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When double-wall carbon nanotubes can become metallic or semiconducting

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Abstract

The electronic properties of double-wall carbon nanotubes (DWCNTs) are investigated via density functional theory. The DWCNTs are separated into four categories wherein the inner–outer nanotubes are metal–metal, metal–semiconductor, semiconductor–metal and semiconductor–semiconductor single-wall nanotubes. The band structure of the DWCNTs, the local density of states of the inner and outer nanotubes, and the total density of states are calculated. We found that for the metal–metal DWCNTs, the inner and outer nanotubes remain metallic for different distances between the walls, while for the metal–semiconductor DWCNTs, decreasing the distance between the walls leads to a phase transition in which both nanotubes become metallic. In the case of semiconductor–metal DWCNTs, it is found that at some distance the inner wall becomes metallic, while the outer wall becomes a semiconductor, and if the distance is decreased, both walls become metallic. Finally, in the semiconductor–semiconductor DWCNTs, if the two walls are far from each other, then the whole DWCNT and both walls remain semiconducting. By decreasing the wall distance, first the inner, and then the outer, nanotube becomes metallic.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since their discovery and synthesis, carbon nanotubes have gradually come to be regarded as one of the fundamental nanostructures for use in the emerging fields of *nanoscience* and *nanotechnology*. They can be regarded as the *fabric* of nanoscale, molecular-scale

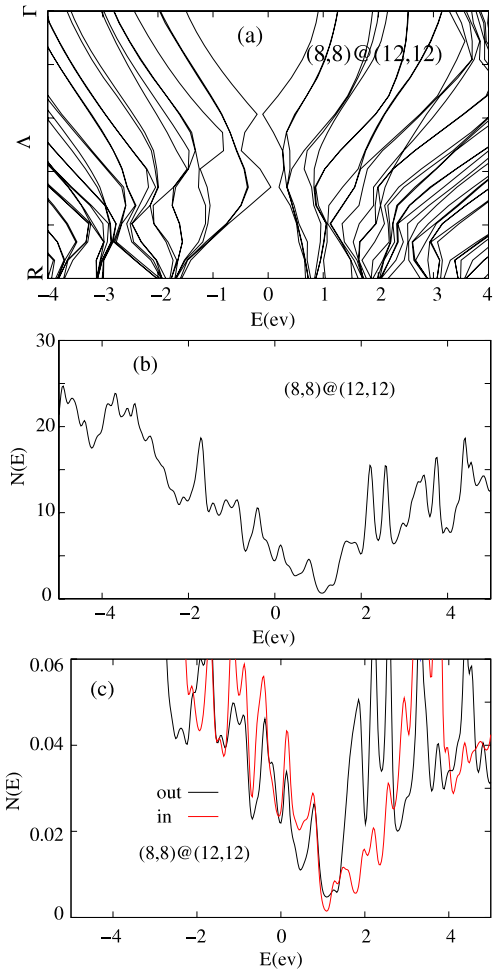

Figure 1. The band structure and density of states of a (8, 8)@(12,12) double-wall carbon nanotube. The results show that the whole double wall, and also the inner and outer walls, are metallic.

and quantum-scale technologies, since they exhibit truly exceptional electronic, mechanical, thermal, and transport properties, depending on their geometrical structures [1]. Single-wall carbon nanotubes (SWCNTs) have very different electronic conduction properties. A graphene sheet is a semi-metallic material with a zero band gap. The electronic states of an infinitely long nanotube, constructed from this sheet, are continuous along the nanotube axis but are quantized along the circumference. For an (n, n) armchair tube, there always exist electronic states that cross the corner points of the first Brillouin zone, and hence these nanotubes always show a metallic behaviour. For an (n, m) tube, if $\frac{(n-m)}{3} \neq$ an integer, the electronic states miss the corner points, and these nanotubes are semiconductors with a band gap that scales with the diameter of the tube (d) as $\frac{1}{d}$ and is of the order of 0.5 eV. For an (n, m) tube with $\frac{(n-m)}{3} =$ an integer, on the other hand, certain electronic states land on the corner points, and these nanotubes would be semi-metallic, but they become small-band semiconductors due to curvature-induced rehybridization [2]. The electronic properties are also highly sensitive to local distortions in the geometry arising from mechanical deformations or the presence of molecular adsorbates. So far, several varieties of nanotube-based electronic devices have been proposed and fabricated, for example a nanoscale bridge between two electrodes with a

