



A comparative study of O₂ adsorbed carbon nanotubes

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Abstract

First-principles, density functional calculations show that O₂ adsorbed single-wall carbon nanotubes (SWNT) show dramatic differences depending on the type of the tube. Upon O₂ physisorption, the zig-zag SWNT remains semi-conducting, while the metallicity of the armchair is lifted for the spin-down bands. The spin-up bands continue to cross at the Fermi level, and make the system metallic only for one type of spin. The singlet bound state of O₂ occurs at the bridge site of the (6, 6) SWNT at small distance from the surface of the tube. However, for the hollow site, the molecule dissociates when it comes close to the surface.

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1. Introduction

Recent studies have shown that the physical properties of single-wall carbon nanotubes (SWNTs) can be modified by the adsorption of foreign atoms or molecules [1–5]. Collins et al. [1] found that exposure to air or oxygen dramatically influences electrical resistance and the thermoelectric power of a semiconducting SWNT. A semiconducting SWNT, which can be reversibly converted to a conductor by a small concentration of adsorbed oxygen has been proposed as a candidate for chemical sensor devices [1]. Several theoretical works aimed at the understanding of physical and chemical mechanisms underlying the enhanced conduction upon O₂ exposure [6–12]. Jhi et al. [6]

were first, who investigated the effect of adsorbed O₂ on the semiconducting (8,0) SWNT by using pseudopotential plane wave method. Furthermore, they found the empty energy bands derived from oxygen states overlap with the valence band of SWNT and gives rise to a finite density of states at E_F . In view of these results, they attributed the observed reduced resistance of the semiconducting SWNT upon O₂ exposure [1] to the hole-doping [6]. In contrast to this finding, the experiments by Derycke et al. [13] have showed that the main effect of oxygen physisorption is not to dope the bulk of the tube, but to modify the barriers of the metal-semiconductor contact. While hole-doping picture for the O₂ physisorbed on the zig-zag semiconducting tube has been refused by recent first-principle studies [14,15], very little known about the O₂ physisorbed armchair SWNTs.

This Letter presents an extensive comparative study of O₂ adsorption on the zig-zag and

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armchair SWNTs as a function of molecule-tube distance, and points out dramatic differences in their behavior.

2. Method

We performed first-principles total energy and electronic structure calculations using pseudopotential planewave method within spin-polarized, generalized gradient approximation (GGA) [16]. Calculations were carried out using periodically repeating tetragonal supercell with in-plane lattice constants $a_{sc} = b_{sc}$ and c_{sc} along the axis of the tube. To reduce the O_2 – O_2 coupling, we used $c_{sc} = 2c$, i.e., double cell (c being the one dimensional lattice constant of the tube). Ultrasoft pseudopotentials [17] for C and O, the kinetic energy cut-off up to 400 eV and 6–12 Monkhorst–Pack [18] special \mathbf{k} -points were used. For all systems we studied all atomic positions of adsorbate and SWNT, as well as c are fully optimized by using the conjugate gradient method. We studied the adsorption of O_2 on the (8,0) zig-zag SWNT and (6,6) armchair SWNT. The bare (8,0) tube is a semiconductor with a band gap of 0.64 eV. The (6,6) tube is a metal with π^* -conduction and π -valance bands crossing at E_F . The contribution of the short range (chemical) interaction to the binding energy is calculated by using the expression

$$E_b = E_T[\text{SWNT}] + E_T[\text{O}_2] - E_T[\text{O}_2 + \text{SWNT}] \quad (1)$$

in terms of the total energies of the fully optimized bare SWNT, ($E_T[\text{SWNT}]$), the individual molecule, ($E_T[\text{O}_2]$), and O_2 adsorbed on the SWNT, ($E_T[\text{O}_2 + \text{SWNT}]$), which are calculated by using the same supercell, and the same parameters of calculation. By definition, $E_s > 0$ corresponds to a stable and exothermic bonding.

