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Effect of vacancy defect on electrical properties of chiral single-walled carbon nanotube under external electrical field*

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Ab initio calculations demonstrated that the energy gap modulation of a chiral carbon nanotube with mono-vacancy defect can be achieved by applying a transverse electric field. The bandstructure of this defective carbon nanotube varying due to the external electric field is distinctly different from those of the perfect nanotube and defective zigzag nanotube. This variation in bandstructure strongly depends on not only the chirality of the nanotube and also the applied direction of the transverse electric field. A mechanism is proposed to explain the response of the local energy gap between the valence band maximum state and the local gap state under external electric field. Several potential applications of these phenomena are discussed.

Keywords: chiral carbon nanotube, mono-vacancy defect, energy gap, external electric field
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Ever since their discovery in 1991,[1] single-walled carbon nanotubes (SWNTs) have emerged as attractive materials for molecular electronic applications.[2−4] Depending on its diameter and chirality, a SWNT can be either metallic or semiconducting, suggesting a variety of electronic applications.[5−8] Among the electronic applications, the SWNT field-effect transistor (FET) is a promising candidate for future electronic devices since the current in SWNTs can be switched on or off by an external electric field. Functional FETs have been successfully demonstrated by several groups[6−10] and the electronic structures of the SWNTs under the external electric field have been also calculated theoretically.[11−14] For example, Brothers *et al.*[15] calculated the polarizabilities of SWNTs under an external transverse electric field using density functional theory (DFT) to discuss the possibility of using SWNTs as shielding for nanoelectrical components. Several experimental observations and theoretical prediction have revealed that structural defects are commonly present in nanotubes and can substantially modify their electronic properties.[16−26] Experimental characterizations for the role of defects in SWNT-FETs are only beginning to emerge,[27] and many theoretical predictions remain to be tested.[28−30]. According to the bandstructure analyses by Kim *et al.*[31] the electrical characteristics of SWNT are modified chiefly by the localized gap states, which are near the Fermi level but far from the band gap edge and are proved to be produced by vacancy-related defects. It is important to find out whether this phenomenon is commonly shared among defective semiconducting SWNTs or not. There are two types of semiconducting SWNTs, i.e., zigzag and chiral semiconducting SWNTs. Previously, we reported the band structure of a zigzag semiconducting SWNT with a mono-vacancy defect (MVD) under a transverse electric field based on DFT calculations.[32] The results show that the responses of the localized gap state, introduced by the MVD, are distinctly different when the nanotube is subjected to an external field. In this study, we used a chiral SWNT to examine the variation in the local energy gap between the valence band maximum

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(VBM) state and the localized gap state according to the direction and strength of an external electric field. Except that there is explicitly mentioned, the local energy gap refers the energy gap between VBM state and the localized gap state in the following. Here, for the first time in literature, a semiconducting chiral SWNT was used to investigate the chirality dependence of the electronic properties of a defected SWNT under a transverse electric field in various directions.

In order to facilitate the computation, a single-walled (10, 5) nanotube was modelled by 140 carbon atoms with one carbon atom missing to represent the MVD. The simulated model was placed within a tetragonal supercell with the lattice constants a, b and c, chosen as the following. The lattice constants a and b were 20 Å (1 Å=0.1 nm) to avoid the influence from adjacent nanotubes. The lattice constant c along the tube axis was set to be the one dimensional lattice parameter of the nanotube, which is subject to change according to the result of the structural optimization. The nanotube was taken along the z axis and the circular cross section was lying in the (x, y) plane. The vacancy site of the defected nanotube was chosen to sit on the $+x$ axis. DFT calculations were performed with the CASTEP code.[33] The geometry optimization was calculated with generalized gradient approximation (GGA).[34,35] The structure of the defected nanotube was fully optimized until the force on each atom during the relaxation was less than 0.005 eV·Å^{-1}. The nuclei and core electrons were represented by ultrasoft pseudopotentials.[36] The fast-Fourier-transform (FFT) grid was set to be 90×90×50 and a kinetic energy cut-off of 240 eV and 12 special k points were used to ensure the convergence in the calculation. To study the effect of the transverse electric field on the electronic structure of the defected nanotube, the potential generated by the external electric field along the x (or y) direction (perpendicular to the tube axis) was modelled as sawtooth-like potential, i.e.

