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Ab-initio calculations for a realistic sensor: A study of CO sensors based on nitrogen-rich carbon nanotubes

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The use of nanoscale low-dimensional systems could boost the sensitivity of gas sensors. In this work we simulate a nanoscopic sensor based on carbon nanotubes with a large number of binding sites using *ab initio* density

Function formalism. We present a recipe where the adsorption process is studied followed by conductance calculations of a single defect system and of more realistic disordered system considering different coverages of molecules as one would expect experimentally. We found that the sensitivity of the disordered system is enhanced by a factor of 5 when compared to the single defect one. Finally, our results from the atomistic electronic transport are used as input to a simple model that connects them to experimental parameters such as temperature and partial gas pressure, providing a procedure for simulating a realistic nanoscopic gas sensor. Using this methodology we show that nitrogen-rich carbon nanotubes could work at room temperature with extremely high sensitivity.

Topics

Ab-initio methods, **Density functional theory**, **Electronic structure methods**,

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Electronic transport, Localized states, Transport properties, Sensors, Nanotubes, Chemical elements, Carbon monoxide

I. INTRODUCTION

The possibility of detecting very low concentrations of chemical species is a fundamental issue for a variety of processes such as in, industrial and environmental monitoring, and medicine.[1–3] In particular, gas sensors are desired for detecting gas molecules which could present high toxicity such as carbon monoxide. Typically, solid-state sensors operate by resistance changes due to alien species binding to the surface of the device. From this perspective it is important to have solid state devices which could operate at room temperature and with higher sensitivity than the present semiconductor-based ones.[4,5] Nanoscopic one-dimensional structures could provide such progress. Due to their high surface area to volume ratio the adsorption of molecules on the surface of one-dimensional systems - even in small concentrations - can lead to significant changes on their electronic and transport properties.

Computer simulations using atomistic methods are an important predictive tool that can, in principle, give precise information about nanostructures in general. However, efforts to use them in nanoscopic sensor design have been largely hindered by the fact these devices comprise a large number of atoms with binding sites unpredictably distributed along the system. Furthermore one needs to associate the results from theoretical atomistic simulations to experimental parameters such as partial gas pressure and temperature.

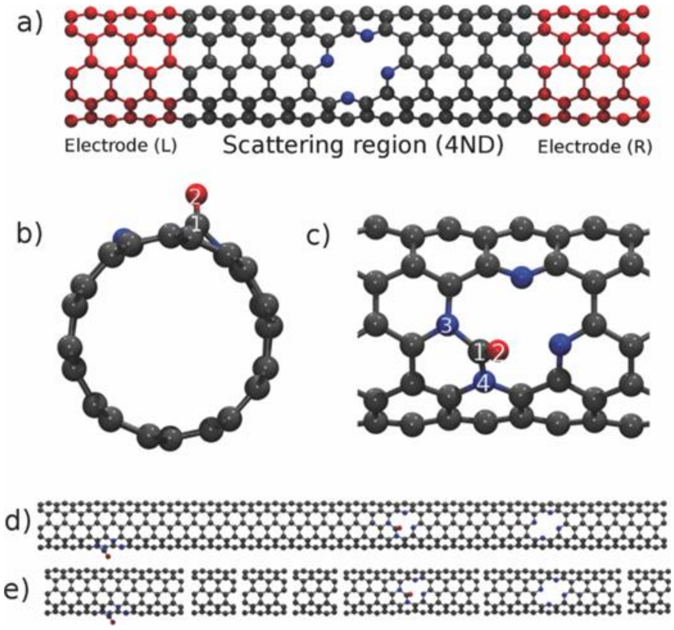
One of the most promising nanostructured materials for the development of new nanoscopic electronic devices is carbon nanotubes (CNT).[6,7] As mentioned above, its one-dimensional character also make it stand out as a candidate for possible gas sensoring applications,[8–12] although it has been demonstrated by theoretical approaches that pristine carbon nanotubes are usually inert to closed shell molecules.[13,14] One promising approach to circumvent this limiting factor is to functionalize them, creating reactive sites where molecules would bind more easily.[15–17] Carbon nanotubes with nitrogen atoms incorporated during growth - the so-called CN_x nanotubes - fall within this category[18,19] and are possible candidates to address this problem. In fact, experimental[20] as well as theoretical[21] works have demonstrated that those nitrogen-rich nanotubes could be assembled into devices that detect a variety of gases.

