

The Effects of Stone-Wales Defect on Quantum Capacitance in Carbon Nanotube

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Abstract

Carbon nanotube is an emerging material for usages in electronic devices due to its efficiency in storing electrical energy. Although fabrications of this material have been developed to nearing perfection where the yield of pristine nanotubes can be most of the time achieved, their structures often contain topological defects known as the Stone-Wales defects. It is widely accepted that the Stone-Wales defects alter the electronic properties of nanotubes. However, the influence of the defects to capacitance of nanotubes remains relatively unexplored. In this work, the effects of Stone-Wales defect to quantum capacitance in carbon nanotube is investigated using a Density Functional theory based a tight-binding method. Our results demonstrate that a single Stone-Wales defect significantly impacts the sign-switching behavior of nanotubes. It is theorized that main contributions to the sign-switching is capacitance due to the changes in exchange-correlation energy caused by the defects, while it is not clear whether the kinetic energy contribution or the density of states of the electrons plays a role. The overall capacitance of carbon nanotube increases by the existence of Stone-Wales defects.

Keywords: Quantum capacitance, Carbon nanotube, Stone-Wales defects

Introduction

The carbon based structures are emerging materials as major components in an electrical devices due to their modifiable electrical properties. Nevertheless, nanotubes usually suffer from various kinds of topological defects arisen during their growth. The Stone-Wales defect are among general defects found. In general, a Stone-Wales defect occurs when the two carbon atoms in carbon nanotube (CNT) are rotated by 90 degree with respect to the center of both atoms. It is known that topological defects impact the electronic properties of nanotubes. For example, defects are known to enhance electrical conductivity of nanotubes [1], decreasing the magnetic resistance [2], reducing the thermal conductivity [3], and changing the band gap among others [4]. Though there is large volume of scientific literature investigating electrical properties of defective nanotubes, to the best of our knowledge the influence of defects to capacitance of nanotubes remain relatively unclear.

Nanotubes are prominent materials for electronic applications because of its efficiency in storing electrical energy. According to the theory of classical electrostatic, the capacitance per unit area (C_{geo}) of a metal-dielectric-metal capacitor depends

on dielectric permittivity (ϵ) and thickness (d) of dielectric sandwiched between two metallic electrodes.

$$C_{geo} = \epsilon/d \quad (1)$$

In addition to the well-known geometric capacitance, the overall capacitance is also influenced by a quantum quantity termed quantum capacitance arisen from the electronic interaction between the electrons. The quantum capacitance is the influencing parameter to the overall capacitance [5]. The quantity of overall capacitance (C_G) is governed by a geometric value (C_{geo}) and the quantum capacitance term (C_Q), as shown in Eq. (2).

$$\frac{1}{C_G} = \frac{1}{C_{geo}} + \frac{2}{C_Q} \quad (2)$$

It is known that a quantum capacitance consists of two parts (1) contributions due to the limiting density of states (C_{DOS}) at Fermi level:

$$C_{DOS} = e^2 \rho(E_F) L \quad (3)$$

where e is electron charge , $\rho(E_F)$ is density of state at Fermi level, and L is the length of one-dimension system, and (2) the contributions due to the many-body effects (C_{xc}) that includes the effects of exchange and correlation energy. Kopp and Mannhart

[6] have demonstrated that the capacitance can be derived from total energy of electron-ion system e.g. Hartree energy, kinetic energy, exchange energy, correlation energy and external energy as:

$$E = E_H + \sum E_{kin} + \sum E_x + \sum E_c + \sum E_{ext} \quad (4)$$

In their article, it has been demonstrated that, for a two-plates electron systems, the quantum capacitance comprises contributions due to the kinetic energy, exchange energy and correlation energy, while the Hartree energy and external energy contribution amounts for the geometric capacitance:

$$\frac{1}{C_G} = \frac{1}{C_{geo}} + \sum \frac{1}{C_{kin}} + \sum \frac{1}{C_x} + \sum \frac{1}{C_c} \quad (5)$$

The kinetic term is, in fact, representing the capacitance due to the density of state (DOS). Therefore, by regrouping terms the quantum capacitance can be written as:

$$\frac{1}{C_Q} = \frac{1}{C_{DOS}} + \frac{1}{C_{xc}} \quad (6)$$

Generally, the magnitude of C_Q is greater than the magnitude of C_{geo} . The overall capacitance depends on geometric capacitance such as the thickness of SrTiO₃/SrRuO₃ capacitor [7]. However, the quantum capacitance plays the critical role in the overall capacitance in some types of material such as the low-dimension conductor of carbon nanotube [5]. Moreover, Eq. (2) hints at the sign of quantum capacitance enhancing overall capacitive characteristics.

