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The Effect of Hydroxyl Group on the Electronic Structure of Carbon Nanotubes with Different Diameters[1]

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Abstract—A single hydroxyl group is functionalized on both sides of one ring of several carbon nanotubes (CNT) as CNT−OH. The electronic structure and chemical bonding parameters are studied with the help of quantum theory of atoms in molecules (QTAIM). Anionic states of the CNT−O as deprotonated hydroxyl are studied in order to get insight into the nature of CNT−OH species, considering frozen and relaxed geometries of CNT−O compounds. The results show a significant difference between inside or outside substituted hydroxyl groups; and also complicated behavior of the CNT's diameter, and it can be concluded that hydroxyl group can be used to tune the CNT's properties, effectively, in interesting application of these nanostructures.

INTRODUCTION

Carbon nanotubes (CNTs) are attracting materials for energy storage, sensors and molecular electronics. Different functional groups have been grafted on CNTs for improving their properties. Recently CNTs were used as catalyst support for oxygen reduction reaction in fuel cells because of their high electronic conductance, high corrosion stability and hydrophobicity [1−12].

Despite many benefits of CNTs, their low specific surface area (compared to activated carbon) and difficulty in direct deposition of metal particles limits their use [1−12].

Density functional theory (DFT) and specially, B3LYP is generally used in molecular modeling studies to predict structure, spectroscopic parameters and energy changes of small, middle and large size molecules [13, 14]. Different studies has been performed for prediction of CNTs with different substituents, such as carboxyl (COOH), hydroxyl (OH), thionyl (SO), sulfonyl (SO_3H), nitrile (CN), nitro (NO_2), carbonyl (CO), ester (C(O)O), and acid anhydride (C(O)O(O)C) groups. Hydroxyl group is the simplest functional group for molecular modeling studies.

Several studies have been reported on hydroxyl functional group on CNTs. The structure, energy and energy gaps of CNTs with hydroxyl group at the end of CNTs with different length and diameters were evaluated by theoretical calculations [13, 14]. Also the role

of −OH, −COOH, and $−CONH_2$ functional groups at the end of CNTs were considered via theoretical and experimental studies [6−14].

In the preset study we optimize different single-walled CNTs from (5.1) to (8.1) with a hydroxyl functional group that are attached outside or inside, and focus on the OH bond, charge and energy of oxygen and hydrogen atoms, and deprotonated structure, in which CNT−OH loses a proton and converts to an anion.

COMPUTATIONAL DETAILS

The geometries and electronic wave functions of the species are obtained at B3LYP/6-311++G** level of theory [15] using Gaussian 03 software package [16]. The electronic structures are analyzed in the context of quantum theory of atoms in molecules (QTAIM) [17] using AIM2000 software [18]. Bonding critical points (BCP) are the first-order saddle points in the electron density scalar field. They play a cornerstone role in the description of chemical bonds [19]. The electron density at BCP, ρ_{BCP}, is a measure of bond strength, while its Laplacian, $\nabla^2\rho_{BCP}$, reflects its sharing character. Two-center delocalization indices between A and B atoms, $\delta(A−B)$, are also reported to estimate the number of delocalized electrons between the corresponding atomic basins [20]. Finally, the difference of atomic charges and energies before and after

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QTAIM parameters of hydroxyl group atoms and their difference with the corresponding anions

