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Theoretical comparison between the response of single- and multiwalled carbon nanotubes based sensor as a function of the gas pressure

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ABSTRACT

We compare the efficiency of semiconducting singlewalled or multiwalled carbon nanotubes in resonator configuration as a function of the gas pressure. The resonance frequency shifts due to the dielectric changes of the resonator upon adsorption of gas are calculated on the basis of an effective polarizability distribution in the tube and the sensed system. Size and geometry of the sensor play an important role at high pressure while at low pressure, no clear difference is shown.

1. Introduction

For many areas in life sciences, the detection of molecules is of crucial interest to diagnostic disease or to screen new drug molecules. Of course, the ultimate goal of these topics is to develop systems showing ultra sensitivity and selectivity to rapidly detect the interesting species [1–7]. For instance several devices present at least only one of the previous properties but no one, to our knowledge is able to combine both of them. For example, semiconductor nanowires sensor based on electrical measurements can lead to selectively detection of DNA molecules or molecular inhibitor depending on their functionalization [8–10]. The SWNTs based sensor presents also interesting properties of ultra sensitivity since it has been shown to detect very small amount of molecules. The measurements based on the variations of the dielectric properties of the SWNT sensor could detect up sub ppm concentrations of acetone [11] but it is not able, however, to predict the composition of a mixing adsorbed on it [11]. These sensors are designed using a simple microchip circular disk resonator coated with singlewalled carbon nanotubes on the surface of the conducting disks. The measurements are conducted using a network analyser that determines the resonator return loss with an accuracy of 0.0125% (see for details Ref. [12]). To measure the presence of an adspecies, a microwave signal is sent to the region around the sensor where it can interact and produce a strong signal at the resonant frequency which depends directly on the dielectric permittivity and the geometry of the resonator. When adspecie is present this resonant frequency is shifted away leading to a detection of the molecule with an high sensitivity. Chopra et al. have also tried to increase the sensor capabilities by studying the behavior of MWNT based sensor compared to the SWNT based one [12,13]. The differences were minor at low concentration whereas high coverage of the sensor shows a real advantage in terms of sensitivity for the SWNT based sensor.

Besides, calculations based on a self-consistent description of the linear dielectric susceptibility of the SWNT at the atomic scale display a very good agreement for the behavior of the NT dielectric permittivity change *vs.* the adsorption of a sample of species including Ar, N_2, CO, etc. when compared to experimental data. Within this model, all the parameters have been widely studied and their influences on the sensor response have been modelized through simple empirical law showing the limitations of the sensor in terms of sensitivity.

Nevertheless, such a complete theoretical treatment is quite hard to perform when interested by larger molecule to detect (such as proteins or viruses) or by large specific area of the sensor (long SWNT or MWNT). To reach mesoscopic scale, an intermediate method has been proposed which incorporates a quasicontinuum description of the tube polarizabilities. This model has been developed to well reproduce detection of small molecule on a single SWNT [14] or biological molecules on MWNT [15] but no comparison has been performed to interpret the data of Chopra et al. [13]. The goal of this paper is to develop the model sensor based on a single SWNT to a well organized assembly of SWNT in order to obtain specific surface comparable to the MWNT. Saturation of the sensor at high coverage should also be improved in order to reproduce experimental data. After developing the model in Section 2, we present the system studied in this paper (Section 3) and the results observed (Section 4) for two particular gases (Kr a rare gas and HF a very toxic specie).

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2. Extension of the model

Microwave resonant sensors coated with semiconducting SWNT can detect a variety of molecular species through the change of their dielectric constant during adsorption. Upon exposure of few ppm of molecules, the relative frequency shift can be written

$$\frac{\Delta f}{f_0} = 1 - \left(\frac{\epsilon_{r0}}{\epsilon_r}\right)^{1/2} \tag{1}$$

f_0 is the resonant frequency of the nanotube without adspecies while Δf represents the shift of the resonant frequency upon adsorption of the gas. ϵ_r is the relative permittivity of the resonator including the admolecules influences and ϵ_{r0} the permittivity of the nanotube alone. Within the linear dielectric response of the system to a probe electric field $\vec{E}_0$, this relative shift can be written

