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Carbon Nanotube Chemical and Mechanical Sensors

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I. Introduction

A single-walled carbon nanotube (SW-CNT) is a nano scale tube formed by a cylindrical shell of single atomic layer of carbon atoms. Nanotubes have diameter of a few nm and length up to 100μm so that they form extremely thin wires. The atomic structure of SW-CNT can be formed by wrapping a stripe of single atomic layer of graphite sheet along a certain direction, and this direction determines the diameter and chirality of the nanotubes. Experimental and theoretical studies have found that these nano-meter sized CNTs have novel electronic properties, which can be metallic or semiconducting, depending on their radius or chiralities [1-6]. Nanotubes can be used as electronic wire between two metal electrodes as shown in Fig. 1, and the conductance between the electrodes can be measured as a function of the gate bias voltage. Since the nanotube electronic property is a strong function of its atomic structure, mechanical deformations [7-8] or chemical doping can induce strong changes in conductance. Such changes can be easily detected by electron current signals, and these properties make CNTs extremely small sensors sensitive to their chemical and mechanical environments. In this paper, we present our theoretical and experimental studies on the subject of using SW-CNT as chemical and mechanical sensors.

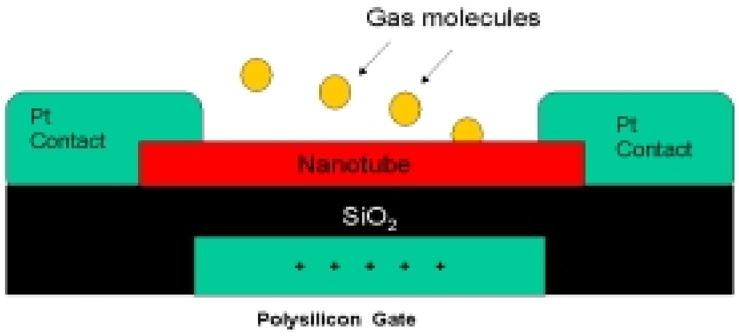


Fig.1 Schematic of a nanotube-based chemical sensor. The conducting properties of the nanotube change when chemicals in the surrounding environment bond to the tube. The absorbed molecules can act as dopants, shifting the Fermi energy of the nanotube. Similarly, the bonds formed between absorbed chemicals and the nanotube change the band-structure of the tube.

II. Nanotubes as Chemical Sensors: Chemical Adsorption of Gas Molecules

A. Experiments

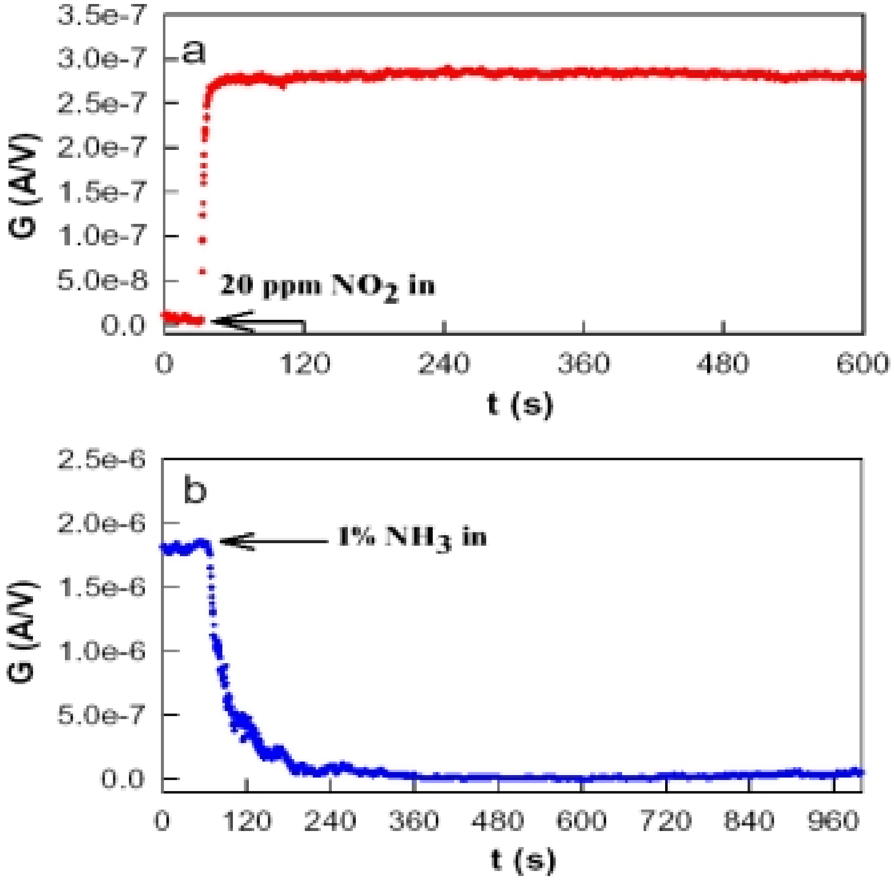


Fig. 2 Change of nanotube conductance when exposed to (a) NO_2 and (b) NH_3 gases.

