

# Electronic Properties of Graphite and Single Walled Carbon Nanotubes- A DFT Study

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## Abstract

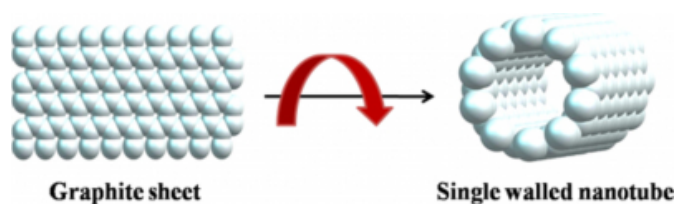
Density functional theory has been used to model graphite and single walled carbon nanotube. The results indicate that three dimensional graphite is a semi metal and two dimensional graphite is a semiconductor with zero gap. Density of states and band structure plots indicate that carbon nanotubes with chirality (10,10), (9,0) are metallic and (10,0) tube is semiconducting.

## INTRODUCTION

Graphite is one of the allotropic forms of natural carbon. It is a material made of hexagonal-symmetry carbon layers. The 3D structure of graphite is not a simple stacking of planes. Every other plane is shifted in the horizontal plane and gives the stacking of AB AB AB. The 2D structure of graphite is considered as a monolayer of 3D graphite. A single- walled carbon nanotube can be considered to be formed by the rolling of a single layer of 2D graphite (Figure 1).

### Figure 1

Figure 1. Structures of a graphite sheet and a single walled carbon nanotube

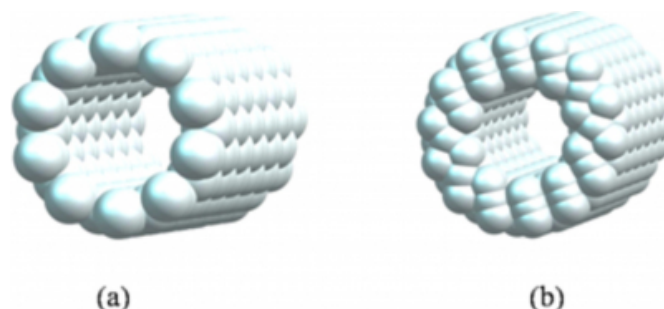


In 1991 Sumio Iijima, a Japanese electron microscopist who was synthesising fullerenes, discovered graphitic carbon needles with outer diameters of 4-30 nm and a length of up to 1  $\mu$ m.<sup>1</sup> These tubules were found to consist of two or more graphene cylinders with a concentric arrangement and were called multi-walled carbon nanotubes (MWNT).<sup>1</sup> Single-walled carbon nanotubes which are made of a single graphene sheet were first reported in 1993 by Iijima et.al.<sup>2</sup> Single walled carbon nanotubes (SWNT) are simpler in structure and have a smaller range of diameters compared with MWNTs (Figure 2). Their diameters range from 0.4 to 2-3 nm and their length is usually of the micrometer order.<sup>1</sup> In the absence of interactions between neighbouring tube

walls found in MWNTs, it is easier to predict physical properties of SWNTs, using computer calculations and theoretical models

### Figure 2

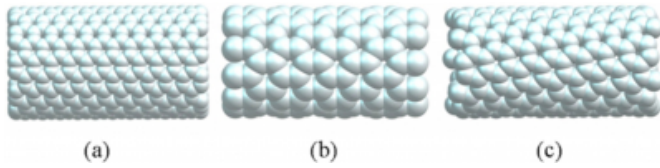
Figure 2. Structures of (a) single-walled, (b) multi-walled carbon nanotube



Carbon nanotubes may be further classified as achiral or chiral depending on symmetry.<sup>3</sup> An achiral carbon nanotube is defined by a carbon nanotube whose mirror image can be superposed on to the original one.<sup>3</sup> Chiral nanotubes exhibit a spiral symmetry and their mirror images are not identical to the original ones.<sup>3</sup> In this regard armchair and zigzag nanotubes are achiral nanotubes. Representative structures for the armchair, zigzag and chiral nanotubes are shown in Figure 3.

**Figure 3**

Figure 3. Structures of (a) armchair, (b) zigzag and (c) chiral nanotube



In this study, we use density functional theory (DFT) calculations to evaluate the change in the electronic properties of graphite and carbon nanotubes (armchair and zigzag).

### COMPUTATIONAL DETAILS

The calculations are based on first-principles density functional theory. SIESTA code<sup>4</sup> was used. Local density approximation (LDA) was used for the exchange-correlation term parameterized by Ceperley and Alder.<sup>5</sup> Core electrons are replaced by non-local, standard norm conserving Troullier-Martins pseudopotentials<sup>6-8</sup> for C. The reference electronic configuration, cut-off radius and partial core cut-off radius for C pseudopotential employed here are tabulated (Table 1).

**Figure 4**

Table 1. Reference configuration and cut-off radii (a.u.) of the pseudopotential used in this study.

