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LETTER TO THE EDITOR

Can electric field induced energy gaps in metallic carbon nanotubes?

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Abstract

The low-energy electronic structure of a metallic single-walled carbon nanotube (SWNT) in an external electric field perpendicular to the tube axis is investigated. Based on tight-binding approximation, a field-induced energy gap is found in all (n, n) SWNTs, and the gap shows strong dependence on the electric field and the size of the tubes. We numerically find a universal scaling that the gap is a function of the electric field and the radius of SWNTs, and the results are testified by the second-order perturbation theory in weak field limit. Our calculation shows the field required to induce a 0.1 eV gap in metallic SWNTs can be easily reached under the current experimental conditions. It indicates the possibility of applying nanotubes to electric signal-controlled nanoscale switching devices.

The prospect of nanoscale electronic devices has engaged great interest, because it could lead to conceptually new miniaturization strategies in the electronics and computer industry. Single-walled carbon nanotubes (SWNTs) can be used as nanoscale devices [1] due to their extraordinarily small diameter and versatile electronic properties [2]. It is suggested that individual SWNT may act as devices such as field-effect transistors (FET) [3], single-electron-tunneling transistors [4,5], rectifiers [6,7], or p–n junctions [8]. The most exciting expectation lies in the devices fabricated on a single tube [9].

In recent years, the interplay between mechanical deformation and electrical properties of SWNTs have been extensively studied [9–12]. Among them, some structural deformations such as twisting, bending, stretching, and topological defects are not compatible with desirable stable contacts for reversibly controllable devices [13]. More recently, Tombler *et al* [14, 15] used an atomic force microscope tip to manipulate a metallic SWNT, leading to a reversible two-order magnitude change of conductance, and Lammert *et al* [13] applied a uniaxial stress to squash SWNTs and detect a similar reversible metal–insulator (M–I) transition. Since the tube ends do not need to move and they are easily controlled, the studies pointed to the possibility that a metallic SWNT may be used as an ultrasmall electromechanical switch.

It is also well known that a magnetic field can change the conductance of carbon nanotubes [16–18]. The magnetic field either parallel or perpendicular to the axis can change

the low-energy electronic properties of the tubes. However, a possible electric field-controlled M–I transition is more exciting because of its easy implementation in the actual applications. Now, a question remains: can an electric field change the electronic properties of a tube?

In previous studies on electronic transports [19], since the bias voltage is a slow-change variable in the range of the primitive unit cell, the possible change of the energy-band structure induced by the bias voltage is neglected. The controlled potential, such as the gate voltage in the case of FET [3], does not induce a voltage drop in the direction perpendicular to the tube axis, and it only shifts Fermi level or changes the carrier concentration. In the literature, to our knowledge, the fact that the properties of the longitudinal electronic transports are changed by a transverse electric field has not been studied. In fact, because of the small diameter of SWNTs (≈ 1 nm), it is easy to exert a strong electric field ($|\vec{E}| \sim \mathrm{V\ nm^{-1}} \sim 10^{8-9}\ \mathrm{V\ m^{-1}}$) perpendicular to the axis. In (n, n) metallic SWNT, the electrons near Fermi energy are nonlocal in the circumference of the tube as their circumference Fermi wavevector is zero [2], and the classic wave-package approximation in slow-change voltage may be not suitable in the presence of the strong transverse electric field. The $\mathrm{Vnm^{-1}}$ order electric field is enough to break the rotational symmetry about the tube axis, and create new interband and inter-wavevector coupling, which may change the low-energy electronic properties of SWNTs, and hence affect the electronic transport. On the other hand, the field is still 2–3 orders less than the atomic interior electric field, and can be treated as perturbation.

In this letter, based on a tight-binding (TB) model, we calculate the low-energy electronic structure of SWNTs in an external electric field perpendicular to the tube axis (see figure 1). The result shows valuable effects: (1) the electric field can always induce an energy gap in (n, n) metallic SWNTs; (2) there is a maximal gap strongly dependent on the radius of the tubes; (3) a universal scaling is found for the gap as a function of the field and the size of the tubes; (4) using the dielectric function of tubes obtained by Benedict *et al* [20], we find the magnitude of the required electric field falls into the range of current experimental conditions, therefore this allows the possibility of applying SWNTs to the electric-field-controlled nanoscale switching devices.

