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New insights in the adsorption of oxygen molecules on single walled carbon nanotubes

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ABSTRACT

We study the adsorption of molecular oxygen, both singlet and triplet forms on single-walled arm chair and zig-zag carbon nanotubes (CNTs) using density functional calculations. It is found that singlet oxygen has more potential of chemisorption than the ground state oxygen on the walls of the pristine CNTs and that the adsorption behaviour is different for semiconducting and metallic nanotubes. Molecular oxygen in its singlet state is found to adsorb strongly on semiconducting pristine nanosurfaces with appreciable binding energies and is found at bonding distances, ~1.47 Å from the side walls. Ground state oxygen is found to be only weakly physisorbed with distances in the range of 3.3–3.5 Å from the tube confirming the previous investigations. The effect of substitutional doping on the adsorption behaviour is studied and the adsorption is found to be enhanced with ground state oxygen coming closer at distances of ~1.5 Å, with appreciable charge transfer, on semiconducting nanotubes doped with boron, in contrast to the weak physisorption of triplet oxygen on the intrinsic tubes. This is an interesting finding, and as substitutional doping offers a permanent solution for possible use as sensor, CNTs doped with boron can find application as a potential molecular oxygen sensor. On doping the metallic nanotubes with boron, the adsorption of singlet oxygen is found to be enhanced with appreciable charge transfer compared to adsorption on the pristine form. We also find that singlet oxygen molecule dissociate near the semiconducting nanotube walls and chemically adsorb onto the surface to form a four membered dioxetane like ring. All the cases of relevant adsorption are accompanied by significant amount of charge transfer from the nanotube to the molecule.

1. Introduction

It has been established experimentally and theoretically that the properties of single-walled carbon nanotubes (SWCNT) can change appreciably with the presence of gaseous molecules and is demanding attention owing to its variety of applications in science and technology [1–8]. High surface to volume ratio, delocalized π electronic system and all carbon molecular structure makes them find their application in wide variety of fields like nanoelectronic devices, energy storage, chemical probes, biosensors, and field emission display [9–11]. The extremely high surface to volume ratio and hallow structures of nanomaterials are ideal for the adsorption of gas molecules. The most common gas sensing principle is the adsorption and desorption of gas molecules on sensing materials. Therefore increasing the contact interfaces between adsorbent and adsorbate, the sensitivity can be enhanced. It has been demonstrated that the electronic properties of CNTs are very sensitive to certain gas exposure [12,13]. CNTs are promising nanoscale molecular sensors for detecting gas molecules with fast response time and high sensitivity at room temperature. It has been reported that the semiconducting nanotubes show sensitivity towards parts per million concentrations of gas molecules [1,13]. The sensing mechanism is to detect the conductance change on CNTs induced by charge transfer to or from the gas molecules adsorbed on nanotube surface [14].

It has been reported experimentally, that small gap semiconducting nanotubes can be made conducting upon exposure to a very small amount of oxygen [1]. However the molecules that can be detected by CNT sensors are limited to the molecules that have large binding energies and charge transfers. Since the electronic properties of CNTs are strongly dependent on the delocalized π electron system, any chemical modification will influence their properties. Thus by the proper choice of the type of modification, the electronic properties of a CNT can be altered. When an intrinsic CNT is substitutionally doped with hetero atoms through the replacement of carbon atoms the local physical properties around the hetero atoms would undergo a significant change resulting in the change of the local chemical reactivity. Peng and Cho [14] studied theoretically the adsorption properties of carbon monoxide and water on semiconducting (8,0) single walled carbon nanotube doped with boron and nitrogen and found that doped

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SWCNTs showed sensitivity towards carbon monoxide whereas the intrinsic SWCNTs are insensitive.

Boron and nitrogen are the natural choice for doping CNTs since they differ in only one valence electron from the carbon atom and a relatively easy incorporation into the carbon honey comb lattice is achievable. Nitrogen atom substituted in graphite like way was calculated to differ only by 0.01 Å from the equilibrium position of a carbon atom [15]. In contrast, boron atoms are comparatively bigger than carbon atoms which produce a higher lattice strain and consequently a stronger deviation from the atom potential of the carbon honey comb lattice is expected [16]. Experimentalists have already demonstrated the growth of boron and nitrogen doped CNTs and $B_xC_yN_z$ nanotubes synthesized by carbon nanotube substitution reactions [17]. In these reactions, carbon atoms of pure CNTs have been substituted partially or totally by boron upon reaction with B_2O_3 with CNTs under inert atmosphere and substitution by nitrogen [18] occur by chemical vapour deposition using imidazole as the carbon–nitrogen precursor, with ferrocene as the catalyst.

There are few studies reported about ground state oxygen adsorption on CNTs [3,4,6,12]. The interaction of oxygen with CNTs has been investigated by few theoretical studies mostly using Density Functional Theory (DFT) with the Local Density Approximation (LDA) [3–7,19,20]. Peng and Cho [14] found that oxygen molecule physisorbs weakly on the outer surface of a (10,0) semi-conducting nanotube. Calculations based on local density approximations (LDA) of Density functional Theory (DFT) concluded that molecular oxygen binds to a semiconducting (8,0) nanotube with binding energy E = 0.25 eV at a distance of 2.7 Å [6]. In a similar study, based on LDA it was reported a binding energy of 0.08 eV at a distance of 2.9 Å, and using gradient functional methods (PBE), yielded binding energy of 0.004 eV and distances of 3.68–3.70 Å [20]. Oxygen molecule was found to be around 2.3–2.5 Å with a binding energy of 0.5 eV with various semiconducting SWCNTs employing DFT using LDA [3]. These previous results, by different methods, conclude that oxygen molecule in its ground state physisorb only weakly to the CNTs, though some results show an overestimation of binding energy as an artefact using LDA method.

