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Band structure of metallic single-walled carbon nanotubes

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Abstract - *Carbon Nanotubes are one-dimensional nanostructured materials that play a key role in future electronics since Moore's Law is proceeding to its end. The electronic structure of a single-walled zigzag carbon nanotube has been studied theoretically by employing extended Huckel theory. For the (n, 0) nanotube with n=3p where p ∈ [2, 8] the observed bandgap ranges from 0.126 to 0.009 eV. Computed results arise from hybridization between π and σ orbital, caused by the curvature effects. The results reveal that "metallic" zigzag CNT studied are not actually metals but exhibit narrow gap semiconductor behavior. Computed data indicate that the bandgap depends inversely on the square of the diameter of the tube.*

Keywords: CNT, Band structure, Bandgap, Semiconducting, diameter

1. INTRODUCTION

Semiconductors are the basics of electronics. The first transistor was discovered by Bardeen & Brattain, 1949 using a semiconducting germanium block [1]. Moore's law [2] has been a prominent pathway to assign the pace at which transistor dimensions are continuously decreasing. But, since Moore's law is proceeding towards its end, new semiconducting one-dimensional nanostructured materials may play a prime role in future electronics. In particular, Carbon Nanotubes (CNT) has been the focal point of interest among researchers due to their wide spectrum of applications ranging from nanoelectronics to chemical and biological sensors [3-11]. Recent findings [12,13] using density functional theory (DFT) calculations predict the potential application of zigzag CNTs as an anode for Mg-ion batteries.

CNT discovered in 1991 by Ijima [14] are regarded as the most fascinating materials due to their unique electrical, mechanical and thermal properties. Single-wall carbon nanotubes (SWCNT) are hollow cylinders of carbon atoms bound together in a hexagonal pattern and are formed by rolling a two-dimensional graphene sheet [15]. A multiwall nanotube is made up of more than one SWCNT with different diameters and a common axis. In comparison to multi-walled nanotubes, the SWCNT are principally narrower and have a diameter near to one nanometer. The SWCNT has a feature that they tend to be curved rather than straight [16].

The geometry, as well as the electronic properties of CNT, are described by a chiral vector $\vec{C} = n\vec{a} + m\vec{b}$, where a pair of indices (n, m) correlates the two crystallographic equivalent sites on the graphene sheet [17]. On the basis of Chiral indices (n, m) CNT is classified as a zigzag, armchair, or chiral. When either n or m is zero, the rolling of the graphene sheet leads to the formation of zigzag CNT. When n=m the CNT is armchair and the conditions when n≠m CNT has chiral structure.

The diameter and the helical arrangement are the two important factors that decide whether CNT will be metal or semiconductor [18]. Armchair (n, n) CNT is always metallic in nature. But the nature of zigzag CNT for chirality (n, m), for n=3p and m=0, is controversial. The simple zone folding tight binding theoretical calculations [19] predicts that (3p, 0) tubes are metallic and other zigzag CNTs are semiconducting. However, on the basis of low-temperature atomically resolved scanning tunneling microscopy, Ouyang et al [20] showed that some (3p,0) zigzag nanotubes have a fundamental gap and hence are semiconductors. B3LYP hybrid density functional theory [21] also indicated that (3p, 0) nanotubes have a small bandgap. To get a clear picture there is a need for more experimental work in this area but they are very complicated and costly as well. Hence, keeping this in mind the electronic band structure of (3p, 0) zigzag nanotubes is explored using a non-equilibrium green function approach with self-consistent calculations [22].

2. STRUCTURE OF CNT

Carbon nanotubes are cylindrical shaped allotropes of carbon. CNT are 1-Dimensional nanostructured materials obtained by rolling up of a graphene sheet into a cylinder [6]. A graphene sheet is a single layer of carbon atoms packed into 2-dimensional honeycomb lattice structure. The diameter of CNT is of the order of few nanometers and micrometer sized length. They are capped at their ends by one half of a fullerene-like molecule. CNT belong to the family of fullerene, which also incorporate buckyballs. Buckyballs are spherical in shape whereas CNT is cylindrical. They are most promising material in the field of nanotechnology.

Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometers. The material used to exhibit peculiar applications at this dimensional scale. At this small scale, to

be more precise at nanoscale the physical, chemical properties of material are entirely different from the properties of individual atoms or molecules. A nano meter is one Billionth of a meter and numerically it is written as 10^{-9}m or 10Å.

The name CNT is derived from their size, as the diameter of CNT is of the order of few nanometers [14]. The chemical bonding in CNT is mainly composed of sp^2 bonds. This bonding structure results in a molecular structure which has unique strength, it is even stronger than sp^3 bonds present in diamond. Carbon nanotubes are strongest material as explored by human being. The value of Young's moduli of CNT is higher than 1TPa, which is five times higher than steel. Carbon nanotubes are much lighter than steel making them a true material for reinforcements in polymer matrix composites. Due to exceptionally unique properties it can be regarded as the material of 21st century and is gaining the attention of scientific community.

3. BACKGROUND BEHIND THE THEORY

Condensed matter Physics is the branch of Physics that deals with the study of matter in its condensed state, broadly linked with solid and liquid phase materials. The matter in the sold phase can be easily understood by adopting solid state physics. This branch of Physics depends on numerous numbers of experimental, theoretical and computational techniques for a detailed and in depth knowledge of these materials. The electronic band structure of materials can be explored through the use of computational techniques. The band structure of various materials having different length scale ranging from macro scale to sub atomic scale can be computed.

Initially Physicist relies on classical or Newtonian mechanics to explain various conceptual phenomena. At macro scale, classical mechanics is successful in explaining the entire phenomenon. Inconsistency is seemed at smaller length scales and rules of classical mechanics are not rigidly followed in this length scale. On atomic and sub atomic scales there was a need of new concepts that are capable of explaining the observed experimental results. Later, with the advancements Physicist adopted a new approach named Quantum mechanics, which is capable of furnishing proper explanation of experimental findings at atomic and subatomic scales. Schrodinger proposed the wave equation, which opened the door to completely explain the properties of materials.

4. THEORY

The model incorporates atom-like orbitals as the basis functions. The adjusted parameters in the theory are only the diagonal matrix elements of the Hamiltonian and the slater-type orbitals (STO) as a basis set [23]. STOs are the product of radially decaying functions and spherical harmonics. The knowledge of defined basis function is used to compute the overlap matrix element S and hence it leads to the determination of the off-diagonal Hamiltonian matrix elements H. The extended Huckel theory is associated with a non-equilibrium Green function to determine the transport properties of nanotubes. To accomplish this task, the band structure of (3p, 0) (with p=2 to 8) zigzag CNT has been computed using simulation technique CNTbands in nanoHUB [24].

5. COMPUTATIONAL DETAIL

For computation of electronic properties of SWCNT the nanohub simulator CNTbands [24] has been used. The output of the simulator incorporates physical and electronic properties, including diameter, band structure and band gap. CNTbands is a rappturized suite of simulation tool for carbon nanotube and graphene nanoribbons. This rappturized (Rapid Application Infrastructure) suite of simulation tool generates a graphical interface of electronic structure once the user defines the outputs and inputs. . Rappture, a toolkit on nanoHUB has been the major source for the rapid development and robust deployment of simulation package. With a consistent interface, one can easily achieve the goal in less time and cost as compared to the experimental scenario developed for this specified purpose. The simulator needs input, one of the inputs being structure. Structure has to be chosen as the input parameter. Two carbon nanostructures CNT and GNR are available on the simulator. If CNT is selected then one can adopt the Extended Huckel Theory model—which take into account carriers from a single s, P_z, P_x, and P_y orbital for each carbon atom. Other important parameter that is needed as input is Chirality. The chirality (n.m) defines the type of carbon nanotube. Here n and m must be positive integers. Upon execution of simulation and using these input parameters the rappturized suite of simulation tool generates a graphical interface of the electronic structure of nanoribbons having varying chirality (width). Rappturized software has an advantage that it is user friendly as well as one can easily achieve the goal in less time and cost but has the disadvantage of being less rigorous.