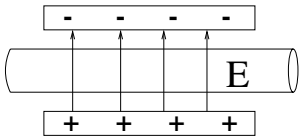

Figure 1. A uniform external electric field perpendicular to the axis of SWNT.

The nearest-neighbour TB approximation has been used successfully for calculating the electronic structure of graphite sheet and nanotubes [2], and the polarization of SWNTs [20]. For the low-energy electronic properties of tubes in the presence of electric field, we will only use the π-electron single-orbital TB approximation [21].

In the presence of a transverse electric field $\boldsymbol{E}$, there is an additional coupling between the nearest-neighbour atoms, reflected in the TB Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 \tag{1}$$

where $\mathcal{H}_0$ is the unperturbed Hamiltonian, and $\mathcal{H}_1 = eV(\boldsymbol{r})$. Here e is the charge of an electron, and $V(\boldsymbol{r})$ is the electrostatic potential of the total electric field which is equal to the sum of an external field $\boldsymbol{E}_0$ and the polarized field induced by $\boldsymbol{E}_0$. For a uniform field [22], the potential in the cylindrical surface of SWNT is

$$V(\boldsymbol{r}) = -V_0 \cos\phi \tag{2}$$

where $V_0 = RE$ is the transverse voltage drop of the tube, and ϕ is the azimuth of the cylinder. Here R is the radius of SWNT, and E is the total electric field strength.

The main role of the electrostatic potential is to change the electronic energy of the ith carbon atom by $eV(\boldsymbol{R}_i)$, where $\boldsymbol{R}_i$ is the position vector of the ith atom. The hopping correction due to the electric field between site i and site j is very small, about the order of s. Here s is the overlap integral of two nearest neighbour atom i and atom j, $s = \int \phi_i^*(\boldsymbol{r})\phi_j(\boldsymbol{r})\mathrm{d}^3\boldsymbol{r} \approx 0.129$ [23], where $\phi_i(\boldsymbol{r})$ is the π-electron wavefunction of the ith atom. The perturbed Hamiltonian matrix elements are:

$$\langle\phi_i|\mathcal{H}_1|\phi_i\rangle = eV(\boldsymbol{R}_i) \tag{3}$$

$$\langle\phi_i|\mathcal{H}_1|\phi_j\rangle \approx esV(\boldsymbol{R}_{ij}^c) \tag{4}$$

where $\boldsymbol{R}_{ij}^c = (\boldsymbol{R}_i + \boldsymbol{R}_j)/2$ is the position of the mass centre of the two nearest neighbour i atom and j atom. Equation (3) is precise because of the symmetry of wavefunction, but in equation (4), we have neglected the electrostatic potential change in the overlapping range of electronic clouds. After gaining these Hamiltonian matrix elements, we can easily calculate the electronic structure of a nanotube in the presence of an electric field.

Figure 2 shows our result on the electronic energy bands of a (10, 10) tube in the presence of electric fields with different magnitudes. When $V_0 = 0.5$ V, a gap of $E_g \sim 0.3$ eV is found at K_0, the Fermi wavevector in zero field. As V_0 increases, the gap increases, and when $V_0 = 1.5$ V, we find that the band structure is obviously deformed. It is surprising to find that the gap decreases as V_0 increases further. When $V_0 = 3.0$ V, the zero gap is found, but the Fermi point dramatically moves to a different position from K_0. The results reveal that a controlled electric field of 1 Vnm^{-1} order can obviously affect the transport properties of a (10, 10) tube.

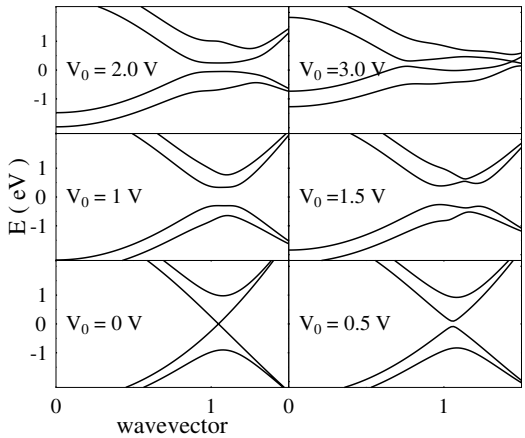

Figure 2. The energy bands of (10, 10) SWNT in the vicinity of Fermi level under the application of a transverse electric field V_0. (10, 10) tube is metal at $V_0 = 0$ V, and it is a semiconductor in the weak field range.

