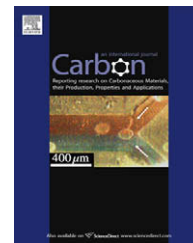


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Ab initio density functional studies of the restructuring of graphene nanoribbons to form tailored single walled carbon nanotubes

Sumit Saxena, Trevor A. Tyson *

Department of Physics, New Jersey Institute of Technology, Newark, NJ 07102, USA

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ABSTRACT

A method based on density functional theory calculations is proposed for the preparation of chiral controlled single walled carbon nanotubes (SWCNTs) by tailoring the edges of bi-layered graphene nanoribbons (GNRs). We find that armchair edged bi-layered GNRs are highly stable and need to be compressed to overcome the energy barrier to form zigzag SWCNTs, while the zigzag edged bi-layered GNRs are intrinsically highly unstable and immediately form armchair SWCNTs. We have investigated the rehybridization of orbitals of carbon atoms in the process of nanotube formation. Nanotube formation is found to be assisted by the edge ripples along with the intrinsic edge reactivity of different types of bi-layered GNRs. Utilizing these results we show that it may be possible to produce high specificity chiral controlled SWCNTs and pattern them for nanoscale device applications.

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1. Introduction

Unique properties of carbon nanotubes have attracted the multidisciplinary applications of carbon nanotubes. They are characterized by the chiral angle quantified by (n, m) indices which determine their properties [1–3]. The availability of wide range of properties for different single walled carbon nanotubes (SWCNTs) produced during synthesis imposes a bottleneck and has stranded the development of carbon nanotube nanodevices [4]. Many different approaches such as chemical functionalization [5], dielectrophoresis [6] for separation and use of bimetallic catalysts [7–10] for selective growth of SWCNTs have been explored, but thermal vibrations of the catalyst particles during synthesis prevent the realization of diameter control in SWCNTs [11]. Thus a bottom-up approach seems far beyond reach and no optimal process of chirality or diameter control is available to date. The process of unzipping carbon nanotubes to produce graphene nanoribbons (GNRs) has

been demonstrated recently [12]. This suggests the idea of producing SWCNTs using GNRs reversibly by zipping it up. However both experiments and theory have shown formation of nanoscrolls [13,14] instead of carbon nanotubes. Moreover it is not only difficult to achieve site specific functionalization [15] but also align opposite edges of a GNR while rolling for nanotube formation [16] as suggested earlier. Here we explore the possibility of tailoring the edges in bi-layered GNRs by compression to produce chiral controlled SWCNTs. We exploit the availability of parallel edges in bi-layered GNRs and analyze this process of nanotube formation which is associated with the rehybridization of orbitals in carbon atoms using ab initio density functional theory. The ability to efficiently control the chirality/diameter of SWCNTs will not only enable the development of large scale high performance carbon nanotube-based devices like arrays of top gate CNTFET [17], interconnects [18] but also unleash the potential of carbon nanotubes for use in nanodevices.

* Corresponding author: Fax: +1 973 596 5794.

E-mail address: tyson@adm.njit.edu (T.A. Tyson).

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2. Computational

First principle spin restricted calculations were performed using the Vienna Ab initio Simulation Package (VASP) that implements the pseudopotential approximation and plane wave basis set into the framework of density functional theory. Highly efficient ultrasoft pseudo potentials (USPP) employing the exchange correlation form of Ceperley and Alder [19], parameterized by Perdew and Zunger [20] were used. A high energy cutoff of 550 eV was chosen for the plane wave basis. The atoms were relaxed using the conjugate gradient algorithm such that the forces on each atom were smaller than .001 eV/Å. Highly accurate projected augmented wave (PAW) potentials using exchange correlation of Perdew-Burke-Ernzerhof (PBE) were used to calculate the site specific partial density of states. The irreducible Brillouin zone was sampled using K points generated by the Monkhorst Pack scheme.