II. THEORETICAL FRAMEWORK

In this work we theoretically address the possibility of using functionalized carbon nanotubes for detecting CO molecules. This is achieved via a combination of *ab initio* density functional theory (DFT)[22,23] calculations and recursive Green's function methods.[19,21,24–27] This technique allows for precise atomistic simulations of the electronic transport properties of disordered systems as one would expect in experimental setups. We study the binding process of CO molecules as well as changes to the conductance due to different relative site occupancy in a disordered system; which provides information about the sensitivity of the device. We then combine our results to a simple model based on Lagnmuir's isotherm.[28,29] The key point is that this recipe directly links our theoretical calculations to experimental parameters such as temperature and pressure, and thus a route to realistically performing simulation-aided sensor design using one-dimensional systems. In the particular case of this work we use this recipe to infer that a CN_x nanotube could be used as a room-temperature CO sensor in the part per million (ppm) sensitivity range.

Previous theoretical calculations[19,21] show that the 4ND defect (shown in Fig. 1(a)) is the nitrogen defect with the lowest formation energy (by approximately 1 eV) in carbon nanotubes for a wide range of chemical potentials. Furthermore recent experiments[30] have obtained porphyrin-like defects such as these containing transition metal atoms. This is the defect used in our simulations. It consists of a divacany surrounded by four substitutional nitrogen atoms (4ND). Firstly, we have studied the absorption process of the carbon monoxide onto the nanotube defect by means of *ab initio* calculations using Density Functional Theory[22,23] as implemented on the SIESTA code.[31] For all total energy and structural relaxation calculations we have used the Generalized Gradient Approximation (GGA-PBE)[32] to treat the exchange-correlation potential, double-ζ polarized basis set (DZP) and standard norm-conserving pseudopotentials.[33] All calculations were spin polarized. For the nanotube with the 4ND defect, we have used a super cell of (25 Å × 25 Å × L_z), where L_z = 22.45 Å, which corresponds to 9 unit cells of a pristine (5,5) nanotube. Convergence tests showed that such a super cell size is enough to avoid image interaction due to the periodic boundary conditions used by SIESTA. The structural configurations were optimized through fully relaxing the atomic coordinates with a force criteria of 0.02 eV/Å.

FIG. 1.



Ball-and-Stick representation of: a) the whole device consisting of the scattering region (4*ND* defect) and the left-right-hand side electrodes. b) and c) correspond to the final structure achieved of the system 4*ND* + CO after the relaxing process viewed from different perspectives. d) A segment of the nanotube consisting of randomly distributed defects. e) Sliced segment showing examples of building blocks containing defects and pristine pieces that can be used to built the system.

For our transport calculations

we use a combination of DFT and the Non-Equilibrium Green's Function Formalism (NEGF).[35–38] In order to perform those calculations, the system is divided into three parts, namely, a central scattering corresponding to the 4ND defect - with or without the CO - and two (left- and right-hand side) electrodes as shown in Fig. 1(a).[39] Here, the electrodes are taken as pristine (5,5) carbon nanotubes. From the system's Green's function in the linear regime (including the effects of the electrodes via self-energies), the problem reduces to the Landauer Buttiker formalism and one can calculate the transmission coefficients $T(E)$.[40,41]