Past research reports have shown that the behavior of quantum capacitance are governed by the screening potential between the device and metallic gate [8]. The screening phenomenon occurs when inducing electronic field on the nanotube. The corresponding bias drives the accumulated electrons on the surface of nanotube to screen the inducing electronic field. Notably, the types of screening can be explained as following. (a) Partially screening occurs when accumulated electrons on the surface of nanotube are not enough to screen the induced electronic field. (b) Complete screening implies the accumulated electrons can screen all inducing electronic field is completely screen. Lastly, (c) overscreening occurs when the electrons are accumulated more than needed. The aforementioned screening types are summarized in term of electronic potential nearing the surface of a nanotube in Figure 1. The potential vanishes at the center of the tube in the case of

complete screening. It is positive and negative in the case of partial screening and overscreening respectively.

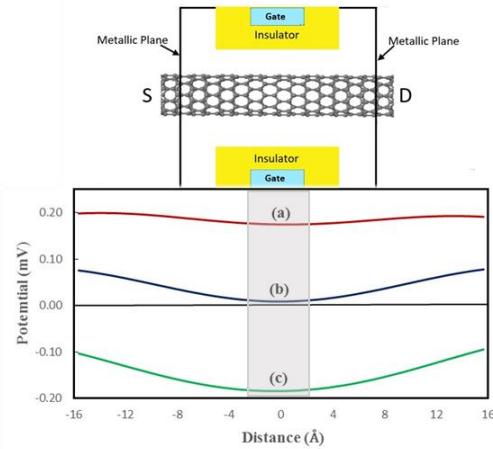


Figure 1. The electrostatic potential of the distance for each carrier densities are shown (a) the positive potential at the center of device due to the effect of partially screen. The electrons are not accumulated enough, (b) the zero potential at the center of device due to the effect of completely screen, (c) the negative potential at the center of device due to the effect of overscreening. The electrons are accumulated more than needed.

In this paper, we focus on how a Stone-Wales defect impacts the capacitive properties of nanotubes using the density functional tight binding (DFTB) approach. Our calculation approach is outlined in Section 2. The details of computational set up is discussed in Section 3. In Section 4, it will be shown that defects have influences on the quantum capacitance.

Theory and related works

Giving a stimulus potential, carbon nanotubes induce charges on their surface. To model this charge accumulation, we have employed techniques derived from the principles in the Density Functional based Tight-Binding (DFTB) theory. DFTB is a widely used computational technique capable of solving the problems in electronic structures. A DFTB calculation is based on adjusting the electron wave function as a function of atomic orbitals and solving Hamiltonian operator of spin quantum number. Specifically, we used the DFTB+ package in this study and the exchange and correlation functional is based on a local density approximation (LDA) [5]. The DFTB+ code is suitable for several

calculation modes, for example structural optimizations, and total energy calculations, among others.

Zheng *et al.* reported that the performance of DFTB+ package is comparable to regular Density Functional Theory (DFT) calculations in term of calculating the equilibrium geometries and isomers of C₆₀-C₈₆ fullerenes [9]. The energies of very large system dissolved carbon nanotube in aromatic solvents are calculated using DFTB [10]. The DFTB simulated band gap of the various doped-site carbon nanotube have been investigated [11]. DFTB methods are used to computes the energies depend on the length of carbon nanotube [12]. The DFTB simulated band gap of strain-induced carbon nanotube is comparable to the experimentally band gap [13]. Specifically, relating to this work Latessa *et al.* have reported that DFTB atomistic simulations of the nonequilibrium transport properties of carbon nanotube field-effect transistors [14].