3. Results and discussion

The nomenclature followed for naming the GNRs merits a small review before we proceed any further. The GNRs are categorized by the arrangement of atoms and the width of the nanoribbons. Nanoribbons with armchair edges are specified by the number of dimer lines across the ribbon width. For example a nanoribbon with armchair edge consisting of eleven dimer lines across the ribbon width is referred to as 11AGNR. For zigzag nanoribbons the number of zigzag chains across the ribbon width is used to classify them. Zigzag edged nanoribbon with eight zigzag chains across the cross-section will be called 8ZGNR [21].

Bi-layered system of GNRs offer aligned parallel edges and reduce the problem of inducing 2π curvature in flat ribbons to just $\pi/2$ at each edge for nanotube formation. The idea of using bi-layered GNRs is supported by recent experimental observations suggesting closing of the edges of graphene lay-

ers at very high temperatures [22,23]. The edges of GNR may primarily be armchair or zigzag type. The properties of edge carbon atoms in large hexagonally symmetric systems depend strongly on the local structure [24]. Hence one may expect varying reactivity for different type of edges in the nanoribbons. We find that the armchair edges are unreactive and hence highly stable bi-layered armchair graphene nanoribbons (AGNRs) need to be compressed to form zigzag SWCNTs as illustrated in Fig. 1(a–c). The zigzag edges are highly reactive and the bi-layered zigzag graphene nanoribbons (ZGNRs) stabilize by forming armchair SWCNTs almost instantaneously as seen in Fig. 1(d–e). The process of formation of nanotubes from bi-layered GNR involves the rehybridization of the orbitals in carbon atoms from sp^2 to sp^3 . In subsequent part of this letter we initiate an intuitive understanding of this process of SWCNT formation from AB stacked bi-layered GNRs by discussing electron localization functions, electronic band structures and site projected partial density of states. Finally we discuss this entire process of nanotube formation using AB stacked bi-layered GNRs in detail.

The electron localization function (ELF) is a “chemically intuitive” way to analyze the electron localization and has values between 0 and 1. A high value implies that there is a high probability of finding two electrons of opposite spins in a given region of space along with small probability of exchange with other electrons outside the region. The ELF was calculated using the formulation of Silvi and Savin [25] for both armchair and zigzag edge bi-layered GNRs. Fig. 2a shows the ELF for bi-layered AGNRs with an isosurface value of 0.80. The core and bonding point attractors are found to be located at positions indicated by atoms and the regions shown by the isosurface between pair of atoms, respectively. It appears that the dangling edge bonds seem to heal at the armchair edges. This is attributed to the close presence of strong adjacent sp^2 hybrid orbital. The ELF was also calculated for the armchair

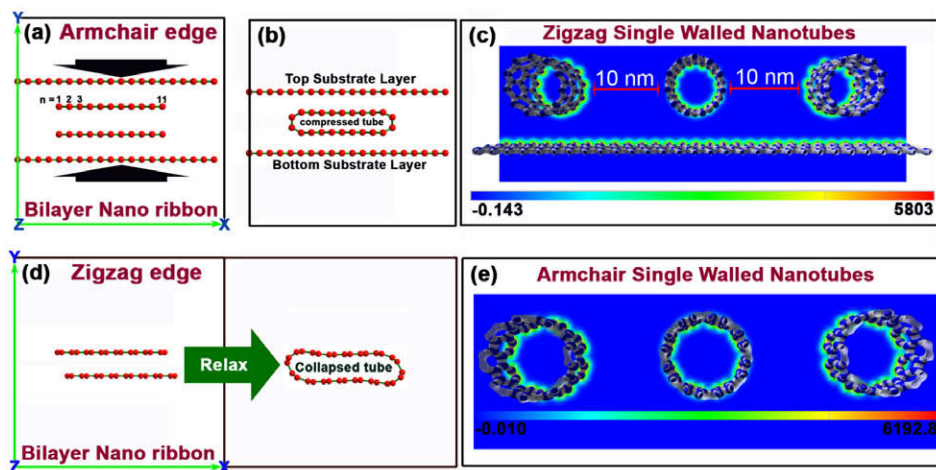


Fig. 1 – (a) Unit cell for bi-layer 11AGNR in AB stacking sandwiched between graphite substrates represented by rigid graphene sheets. (b) Shows the unit cell of compressed (11, 0) zigzag tubular patterned array. (c) Shows the charge density plot along with relaxed geometry of (11, 0) tube patterned array obtained after removing top substrate. (d) Shows AB stacked bi-layered 8ZGNR with the charge density of tubular the geometry obtained for resulting (8, 8) armchair nanotube given in (e). Unit cell is marked by green lines in (a) and (d). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

