e is the electronic charge and \mathcal{G} denotes the voltage constant of the analyte and is determined graphically by fitting the values of τ in (2). Higher value of \mathcal{G} signify that larger energy is required to completely drive away the chemisorbed molecules from the sensor surface.

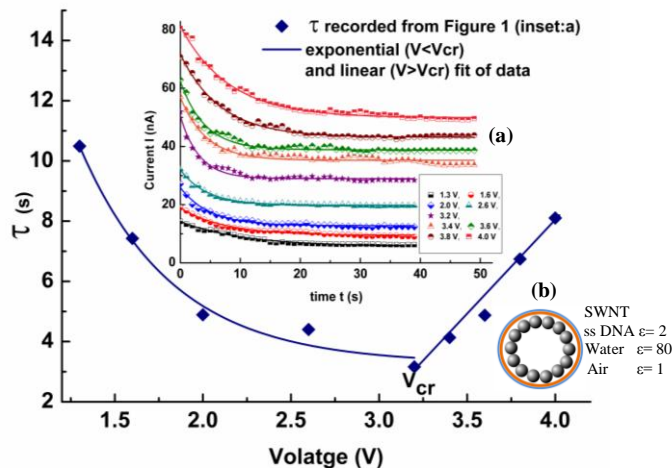


Figure 1: Variation of τ with the applied voltage in the range 1.3-4 V, (Inset a): Output current I vs. time t plot obtained for different bias voltage when the RH was relaxed from 80% to 40% , (Inset b): Cross sectional view of DFC showing the ultra thin layer of water molecules ($\epsilon=80$) sandwiched between layers of ssDNA ($\epsilon=2$) and air ($\epsilon=1$).

Beyond V_{cr} we observe a linear increase in τ :

$$\tau = 6.159V_{DS} - 16.89, \quad V_{DS} > V_{cr} \quad (3)$$

which is due to charge entrapment within ultrathin layer of water sandwiched between dielectric layers of DNA and air that prevents fast desorption of water molecules. The

phenomena are described in details in the following section.

III. DISCUSSIONS

Water molecules are bound to the surface of the DFC through chemisorption occurring due to overlap of atomic orbitals between the water molecules and the phosphate backbone (PB). Desorption of water molecules from the DFC bed accounts for the dissolution of these short range forces.

A. Electric field assisted desorption (EAD)

The exponential decay of τ with $V_{DS} < V_{cr}$ is attributed to the orientation polarization of molecular dipoles of water in the direction of applied electric field E which raises the mutual potential energy of adjacent dipoles, assisting the desorption of water molecules from DFC. Molecular desorption [8] of water from the surface of the DFC can be explained through:

$$\frac{dn}{dt} = -\sigma Cn \quad (4)$$

where n , σ and C represent the number of adsorbed molecules, molecular desorption coefficient and concentration of the water molecules respectively. The solution of (4) is:

$$n = A.e^{-\frac{t}{\tau}} \quad (5)$$

where A is a constant and $\tau = 1/(\sigma C)$.

For a particular desorption process at a fixed V_{DS} the constant τ is physically interpreted as the characteristic life-time of the molecular dipoles of water on the surface of DFC caused by an instantaneous reduction in RH. The exponential decay in n manifests as an exponential decay in I with the same characteristics time constant τ for a given V_{DS} .

The decrease in τ with V_{DS} can be explained by the orientation polarization between two interacting dipoles ${}^{H_2O}_i\vec{\mu}$ and ${}^{H_2O}_j\vec{\mu}$, whose potential energy Φ_{ij} is:

$$\Phi_{ij} = \frac{1}{4\pi\epsilon_0 r_{ij}^3} \left[{}^{H_2O}_i\vec{\mu} \cdot {}^{H_2O}_j\vec{\mu} - 3 \frac{({}^{H_2O}_i\vec{\mu} \cdot \vec{r}_{ij})({}^{H_2O}_j\vec{\mu} \cdot \vec{r}_{ij})}{r_{ij}^2} \right] \quad (6)$$

where ϵ_0 and r_{ij} denotes the permittivity of free space and distance between dipoles respectively. Φ_{ij} depends on the dipole orientation and is maximum when the two dipoles water are aligned.

In the absence of externally applied dc electric field E the dipoles of the water molecules adsorbed on the PB are randomly oriented and bear a zero net dipole moment, $\langle {}^{H_2O}\vec{\mu} \rangle_{E=0} = 0$. With increase in electric field E (or V_{DS}) the

dipoles increasingly align themselves in the direction of the field to form a polarized system of mutually interacting dipoles and thereby increasing the potential energy of the system. It should be noted that thermal energy kT prevents the dipoles from perfectly aligning with E . Desorption allows the dipoles to return to a state of lower potential energy. Thus higher the state of polarization in DFC, more rapid is the rate of release of water molecules from its surface when the external stimulus (RH) is withdrawn. Consequently, τ strongly reduces with increase in V_{DS} .

As stated above, the average polarization $\langle P \rangle$ was maximum and τ was at a minimum at bias voltage V_{cr} . When $\langle P \rangle$ counteracted by thermal energy reaches the state of orientational equilibrium, the molecular dipoles by the virtue of maximum interacting Φ_{ij} induce the fastest desorption of the molecular dipoles of water from the surface of the DFC network.

B. Electric field induced trapping of charge carriers

Further investigation into the EAD mechanism at higher $V_{DS} (> V_{cr})$ yielded surprising results. The characteristic time τ which was predicted to saturate beyond $V_{DS} > V_{cr}$ due to maximum alignment of dipole moment along E , was found to increase almost linearly with V_{DS} between 3.4 V and 4.0 V.

