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Considering the effect of different arrangements of pentagons on density of states of capped carbon nanotubes

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ABSTRACT

We have used a non-equilibrium surface Green's function matching formalism combined with a tight-binding Hamiltonian to consider the effect of different arrangements of pentagon rings on localization of density of states at the tip regions of semi-infinite capped carbon nanotubes. The transfer matrixes are obtained by an iterative procedure. The results demonstrate that the positions of the peaks near Fermi energy are remarkably affected by the relative locations of pentagons. It is observed that in thin nanotubes, carbon atoms belonging two neighboring pentagon rings have significant contribution in the localized states near fermi energy. From our calculations, it turns out that the metallic or semiconducting behavior of capped nanotubes in the tip regions depends on the metallic or semiconducting nature of their nanotube stems.

1. Introduction

The quality of the localization and distribution of emitting states on the caps of carbon nanotubes have considerable effects on field emission patterns and currents [1–3]. Electron holography experiments on field emitting carbon nanotubes exhibit that the local electric field and hence the associated emission current are concentrated precisely at the tips of carbon nanotubes and not at side-walls [4]. Evidence from scanning tunneling microscopy (STM) experiments combined with tight-binding calculations indicates that the topology of the carbon bond network at the tip, and in particular the respective location of pentagons are responsible for the electronic properties of the tubes [5,6].

The number of pentagon rings and their relative positions at the tip control the morphology and sharpness of the tip of capped carbon nanotubes. According to Euler's rule, the presence of 12 pentagon rings is enough to make a carbon cage. Consequently, a carbon nanotube can be closed from one side by the presence of six pentagon rings. In this regard, a direct proof of the presence of six pentagons on the tip of a closed carbon nanotube has already been yielded from filed emission experiments [7]. Theoretically it is shown that depending on the diameter of nanotubes, there are many different cap geometries with different arrangements of pentagons that can be used for closing a nanotube [8,9]. For example, there are at least 677 possible cap configurations for a (13,2) nanotube [9]. Similarly through reparative field evaporation techniques, it is demonstrated that in the experiments a verity of cap structures can be produced on the same nanotube [10]. Both experimental and theoretical studies indicate that different cap geometries have different electronic structures. In other words, the topology of the cap influences the strength and position of the peaks observed in density of states spectra near the Fermi energy [5,6,11–14]. Hence, it has been suggested that the density of states near the tip, which is measurable in tunneling spectroscopy experiments, can be used to discriminate between different tip structures [5,6,13].

Almost all previous first-principles or tight-binding electronic structure calculations done on nanocones, nanohorns or carbon nanotubes indicate that the pentagon sites at the caps determine the essential features of the electronic structure near the Fermi energy [11–14]. However, there is still no general rule to predict the possible caps for a set of tunneling spectroscopy data without performing very large number of calculations. In our previous field emission calculations, from the local density of states (LDOS) patterns, it was observed that the LDOS reaches a maximum at the pentagon rings and/or the bonds connected to the pentagon rings [2]. In this work we have systematically studied how the relative positions of pentagon rings at the tips of capped carbon nanotubes affect the electronic structure of the nanotubes near the Fermi energy. From our calculations, it is observed that at the

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pentagon rings and the bond that connect two neighboring pentagons have significant contributions in the states localized near Fermi energy. We hope that our study will have some implication in discrimination of the nanotubes with different cap geometries.

2. Models and computational details

To investigate the relation between the confinement of the pentagon rings and local density of states of capped carbon nanotubes, we have employed an efficient approach based on the surface Green's function matching formalism [15]. Using the above approach the capped carbon nanotubes are simulated with their semi-infinite length similar to ones, which are observed in experiments. In detail, we have adjusted the general approach proposed by Farajian et al. for calculating the quantum transport properties of contact-molecule-contact systems to our case study, which is like contact-molecule systems [15]. In other words, the approach as mentioned before is well adopted such that only the terms related to left contact and molecule regions are kept, and the terms related to the effect of right contact are eliminated. In fact, in our case studies, the left contact is the semi-infinite nanotube body and the molecular region is the cap geometry.

In Green's function approaches, the density of states of electrons (DOS) is defined as:

$$DOS = -\frac{1}{\pi}\mathrm{Im}(Trace[G_M]) \tag{1}$$

where G_M is the Green's function of the molecular region. The rest of this section is devoted to calculation of G_M.