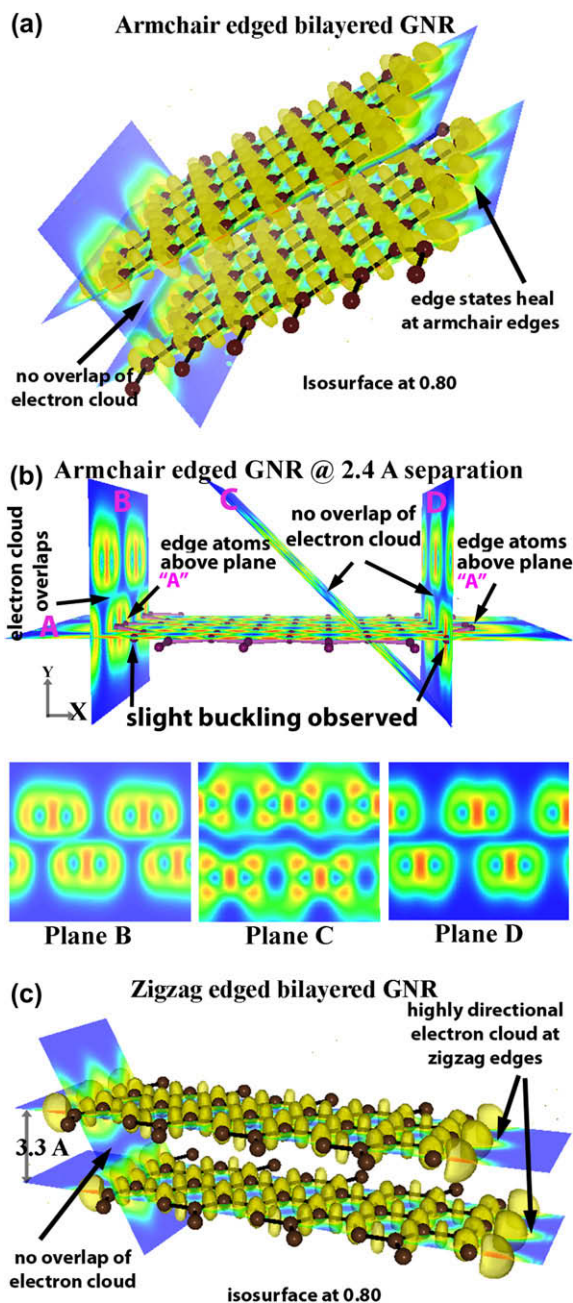


Fig. 2 – Electron localization function for (a) bi-layered 11AGNR at graphitic separation, (b) bi-layered 11AGNR at 2.4 Å, the planes A, B, and C containing the ELF are shown. (c) Bi-layered 8ZGNR at normal graphitic separation.

bi-layered system at a reduced interlayer separation of about 2.4 Å. In Fig. 2b vertical cross-sectional plane B, we clearly observe that for this separation the electron cloud at the edges start to overlap however no overlap of the electron cloud is observed at sites other than the edges as in cross-sectional planes C and D. It is also observed that the edges start to buckle towards each other inducing a slight sp^3 character to the carbon atoms neighboring the edges. The edges of the bi-layered ZGNRs seem to be highly directional and hence expected to be reactive, from the ELF in Fig. 2c. We observe that there is no overlap of the electron cloud between the mono-

layers in either of the bi-layered nanoribbons. Presence of highly directional edge dangling bonds is understood to induce structural instability to these zigzag edge bi-layered nanoribbons by increasing the overall energy; this assists in initiating the reconstruction of edges in zigzag bi-layered nanoribbons to form nanotubes.