Using the experimental structure shown in Fig. 1, Kong et al. found that nanotubes can be used for miniature chemical sensors to detect small concentrations of gas molecules with high sensitivity at room temperature [9]. Chemical sensors based on individual or ensembles of single-wall nanotubes can detect chemicals such as nitrous oxide (NO_2) and ammonia (NH_3) [9]. For a semiconducting single-wall nanotube exposed to 200 ppm of NO_2, it was found that the electrical conductance can increase by up to three orders of magnitude in a few seconds (Fig. 2a). On the other hand, exposure to 2% NH_3 caused the conductance to decrease by up to two orders of magnitude (Fig. 2b). As a general comparison, conventional solid-state sensors for NO_2 and NH_3 typically operate at temperatures over 400°C, and conducting polymers provide only limited sensitivity. Sensors made from single-wall nanotubes have high sensitivity and a fast response time at room temperature, which are important advantages for sensing applications.

B. Theory

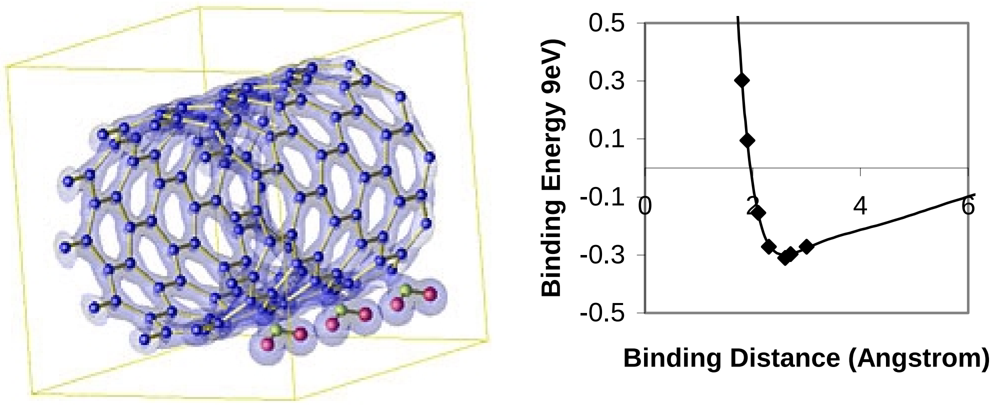


Fig 3 Left: Total valence electron charge density plot. The value of charge contour is 0.0015 (el/Å^3) showing the binding charge between the SWNT (10,0) and the NO_2 molecule. Three units are shown in this figure. Right: Binding energy curve for NO_2 interacting with (10,0) SWNT as a function of distance from NO_2 to the nanotube. The solid line curve is a fitting with universal binding curve.

The first-principles calculations are carried out on several representative molecules (NO_2, CO, NH_3, O_2, and H_2O) and SWNT using density functional theory. Figure 3 shows one binding configuration for NO_2 gas molecule on the (10,0) SWNT with three units. NO_2 gas molecule of this configuration is found to bind with SWNT with adsorption energy of 0.3 eV, and it is also found that the molecule has high diffusion kinetics on nanotube surfaces. Electron density analysis shows that charge transfer is induced from C atom to the NO_2 gas molecule leading to hole (or p-type) doping of semiconducting (10,0) nanotube. This increases hole carriers in the SWNT is responsible for the increase of conductance shown in Fig. 2a.

The simulation results for CO and SWNT system show no binding indicating that a bare nanotube may not work as a CO sensor, and this is in agreement with the experiment results [9]. For NH_3 and SWNT system, the molecule has stable binding energy when hydrogen atoms are pointing to the nanotube. The charge transfer is calculated to happen from NH_3 to nanotube leading to n-type doping (or hope compensation) of the nanotube corresponding to decreasing conductance shown in Fig. 2b. For O_2 case, O_2 can form a weak stable adsorption configuration with the (10,0) nanotube. Electron transfer direction is from the nanotube to the O_2 molecule that is consistent with experimental observation [10]. For H_2O case, one simulated molecular configuration shows repulsive interaction, and no charge transfer is observed when the water molecule is placed close to the nanotube surface. This result is consistent with experimental observation that the nanotube conductance is not significantly changed even when the nanotube is fully immersed in water. This finding demonstrates an important possibility of using nanotubes as biochemical sensors operating in water at physiological temperature.