Atom		C
Reference		$2s^2 2p^2 3d^0 4f^0$
Core radius	$s$	1.25
	$p$	1.25
	$d$	1.25
	$f$	1.25
Core cut-off		0.00

The quality of the pseudopotential was tested comparing the eigenvalues and excitation energies of all-electron calculations on the same series of atomic configurations. The

cross-excitation energies for C pseudopotential were not more than 0.04 eV respectively indicating the excellent transferability of these pseudopotentials.

The one-electron Kohn-Sham eigenstates were expanded in a basis of strictly localized NAOs.<sup>9</sup> For C a double  $\eta$  basis set for 2s and 2p valence states and a single  $\eta$  basis set for 3d were used.

Structure optimizations were performed using a conjugate gradient algorithm and the forces on the atoms were obtained from the Hellmann-Feynman theorem including Pulay corrections. In all optimised structures forces on the atoms were smaller than 0.04 eV/Å and the stress tensor was less than 0.02 GPa. To represent the charge density a cut-off of 250 Ry for the real space grid integration was used in all calculations. For graphite, 60 k points were used to plot density of states (DOS) and band structure. For the zigzag nanotubes, a number of k points between 10 and 15 were sufficient for the calculation. But for the arm chair tubes it was 60 as it has the shortest periodicity. Cubic super cells with 20 Å were used to model nanotubes to make sure that the two adjacent structures do not interact with each other.

### ELECTRONIC PROPERTIES OF GRAPHITE AND CARBON NANOTUBE

The unique electronic structure of a two dimensional graphene sheet together with the nanometer dimensions of the carbon nanotubes make the electronic properties of these one dimensional carbon nanotube structures highly unusual. The electronic structure and properties of a single walled carbon nanotube can be deduced from the electronic properties of the graphene sheet.<sup>10</sup> A graphene sheet may be regarded as an infinitely extended system and its unit cell contains two carbon atoms. Each carbon atom has four valence electrons. According to a tight binding scheme, graphene contains four valence bands and four conduction bands.<sup>3</sup>  $\pi$  valence bands and  $\pi^*$  conduction bands are obtained from the  $sp^2$  hybridised orbitals.  $\pi$  valence bands and  $\pi^*$  conduction bands are formed by the  $p_z$  orbitals of the carbon atoms oriented perpendicularly to the graphene sheet.<sup>3</sup> If we see the band structure (energy vs wave vector relation) and the hexagonal shape of the Brillouin zone of graphene, it is interesting to note that the valence band ( $\pi$ ) and conduction band ( $\pi^*$ ) touch at the points of the Brillouin zone (corner of the hexagonal Brillouin zone) and due to this touching, the graphene sheet becomes a zero gap semi conductor.<sup>11</sup> Due to the weak overlap between valance and conduction bands, three dimensional graphite exhibits semi metallic behaviour.

The main difference between graphene and a nanotube lies in the periodic boundary conditions. For an infinite nanotube, the boundary condition along the tube axis is the same as for graphene and along the circumference direction a periodic boundary condition is imposed or a wave vector around the circumference direction is quantized.<sup>12</sup>

The electronic band structure of a single wall nanotube could be derived from that of a graphene sheet by a zone folding method.<sup>12</sup> In this method the rolling up of a graphene sheet is neglected and the nanotube is simply treated as a graphene rectangle and this method provides an approximate picture of the band structure near the Fermi level. It totally ignores the effects of deviation from pure  $sp^2$  hybridisation due to tube curvature. The 1D band structure of a given SWNT consists of the 2D band structure of the graphene sheet along the tube axis. For a given metallic nanotube, one of the lines passes through a k point of this zone and the band structure of the nanotube will be characterised by a zero energy gap.<sup>12</sup> For a semiconducting nanotube, none of these lines passes through a k point and the tube will have a finite energy gap. Analysis shows that an (n, m) tube is metallic when  $n = m$ , or when  $n - m = 3i$  where i is an integer while carbon nanotubes with  $n - m \neq 3i$  are semiconducting.<sup>12,13</sup>

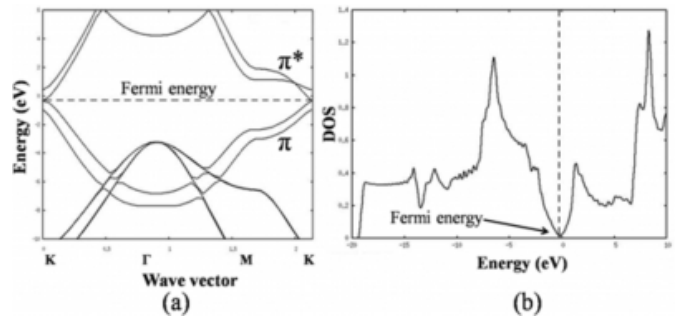
## RESULTS AND DISCUSSION

### (a). Three dimensional graphite (3D) and two dimensional graphite (2D)

The band structure of three dimensional graphite calculated with SIESTA predicts that valence ( $\pi$ ) and conduction ( $\pi^*$ ) touch at the k point in the Brillouin zone of the graphite and there is a very small density of states at the top of the valence band. These features clearly show that 3D graphite is a semi metal (Figure 4). The splitting pattern of bands in 3D graphite is due to the doubling of the C atoms in the unit cell. The band structure of 2D graphite (graphene) and density of states shows that it is a semiconductor with zero gap (Figure 5).