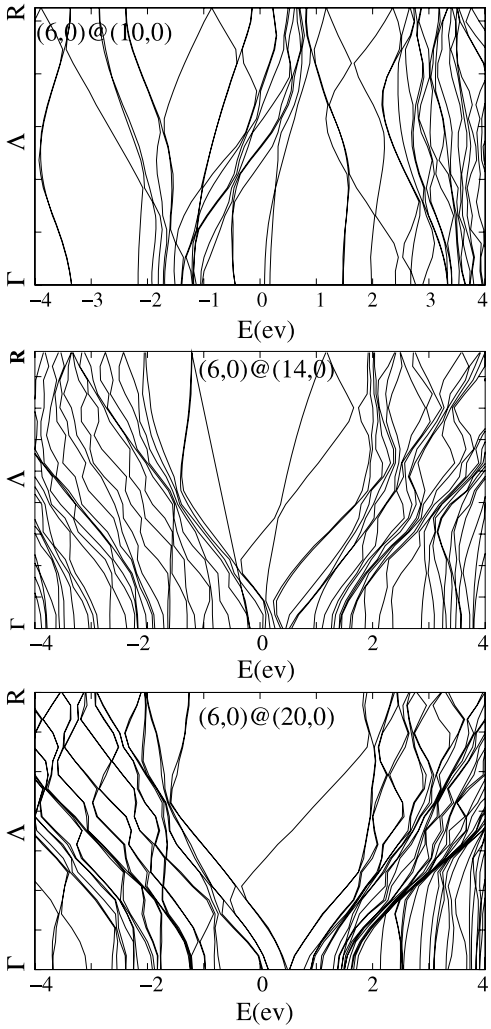

Figure 2. The band structures of (6, 0)@(10, 0), (6, 0)@(14, 0) and (6, 0)@(20, 0) DWCNTs, where initially the separate inner SWCNT is metallic, while the outer SWCNT is a semiconductor. The band structure shows that the whole double-wall structure is metallic.

separation of less than 30 nm, acting as a *nanowire* [3] in the field of molecular electronics. More recent exploitation of the electronic properties of nanotubes is in the field of spin-electronics, or *spintronics*, a field that manipulates the electron's spin degree of freedom for transfer and storage of information and communication. Nanotubes, as one-dimensional ballistic conductors, provide ideal objects for spin transport over long distances.

Although the electronic properties of SWCNTs are quite well known [4–6], the same cannot be said about the multi-wall carbon nanotubes (MWCNTs). Experimentally, the currents carried by the outer nanotube [7], and by inner nanotube [8] of MWCNTs are measured in low-bias and high-bias regimes respectively. The most simple type of MWCNT is a double-wall carbon nanotube (DWCNT). A DWCNT with metallic layers can be used as a coaxial cable or a capacitor. For other combinations of conductivities of the inner and outer nanotubes, there are applications in such fields as field emission transistors (FETs), biosensors, etc. Although DWCNTs are constructed from two SWCNTs with the same, or different, chiralities, the electronic properties of each nanotube within a DWCNT can be different from those of an isolated SWCNT.