We analyze the electronic band structure and site projected partial density of states (PDOS) to further understand this process of rehybridization of orbitals and edge reconstruction in GNRs. The density of states near the Fermi level provides a quantitative estimate of the chemical reactivity for a given system [26]. All structures with edge states crossing the Fermi level or in its immediate vicinity are expected to be highly reactive. The band structure plot in Fig. 3a shows that bi-layer 11AGNR has a very small band gap at the Fermi level. The edges of these nanoribbons were terminated by hydrogen atoms to look at the states due to edges. It was observed that the edge dangling states of the armchair nanoribbons lie away from the Fermi level making them relatively chemically inert and hence helps in stabilizing these bi-layered armchair structures. The band structure for bi-layered 11AGNR at interlayer separation of 2.4 Å showed that the lowest conduction and the highest valence band lie symmetrically within about 10 meV about the Fermi level at the Gamma point. This narrowing of the bandgap is understood to be due to the p_y electron states which lie closer to the Fermi level as seen in the site projected PDOS at one of the edge in Fig. 3e and f. The p_y orbitals are oriented normal to the plane of GNRs. Modification of PDOS corresponding to s , p_x and p_z orbitals is also observed. Once nanotubes are formed the band gap opens up again forming a semiconducting (11, 0) zigzag SWCNT [27] as in Fig. 3b. The band structure of bi-layered 8ZGNR in Fig. 3c shows the availability of edge dangling states as well as bands due to localized states at the edges suggesting highly reactive edges. As the separation between the two graphene layers in the bi-layered system decrease to normal graphitic separation, the interaction between the two layers start to build up causing a small split in the bands representing the edge dangling bonds shown by magenta arrows and the localized states shown by green arrow in Fig. 3c at the zigzag edges near the Fermi level. As both layers in the bi-layer system approach each other the interaction of the edge dangling bonds among the layers increases and flat bands in the Fermi level starts to split further, ultimately the metallic band structure of armchair due to crossing of bands corresponding to π and π^* orbitals is observed in Fig. 3d, the electronic band structure plot for (8, 8) Armchair SWCNT [28].

Experimental evidence of scrolled and staggered edges in free standing graphene is available [29]. The finite element model has shown that the amplitude of the ripples at the zigzag edges is about twice the amplitude of the ripples at the armchair edges. Such vibrations are understood to occur in monolayer nanoribbons because of stretching of atomic bonds due to out of plane motion of the atoms. The typical amplitudes of the ripples at the zigzag edges have been predicted to be about 2.6 Å [30]. Considering bi-layer graphene system as composed of coupled identical entities and assuming normal modes of oscillation of the sheets would mean that with highly directional dangling bonds at the edges of zigzag edges in both the sheets of the bi-layered graphene