Based on the explanation as above and shown in Fig. 1, our system composed of a molecular region (cap geometry) connected to a source contact (semi-infinite tube). The source contact is divided into successive principal layers. A principal layer is defined as the smallest number of unit cells such that only nearest neighboring interactions exist between principal layers. The source contact includes infinite number of principal layers. The first principal layer between molecular and source contact is called surface layer. Moreover, the molecular junction is assumed to have direct interactions only with the surface principal layers of the source contact. For such systems, G_M is calculated as follow:

$$G_M = \left(zS_M - H_M - \sum_S\right)^{-1} \tag{2}$$

where H_M and S_M are the Hamiltonian and overlap matrixes of the molecule. z is the complex energy. $\sum_S$ is the surface energy of the source contact, which is calculated as:

$$\sum_S = (H_{SM} - zS_{SM})^{+} G_{s;S}(H_{SM} - zS_{SM}) \tag{3}$$

where H_{SM} and S_{SM} are the Hamiltonian and overlap matrixes which couple the molecular to the first layers of the source contact (surface principal layer in Fig. 1). $G_{s;S}$ is the surface Green's functions of the source which is derived as

$$G_{s;S} = [zS_S^{0,0} - H_S^{0,0} - (H_S^{-1,0} - zS_S^{-1,0})T_S]^{-1} \tag{4}$$

where $H_S^{0,0}$ and $S_S^{0,0}$ are the Hamiltonian and overlap matrixes of the surface region. $H_S^{-1,0}$ and $S_S^{-1,0}$ are the Hamiltonian and overlap matrixes, which couple the surface layer to its neighboring principal layer. T_S is the transfer matrix which can be calculated by the iterative method proposed by Sancho et al. [16,17]. The advantage of this iterative scheme has been already demonstrated in near the singularities of density of states when the other schemes converge slowly [16,17]. Hence, this iterative method helps to save a considerable amount of computing time. Based on Sancho's method, T_S is calculated iteratively as

$$T = t_0 + \tilde{t}_0 t_1 + \cdots + \tilde{t}_0 \cdots \tilde{t}_{n-1} t_n$$

where t_i and $\tilde{t}_0$ are defined via the recursion formulas:

$$t_i = (I - t_{i-1}\tilde{t}_{i-1} - \tilde{t}_{i-1}t_{i-1})^{-1} t_{i-1}^2$$

$$\tilde{t}_i = (I - t_{i-1}\tilde{t}_{i-1} - \tilde{t}_{i-1}t_{i-1})^{-1} \tilde{t}_{i-1}^2 \tag{5}$$

and

$$t_0 = (z - H_{00})^{-1} H_{01}^{+}$$

$$\tilde{t}_0 = (z - H_{00})^{-1} H_{01} \tag{6}$$

The iteration process is repeated until t_n, $\tilde{t}_n < \varepsilon$ with ε arbitrarily small. For more details of the used Green's function equations and the iterative method, see Refs. [15–17]. We have calculated all the necessary Hamiltonian and overlap matrixes based on a simple tight-binding model with one p orbital per carbon atom. The interactions are limited to first nearest neighboring atoms. This tight-binding model can be justified because, as shown in many different studies, the states around Fermi energy are essentially π or π^* type [18–22]. Values for the hoping integral, $V_{pp\pi}$, are reported in the literature from -2.4 to -2.9 eV [18–22]. We have carried out our calculations using a hopping parameter of -2.6 eV, which has been widely used in previous studies. It is worth mentioning that we have repeated our calculations with several other hopping values in the above range of energies, but no significant changes in the results is observed. It should be noted that the method we have used here is quite general and can be applied to any type of semi-infinite systems in any level of accuracy, e.g., tight-binding and ab initio.

To prove the reliability of the developed method, we have performed a set of test calculations on zigzag and armchair carbon nanotubes with different tip geometries and we have compared our results with the previous calculations in the literature. As depicted (see Supporting information), the local density of states has been calculated for different atomic layers of an open-ended (10,0), a close-ended (10,0) and a close-ended (10,10) nanotube. Our results are in well agreement with the previously reported results by Vita et al. on the same nanotube geometries [11]. It is seen that although the implemented formalism [23] by Vita et al. for calculating the electronic density of states is different as ours, the final results are the same. For the sake of assurance, we have further developed our methodology—considering of the systems contact–molecule-contact systems. With the full-developed program, we were able to compute the density of states and conductance of infinite armchair and zigzag nanotubes. All the test results are in well agreement with the previous calculations in literature, but owning not relating the main purpose of this paper, which is about density of states of capped carbon nanotubes (contact-molecule systems), we have included them in Supporting information.