In principle the NEGF+DFT methodology can be used for calculating the transport properties of any system size. Nonetheless, in practice, for a description of a large number of molecules randomly distributed along the nanotube, as it is the case of a more realistic device, one must consider a system with tens of thousands of atoms using an atomistic description. We solve this problem using the recursive Green's function method.[19,21,24–27] Within this framework one can note that - in the case of a long one-dimensional system written in terms of a localized basis set - the total Hamiltonian can be written in tri-diagonal form. This is achieved by slicing the nanotube into segments as shown in figure 1(e). Each segment can be either a piece of the nanotube containing the nitrogen defect (with or without CO molecules adsorbed on them) or a segment of the pristine nanotube. It is noteworthy that each building block only couples to immediately adjacent ones and for non-adjacent segments the coupling is considered to be zero. The segments can be chosen in such a way that this condition is always satisfied. Each building block - on-site Hamiltonian and coupling matrix - of the final Hamiltonian for the entire system is obtained by an isolated DFT calculation, thus performed on a significantly smaller number of atoms. The total device is then assembled by randomly selecting segments for a fixed system length. For a system written in this form it is possible to show that the only required elements of the Green's function for a transport calculation are the ones connecting the left and right electrodes. In order to avoid calculating all Green's function elements we can remove exactly the degrees of freedom of each building block by decimating them into the posterior and anterior segments. This procedure can be repeated until there are no orbitals left inside the scattering region. Essentially, this recursive procedure consists of mapping the problem of a long disordered system into one of two electrodes coupled via an effective potential. More importantly, not all elements of the Green's function need to be calculated and the problem becomes tractable.

III. RESULTS AND DISCUSSIONS

A. Energetic properties and absorption process study

The questions one needs to address first is whether the CO molecule would bind to the 4ND defect, and furthermore, if other molecules present in air would have a similar effect. Our procedure consisted of building up several structures of 4ND nanotube + CO by positioning the molecule close to different atoms of the defect region. We have changed the distance and the molecule orientation relative to the nanotube. For all structures built, we performed total structural relaxation using a conjugate gradient (CG) method. Our results show that, independent of the initial configuration, the final geometry was identical to the one shown in Fig. 1(b) and 1(c). Moreover, in all cases we noted that binding occurred without a barrier.

The binding energy,

$$E_b = E_{total}(4ND + CO \qquad (1)$$

$$- E_{total}(CO),$$

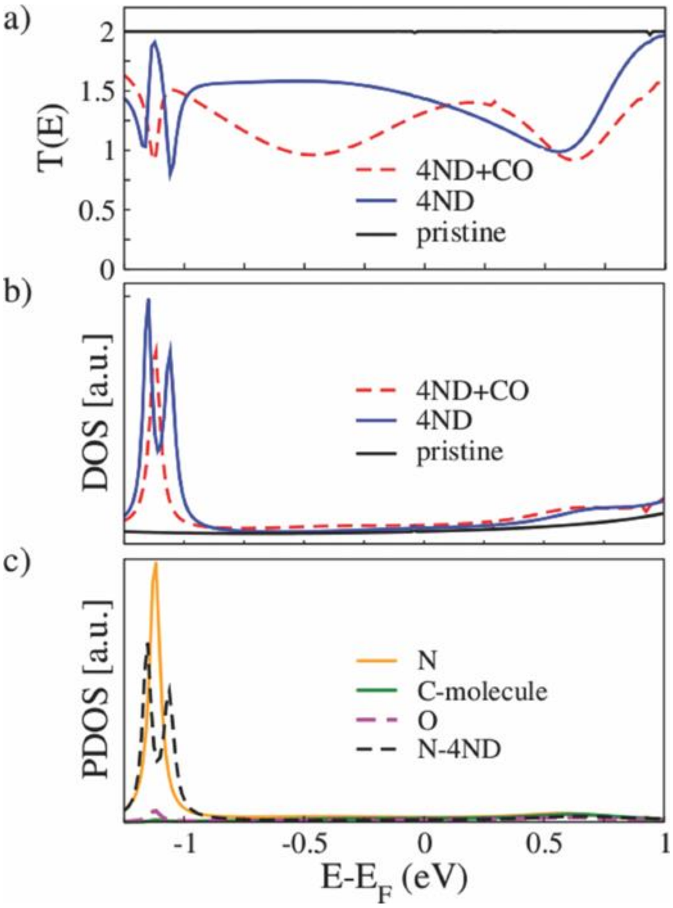
was also calculated by taking the difference in total energy E_{total} of the isolated constituents (nanotube with a 4ND defect and the CO molecule) with that of the final structure (dissociated molecule onto the nanotube). The value of $E_b = -0.75$ eV indicates that the molecule is strongly bonded to the defect and is in accordance to that found by others for CO bound to other types of nitrogen-doped nanotubes.[42] We attempted to absorb a second CO molecule onto the defect, however $E_b \simeq -0.026$ eV, which is approximately the thermal energy (K_BT) at room temperature, thus we can conclude that it is unlikely that a second molecule would remain at the anchoring site. Following the same procedure, we investigated the absorption process of other gases such as N_2, O_2, H_2 and H_2O - the main constituents of air. We have also considered CO_2 since in a incomplete combustion reaction one would expect this gas as sub product along with CO. Again, several structures were built changing the molecules' initial orientation related to the nanotube surface. For all of them, the molecules did not bind or dissociate onto the nanotube surface. Actually they turned away from the nanotube. Consequently one can conclude that the most important molecules present in air do not interfere when detecting CO. Furthermore, we do not expect a significant change with respect to nanotube diameter or chirality.[12,42]