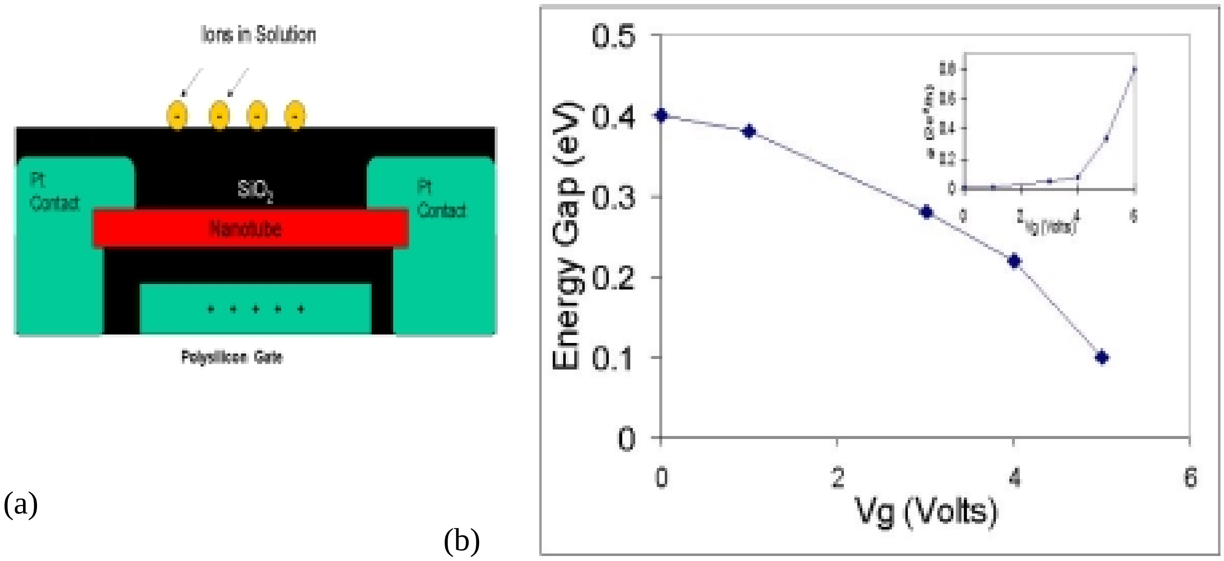


Fig.4 Schematic of an electrolyte insulator semiconductor (EIS) sensor, incorporating a nanotube sensing mechanism. A gate voltage Vg is applied to the semiconducting substrate and causes ions in the electrolyte to gather at the oxide surface. The conductance of the nanotube is modulated by the resulting electric field set up across the oxide. The strength of the electric field is used to identify the density and size of ions in the electrolyte.

We have discovered a novel electronic property of nanotubes which can be used to develop another sensing mechanism of ionic species without inducing charge transfer or doping effects. Fig. 4b shows the electric field induced band gap change of a semiconducting nanotube. Even though the gate voltage (Vg) does not induce doping, the reduced band gap leads to significant increase in conductance as shown in Fig. 4b inset.

An Electrolyte-insulator-semiconductor (EIS) structure can be used to measure ion concentrations and types. In a typical EIS sensor a voltage applied to the semiconductor back gate (Vg) attracts ions in the electrolyte to the oxide surface. The arrangement of ions in response to a specific Vg is determined by the size and charge of the ions. Measuring to gate capacitance (Cg) versus Vg can allow the ion species and concentration to be determined.

In Fig.4a, a carbon nanotube is used to modify the EIS sensor. In this design a semiconducting carbon nanotube is placed in the center of the dielectric. When ions are present in sufficient concentrations, a large electric field occurs across the insulator. This field narrows the energy-gap of the semiconducting nanotube, leading to an increased source-drain conductance. If there are insufficient ions in the electrolyte the resulting electric field intensity is weak and the nanotube energy gap change is reduced. Fig.4b illustrates the energy-gap change with Vg for the case of a large ion concentration.