$$V_{\text{ext}}(r) = |e|\,Ex, \quad \left(-\frac{L}{2} < x \leq \frac{L}{2}\right), \tag{1}$$

where E is the magnitude of the screened electric field and L is the size of the supercell, chosen to be large enough so that the tube is located at the centre of the supercell to avoid discontinuity at the boundary. A screened electric field was used in Eq. (1), since the DFT calculations[37] demonstrated that the charge screening of the external electric field can be welldescribed simply by changing the slope of the external potential.

After geometry optimization, the band structures of both perfect and defected chiral (10, 5) SWNTs were shown in Fig. 1.

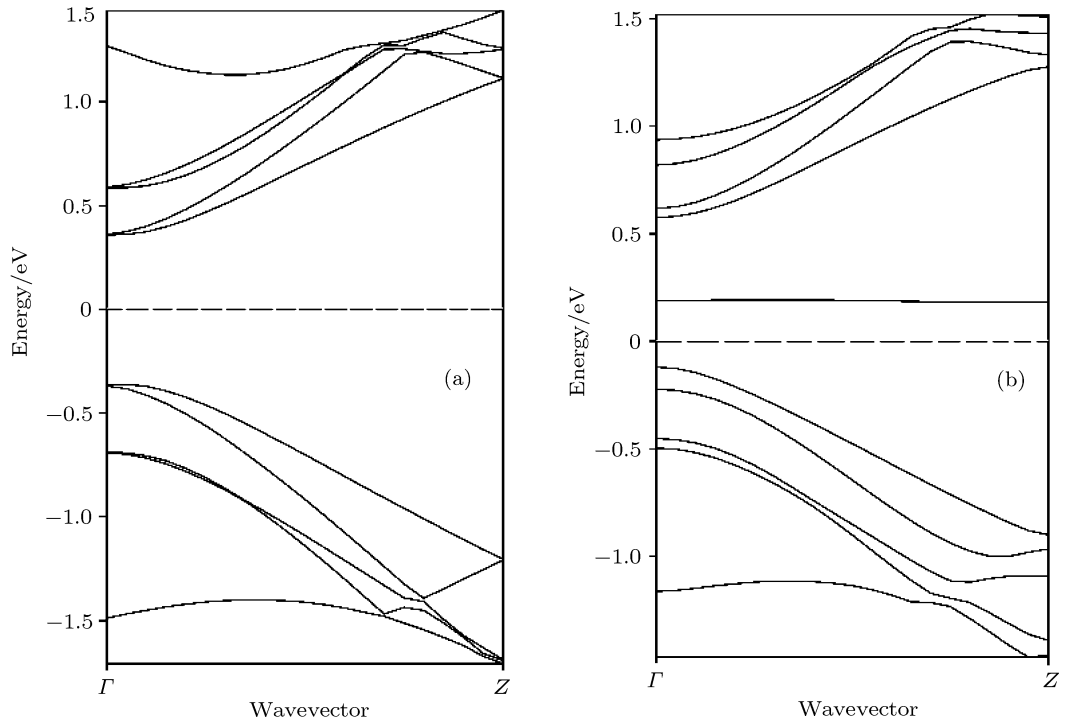

Fig. 1. The band structures of a chiral (10, 5) SWNT. (a) The band structure of a perfect nanotube. (b) The band structure with a mono-vacancy defect. The dash line indicates the Fermi level.

The local energy gap of the defective nanotube between the VBM state and local gap state is 0.3 eV at the point of the Brillouin zone, smaller than the bandgap of the corresponding perfect nanotube, 0.722 eV due to a defected band just above the Fermi level, similar to those found in zigzag defected SWNTs.[32] The band structures of the defected SWNT under x- and y-axes with various field strengths are shown in Figs. 2 and 3, respectively.