Ab initio molecular dynamics calculations[34] were also performed considering 7 molecules of carbon monoxide inside the super cell box randomly distributed around the defect. We have used a temperature controlled Nosé thermostat ($T=300$ K and a generalized Nosé mass $Q = 10$ Ry fs^2) and a time step of 0.5 fs. A total of 4000 time-steps for the simulation were considered. After ~0.5 ps, a CO molecule binds onto the defect in the same way as the previously built structures and remains there throughout the rest of the simulation period, which reinforced our CG calculations.

B. Transport properties of a single defect

Subsequently, we turned to an investigation of the transport properties of a single 4ND nanotube with and without the dissociated molecule. In Fig. 2(a) we compare the transmittance as a function of energy for the systems 4ND molecule-free and 4ND plus carbon monoxide (the horizontal line at 2 G_0 represents the transmittance of a pristine (5,5) nanotube for the energy range considered here). It can be noted that the presence of the molecule significantly changes the shape of the curve, specially for energies close to −0.5 eV and −1 eV with respect to the Fermi energy (E_F). From the DOS shown in Fig. 2(b), we can see that there are localized states around −1 eV and those states are associated mainly with the nitrogen atoms of the defect, more specifically with their *p* orbitals. Those states are responsible for the variation of the transmittance for the same range of energy. Yet, the presence of the molecule does not remove all those states from the energy window. the Projected Density of States (PDOS) over the nitrogen and molecule atoms shown in Fig. 2(c) indicates that the minimum in the transmittance curve around −0.5 eV for the system 4ND+CO can not be associated to localized states created by the presence of the molecule. It is associated with a delocalized state over the entire defected tube. The shape of the transmission curve presents an overall behaviour around the Fermi level similar to the one observed for ammonia dissociation.[21] Most importantly there is a drop in the total transmission after adsorption of approximately 12%.

FIG. 2.



Transmittance (a) and DOS (b) of the 4ND+CO compared to 4ND molecule-free and pristine nanotube as function of energy; (c) Projected Density of States (PDOS) of 4ND+CO on the four nitrogen atoms of the defect region and on the atoms of the CO molecule.