To probe the above effect in general, we performed the computation for a series of (n, n) tubes. Figure 3 shows the gap as a function of the electric field in (n, n) tubes, where n is from 5 to 15. From figure 3, we find the determined effect: the electric field can always induce a gap, i.e. a metal–insulator transition, in (n, n) tubes, and the size of the gap strongly depends on the magnitude of the transverse field and the tube parameter n. For any (n, n) tubes, the gap first increases with increasing field, and reaches a maximal value E_{gm} at the $V_0 = V_{0m}$,

then drops again. Both the maximal gap E_{gm} and the corresponding V_{0m} are approximately proportional to $1/n$, and hence inverse proportional to the radius of tubes, i.e.,

$$E_{gm} \approx 6.89\ \mathrm{eV}/n \tag{5}$$

$$V_{0m} \approx 12.09\ \mathrm{V}/n. \tag{6}$$

The finding, which is shown in (5) and (6) that the maximal gap E_{gm} quickly decreases as the size of conductor increases, indicates the electronic structure change is very small in the large materials even though at very strong electric field. This might be the reason why people have not yet recognized the effect in previous studies on large conductors. In the strong field range, figure 3 shows a more complicated field dependence of the gap, which can also be negative. The field dependence of the gap is quite similar for tubes with various radii, which invokes us to scale both E_g and V_0 up to n times their original values. The obtained results are shown in figure 4. From it we do find the scaled gap to be a universal function of the scaled electric field for all (n, n) tubes. In the weak field range, for all eleven calculated (n, n) tubes there exists a simple relation: $nE_g = \lambda(neV_0)^2$, where λ is a constant, about 0.07 $(\mathrm{eV})^{-1}$. In the middle field range, apart from a few small-radius tubes such as (5, 5) and (6, 6) tubes, the universal scaling law still holds.

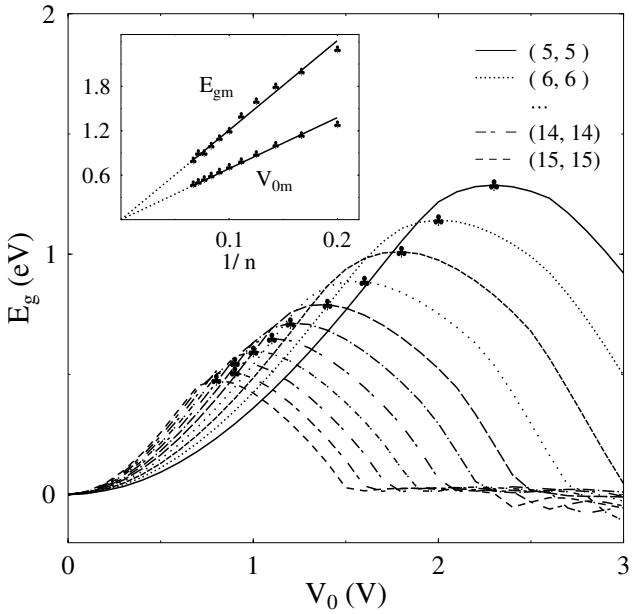

Figure 3. Field-induced gap of (n, n) tubes versus the field. From the top to the bottom, the tube parameter n increases from 5 to 15. The clubs denote the position of the maximum gap point. In the inset, both the maximum gap E_{gm} and V_{0m} (see text) are found to be proportional to $1/n$ The lines are fitting results.