3. Results and discussions

3.1. Triplet-physisorption state

Four possible adsorption sites on the (8,0) zig-zag tube are on top of the axial C–C bonds (A-site); above the center of the hexagonal carbon

rings (H-sites); on top of the zig-zag C–C bond (Z-site) and perpendicular to the axis of the tube and above two adjacent zig-zag bonds (T-site). The spin-polarized GGA total energy calculations, which were performed by optimizing the positions of 64 C and two O atoms, as well as c_{sc} , yield the magnetic (triplet) ground state with the magnetic moment $\mu \sim 2\mu_B$ (Bohr Magneton). The corresponding chemical binding energies, E_s , were calculated -5 , 4 , -27 and 37 meV at A-, H-, Z-, T-sites, respectively [14]. Owing to the double-cell, the contribution of O_2 – O_2 coupling is negligible in the calculated binding energies. These energies indicate that the chemical interaction between O_2 and (8,0) tube is very weak and the character of the bond is physisorption. By including the Van der Waals energy, E_{vdw} , which is calculated in terms of the asymptotic form of the Lifshitz formula [19–21], the total binding energies, $E_b + E_{vdw}$, are found 120, 159, 158 and 191 meV, for A-, H-, Z-, and T-sites, respectively, and the average O_2 –SWNT distance $d \sim 2.9 \text{ \AA}$. Apparently, the physisorption bond of O_2 on the (8,0) SWNT is stabilized by Van der Waals interaction. The physisorption energy was measured [22] to be 190 meV, which is in agreement with our calculated binding energy at T-site.

In the supercell geometry, the electron energy states of the individual molecule physisorbed on the SWNT form spin-up and spin-down energy bands. The energy band structure corresponding to physisorption of O_2 at the A-site of the (8,0) SWNT is presented in Fig. 1. We see that $\text{Opp}\pi^*(\downarrow)$ and $\text{Opp}\pi^*(\uparrow)$ bands split by ~ 2 eV. There occurs a band gap of ~ 0.2 eV between the top of the valance band of SWNT (E_V) and empty $\text{Opp}\pi^*(\downarrow)$ band. As pointed out by recent studies [14,15] this situation invalidates the metallization or the hole-doping.

The physisorption of O_2 on the (6,6) armchair SWNT has been investigated for the bridge (B-) and hollow (H-) sites described as inset in Fig. 2. Similar to the (8,0) tube, O_2 adsorbed on the (6,6) SWNT has magnetic ground state ($\mu \sim 1.9\mu_B$) for both sites. The spin-polarized electronic energy band structures are presented in Fig. 2. Because of relatively weak O_2 –SWNT interaction, the overall features of the bands associated with O_2 are

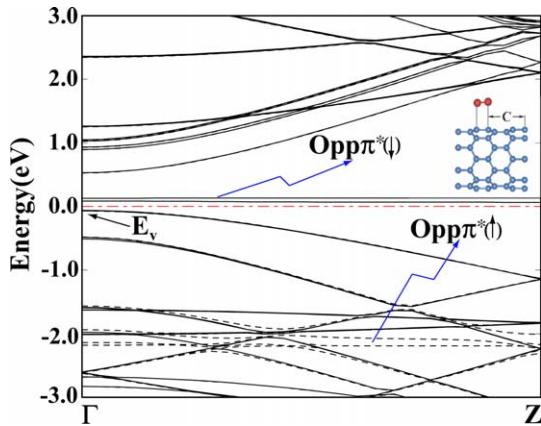


Fig. 1. Electronic structure of O_2 physisorbed on the A-site of the (8, 0) SWNT (described by inset) calculated by spin polarized GGA with the atomic structure fully optimized in the double-cell. The spin-up and spin-down bands corresponding to the triplet ground state are shown by broken and continuous lines, respectively. The zero energy is set at the Fermi level. E_v indicates the top of the valance band.

similar. The π^* -conduction and π -valence bands of the bare (6, 6) SWNT, which normally cross at E_F , split upon O_2 physisorption. While the spin-up bands continue to cross, spin-down bands open a gap. At the middle of the gap two $O_{pp}\pi^*(\downarrow)$ bands are located. Accordingly, the metallic (6, 6) SWNT continues to be metallic with a constant density of states at E_F only for spin-up electrons. Such a situation may occur due to symmetry breaking [23] and is certainly important for spintronics.