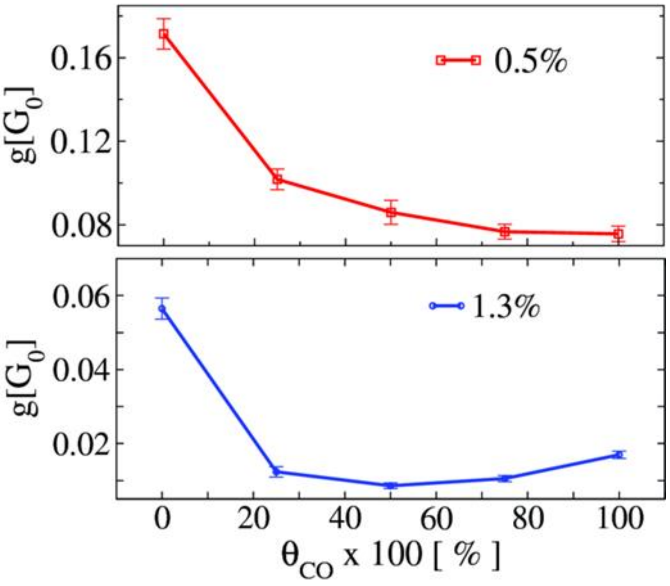
C. Transport properties of the disordered system

Although the conductance for a single impurity has dropped, it cannot be directly related to experiments. The processes of growing N-doped carbon nanotubes do not allow one to spatially control the position of the defects in these materials. Nonetheless, it is possible to have a reasonable control over the heteroatoms concentration.[43] Thus, those defects are actually randomly distributed along the nanotube length, not only in distance, but in relative orientation as well. It is also expected that, upon exposure to a particular molecule, not all binding sites will be populated. This is a key point in the sensitivity of the device and will largely depend on experimental conditions such as partial gas pressure as well as temperature.

Therefore, we turn to a more realistic system constituted by a very long carbon nanotube with randomly distributed 4ND defects. To achieve this we use the methodology discussed earlier. From independent DFT calculations, we obtain the Overlap and Hamiltonian matrix of each segment which are stored to built the whole scattering region matrices. In this work we have considered a ∼220 nm-long CN_x nanotube with 0.5% and 1.3% of nitrogen-mass concentration, which corresponds to a mean distance between defects of 9 nm and 3 nm, respectively. As mentioned previously, the whole system is built by randomly combining blocks containing defects and pristine ones (as shown in Fig. 1(d) and 1(e)) for a fixed CNT length and defect concentration. In addition to the randomness of the distribution of building blocks, our simulations were made considering defects with and without carbon monoxide in different complimentary proportions, i. e., the coverage $\theta_{\mathrm{CO}} = N_{\mathrm{CO}}/N_{\mathrm{4ND}}$, where N_{CO} corresponds to the total number of molecule-occupied sites and N_{4ND} is the total number of binding sites. This will yield important information on the sensitivity of the device, since it provides the relative change in conductance as one increases the coverage of CO molecules. Finally, since we have considered blocks of defects randomly distributed, we made approximately 50 realisations and calculated the average and the mean error of the conductance for each value of θ_{CO} and concentration.

In Fig. 3 the average of the conductance as a function of the gas coverage is shown. As more molecules are adsorbed onto the anchoring sites, the average of the conductance decreases following the trend observed for the isolated defect. For nitrogen-mass concentration of 1.3%, the average of the conductance decreases by 80% when the CO concentration goes from 0% to 50%. When the same analysis is done for nitrogen-mass concentration of 0.5%, the decreasing in the average of the conductance is 50%. This indicates that the sensitivity of the device is higher with higher concentrations of defects. However, it is important to note that, as the nitrogen-mass concentration changes from 0.5% to 1.3%, the absolute value of the average of the conductance decreases by a factor of 3; for example, for the respective conductance points with 0% CO, the conductance changes from $0.17G_0$ to $0.06G_0$, which could undermine the measurement. So, it is important to balance the concentration of defects and the decreasing of the absolute value of the conductance in order to achieve the best combination for gas sensors applications. It is also noteworthy that one would not expect qualitative changes to our results as we increase the diamenter of the nanotube as long as it remains metallic. For the case of semiconducting nanotubes, changes in conductance are expected provided a gate voltage is applied. This gate voltage could, in principle, be tuned to even enhance the effect.

FIG. 3.