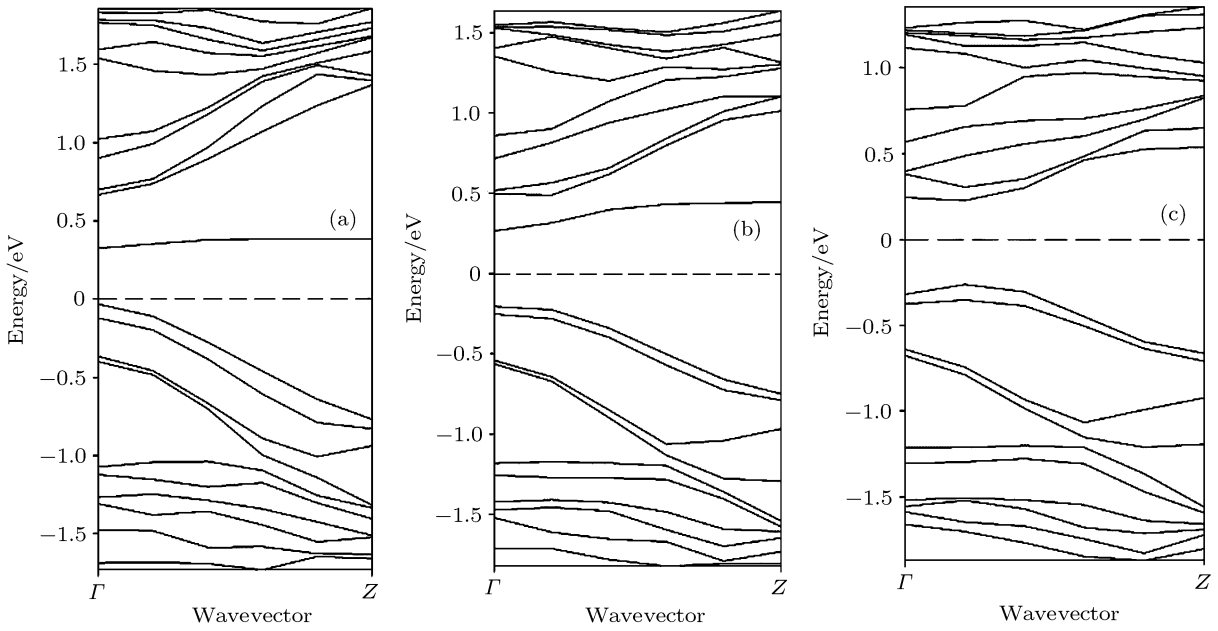

Fig. 2. The band structures of a chiral defected (10, 5) SWNT under a x-axis external electric field. (a) The band structure under 0.1 V/Å. (b) The band structure under 0.3 V/Å nanotube. (c) The band structure under 0.5 V/Å. The dash line indicates the Fermi level.