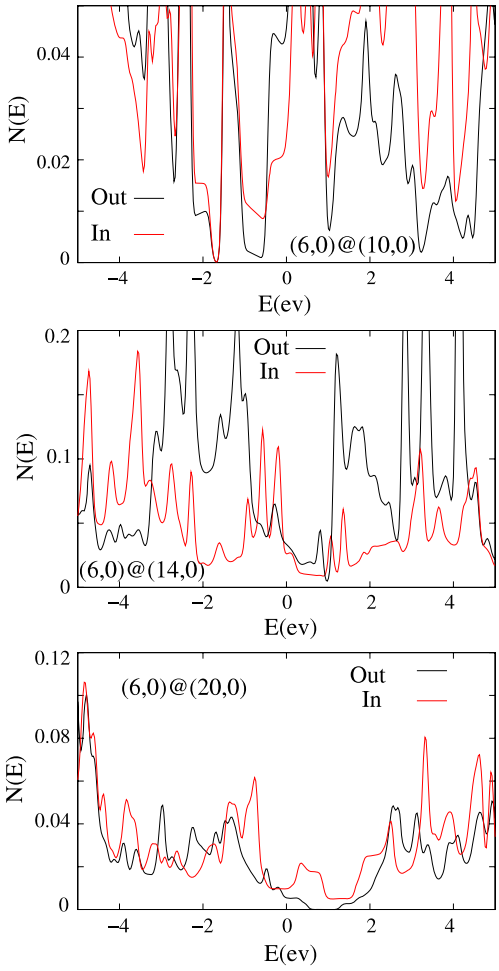

Figure 3. The densities of states for individual (6, 0)@(10, 0) and (6, 0)@(14, 0) and (6, 0)@(20, 0) SWCNTs when they are parts of the DWCNTs. The results show that the separate SWCNTs in the (6, 0)@(10, 0) and (6, 0)@(14, 0) DWCNTs are metallic, while in the (6, 0)@(20, 0) DWCNT the inner SWCNT remains metallic and the outer SWCNT remains semiconducting.

In the most synthesized MWCNTs, the reported interlayer distance is approximately the graphite interlayer distance, 3.4 Å, [9–11]. Also, it is claimed that the interlayer spacing is not constant at 3.4 Å, but it has a range from 3.4 to 4.1 Å [12] or from 3.4 to 4.7 Å [13], or for the case of being smaller than 3.4 Å, it has been reported to be in the range from 2.75 to 3.5 Å [14], and the inter-wall distances have been decreased by 10%–15% [15]. Furthermore, it is reported that in the carbon anions the distance between lattice planes decreases from outside to inside where the lowest value is 2.2 Å [16].

In this paper, our aim is to investigate the influence of the inter-wall distance between the two SWCNTs on the density of states and the band structure of the resulting DWCNTs, as well as on the individual SWCNTs within the DWCNTs. These computations are performed via first-principles full potential linearized augmented plane-wave density functional theory, as implemented in the WIEN2k code [17]. A simple case of this work done by density functional theory using a pseudo-potential with eight k-points [18] in the first Brillouin zone. They found that a curvature of $(7, 0)$ induced metallization in the $(7, 0)@(16, 0)$, $(7, 0)@(17, 0)$, $(7, 0)@(19, 0)$ and $(7, 0)@(20, 0)$ DWCNTs, while for DWCNTs with thicker inner walls the double walls remained semiconducting. So they conclude that the curvature of inner wall, $(7, 0)$, of such DWCNTs caused metallization of whole DWCNTs. Their calculation is done