Most of the existing theoretical methods concentrate only on triplet oxygen adsorption which binds weakly to the nanotubes [6,20]. Moreover the behaviour of singlet oxygen near nanotube surfaces is unknown but is very interesting from the point of view of fundamental understanding. Most recently, Kinoshita and coworkers [21] studied singlet oxygen adsorptions onto surfaces of graphene-like aromatic hydrocarbon molecules and found that singlet oxygen has the potential of chemisorption on to benzene, naphthalene and pyrene.

The study of singlet oxygen adsorption is also interesting because of the recent interest in its application in photodynamic therapy. Recent research suggests interesting application of oxygen adsorption on carbon nanotubes in radiotherapy that the carbon nanotubes can adsorb oxygen and deliver it into the oxygen deficient tumor cells [22]. The spin state can play a vital role in these applications since singlet oxygen can cure cancerous tissues and may find application as an alternate to photodynamic therapy [23] as there are serious limitations to this technique, for example, the inability of the photosensitizer to reach thick tissues. If the CNTs can be used to selectively bind and deliver the singlet oxygen to the damaged tissues the limitations with photodynamic therapy can be rectified.

In this work, we have investigated the behaviour of singlet and triplet oxygen molecules near intrinsic and doped zig-zag and arm-chair nanotubes using density functional calculations. Although the properties of carbon nanotubes are nothing short of exceptional, there are nonetheless many areas in nano and molecular-electronics, optics, electromechanics or chemistry where pristine tubes are not the most appropriate. This is because of their rather wide spread characteristic physical and chemical properties, which is a result of the diameter and helicity variations of nanotube samples. Substitutional doping of nanotubes is expected to provide solutions for these limitations. Indeed, the incorporation of boron and nitrogen atoms into the honeycomb lattice leads to chemical activation of the rather passive surface of a carbon nanotube and adds additional electronic states around the Fermi level [16]. We have also done substitutional doping with hetero atoms, boron and nitrogen to understand the effect of doping on adsorption properties of oxygen, both singlet and triplet forms on the nanotubes.

2. Model and computational method

We have used the Kohn–Sham density functional theory and made use of the most popular B3LYP hybrid functional in Gaussian09 which applies corrections for both gradient and exchange correlations [24]. DFT methods are attractive because they include the effects of electron correlation and take into account for the instantaneous interactions of pairs of electrons with opposite spin. The B3LYP functional combines the Becke generalized gradient approximation (GGA) exchange potential based with HartreeFock (HF) exact exchange plus the Lee–Yang–Parr correlation functional.B3LYP has been found to provide accurate cohesive energies, ionization potentials and electron affinities for a range of finite molecules. The inclusion of HF exchange helps to correct for the self energy problem with regular DFT formulations. Among the most popular functionals of GGA are PW91, PBE (Gradient corrected correlation functionals) and Local density approximations VWN [25–27]. PW91 is particular for a GGA functional, is the combination of exchange and correlation functional, developed by Perdew and Wang. VWN is an exchange correlation potential given by Vosko, Wilk and Nusair which is widely used in LDA calculations which reproduces the random phase approximation results for a uniform electron gas [27]. The accuracy of DFT depends on the choice of approximation of the universal exchange correlation functional.

Density functional theory (DFT) with hybrid functional B3LYP with basis set 6-31G (d) has been employed for optimization studies of various gas molecules along the side walls of SWCNTs. Semiconducting zig-zag (5,0), metallic arm chair (5,5) SWCNTs with eight layers constituting 80 carbon atoms and (8,0) semiconducting zig-zag SWCNT with 6 layers constituting 96 carbon atoms are considered and end carbon atoms of the tube are saturated with hydrogen atoms in order to satisfy the valence in all the cases. Adsorption energy is calculated using the formula,

$$E_{ads} = \text{Energy of } (CNT + O_2) - (\text{Energy of CNT} + \text{Energy of } O_2).$$

In the case of doped systems, one of the carbon atoms is replaced by boron or nitrogen and the adjacent bonds of the hetero atom were made single in order to satisfy the valency.

3. Results and discussion

3.1. Adsorption on pristine nanotubes

We have studied the behaviour of oxygen in its singlet and triplet forms on the side walls of (5,0), (8,0) and (5,5) nanotubes. The results of these calculations are compiled in Table 1. Adsorption energy in eV per mole, distance of the molecule from the nanotube (Å) and charge transfer from Mulliken population analysis are given. Negative sign indicates charge transfer from the nanotube to gas molecule and positive sign indicates charge transfer from the gas molecule to nanotube. Singlet oxygen is found to be at a distance of 1.46 Å from the (5,0) and 1.47 Å from the (8,0) semiconducting CNTs which shows a very good affinity and there is