	Ia	IIa	IIIa	IVa	Ic	IIc	IIIc	IVc
$\rho BCP(O-H)$	0.362	0.340	0.344	0.351	0.383	0.370	0.363	0.362
$\nabla^2 \rho BCP(O-H)$	−2.095	−2.045	−2.059	−2.085	−2.427	−2.144	−2.080	−2.072
$q(H)$	0.608	0.630	0.629	0.607	0.633	0.596	0.600	0.606
$E(H)$	−0.341	−0.313	−0.317	−0.336	−0.346	−0.357	−0.348	−0.344
$\delta(O-H)$	0.606	0.509	0.529	0.567	0.488	0.575	0.603	0.605
$\Delta qf(O)$	0.061	0.057	0.115	0.104	0.051	−0.014	0.082	0.099
$\Delta Ef(O)$	0.366	0.338	0.389	0.385	0.362	0.303	0.367	0.368
ΔEf	0.614	0.635	0.625	0.618	0.566	0.590	0.602	0.608
$\Delta qr(O)$	−0.147	−0.216	−0.228	−0.227	−0.016	0.038	−0.009	−0.184
$\Delta Er(O)$	−0.254	−0.298	−0.316	−0.311	−0.243	−0.328	−0.414	−0.294
ΔEr	−0.014	−0.030	−0.025	−0.024	−0.089	−0.036	−0.050	−0.012
$\Delta q(O)$	−0.086	−0.159	−0.113	−0.123	0.035	0.023	0.072	−0.085
$\Delta E(O)$	0.112	0.040	0.073	0.074	0.119	−0.025	−0.047	0.075
ΔE	0.600	0.605	0.600	0.594	0.476	0.554	0.552	0.595

the loss of hydrogen are computed, for both frozen and relaxed anions' geometries.

RESULTS AND DISCUSSION

The optimized neutral and anionic (after removal of hydroxyl's hydrogen atom) molecular structures are shown in the figure, and labeled from **I** to **IV**, corresponding to the CNT's number of lateral rings from 5 to 8; **a** to **b**, corresponding to neutral and anionic states for hydroxyl group placed outside; and **c** to **d**, the same as **a**, **b**, for hydroxyl group placed inside.

Table contains QTAIM analysis data, including electron density at the hydroxyl O−H bond's BCP, $\rho BCP(O-H)$, and its Laplacian, $\nabla^2 \rho BCP(O-H)$, delocalization index, $\delta(O-H)$, charge and energy of hydroxyl's hydrogen atom, $q(H)$ and $E(H)$, respectively. Difference of charge and energy of hydroxyl's oxygen atom between three states including, neutral, frozen anion, and relaxed anion, are also displayed in table, where the molecular geometry of frozen anion is not optimized, in contrast to relaxed anion which is optimized under no constrain. The subscript indices in $\Delta q(O)$ and $\Delta E(O)$, as f and r denotes charge and energy differences for the oxygen atom for frozen and relaxed geometries, respectively.

The values of $\rho BCP(O-H)$ reveal that the strongest OH bond belongs to the smallest CNT, which is also reflected in $\nabla^2 \rho BCP(O-H)$ values which predicts higher sharing character for this bond in the smallest CNT. Although delocalization indices show higher electron delocalization between hydrogen and oxygen atoms in outside hydroxyl in smallest CNT, the reverse

is true for inside hydroxyl in which the smallest CNT possesses the less delocalization index. Charge and energy values of hydrogen and oxygen atoms do not vary orderly with the above trends which is a result of multicharacter of OH bonding as partially covalent, partially electrostatic.