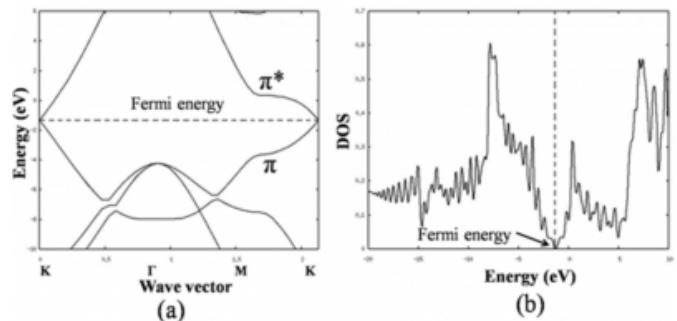
**Figure 5**

Figure 4. (a) band structure (b) DOS of 3D graphite



**Figure 6**

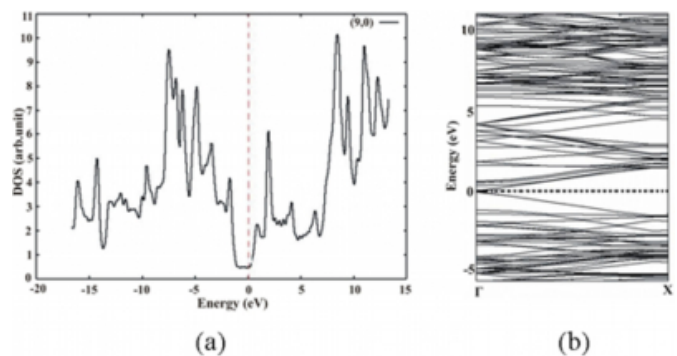
Figure 5. (a) band structure (b) DOS of two dimensional graphite (b). Carbon nanotubes



A (9, 0) carbon nanotube is metallic, so the DOS plot should contain density at the Fermi level and in the band structure, valence and conduction bands should intersect at the Fermi level. Calculated DOS and electronic band structures for a (9, 0) nanotube are given in Figure 6.

**Figure 7**

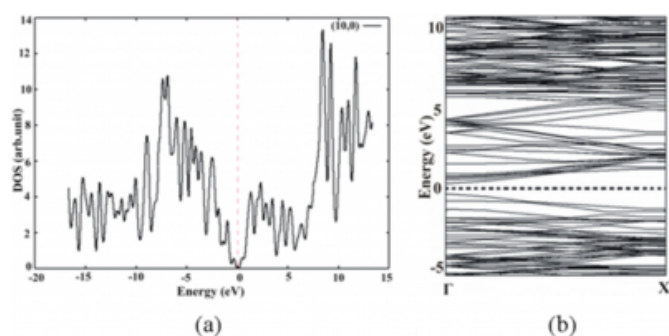
Figure 6. (a) DOS (b) band structure of a (9,0) tube



A (10, 0) carbon nanotube is semiconducting tube. So the DOS plot should contain no density at the Fermi level; there should be a band gap at the Fermi level. Calculated DOS and electronic band structures for a (10, 0) nanotube are given in Figure 7.

**Figure 8**

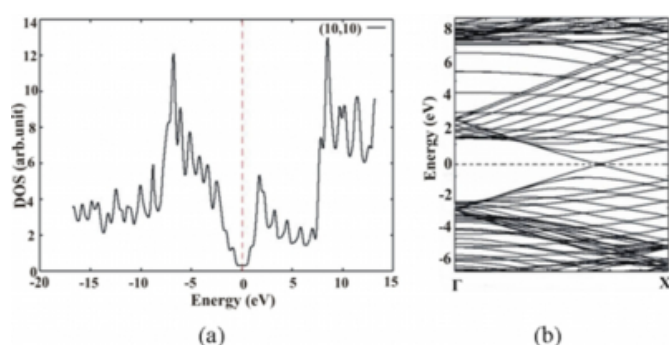
Figure 7. (a) DOS (b) band structure of a (10,0) tube



A (10, 10) carbon nanotube is metallic. So the DOS plot should contain density at the Fermi level and valence and conduction bands should intersect at the Fermi level. Calculated DOS and electronic band structures for a (10, 10) nanotube are given in Figure 8.

**Figure 9**

Figure 8. (a) DOS (b) band structure of a (10,10) tube



## CONCLUSIONS

The band structure of 3D graphite calculated with SIESTA predicts that valence ( $\pi$ ) and conduction ( $\pi^*$ ) touch at the k point in the Brillouin zone of the graphite and there is a very small density of states at the top of the valence band. These

features clearly shows that 3D graphite is a semi metal. The band structure of 2D graphite and density of states shows that it is a semiconductor with zero gap.

DOS and Band structures were plotted for nanotubes with chirality (9,0), (10,0) and (10,10). Calculations reveal that tubes with chirality (9,0), (10,0) are metallic and (10,0) tube is semiconducting.

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