III. CNT as Mechanical Sensor

A. Experiments: Electromechanical Properties of SWNTs

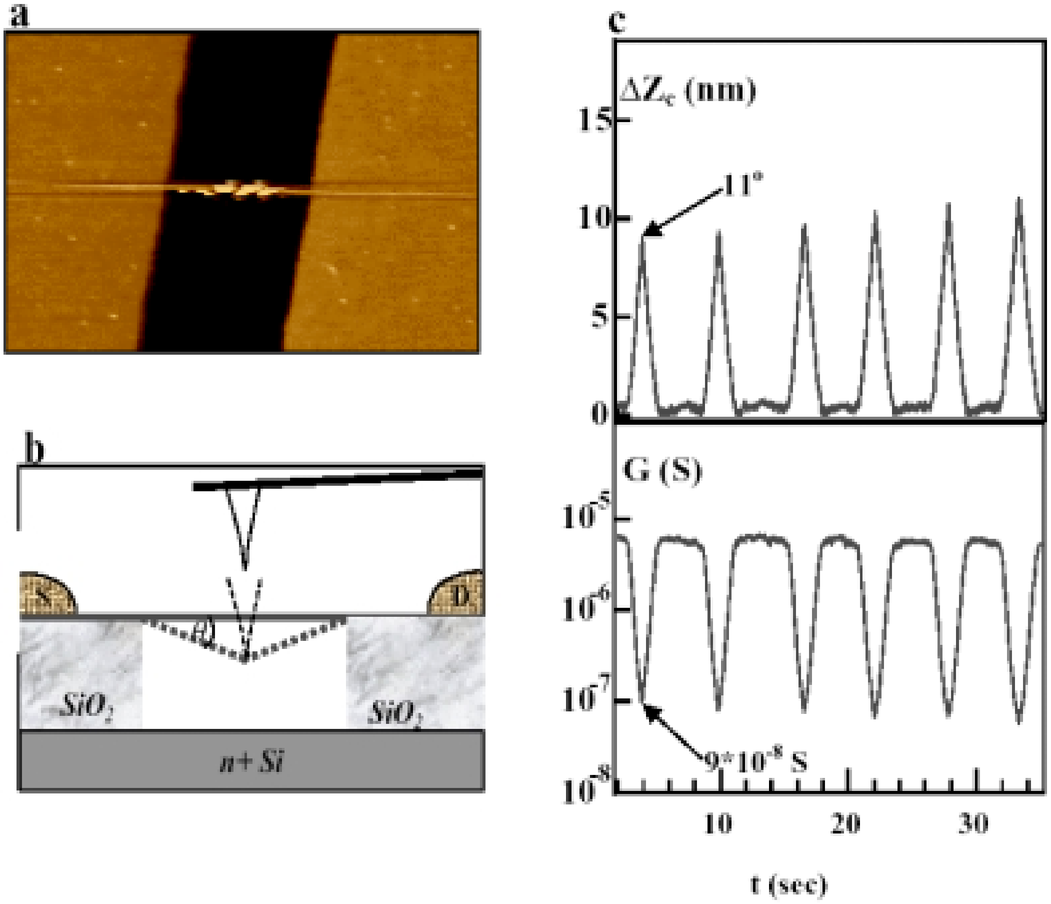


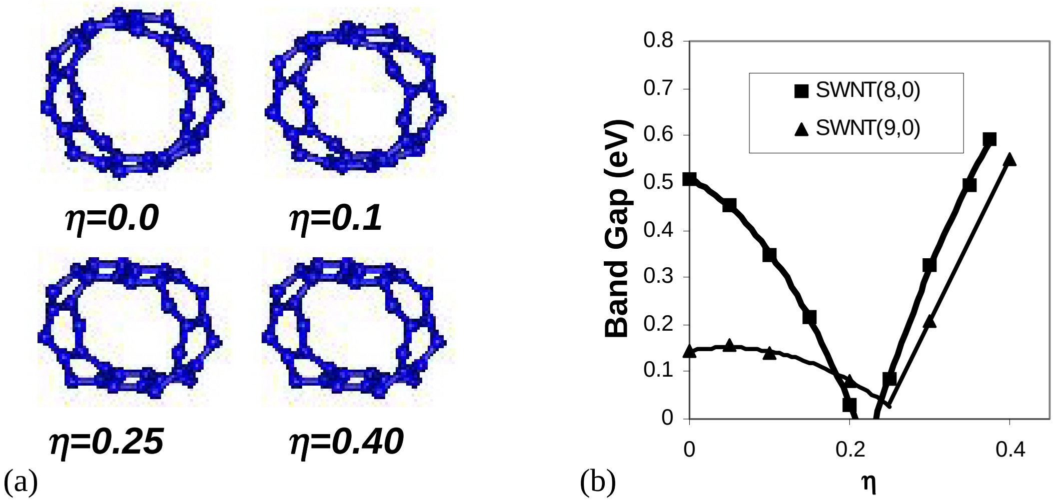
Fig. 5 Reversible conductance change induced by mechanical deformation of metallic nanotube using AFM tip. (a) AFM image of the nanotube on the trench. (b) Schematic illustration of the suspended nanotube and AFM tip induing the deformation. (c) Vertical displacement (ΔZ_C) and conductance (G) of nanotube during six reversible deformations with 6 sec interval.