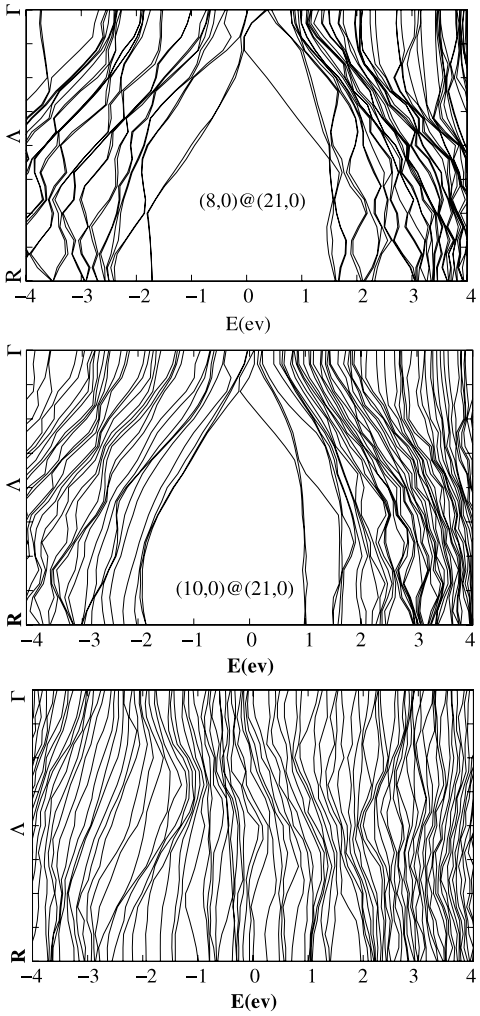

Figure 4. The band structures of (8, 0)@(21, 0), (10, 0)@(21, 0) and (14, 0)@(21, 0) DWCNTs where their initial SWCNTs semiconducting gaps are overlapped. By decreasing the distance between layers, a semiconductor-to-metal phase transition takes place.

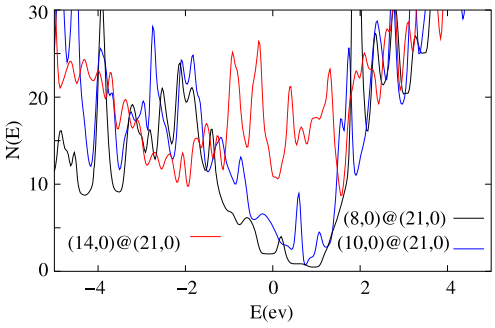

Figure 5. The densities of states of (8, 0)@(21, 0), (10, 0)@(21, 0) and (14, 0)@(21, 0) DWCNTs.

for small number of k-points (eight); the band structure and density of states are very sensitive with respect to the number of k-points when the number of k-points is low. Our calculations are done in the range of 100–200 k-points. Some of our results are different from their results; for example, they claimed that the $(10, 0)@(20, 0)$ tube is a semiconductor while our calculation

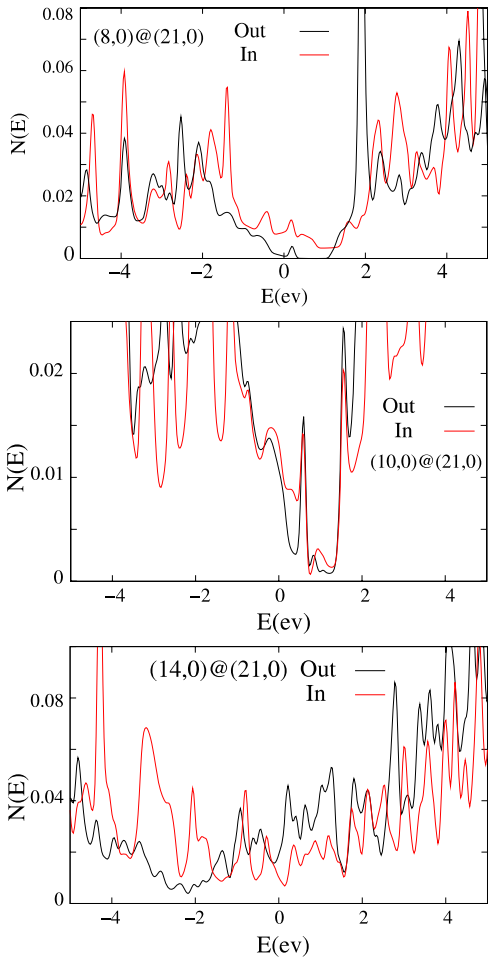

Figure 6. The inner wall and outer wall local densities of states for (8, 0)@(21, 0), (10, 0)@(21, 0) and (14, 0)@(21, 0) DWCNTs. For the (8, 0)@(21, 0) DWCNT, the inner wall is metallic while the outer wall is a semiconductor, where they are interchanged to metallic–semiconductor respectively. By increasing the inner wall radius, interactions between walls leads to a metal-to-semiconductor phase transition for inner wall.

shows that it is metallic. To clarify our results, the inner wall and outer wall local densities of states, the total density of states and the band structure are calculated. We found that when the energy gaps of the individual SWCNTs of a DWCNT overlap and the inter-wall distance is big then the DWCNT is semiconducting, but for other cases the DWCNTs are metallic. We also we found two factors that could lead to metallization of a semiconducting DWCNT, first the interaction between walls due to overlap of π orbitals of the inner and outer walls when the inter-wall distance is small, and second, the states of the inner wall fill the energy gap of outer wall and vice versa.