To understand the above scaling relation, we use perturbation theory to calculate the field-induced gap in weak field limit. The first-order perturbation approximation only causes a shift in the Fermi level, showing no contribution to the gap. Calculating up to the second-order perturbation at K_0 point, we obtained the following analytic result

$$E_g \approx \frac{\sqrt{3}}{2\pi\gamma} ne^2 {V_0}^2 \tag{7}$$

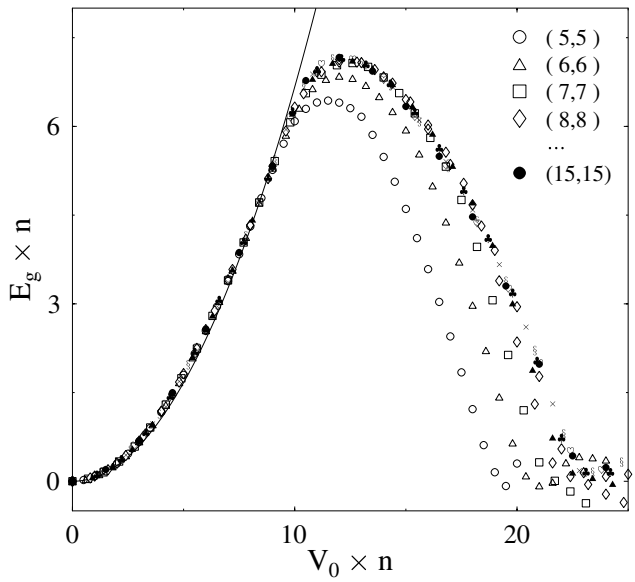

Figure 4. Universal scaling are found for the gap as a function of V_0 in different (n, n) tubes. At weak field, the data of all tubes are very much consistent with the scaling relation $nE_g = \lambda(neV_0)^2$, as expected by the second-order perturbation theory. The line is the fitting result. Except for (5, 5) and (6,6) tubes, the universal scaling is satisfied well up to strong field region.

where γ (=3.033 eV) is the hopping parameter in the absence of the electric field [23, 24]. The contribution of the overlap integral s, which is very small, is neglected. The second-order perturbation calculation gives almost the same scaling relation as the numerical results in the weak field, though the obtained $\lambda \approx 0.09$ (eV)$^{-1}$ is slightly larger than the numerical result 0.07 (eV)$^{-1}$. In the strong field range, since the Fermi wavevector is away from K_0, the perturbation theory becomes unsuitable. In fact, the weak field range may be more compatible with the practical application. In order to open a 0.1 eV gap in the energy bands of (n, n) tubes, according to equation (5) n must be smaller than 68, and the required electric field is,

$$E = \frac{2\pi}{3r_0 e}\sqrt{\frac{E_g}{\lambda}}n^{-\frac{3}{2}} \tag{8}$$

where r_0 (=1.42 Å) is the bond length of carbon atoms in SWNT. Therefore, for example for a (10, 10) tube, the required field is about 5×10^8 Vm^{-1}, and for a (60, 60) tube, it is about 3×10^7 Vm^{-1}. Since the total field $\boldsymbol{E}$ is equal to to the sum of the external field $\boldsymbol{E}_0$ and the polarized field, we have $\boldsymbol{E} = \boldsymbol{E}_0/\epsilon$, where ϵ is the dielectric function. Under the homogeneous polarization approximation, Benedict *et al* [20] calculated the ϵ of some tubes within random phase approximation. Based on their results, we have [25],

$$\epsilon = 1 + 5.2\frac{R^2}{(R + \delta R)^2} \tag{9}$$

where R is the radius of tubes. Benedict gave δR about 1.2 Å. So the required external field is approximately 6 times that of the calculated total field $\boldsymbol{E}$. Since such a magnitude of the electric field can be easily reached by the current experimental conditions, we would like the above prediction to be checked in near future.

In summary, we have proposed an electric-field-induced M–I transition in (n, n) SWNTs for the first time. The universal relationship between the gap and the electric field has been

obtained in SWNTs by using the TB model. The results support the argument that SWNTs can be applied as nanoscale electric signal-controlled switching devices.

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[25] $\epsilon = \alpha_0/\alpha = 1 + \frac{2\alpha_0}{R_{eff}^2}$, where α_0 and α are the unscreened and screened polarizability of tubes, respectively. $R_{eff} = R + \delta R$ is the effective radius of tubes due to the screened charge is out of the wall of tubes. Benedict *et al.* showed $\alpha_0 \approx 2.6R^2$ for all tubes (see figure 2 of reference [20]).