Experimental investigation of the electromechanical properties of nanotubes can be carried out with suspended nanotubes as shown in Fig. 5. [11]. A nanotube can be grown from patterned catalyst sites across pre-fabricated trenches on SiO_2/Si substrates [11]. This leads to an individual SWNT that is partially suspended over the trenches (Fig. 5a). The suspended part of the nanotube can be manipulated with an AFM tip, while the resistance of the sample is being monitored (Fig. 5b). The nanotube conductance decreases each time the AFM tip pushes the nanotube down, but recovers as the tip retracts (Fig. 5c). The full reversibility of the nanotube electrical conductance upon tip retraction suggests that the metal-tube contacts are not affected each time when the tip deflects the suspended part of the nanotube. The observed change in sample conductance is entirely due to the mechanical deformation of the SWNT caused by the pushing tip, and this measurement demonstrates a possibility of developing nanotubes as mechanical sensors.

B. Theory of Electromechanical Coupling of Nanotubes

When the AFM tip pushes down the nanotube as shown in Fig. 5, the nanotube experiences several mechanical deformations at the same time. The nanotube length increases leading to tensile strain of the suspended part of the nanotube. This tensile strain induces a force pulling the nanotube section on SiO_2 surface which is rather strongly bound to the surface. As the tension increases over a critical value, the nanotube section on SiO_2 surface will slip to reduce the tension in the suspended section. The nanotube section in contact with the AFM tip will experience the cross sectional flattening. As the tip is removed from the nanotube, the nanotube returns to the initial straight configuration to reduce the strain energy. We will analyze in detail the nanotube electronic structure changes to elucidate the mechanism of the experimentally observed reversible conductance changes in Fig. 5.

Electronic structure of flattened CNTs. - The effects of cross section flattening distortion of SWNTs on their electronic properties are investigated through first-principles calculations. The geometry of a flattened nanotube is described in Fig. 6a. A deformation parameter η is defined as $\eta = (D_0\text{-}d)/D_0$, where D_0 is the original diameter of the nanotube, and d is the smallest diameter of the flattened cross section. For semiconduting (8,0) SWNT, the band gap first decreases leading to semiconductor-metal transition and then reopens leading to metal-semiconductor transition as a function of η. Similarly, metallic (or small band gap semiconducting) (9,0) SWNT undergoes band gap increase corresponding to metal-semiconductor transition as η increases. These results in Fig. 6b show that mechanical deformation can change electronic property of the nanotube from semiconductor to metal and vice versa.



(a) (b)

Fig.6 (a) The flattening of (9,0) carbon nanotube with four different degrees of deformation. (b) Energy band gap as a function of η for (8, 0) and (9, 0) SWNTs. The continuous lines are fitted through either quadratic or linear function.