$$\frac{\Delta f}{f_0} = 1 - \left(\frac{3 + Tr\left[\overleftrightarrow{\chi}_0\right]}{3 + Tr\left[\overleftrightarrow{\chi}\right]}\right)^{1/2} \tag{2}$$

where $Tr\left[\overleftrightarrow{\chi}_0\right]$ and $Tr\left[\overleftrightarrow{\chi}\right]$ means the trace over the three field directions of the linear susceptibility tensors of the bare CNT and molecule M adsorbed CNT. These tensors become tractable through semi-continuum approach both for long SWNT [14] or for MWNT [15] based sensor and depend only on the effective polarizability of the tube in each direction modified or not by the presence of the adspecies. For SWNT they can be written as

$$\overleftrightarrow{\chi}_0 = \frac{L}{V_T}\overleftrightarrow{\tilde{\alpha}}_T \tag{3}$$

for the bare SWNT with length L, volume V_T and carbon polarizability tensor $\overleftrightarrow{\tilde{\alpha}}_T$, and

$$\overleftrightarrow{\chi} \approx \frac{1}{V}\left[L\overleftrightarrow{\tilde{\alpha}}_T + \overleftrightarrow{\tilde{\alpha}}_m + \int_{-L/2}^{L/2}\overleftrightarrow{\approx{\alpha}}_T\,\mathrm{d}z\int\overleftrightarrow{T}(\vec{u}(z,\vec{r}_k))\overleftrightarrow{\tilde{\alpha}}_m\,\mathrm{d}\vec{r}_k + \int\overleftrightarrow{\tilde{\alpha}}_m\int_{-L/2}^{L/2}\overleftrightarrow{T}(\vec{u}(\vec{r}_k,z))\overleftrightarrow{\tilde{\alpha}}_T\,\mathrm{d}z\right] \tag{4}$$

for the total system SWNT + molecule with volume $V = V_T + V_M$, with $\overleftrightarrow{\tilde{\alpha}}_m$ the effective polarizability tensor of the m_{th} atom in the molecule M. $\overleftrightarrow{T}$ is the double gradient action tensor between one atom of the NT and one atom of M. $\overleftrightarrow{\approx{\alpha}}_T$ represents the effective polarizability tensor of the carbon atoms in the presence of an adspecies *M* [14].

It has been shown recently that when a MWNT is submitted to an external electric field $\vec{E}_0$, the carbon atoms are mutually polarized leading to an effective polarizability tensor $\overleftrightarrow{\tilde{\alpha}}_T$ per length unit. The parallel component is the sum of the parallel polarizabilities for each coaxial tube

$$\tilde{\alpha}_T^{//} = \sum_{R_T^i}^{R_T^O} 2\pi R_T da \tag{5}$$

while the perpendicular component $\tilde{\alpha}_\perp$ comes mainly from the few outer tubes in the MWNT. $\tilde{\alpha}_\perp$ can be approximated within a few percent ($\leq 5\%$) by the perpendicular component of the outer tube, as

$$\tilde{\alpha}_T^{\perp} = 2\pi (R_T^O)^2 db \tag{6}$$

$a = 0.5787$ and $b = 0.0187\,\text{Å}^{-1}$ are parameters calculated in Ref. [14]. Here, such a MWNT is characterized by its length L, its inner R_T^i and outer R_T^O radii with concentric coaxial stacking of tubes distant by $d = 3.4\,\text{Å}$. Note that $\overleftrightarrow{\approx{\alpha}}_T$ is expressed in the same terms than $\overleftrightarrow{\tilde{\alpha}}_T$ by replacing a by $a' = 0.5156$ and b by $b' = 0.0227\,\text{Å}^{-1}$.