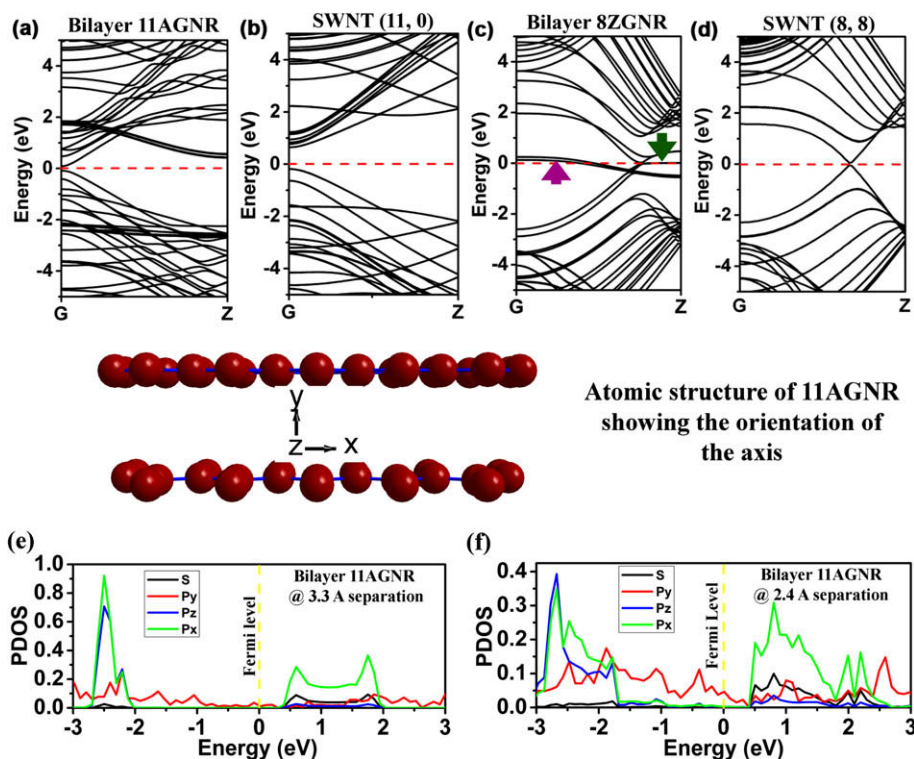


Fig. 3 – Band structure for (a) bi-layered 11AGNR (b) (11, 0) SWCNT (c) bi-layered 8ZGNR and (d) (8, 8) SWCNT. The Fermi level is adjusted to 0 eV and represented by red dashed line. The arrows in (c) show the bands due to dangling bonds (magenta) and due to localized states (green). The inset in the figure shows the orientation of the axis with respect to the ribbon. Partial LDOS at an edge atom of 11AGNR at interlayer separation (e) at normal graphitic separation and (f) at 2.4 Å. Fermi level in (e) and (f) is shown as yellow dashed-dot line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

would readily interact with each other due to overlap of electron cloud during vibration even at graphitic separation. Thus the layers of bi-layer graphene system come close to each other and ultimately forming strong covalent bonds at the edges by overcoming the strain energy associated to sp^3 hybridized carbon atoms in the tubular structure. Once covalent bonds are formed at the edges the strain energy is transferred from the highly stressed curved edges toward the planar sp^2 hybridized carbon atoms on the flat surface of the tubes in order to uniformly distribute the strain over the cross-section ultimately relaxing to regular nanotube structure. For the armchair edged bi-layered GNRs with distributed electron cloud the graphitic separation is too large to enable coupling between the layers. Hence the separation between the layers of the bi-layer system needs to be decreased to less than about twice the amplitude of vibration of the armchair edges. In fact we find that the optimized value of ~ 2.4 Å for separation of the armchair edged layers, obtained as result of trial step movement of rigid graphene sheets is in close agreement with the distance suggested from the finite element model.

Rehybridization of orbitals is expected to occur in response to external or internal perturbations when such a change increases the stability of the system. Bi-layers of AGNRs at graphitic separation, enclosed in a cell, were considered as precursors for zigzag SWCNTs. The cell was chosen such that the separation between the bi-layer nanoribbons in

the adjacent cells was at least 10 Å. Such a large separation ensures minimal interaction between bi-layer nanoribbons in the adjacent cells. Two graphene sheets representing highly rigid surfaces [31] were placed above and below this bi-layer GNRs as show in Fig. 1a. This choice of a unit cell would effectively represent a patterned array of bi-layer GNRs between a pair of highly rigid substrates. Compression was produced by moving the top and bottom graphene sheets simultaneously towards each other in small steps for each layer representing the top and bottom substrate. It is observed that as the separation between the sheets representing the substrates “ d ” is decreased the armchair edge nanoribbons come close towards each other. This is accompanied by increase in total energy of the bi-layer as shown in Fig. 4. It is observed that the edges of the AGNRs start to bend towards each other at a value of d equal to 7.5 Å. At this stage the separation between the layers of the bi-layered GNRs was found to be 2.49 Å. On further compression by reducing “ d ”, it is observed that the edges of the top and bottom layer of bi-layer nanoribbons stick together to form compressed zigzag SWCNT. Once the tubular structure is obtained, the layers representing the substrates are retracted to release the compression and finally the top layer is completely removed, resulting in formation of patterned array of zigzag SWCNTs. The entire process of nanotube formation is observed in Fig. 1a–c. This is accompanied by lowering of the total energy of the tubular structure. The energy difference of the