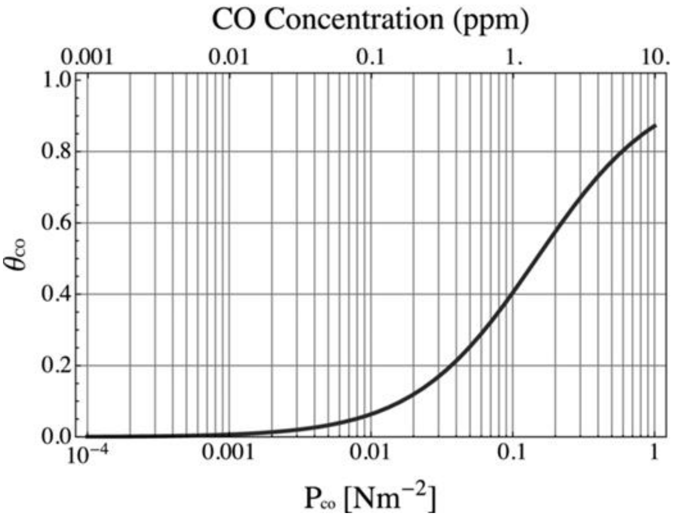


Average of the conductance (in units of $G_0 = 2e^2/h$) as a function of carbon monoxide coverage for 4ND defect for different mass concentration. The length of the nanotube was kept on 220 nm. Each point corresponds to an average of 50 realisations.

D. Room temperature detection

Finally, using a simple model it is possible directly relate our results to experiments. We assume that molecules can adsorb onto a certain number of binding sites with binding energy E_b. At a temperature T molecules will be constantly adsorbing and desorbing from such sites. When the system reaches equilibrium, at any given time θ_{CO} percent of these sites will be populated - on average - depending on gas pressure, temperature and E_b.[28,29] At room temperature and using the binding energy obtained from our DFT calculations one can simulate the so-called Langmuir isotherm for our device. They are shown in Fig. 4. From our results for the differential conductance we note that a coverage of 20 % would already give rise to significant changes. Since only CO molecules bind to the 4ND we only consider a partial pressure due to carbon monoxide, which in turn can be associated with the partial concentration of gas molecules. We can clearly see from our results that a CO concentration in the ppm range would already lead to significant changes in the conductance, thus indicating a device that can work at room temperature with high sensitivity.

FIG. 4.



Partial occupation of binding sites as a function of partial CO pressure (concentration) using Langmuir's isotherm. $E_b = -0.75$ eV and temperature T = 300 K.

IV. CONCLUSION

In summary, we have presented a methodology whereby one is able to use *ab initio* atomistic methods combined with Non-Equilibrium Green's Function electronic transport calculation to realistically simulate a nanoscopic gas sensor. This is achieved by i) first determining the binding properties of the molecule one wishes to detect via DFT calculations, ii) then calculating the electronic transport properties of an isolated defect and, most importantly, of a disordered system where the binding sites are randomly distributed along the device, which in turn allows for different gas coverages to be taken into account. iii) Finally we connect our conductance results to experimental parameters such as temperature and gas pressure. As a point in case we have determined that the 4ND defect in CN_x nanotubes is a very promising system to be used as gas sensor to detect carbon monoxide. As stated before, the molecule binds to the defect region without an energy barrier and with a significant binding energy of $E_b = -0.75$ eV. From charge transport calculations of a single defect, we have shown that the presence of just one molecule significantly changes the transmittance of the tube. Besides, when going from a single defect CNT to a more realistic one - with thousands of atoms and defects randomly distributed along the tube - the percentage change in the conductance goes from 12% to 50%(80%) for nitrogen concentration per mass of 0.5%(1.3%), which represents an ∼5-fold increase in the sensitivity of the device. Finally we directly relate our calculations, via the model presented, to experimentally controlled paremeters. Thus, we have provided a recipe for computer-assisted sensor design, by showing that CN_x carbon nanotubes can be used as yield a room-temperature sensor with ppm sensitivity.

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