6. RESULT

The molecular structure of one-dimensional nanomaterial (n, 0) comprises 2n number of hexagons in a unit cell. The circumference of any CNT is expressed in terms of the chiral vector, which couples two crystallographically equivalent sites on a two-dimensional graphene sheet [17]. With the increase in the value of p in n=3p, the circumference and diameter of nanotubes increases. The distance between the center of any two carbon atoms in the nanostructure is taken to be 1.42 Å and is kept fixed for all zigzag CNT having different diameters.

Firstly, the band structure of an extremely small diameter nanotube (6, 0) is evaluated and is displayed in Fig. 1 (a). It is observed that a very small bandgap = 0.126 eV opens at the Fermi level due to a strong hybridization effect. However, the previous results obtained using the tight-binding method [19] demonstrated that in (6, 0) nanotube the top of the valence band touches the bottom of the conduction band at Γ point. The discrepancy may be due to the fact that in the tight binding method no π- σ hybridization effects were taken. But, for such a small diameter d=0.4697nm the hybridization effects, caused by the curvature of CNT, play a crucial role. Bands higher than the Fermi level are the antibonding π bonds. Bands lower than the Fermi level are bonding π bonds and bonding $sp^2\sigma$ bonds having low energy. The π* and σ* states mix and repel each other and hence resulting in a lower pure π* state.

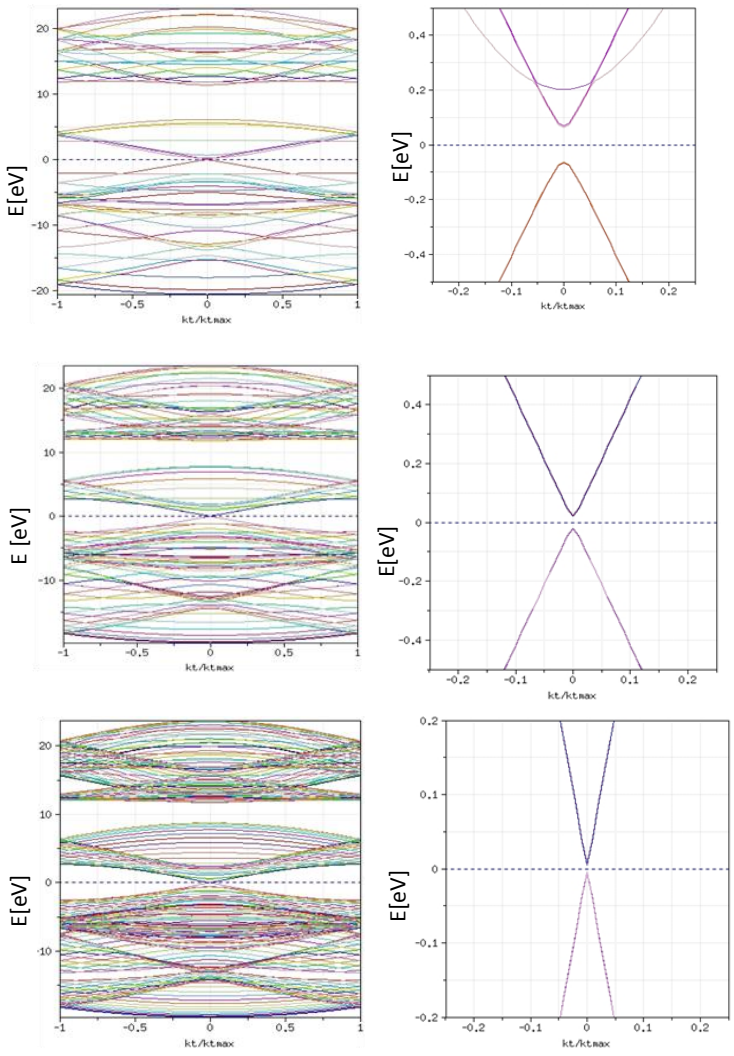

Fig.1: Electronic band structure of (6, 0); (12. 0) and (24, 0) zigzag CNT (Top) with enlarged scale near the Fermi energy (at Right). The Fermi level is at E_F=0.0eV.