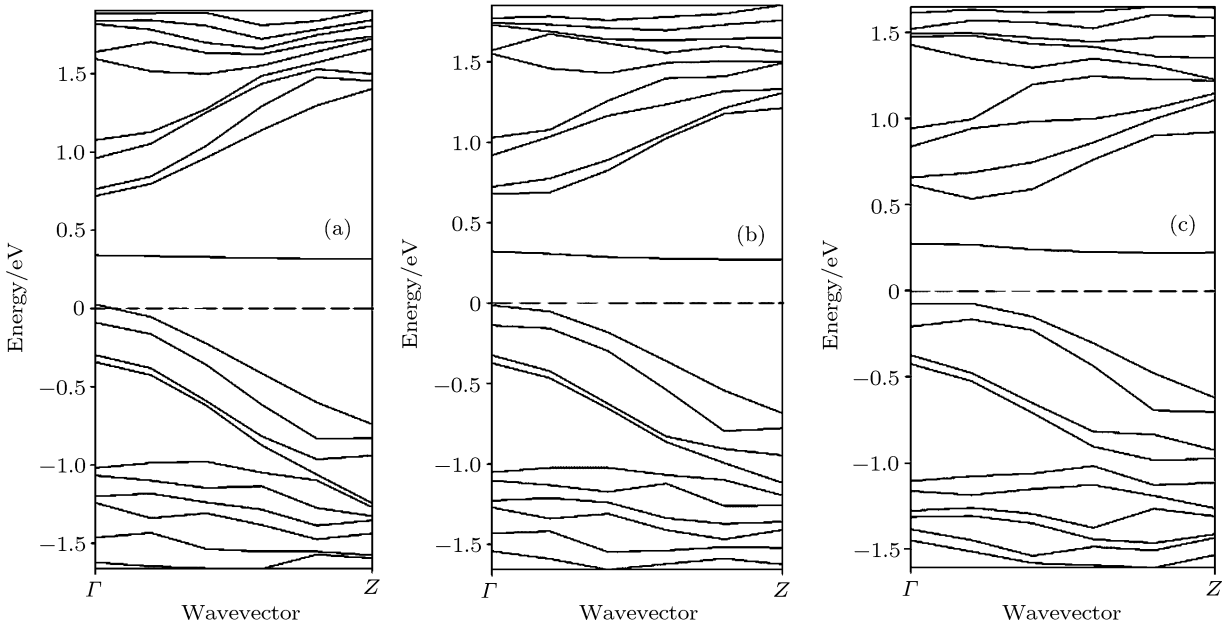

Fig. 3. The band structures of a chiral defected (10, 5) SWNT under a y-axis external electric field. (a) The band structure under 0.1 V/Å. (b) The band structure under 0.3 V/Å anotube. (c) The band structure under 0.5 V/Å. The dash line indicates the Fermi level.

The local energy gaps under a transverse electric field with different applied directions are summarized in Fig. 4. If the field is applied along x axis, the local energy gap of the defective nanotube increases first and later decreases as the field strength increases.

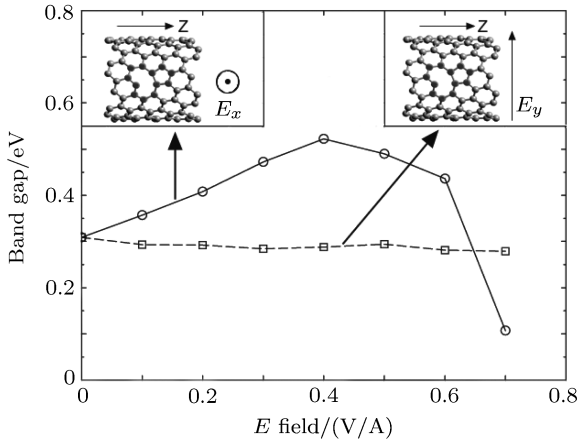

Fig. 4. The variation of the local energy gap for the defective (10, 5) nanotube with 139 carbon atoms under a transverse electric field applied in two different directions, x-axis and y-axis, where the circles represent the electric field in x axis; and squares are in y axis. The inset plot is its optimized structure.

However, if the field is applied along y axis, the local energy gap holds almost constant. Obviously, the above phenomena indicate that the electric properties of the defective nanotube strongly depend on the applied field direction. In order to elucidate the physics governing the local energy gap shrinkage of the defective nanotube in the x-axis field, we analysed their band structures (Figs. 2 and 3) and the charge densities of the VBM and conduction band minimum (CBM) states (Fig. 5).

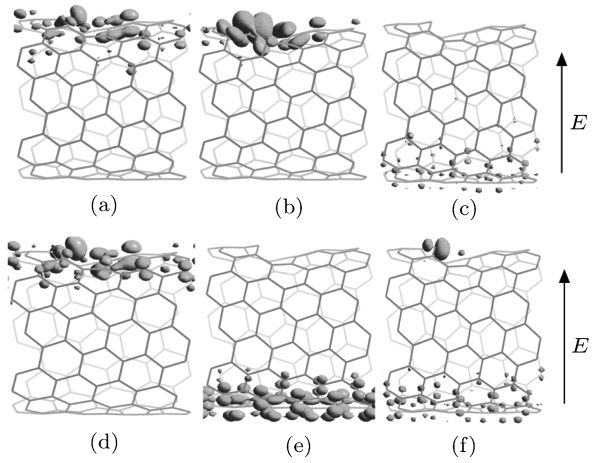

Fig. 5. The orbital density plots of the defective SWNT. (a), (b) and (c) are the VBM, CBM and second CBM states under a x-axis electric field with 0.2 V/Å, respectively. While, (d), (e) and (f) are those under a x-axis electric field with 0.6 V/Å. The arrow indicates the direction of the external electric field.