The values of τ in our work are of the order of seconds which is much higher than the characteristic decay time associated with recombination of holes ($\sim ps$) [13] and annihilation at the electrodes ($\sim \mu s$). So it can be concluded that the decay in I was not a result of aforesaid mechanisms, but attributed to the entrapment of charges due to electric field confinement within the ultra-thin layer of water having higher dielectric constant ($\epsilon=80$), sandwiched between layers of lower dielectric materials, ssDNA ($\epsilon=2$) and air ($\epsilon=1$) [14] as shown in Figure 1 (inset b). The slow relaxation times of photo-carriers have previously been explained by trapping of photo-carriers at the metal/CNT interface, metal/semiconducting CNT contacts and the inter-tube barriers within the CNT networks [15]. Similar phenomenon of electric field assisted trapping of charged carriers when the DFC network was exposed to instantaneous decrease in RH was observed in our work.

Ionic charges are developed on the DFC network not only due to transfer of electrons on exposure to water molecules [11] but also as a result of bond breaking of the phosphate group and self dissociation of water molecules forming H_3O^+ and OH^- ions [16, 17]. The reduction in ion binding energy ($\Delta E_{ion} = \frac{l_c}{E}$) is inversely proportional to the applied dc electric field E where l_c is a constant for a system for a fixed temperature called the confinement length. This external field induced reduction in binding energy helps to retain the ions in their charged state, confined within the ultrathin water layer. The trapped charges take sufficiently long time to incorporate themselves into the electrical pathways in the DFC network and thus prevent the output current from fast recovery to the initial state I_i .

The weak deviation in τ from linear behavior may be due to contribution from Poole-Frenkel (PF) mechanism of electric field assisted lowering of shallow trap potential barrier arising due to defects on the nanotube walls [18]. The PF mechanism occurs at sufficiently high E and is responsible for incorporation of trapped charge carriers in the DFC conductive pathway which lowers τ . Trapping of charges dominates when increase in E lowers the binding energy of the ions facilitating increase of trapped charged species within the molecular layer of water preventing fast decay of I .

C. Conduction Mechanisms

In addition to charge transfer process, tunneling across chemisorbed water molecules on the surface of DFC also contributes to conductance at high RH (Figure 2). Water vapor exposed DFC can be approximated as consisting of several molecular dipoles taking part in the tunneling process which is partially driven by charging energy and partially by polarization [19]. When the DFC is exposed to RH, the transfer of electrons from the PB of the DFC to the water molecules, along with the local formation of ions due to breakage of PB, influences neighboring charge distribution which in turn induces reorientation of molecular orbitals in the π -way. Moreover, the conformational changes in DNA structure occurs on exposure to water molecules [20] which changes π -orbital overlap between the nucleobases and the surface of SWNT. Thus the electronic redistribution in the π -way of the DFC on being exposed to RH changes the conductance of DFC network. Again, interaction between the nucleobases and the water molecules breaks the π -bonds generating delocalized π -electrons which also contribute to the conduction mechanism through the π -way of the DFC.

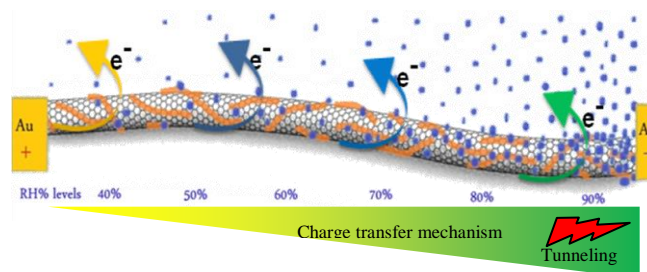


Figure 2 : Schematic representation of conduction mechanisms at low and high RH%

With increase in RH, more charges are transferred to the water molecules which increase the conductance of the DFC network. Due to scarcity of water molecules, tunneling is subdued at low RH due to higher tunneling distance between adjacent water molecules that causes higher potential barrier for tunneling of charges.

IV. CONCLUSIONS

The work demonstrates the electric field assisted desorption (EAD) of water molecules from the surface of the DFC network. With increase in electric field E the dipoles increasingly align themselves in the direction of the field to form a polarized system of mutually interacting dipoles and thereby increasing the potential energy of the system. Desorption allows the dipoles to return to a state of lower potential energy. Higher the state of polarization in DFC, more rapid is the rate of release of water molecules from its surface when the external stimulus (RH) is withdrawn.

In addition to the present study with water molecules reported here, our preliminary results (not reported here) involving N,N dimethylformamide (DMF) and ethanol suggest that DFC is sensitive towards polar molecules in general. The rate of desorption of polar chemical analytes from the DFC surface depends on their respective binding energy with the DFC surface. The stronger the binding energy larger is the

energy expended to drive away the molecules from the DFC surface. Thus relative binding energies of different polar analytes can be determined from the characteristic values of \mathcal{G} for different polar analytes chemisorbed on DFC. The chemical analyte with high \mathcal{G} is more strongly bound on the DFC surface than is an analyte with a relatively low \mathcal{G} . DNA functionalization of CNT not only increases the sensitivity of the humidity sensor but the weak bonds between DFC and water molecules facilitate fast desorption at a relatively low applied voltage.

With further increase in E the average polarization of the molecular dipole is maintained and τ is expected to saturate with E . But to our surprise we noticed that τ increases linearly above $V_{DS} = 3.2$ V. This phenomenon is attributable to the entrapment of charges in the ultrathin water layer which prevent availability of charges in the conducting network. In addition to charge transfer process, tunneling across chemisorbed water molecules on the surface of DFC also contributes to conductance at high RH.

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