2. Computational details and results

For the exchange and correlation terms, the generalized gradient approximation (GGA) is used following [19]. For carbon atoms the 1s state is the core state, while the 2s and 2p states form the valence states. Muffin-tin radii of 1.3 au are used. The total number of k-points in the whole Brillouin zone (BZ) is taken to be equal to 200. Calculations are performed in the supercell approximation within a cubic unit cell. The length of the supercell is 10 Å + outer wall diameter in the x and y directions.

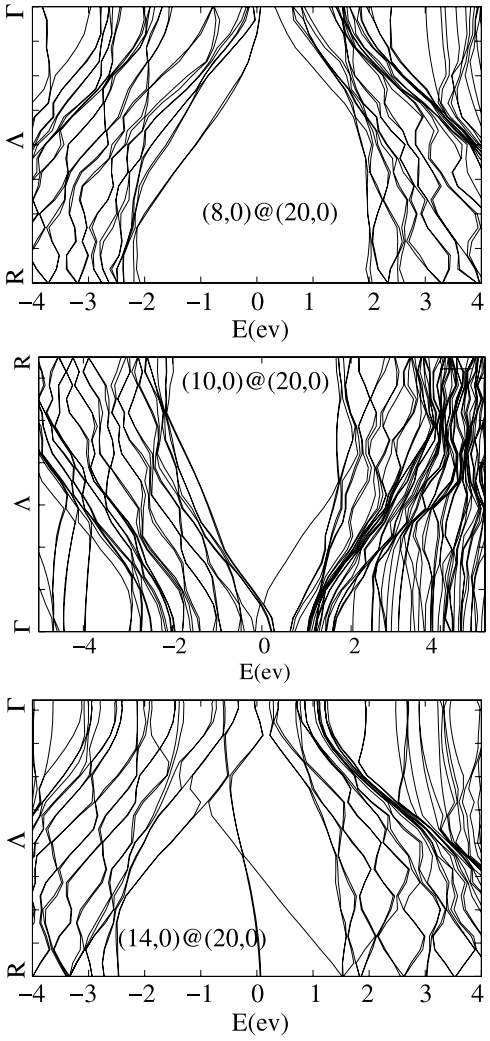

Figure 7. The band structures of (8, 0)@(20, 0), (10, 0)@(20, 0) and (14, 0)@(20, 0) DWCNTs where their initial SWCNTs semiconducting gaps are overlapped. By decreasing the distance between layers, a semiconductor-to-metal phase transition takes place.

Four possible cases are investigated. In the first case, both the inner and outer nanotubes of the DWCNT are initially metallic SWCNTs. Figures 1(a) and (b) show respectively the density of states and the band structure of a (8,8)@(12,12) DWCNT. Figure 1(c) shows the same results for the (8, 8) and (12, 12) SWCNTs separately *when they are parts* of the DWCNT. The results show that both the inner and outer SWCNTs remain metallic, and the DWCNT is also metallic.

In the second case, initially the separate inner SWCNT is metallic, while the outer SWCNT is a semiconductor. In this case, in the resulting DWCNT, the radius of the inner SWCNT is fixed, while that of the outer SWCNT is varied. The combinations considered are (6, 0)@(10, 0), (6, 0)@(14, 0) and (6, 0)@(20, 0). Figure 2 show the band structure of (6, 0)@(10, 0), (6, 0)@(14, 0) and (6, 0)@(20, 0) DWCNTs, and figure 3 shows the densities of states for the individual SWCNTs when they are parts of the DWCNTs. First, the results show that in this case all the DWCNTs always become metallic. Second, the results show that the separate SWCNTs in the (6, 0)@(10, 0) DWCNT and (6, 0)@(14, 0) DWCNT are metallic, while in the (6, 0)@(20, 0) DWCNT, the inner SWCNT remains metallic and the outer SWCNT remains