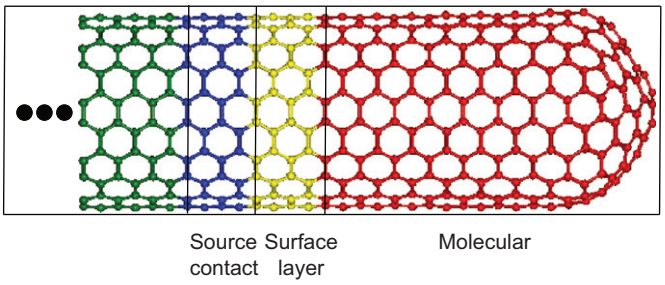

Fig. 1. A typical capped carbon nanotube. The molecular and source regions stand for the cap and the semi-infinite stem of the carbon nanotube, respectively.

3. Results and discussion

To understand the effect of arrangements of pentagon rings on the density of states of thin nanotubes, we have created 12 different capped carbon nanotubes with either metallic ((5,5), (6,6), (10,10), (15,0), (18,0)) or semiconducting (10,0) stems, shown in Figs. 2 and 3. All the structures have six pentagon rings with different distributions. We have arbitrary collected these capped nanotubes from previous studies in the literature [2,8,9,24]. The coordinates of structures in tip regions are presented in Supporting information. The stability of capped carbon nanotubes can be understood appropriately by analyzing the stability of the fullerenes with similar distributions of pentagons. This is because the caps of carbon nanotubes can be constructed by using half of fullerenes. In this regard, recently there is an extensive study on stabilities of different fullerenes and metallofullerenes by Rodríguez-Fortea et al. [24].

As seen from the test calculations (see Supporting information), the effect of cap geometries on the electronic structure of the carbon layers, which are located far from the tips, is negligible. Hence in this study, in order to consider the effect of geometrical structures of caps on the electronic structures rightly, we have used caps with less than 30 carbon layer buffers as the molecular regions in the calculations. Therefore, depending on the tip geometry, the cap regions include more than 300 carbon atoms.

To clarify the effect of arrangements of pentagon rings on the localizations of the states near the cap explicitly, we have focused on analyzing the density of states of the tip regions, which includes all the pentagon rings and just a buffer carbon layer below the last pentagon ring close to the semi-infinite nanotube stem; the top-most 40–55 carbon atoms of each tip. As expected, the calculations show that the localized density of states on the pentagons is identical, for which having the same neighboring carbon network environments. Hence, in Figs. 2 and 3, beside the top view of each cap configuration, the pentagons which are topologically equivalent have been indicated. As it is evident from the cap geometries, any two neighboring pentagon rings are linked together directly with a C–C bond or indirectly through a hexagon ring(s). It will be shown later that the C–C bonds that directly connect pentagons together have noticeable influences on the strength of the peaks in the density of states near the Fermi energy. Here, the studied capped nanotubes are categorized into two main sets: the caps without any direct connected pentagons (Caps 1–4, see Fig. 2) and caps with some connected pentagons (Caps 5–12, see Fig. 3). Since the states near Fermi energy are the most important states for the electronic applications, our discussions will be mainly about the states at the range from -2 to $+2$ eV. However, for more information, the results of density of states are presented at the range from -3 to $+3$ eV. In the total local density of states curve (TLDOS) of each cap, the arrows show the localized states near the Fermi energy. In Figs. 2 and 3, for each cap structure in addition to its TLDOS, the contribution from each set of identical pentagons, each individual pentagon, the C–C bonds that directly connect pentagons have been shown.

Fig. 2 shows the top views of cap configurations without any directly connected pentagons. From the electronic structure of this set of caps, it is observed that the pentagons have significant contributions in the localized states near Fermi energy. In Caps 1 and 2, pentagons are separated from each other with two or more hexagon rings and are distributed with five fold symmetries.