Table -1 Band gap of (3p, 0) SWCNT with different chirality along with structural parameter

Chirality Index	Diameter [nm]	Bandgap [eV]
(6, 0)	0.4697	0.1260
(9, 0)	0.7130	0.0800
(12, 0)	0.9394	0.0440
(15, 0)	1.1820	0.0390
(18, 0)	1.4200	0.0290
(21, 0)	1.6440	0.0126
(24, 0)	1.8780	0.0090

Further, the computed result of the quasiparticle band structure of (9, 0), (12, 0), (15,0), (18,0), (21,0) and (24,0) nanotubes reveal that these materials are semiconducting. However, beyond (24, 0) no bandgap is observed. The narrow bandgap found in (3p,0) nanotube with p = 3, 4 and 5 is strongly in accordance with the experimental data obtained by adopting a low-temperature atomically resolved scanning tunneling microscopy [20]. For p=6, 7 and 8 comparison with experiment cannot be made because of scarcity of available data. Moreover, the results obtained for all (3p, 0) CNTs are also in good accordance with the B3LYP hybrid density functional approach [21] and the results obtained by density hybrid functional theory [25]. The π-π* gap of (3p, 0) tubes are tabulated in Table I. As demonstrated in Fig. 1 (b) and (c), by the example of ZGNR with chirality (12, 0) and (24, 0) nanotubes, the semi-empirical theory leads to a semiconducting state in (3p, 0) tubes. For CNT with significantly low diameter, the structural deformation of graphene sheet to roll to a CNT has an enormous influence on the electronic structure inducing the modification of the overlap of π orbitals and consequently opening a bandgap.

The graphical representation depicted in Fig. 2 reveals an inverse relationship between the energy gap and the diameter of the tube. Inspection of the graph shows that band gaps scale as $\sim A_0/d^2$, in harmony with the model proposed by Ouyang et al [20]. The constant factor A_0 is related to γ_0, the transfer binding matrix element as $A_0 = 3\gamma_0 a^2_{c\text{-}c}/4$. The study showed that finite curvature reduces the overlap between nearest-neighbor π orbitals which in turn lead to the shifting of k_F from the first Brillouin zone corner (K point) of a 2D graphene sheet. Hence, for (3p,0) tubes the Fermi wavevector k_F proceed far away from the K-point along the circumferential direction in a manner that the allowed subband K no longer passes through k_F, leading to the opening of bandgap in these materials.

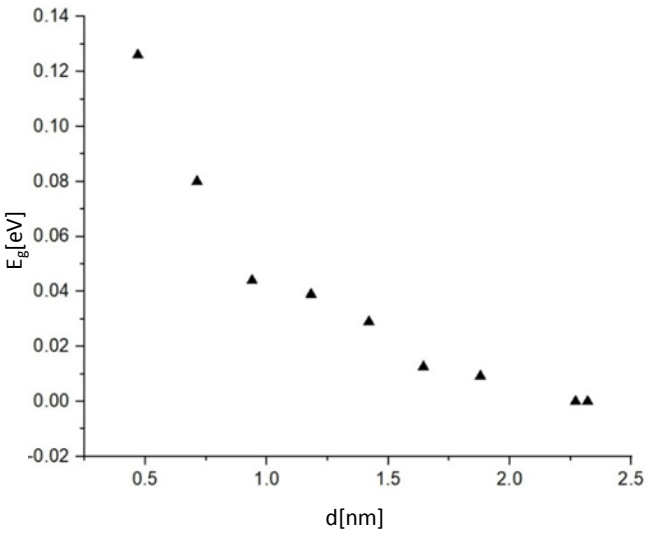

Fig.2: Band gap of (3p, 0) zigzag SWCNT as a function of diameter

7. CONCLUSIONS

Extended Huckel Theory used to evaluate the band structure of zigzag (3p, 0) demonstrated that the sizable band gap arises from the intrinsic properties of CNT. The finite curvature present in CNT modifies the overlapping of π orbitals resulting in a bandgap that is found to decay monotonically with the increase in diameter. Hence, metallic (3p, 0) zigzag CNT is no longer metallic, concluding that they are semiconductors.

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