3.2. Singlet bound state

The interaction of O_2 with SWNT as a function of O_2 -SWNT distance d has been examined by calculating the total energy E_T , bond distance of O_2 , d_{O-O} , magnetic moment μ , and energy gap E_g of the O_2 physisorbed (8, 0) SWNT. In these calculations, d has been constrained, but d_{O-O} has been relaxed. Fig. 3a shows the variation of the ratio of E_T , d_{O-O} , μ , E_g to their corresponding equilibrium value at $d^0 = 2.89 \text{ \AA}$. We see that $|E_T|$ decreases in the range $1.6 \text{ \AA} < d < 2.9 \text{ \AA}$. For a wide range of O_2 -SWNT separation, E_g continues to exist, and the total energy difference between the spin-polarized and spin-unpolarized O_2 +

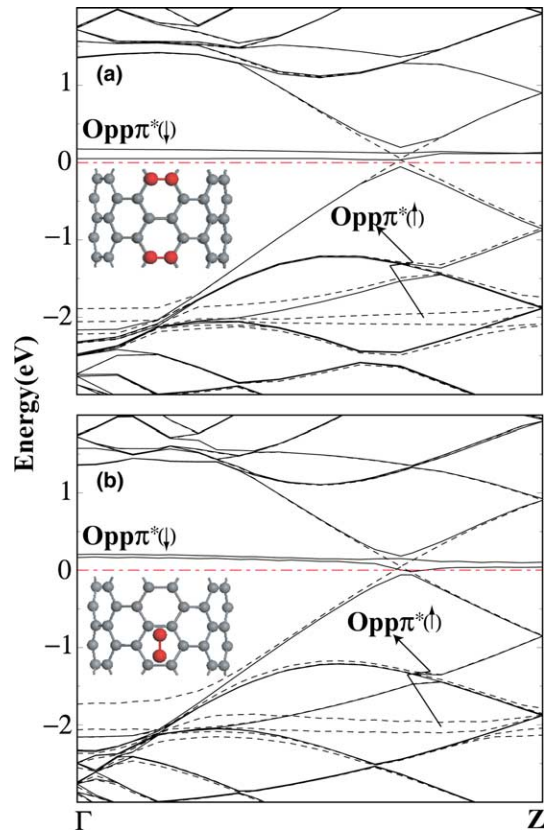


Fig. 2. Energy band structures of O_2 physisorbed on the (6, 6) armchair SWNT. (a) B-site, (b) H-site. Spin-up and spin-down bands are shown by broken and continuous lines.

SWNT, (i.e., $\Delta E_T = 0.86 \text{ eV}$) induces the gap E_g and prevents it from closing. For $\sim 1.6 \text{ \AA} < d < d^0$ a strong perpendicular force F_{\perp} is generated on the O_2 molecule to push it away from SWNT. The magnetic moment of O_2 + SWNT diminishes at a distance $d < 2 \text{ \AA}$. Moreover, the singlet state of adsorbed O_2 leads to a bound state at the Z-site at $d = 1.48 \text{ \AA}$ and 0.8 eV above the corresponding physisorption state. (i.e., $E_T - E_T^0 = 0.8 \text{ eV}$). Similar singlet bound state occurs also at the A-site at $d = 1.47 \text{ \AA}$ and 0.45 eV above the physisorption state of the A-site at $d = 2.89 \text{ \AA}$. These singlet bound states in Fig. 3b correspond to local minima on the Born–Oppenheimer surface and are separated from the more energetic physisorption states by an energy barrier. We note that these states [14,24] are neither easily accessible from the