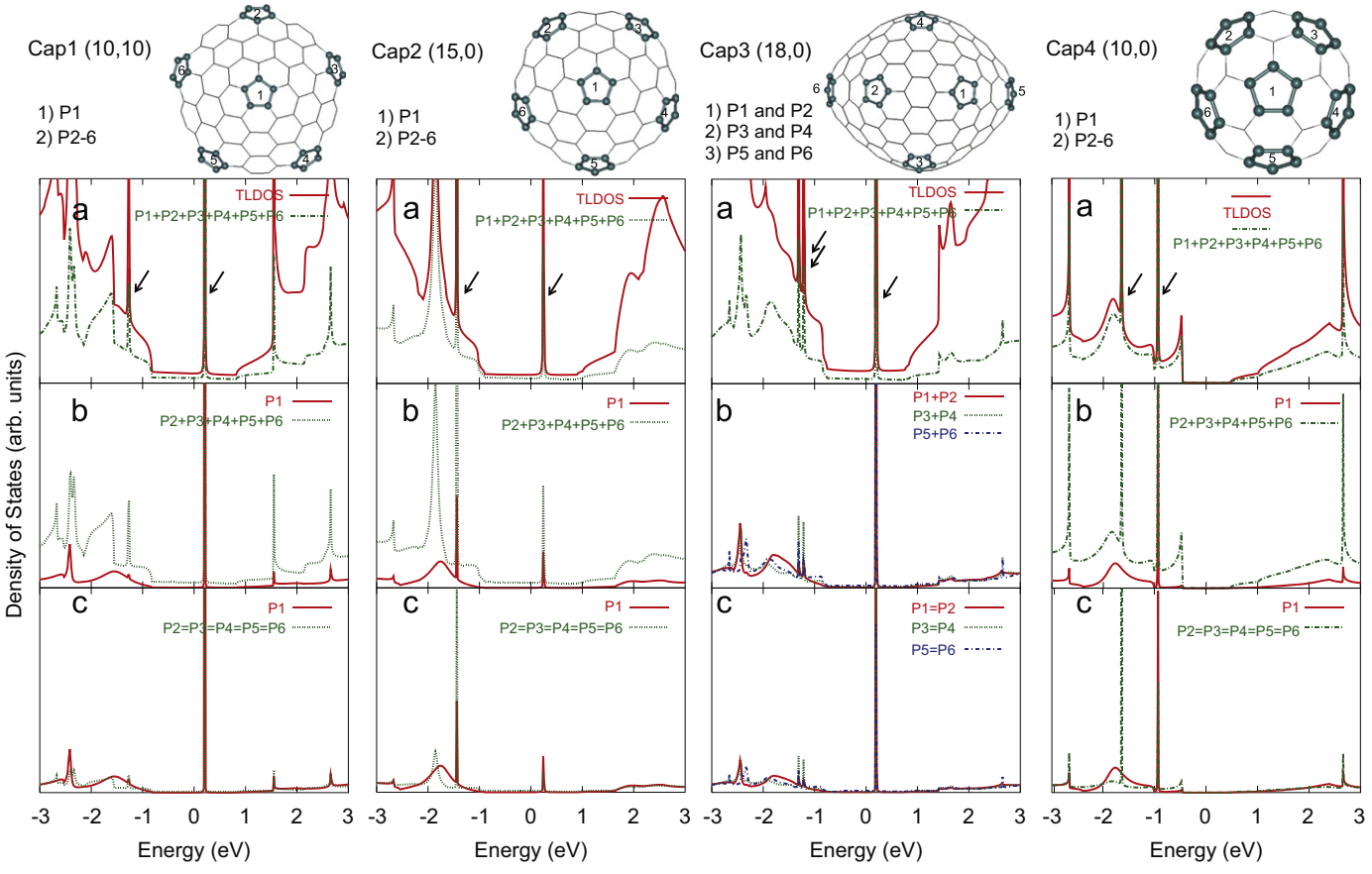

Fig. 2. Top views of the geometrical structures of Caps 1–4 without any directly connected pentagons. The types of nanotube stems and the number of different sets of equivalent pentagons are shown beside each cap. Curves (a) total local density of states (TLDOS) and contribution of all pentagons together, (b) contributions of equivalent pentagons, and (c) contribution of each individual pentagon in TLDOS. Arrows show the main peaks near Fermi energy. Fermi energy is at zero.