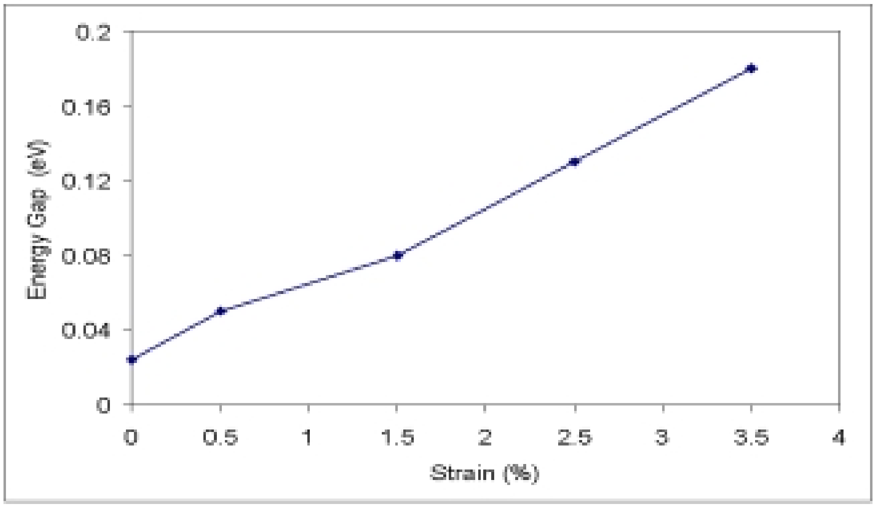


Fig.7 Band-gap versus tensile strain for a (9,0) zigzag nanotube. Under zero strain conditions a 24meV energy gap is predicted using pi-sigma band hybridization in a tight-binding simulation. For increased strain the energy-gap increases linearly. In this way the conductivity of the nanotube is very sensitive to mechanical forces that tend to stretch the tube.

Electronic structures of strained CNTs. - Experiments in Fig. 5 have shown that an atomic force microscope (AFM) tip can be used to gate a single walled nanotube (SWNT). When the AFM tip is pressed against the nanotube a large drop in tube conductance is observed (Fig. 5c), which turns the tube from a conducting channel to an insulator. Several mechanisms have been proposed to account for this gating effect, including localized deformation of the nanotube under the AFM tip as well as long range stretching of the nanotube. Curvature of the tube surface causes some small π-σ hybridization and can give rise to a small energy gap in metallic zigzag tubes. We use π-orbital axis vector (POAV) analysis to model the effect of such hybridization on carbon-carbon bonds. Using this analysis, single orbital tight-binding method [12] predicts a 24meV energy-gap for a (9,0) metallic nanotube. If a tensile strain is applied along the tube axis the π-σ hybridization is increased, and the energy-gap increases linearly with axial strain as shown in Fig.7. In this mechanical effect in nanotube conductivity can be used to measure the strain/deflection from a mechanical actuator shown in Fig. 5.

IV. Discussion and Future Applications

In summary, our experimental and theoretical studies show that CNTs can be used as chemical and mechanical sensors. We found the electronic properties of CNTs are sensitive to the adsorptions of certain type of gas molecules. External electric field is also shown to strongly modify the band structures of CNTs, which make CNTs a good sensor to surrounding ions. We also found that CNTs are sensitive to mechanical deformation such as flattening and tensile strain. The band gap of CNTs can be significantly modified in response to these deformations.

A promising direction to develop CNT as biosensor is to use intermediate materials, such as polymers, between CNT and system to be sensed as illustrated in Fig. 8. Our molecular dynamics (MD) simulation shows that certain polymers (e.g., polyethylene) can be chemically bonded to CNT, and a pyrene molecule can also be adsorbed on CNTs through Van der Waals potentials. These suggest a possibility to use these connecting polymers as channels to passing information from variety of molecular systems to CNTs.

Another possible direction to improve sensing capability is to use AC electron currents as signals. Previous studies are generally based on DC currents. We expect that frequency-dependent responses of the CNTs to external chemical gases and mechanical deformations will provide enhanced ability to distinguish more varied types of signals from environments.

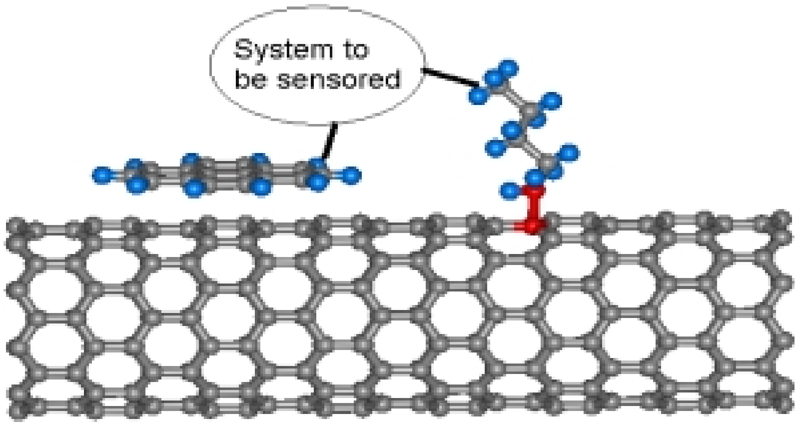


Fig. 8: Polymer-CNT composite system for a functionalized biosensor application. A polyethylene molecule is chemically bonded to a CNT and a pyrene molecular is adsorbed on the CNT through van der Waals interaction potential.

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