In contrast to $\rho BCP(O-H)$ prediction for the strength of OH bond, the least value of ΔE_f belongs to the smallest CNT, and one concludes that the excess electron is more stabilized on the smallest CNT, possibly due to some slight and complicated conjugation of hydroxyl with the rings. Moreover, the smallest CNT has the lowest absolute value of relaxation energy, ΔE_r, for outside hydroxyl, which is predictable as this system is highly constrained and its molecular geometry is not as free as the others. This situation for inside hydroxyls is different, and the smallest CNT is more stabilized by relaxation. This can be also described by the strain phenomenon, where the CNT wall senses higher stress for smaller CNTs when the hydroxyl group is located inside the CNT; and thus smaller CNTs gain higher stabilization by relaxation. The overall deprotonation energies, ΔE, shows least value for the smallest CNT when hydroxyl is inside; and close values for outside hydroxyls. Also, the values of $\Delta E(O)$ show how the smallest CNT is distinguished from the others, in which the oxygen atom is highly destabilized during the deprotonation. An interesting point can be seen in **IIc** and **IIIc**, where the oxygen atom is stabilized by deprotonation, which reveals that the CNT might has compensated the loss of proton for the oxygen atom. In addition, despite to $\Delta q(O)$ for outside hydroxyls which are all negative, they are not
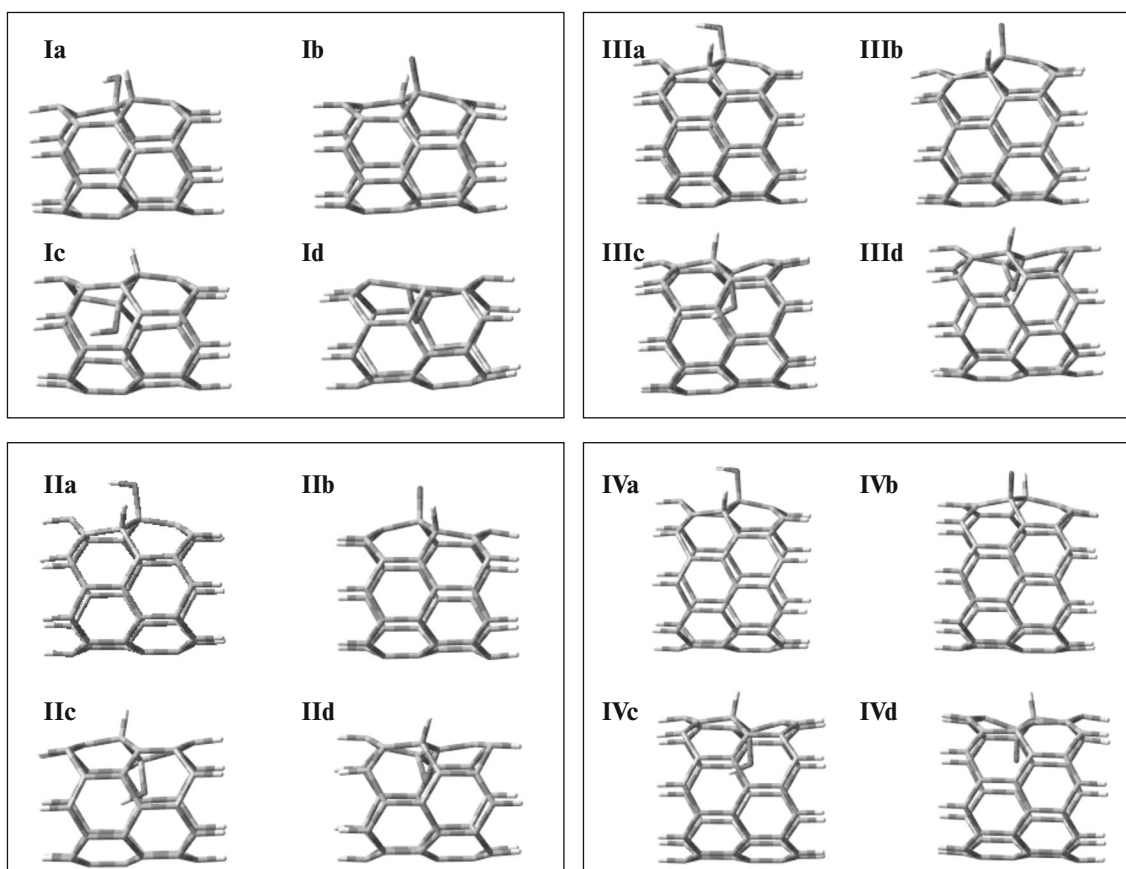
Molecular structures of the studied CNTs functionalized by hydroxyl group and the corresponding deprotonated state as anion.

for inside hydroxyl and three of them are positive; which is a reflection of distinct behavior of inside hydroxyl group.

CONCLUSION

In the present work, the effect of two parameters on the electronic structure of functionalized CNTs are considered: location of hydroxyl group, and size of the CNT. It is shown that if the hydroxyl group is located inside the CNT, it has strong influence on the CNT's properties. Also, the diameter of CNT affects the electronic structure in the complex manner, which might be due to inappropriate conjugation of carbon atoms of the CNT and slight conjugation to the hydroxyl group.

Since CNTs are commonly employed as seminconductors, hydroxyl group can be used as controlling agent to tune the CNT's properties, as the conduction phenomenon is highly sensitive to the electronic structure. Therefore, precise determination of CNT's diameter and location of functionalization with hydroxyl groups makes these materials much more effective in the world of CNT nanoelectronics and nanotechnology.

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