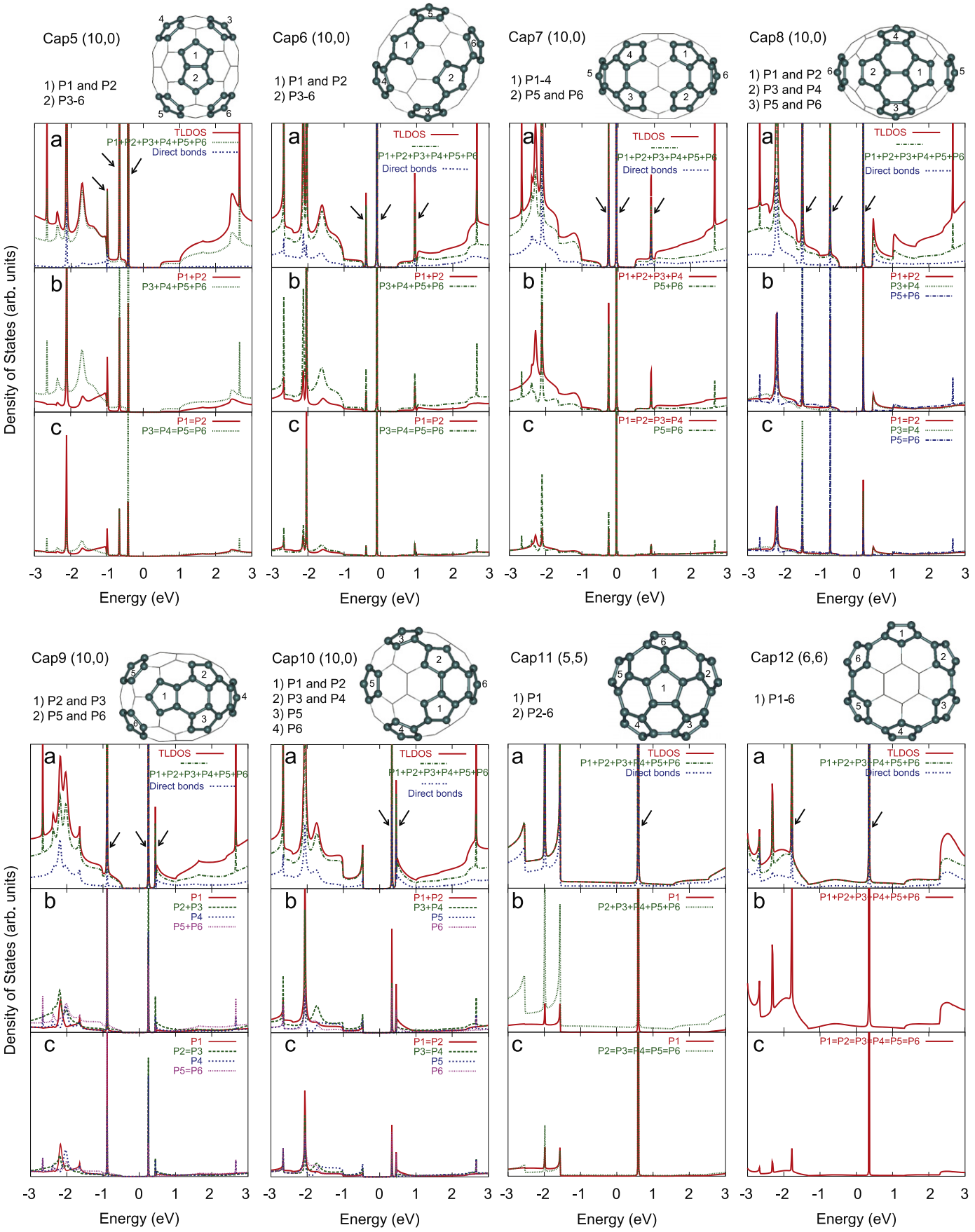

Fig. 3. Top views of the geometrical structures of Caps 5–11 with some directly connected pentagons. Curves (a) total local density of states (TLDOS), contribution of all pentagons together, and contribution of carbon atoms that connect directly two pentagons together (b) contributions of equivalent pentagons, and (c) contribution of each individual pentagon in TLDOS. Arrows show the main peaks near Fermi energy. Fermi energy is at zero.

These pentagons contribute in two localized states at −1.6 and 0.3 eV. The surrounding pentagons around the tube, P2-6 contribute mostly in the localized states at below Fermi energy and the centering pentagon, P1, with highest symmetry contribute mainly in the localized state at above Fermi energy. When the symmetry of distribution of pentagons is reduced, see Cap 3 with two fold symmetries, a new localized state is created at −1.7 eV. In a thin nanotube with nonconnected pentagons, Cap 4, each two pentagons are separated from each other by one hexagon ring. it is observed that two localized states are found below Fermi energy at −1.7 and −1.0 eV, while there is no localized state in the unoccupied electronic levels with low energies (in the range of our interest, from −2.0 to +2.0 eV).