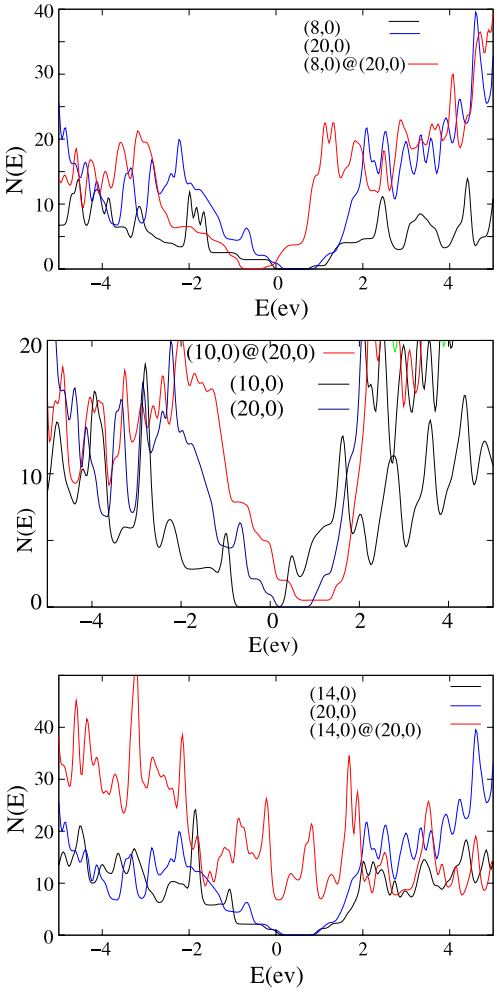

Figure 8. The densities of states of (8, 0)@(20, 0), (10, 0)@(20, 0) and (14, 0)@(20, 0) DWCNTs. The semiconducting gaps of the initial SWCNTs of the (8, 0)@(20, 0) DWCNT are overlapped and the walls are far from each other; hence the (8, 0)@(20, 0) DWCNT is a semiconductor. Although the semiconducting gaps of the initial SWCNTs of the (10, 0)@(20, 0) and (14, 0)@(20, 0) DWCNTs are overlapped, interaction between the walls leads to a semiconductor-to-metal phase transition.

semiconducting. These findings show that the variation of the inter-wall distance results in a semiconductor-to-metal phase transition for the outer SWCNT.

In the third case, initially the separate inner SWCNT is semiconducting, while the outer SWCNT is metallic. In this case, in the resulting DWCNT, the radius of the outer SWCNT is fixed, while that of the inner SWCNT is varied. The combinations considered are (8, 0)@(21, 0), (10, 0)@(21, 0) and (14, 0)@(21, 0). Figures 4 and5 show respectively the band structures and the densities of states of the DWCNTs. The results show that all the DWCNTs become metallic. Furthermore, from figure 6 we see that the separate SWCNTs in the (10, 0)@(21, 0) and (14, 0)@(21, 0) DWCNTs are metallic, while in the (8, 0)@(21, 0) DWCNT the outer SWCNT, which was initially metallic, has transformed into a semiconductor, and the inner SWCNT, which was originally a semiconductor, is transformed into a metal. The results in this case show that, when the inter-wall distance is decreased, both the SWCNTs become metallic, while when this distance is increased, the SWCNTs interchange their identities.

Finally, in the fourth case, the separate inner and outer SWCNTs are both semiconducting. In this case, the radius of the outer SWCNT is fixed, while that of the inner one is varied. The combinations considered are (8, 0)@(20, 0) and (10, 0)@(20, 0) and (14, 0)@(20, 0). Figures 7