This effective treatment can also be applied when the same molecule is adsorbed on both sensor. However when we interested in an assembly of SWNT or/and, respectively, a molecular assembly, these equations should be rewritten as:

$$\overleftrightarrow{\chi}_0 = \frac{L}{V_T}\sum_i\left(\int_{-L/2}^{L/2}\overleftrightarrow{\tilde{\alpha}}_T\,\mathrm{d}z_i + L\int_{-L/2}^{L/2}\int_{-L/2}^{L/2}\overleftrightarrow{\approx{\alpha}}_T\overleftrightarrow{T}(\vec{r}_{ij})\right)\overleftrightarrow{\tilde{\alpha}}_T\,\mathrm{d}z_j\,\mathrm{d}z_i \tag{7}$$

where V_T represents the total volume occupied by the carbon atom of the SWNTs. The susceptibility of the SWNT + adsorbates assemblies becomes

$$\overleftrightarrow{\chi} \approx \frac{1}{V}\Bigg[L\sum_i\int_{-L/2}^{L/2}\overleftrightarrow{\tilde{\alpha}}_{Ti}\,\mathrm{d}z_i + \sum_m\overleftrightarrow{\tilde{\alpha}}_m + L^2\sum_i\int_{-L/2}^{L/2}\int_{-L/2}^{L/2}\overleftrightarrow{\approx{\alpha}}_{Ti}\overleftrightarrow{T}(\vec{r}_{ij})\overleftrightarrow{\tilde{\alpha}}_{Tj}\,\mathrm{d}z_j\,\mathrm{d}z_i + \sum_i\sum_m\int_{-L/2}^{L/2}\overleftrightarrow{\approx{\alpha}}_{Ti}\overleftrightarrow{T}(\vec{r}_{im})\overleftrightarrow{\tilde{\alpha}}_m\,\mathrm{d}\vec{r}_k + \sum_i\sum_m\overleftrightarrow{\tilde{\alpha}}_m\int_{-L/2}^{L/2}\overleftrightarrow{T}(\vec{r}_{mi})\overleftrightarrow{\tilde{\alpha}}_{Ti}\,\mathrm{d}z_i + \sum_m\sum_n\overleftrightarrow{\tilde{\alpha}}_m\overleftrightarrow{T}(\vec{r}_{mn})\overleftrightarrow{\tilde{\alpha}}_n\Bigg] \tag{8}$$

For MWNT, no sum over tube indices is necessary since the effective polarizabilities (Eqs. (5) and (6)) take already into account for the influence of each tube on the other ones.

3. Description of the system

The frequency shifts (Eq. (1)) have been calculated for a SWNT exposed to a very small amounts of small molecules such as N_2, CO, O_2, $CH_3$and CH_3Br described as single polarizable centers, i.e. by limiting $\overleftrightarrow{\tilde{\alpha}}_m$ to the point molecule polarizability tensor in Eqs. (4) and (8). The excellent agreement obtained with concomitant experiments on SWNT coated resonator sensor exposed to the same molecules have led us to improve the approach by considering a biological system, with larger sizes than considered previously adsorbed on a MWNT with experimental characteristic (large external radius and high length). The choice of MWNT for such biological system was consistent since the sensor and sensed system sizes were equivalent to increase the response of the detection.

The goal of this letter is to study and to compare the dielectric response of the resonators (based on SWNT or MWNT) to the adsorption of an assembly of adsorbates (here Kr and HF), to know which sensor is the more efficient to detect molecules. We limit ourselves to a point description of the molecules and the geometry of the sensor is shown in Fig. 1. Each SWNT is described in terms of its length L (we chose $L = 0.1\,\mu$m) and its diameter D (here $D = 1.4$ nm) and arranged in a regular geometry reproducing a SWNT carpet. Indeed, modelizing a bundle does not change qualitatively the response of the sensor since only the external surface of the sensor is exposed to the adsorbate. The number of SWNT is chosen to reproduce the external radius of the MWNT (D_O) as depicted in Fig. 1. Besides, the MWNT presents the same length L and is characterized by its internal (D_I) and external (D_O) diameters respectively [13]. It should be noticed that the perfect circular geometry of the SWNT in the bundle could be modified due to high strain leading to a polygonization or a quasielliptical cross sections for the tubes