The CBM state shows an upward shift with a x-axis field, but remains almost unchanged with increase of the field strength along y axis up to 0.7 V/Å, the maximum field strength in this study. This finding is similar to those found in the defected zigzag SWNT.[32] It indicates that the CBM state is strongly influenced by the direction of the charge polarization caused by the external electric field. While the second CBM state shows a downward shift as the field strength increases no matter of the applied direction. Therefore, the CBM state moves close to the second CBM state and eventually cross over each other when the x-axis field strength reaches over 0.4 V/Å. The charge density is very sensitive to the strength of the external electric field. It is because that the SWNT is polarized and the symmetric distribution of charge densities breaks. The charge distribution of the VBM state are mostly located at the SWNT's upper part; while those of the first and second CBM states are localized at the lower part as shown in Figs. 5(a), 5(b) and 5(c), respectively. Furthermore, when the field strength increases over 0.5 V/Å, the original CBM state will exceed the second CBM state, which becomes the new CBM state, as shown in Fig. 2. As the VBM and CBM states move close to each other, the subband mixing between them becomes more pronounced as the x-axis field strength increases beyond 0.4 V/Å, and therefore the local energy gap starts to shrink. But, for the y-axis electric field, the subband mixing between the above two states are not pronounced as that found in the x-axis electric field because the field polarization induced by the y-axis field does not influence the CBM state significantly. However, as the field strength increases, the energy difference between the CBM state and the second CBM state shrinks more rapidly in the x-axis field than in the y-axis one. It is expected that, as the field strength increases in both the x-axis and y-axis fields, the VBM and CBM states eventually cross each other. From our results, a general variation trend of the local energy gap for a semiconducting chiral SWNT with an MVD under a transverse electric field can be obtained. When a nanotube with the above characteristics is rotated in an external electric field with the setting similar to our simulated model, its local energy gap will vary. The maximum and minimum values of the local energy gap will be found when the directions of the applied field are corresponding to $+x$ axis and $-x$ axis, respectively, provided that the field strength is not too high. One can modulate the local energy gap of a semiconducting chiral SWNT with vacancy defects within certain range by changing the field strength and direction of the transverse electric field. Another

important application is that the existence of vacancy defects in a chiral SWNT can be determined by simply rotating the nanotube in a transverse electric field. Besides, if the local energy gap varies according to the direction of the external electric field, the direction with the maximum of the local energy gap will be the direction of the nanotube where the possible vacancy sites reside. Although the general behaviour of chiral defected SWNTs is very similar to those found in zigzag defected ones, there still exist some differences. There exists a cross-over voltage between the x- and y-axis fields before the semiconducting–metal transition, and this crossover is not observed in semiconducting zigzag SWNTs. The local energy gaps are not always measured at the gamma point for a chiral defected SWNT since the minimum of the energy difference between VBM and CBM states is not at the gamma point for the external field strength larger than 0.5 V/Å.

We demonstrate successfully that a chiral (10, 5) SWNT with an MVD responds quite differently when a transverse electric field is applied in different directions. The defect site of the defective nanotube provides a CBM state with lower energy than that found in the corresponding perfect nanotube. The difference in the response of those states near the Fermi level toward the different applied directions of an external electric field is the main reason to cause the difference of the local energy gap variation for a semiconducting chiral SWN with vacancy-defects. Our results indicate that the local energy gap of a semiconducting chiral SWNT can be modulated similarly to that of a semiconducting zigzag SWNT. This also provides some flexibility to select a suitable local energy gap for specific applications since the energy gap can increase or decrease depending on the direction and strength of the transverse electric field.

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