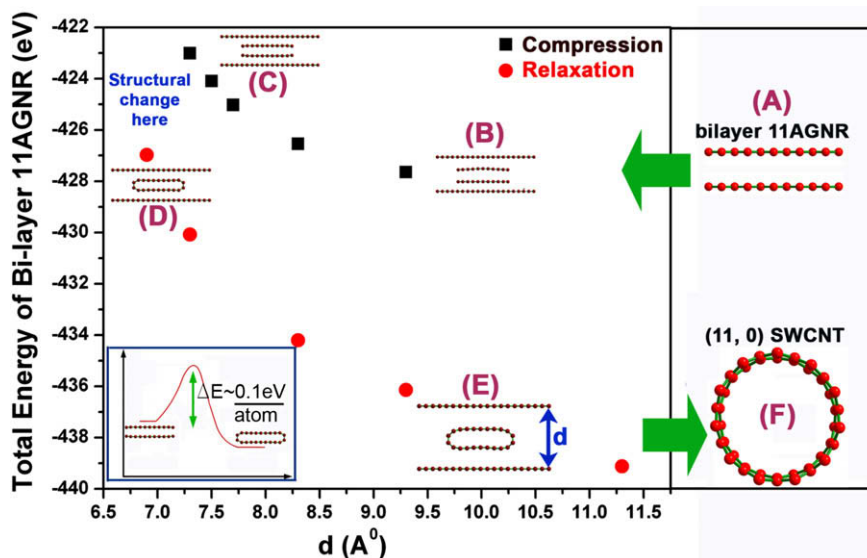


Fig. 4 – Variation of total energy of the bi-layer 11AGNR is plotted as function of the top and bottom substrate layer separation “ d ”. The bi-layer represented by (A) patterned on lower substrate is compressed between graphene sheets shown as (B). As “ d ” is decreased, total energy of highly compressed bi-layered system (C) increases. Once “ d ” is reduced sufficiently, bonds form at edges to form tubular structure (D). Relaxing “ d ” is associated with lowering of energy is observed for (E). Ultimately the tube attains a fully circular cross-section (F). The inset shows the energy difference between nanoribbon and compressed tube.

bi-layered GNR and the compressed SWCNT was found to be ~ 0.1 eV/atom.

The process of formation of armchair SWCNTs using bi-layered ZGNR precursor is less involved. Bi-layered ZGNRs were relaxed in a cell such that the adjacent nanoribbons are separated by at least 10 Å. Both the layers of the bi-layered GNRs in this case exert attractive forces towards each other by relaxing to a stable armchair SWCNT as seen in Fig. 1(d–e). These results are consistent with the nudged elastic band calculations [32] and the zipping mechanism suggested earlier [33]. It is observed that in the case of bi-layered ZGNRs, the energy required to convert sp^2 hybridized carbon atom to sp^3 hybridized carbon atom is provided by the system itself.

4. Conclusion

Finally, the restructuring of the edges of bi-layer GNRs normally or under compression to form carbon nanotubes is possible. We have investigated the process of rehybridization of sp^2 bonded carbon atoms in bi-layered GNRs to sp^3 hybridized carbon atoms in nanotubes based on density functional calculations. Our analysis of ELF along with band structure and site projected PDOS suggest that the restructuring of the edges of bi-layer GNRs normally or under compression is basically due to the availability of states in close vicinity of the Fermi level which makes the edges reactive. We also observe that the amplitude of edge ripples plays an important role in this restructuring. Preliminary investigations have indicated the flexibility of this process to produce a wide range of monodispersed SWCNTs. The ability to pattern nanoribbons would provide an added advantage of patterning arrays of nanotubes.

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