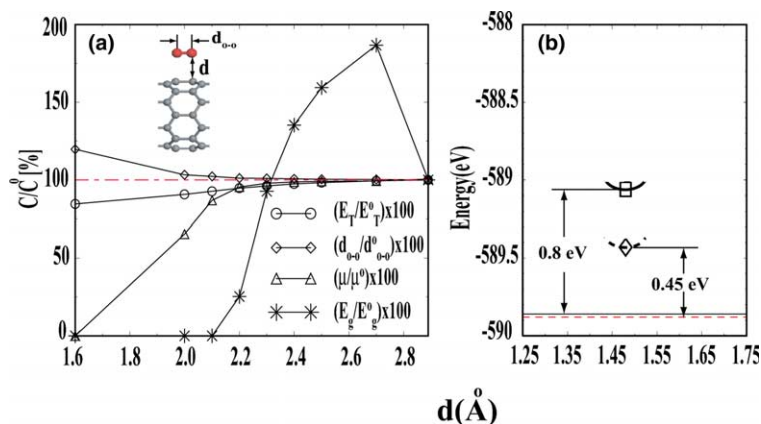


Fig. 3. (a) Variation of the percentage values of C/C^0 (E_T/E_T^0 ; d_{O-O}/d_{O-O}^0 ; μ/μ^0 ; and E_g/E_g^0) with the O_2 -SWNT separation d . E_T^0 , d_{O-O}^0 , μ^0 and E_g^0 corresponds to the stable physisorption state with $d^0 = 2.89$ Å at the A-site. (b) The total energies of the singlet bound states found at small d at Z-site (square) and at the A-site (diamond). The total energy of the triplet ground state corresponding to the physisorption state for the Z- and A-sites at $d \sim 2.9$ Å are shown by continuous and broken lines.

physisorption state, nor supporting the hole-doping picture because the band gap of ~ 0.5 eV. However, O_2 adsorbed at the H-site of the (6,6) SWNT behave differently. In Fig. 4, we show the variation of $E_T(d)$, $F_L(d)$, $\mu(d)$ and $d_{O-O}(d)$ in the range of $1.3 \text{ Å} < d < 3 \text{ Å}$. As d decreases from the physisorption distance, $\mu(d)$ decreases rapidly and vanishes at $d = 2$ Å. The variation of E_T , F_L and d_{O-O} indicates that, at $d \sim 1.25$ Å, d_{O-O} is increased to 2.5 Å and hence the bond is broken, i.e., O_2 molecule dissociates into two O atoms. Passing over a barrier, $|E_T|$ increases and $|F_L(d)|$ decreases. In contrast to this site, the O_2 molecule has a bound singlet state at the B-site with $d_{O-O} = 1.51$ Å.

In conclusion, our first-principle, plane wave calculation carried out for $1.3 \text{ Å} \lesssim d \lesssim 3.1 \text{ Å}$ show that O_2 can be physisorbed to both (8,0) and (6,6) SWNT, and has a triplet ground state. Binding is stabilized by the Van der Waals interaction. In the case of (8,0), the empty $O_{pp}\pi^*(\downarrow)$ state of O_2 occurs ~ 0.2 eV above the top of valance band. The metallic (6,6) tube continues to be metallic for spin-up bands of SWNT which cross at E_F . Spin-down bands of SWNT open a gap, and empty $O_{pp}\pi^*(\downarrow)$ states are located in this gap. We obtained different behavior for different tubes as d decreases. While O_2 physisorbed at the H-site of the (6,6) SWNT is dissociated at $d \sim 1.25$ Å.

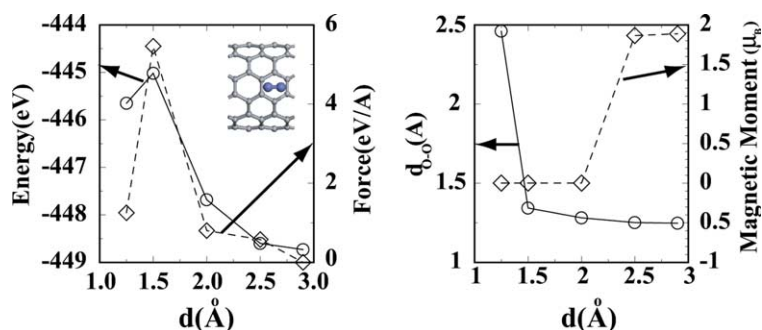


Fig. 4. Variation of the total energy, E_T ; force acting on the O_2 molecule, F_L ; bond distance of O_2 , d_{O-O} ; and magnetic moment, μ with O_2 -(6,6) SWNT distance d for O_2 adsorbed on the H-site of the (6,6) SWNT. Calculations have been performed in the double-cell.

Singlet bound states of O₂ occur at $d \sim 1.47 \text{ \AA}$ for the A- and Z-sites of the (8, 0) SWNT, and for the B-site of the (6, 6) SWNT. These conclusions are expected to be valid for similar tubes with different radii, except that the binding energies are modified due to the curvature effect [4,5].

Acknowledgements

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