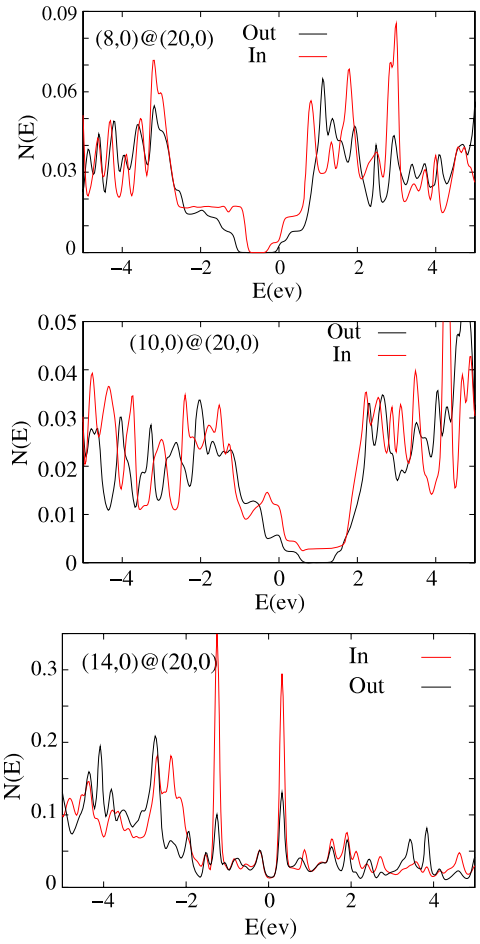

Figure 9. The local density of states at a carbon atom position on the inner and outer walls of (8, 0)@(20, 0), (10, 0)@(20, 0) and (14, 0)@(20, 0) DWCNTs. In this case we found that, by decreasing the inter-wall distance, the interaction between walls could lead to a semiconductor-to-metal phase transition for the inner wall, and by decreasing more to a semiconductor-to-metal transition for both walls.

and 8 show the band structures and the densities of states for these DWCNTs. The results show that the (8, 0)@(20, 0) DWCNT is a semiconductor, while the other two DWCNTs become metallic.

Furthermore, figure 9 show that the separate SWCNTs in the (8, 0)@(20, 0) DWCNT remain semiconducting, while in the (10, 0)@(20, 0) DWCNT the inner SWCNT becomes metallic and outer SWCNT remains semiconducting. In the (14, 0)@(20, 0) DWCNT, both the inner and the outer SWCNTs transform into metals.

The behaviour of the (8, 0)@(20, 0) DWCNT is explained in terms of two factors which influence its electronic conduction properties. First, there is the overlap of the semiconducting gaps of individual SWCNTs as shown in figure 8. Second, the interaction between the walls of the inner and outer SWCNTs due to $2p_z$ orbitals which are perpendicular to the cylindrical walls surface, which causes a phase transition when the distance is small (smaller than 4.7 Å), has no effect since the inter-wall separation is large. This should be contrasted with the result for (10, 0)@(20, 0) and (14, 0)@(20, 0) DWCNTs; they transform into metals, even though there is an overlap of the semiconducting gaps. The reason is that the inter-wall separation for these two DWCNTs is small (3.92 and 2.35 Å respectively), hence causing the transformation into the metallic state.

3. Conclusion

We have investigated the electronic conduction properties of DWCNTs via density functional theory as implemented in the code WIEN2k. All possible combinations of SWCNTs making up a DWCNT are considered. In the first case, when the SWCNTs are both metallic, our results shows that the DWCNT is also metallic. In the second case, when the inner SWCNT is metallic and the outer SWCNT is a semiconductor, we found that the DWCNT is metallic, while the individual SWCNTs remain the same when their inter-wall distance is large, but transform into metals when this distance is small due to overlap of $2p_z$ orbitals which are perpendicular to the cylindrical wall surfaces. In the third case, the inner SWCNT is a semiconductor, and the outer SWCNT is metallic. We found that in this case the DWCNTs are metallic. In two of the DWCNTs, the individual SWCNTs become metallic, while in the third DWCNT, (8, 0)@(21, 0), they interchange their conduction properties. Finally, for DWCNTs where both SWCNTs are semiconductors, we found that when the SWCNTs' semiconducting gaps do not overlap, the resulting DWCNTs are metallic. However, if these semiconducting gaps do overlap, the inter-wall distance then determines if they remain semiconductors. If this distance is large, the SWCNTs remain semiconductors as they were originally, and if the distance is small, they transform into metals. The phase transition (semiconductor to metal) of the inner and outer walls of a DWCNT for small inter-wall distances is due to overlap of the $2p_z$ orbitals of the walls. Our results can open interesting avenues in research concerned with the use of carbon nanotubes in the emerging field of nano-electronics.

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