Fig. 3 shows the top views of caps with some directly connected pentagons. Similar to electronic structure of Caps 1–4, the pentagons in Caps 5–12 have significant contributions in the localized states near Fermi energy. However, the TLDOS curves of Caps 5–12 are much more complicated than the TLDOS curves of Caps 1–4. This shows that in Caps 5–12 as the pentagons get closer to each other, the localized states on them interact significantly together. However, still some general features from LDOS of Caps 5–12 can be deduced. In Cap 5, there are two pentagons that are connected together with a common C–C bond. In comparison to Cap 4, when two pentagons are attached together, one additional localized state appears below Fermi energy. The localized states of Cap 5 are closer to Fermi energy (−1.0, −0.75, and −0.5 eV) than the localized states of Cap 4. In Caps 6 and 7, three pentagons are directly connected together. It is observed that in such caps, there are two localized states at below fermi at ∼−0.3 and ∼−0.1 eV, and a localized state appears at above Fermi energy at 0.9 eV. It is found that in Cap 7 with more confined pentagon configurations (each pentagon is connected to two pentagons), the localized peaks get closer to Fermi energy. When the number of connected pentagons in caps exceed more than three—Caps 8 and 9 with four, Cap 10 with five, and Caps 11 and 12 with six connected pentagons—the localized states at below Fermi energy move to lower energies and the localized state(s) at above Fermi energy get closer to Fermi energy. The pentagons with higher number of direct connections with other pentagons have significant contribution in the localization of the states above Fermi energy. In particular, the carbon atoms that directly connect two pentagons together have larger contributions than other carbon atoms of the pentagons at localizations of the states below and above Fermi energy. It is seen as the symmetry of the distribution of the pentagons at the cap decreases, the more states above Fermi energy are created.

In Caps 8–10, in addition to directly connected pentagons, they have one or two pentagons that is/are indirectly connected to other pentagons with hexagons. It is observed that finger prints of these pentagons in the localization of the states at below Fermi energy are very similar to localization of the states in Cap 4 with relatively similar pentagon distributions.

The above-mentioned trends are almost seen in the density of states of nanocones with one to five pentagons, calculated by Charlier and Ringanese, and by Qu et al. [12,14]. The reported TLDOS curves by Charlier and Rignanese have been obtained from similar tight-binding model as us [12], and the calculations performed by Qu et al. are ab initio [14]. As we discussed above, the peaks near Fermi energy are mainly resulted from the pentagon rings, in particular the C–C bonds that connect directly the pentagons together. Above results support the conclusion of our previous first-principles calculations that pentagon rings and/or the bonds connected to the pentagon rings have significant contributions in the field emission patterns [2].

Since in this study, we have used many different caps with metallic or semiconducting body, the above-observed trends are general. It shows that the chirality of nanotubes does not significantly affect the localization of the states at the tip area.

It is worth mentioning that from TLDOS of Caps 1–12 it is observed that the metallic or semiconducting nature of caps follow the metallic or semiconducting nature of the nanotube stems. It means the caps with metallic stems have metallic TLDOS at the cap region and the caps with semiconducting stems have semiconducting TLDOS at the cap region. From our calculations, it is found that even at thin nanotubes, different distribution of pentagons cannot change metallic or semiconducting behaviors of nanotubes.

4. Conclusion

We have adjusted the Green's function method proposed by Farajian et al. [15] to consider the electronic density of states of semi-infinite contact-molecule systems. For calculating the transfer matrixes, the iteration scheme proposed by Sancho et al. has been used [16,17]. By using tight-binding Hamiltonian we have applied the above methodology to consider the effect of different arrangements of pentagon rings on the top of capped carbon nanotubes. Our calculations show that in thin capped carbon nanotubes, the pentagon rings have significant contributions in the peaks near Fermi energy in particular at the range of between −1.0 and +1.0 eV. The pentagons, which have indirect connections with other neighboring pentagons, contribute in the peaks at lower energies at the range from −1.0 to −0.5 eV. The more numbers of C–C bonds connecting directly a pentagon to other nearest neighboring pentagons, the closer localized states are found near Fermi energy at the range from −0.5 to 1.0 eV. The caps, which have pentagons that are connected with one or two C–C bonds to their nearest neighboring pentagon rings, have a very sharp peak below Fermi energy between −0.5 and 0.0 eV. The caps with pentagons that are connected with three or more C–C bonds to the nearest neighboring pentagon rings, have a very sharp peak above Fermi energy between 0.0 and 0.5 eV. This study is expected to provide a framework for better understanding of electronic properties of real carbon nanotubes since their cap topologies are frequently omitted.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.physb.2011.07.017.

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