In this work, the quantum capacitances are determined by considering three types of screening behaviors namely; (1) completely screening, (2) partial screening, and (3) overscreening, have been shown in introduction section. The setup of quantum capacitance model consists of four components; (a) metallic electrode, (b) ideal SiO₂ insulator, (c) metallic plane at the end of nanotube, and (d) the nanotube, as shown in Figure 2 (a). This setup can be interpreted into the circuit model, as shown in Figure 2 (b). The capacitance between carbon nanotube and insulator is $C_{\text{ins},1}$ and $C_{\text{ins},2}$ is the capacitance inner the nanotube. The capacitance of external metallic plane is C_{ext} . Finally, C_Q is the quantum capacitance of this geometric setup which can be obtained knowing the other capacitances as shown in Eq. (5).

Past research have been shown the behavior of quantum capacitance of carbon nanotube is governed by the carrier density [5]. It corresponds to the charge accumulation on the nanotube surface which can alter the types of screening.

$C_Q(n)$ is the quantum capacitance as a function of a one-dimensional carrier density (n). The externally controlled gate voltage is δV_G . $\delta Q(n_{\text{crit}})$ is a total charge induced on carbon nanotube at critical value of the carrier density (n_{crit}) when complete screening is observed. The total charge induced at each doping level of carrier density is $\delta Q(n)$. By examining calculation results, the capacitance of the external metallic plane C_{ext} and the capacitance caused by the inner surface of the

nanotube $C_{\text{ins},2}$ are insignificant. In the case of complete screening the overall capacitance complete screening is given by $1/C_G = 1/C_{\text{ins},1} = \delta V_G / \delta Q(n_{\text{crit}})$ whereas in the other screening regimes, the overall capacitance is $1/C_G = 1/C_{\text{ins},1} + 1/C_Q(n) = \delta V_G / \delta Q(n)$. By comparing these two expressions, the quantum capacitance can be easily solved to yield.

$$C_Q(n) = C_{\text{ins},1} \left[\frac{\delta Q(n_{\text{crit}})}{\delta Q(n)} - 1 \right]^{-1} \quad (7)$$

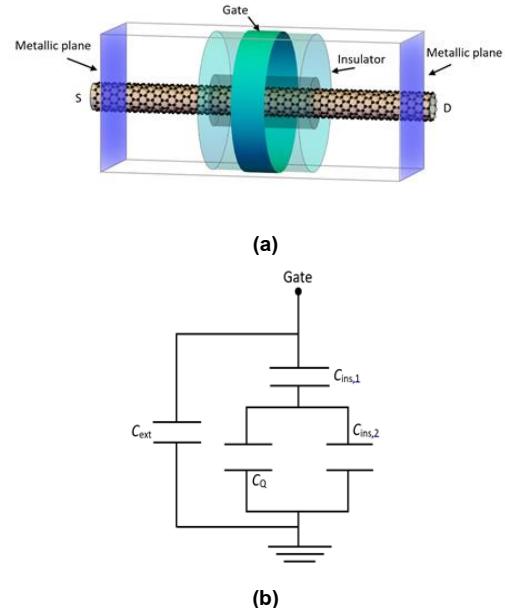


Figure 2. (a) The setup of the quantum capacitance model of a nanotube and (b) circuit model [15]

Computational details

The quantum capacitances are obtained by computing the induced charge on nanotube as it is biased by an external potential described in the previous section. This induced charge is also viewed as a function of the uniform carrier density as shown in Eq. (5).

In this work, a pristine (10,0) carbon nanotube and a corresponding defective carbon nanotube with a single Stone-Wales defect (as shown in Figure 3) are investigated. Both materials consist of 2,160 atoms of carbon and the length of both nanotubes are about 22.6 nm. The DFTB packages have been modified to allow for transport calculations of coaxially gated nanotubes. CC_pz.sk file is used as a parametrization file. For the Brillouin-zone sampling we set k-point according to the 256 x 1 x 1 according to the Monkhorst-Pack sampling pattern. The optimization of each structure is done by the total energy

calculation of the equilibrium structures. In the transport calculation, the source and drain of current are placed next to the equilibrium structure as shown in Figure 2.

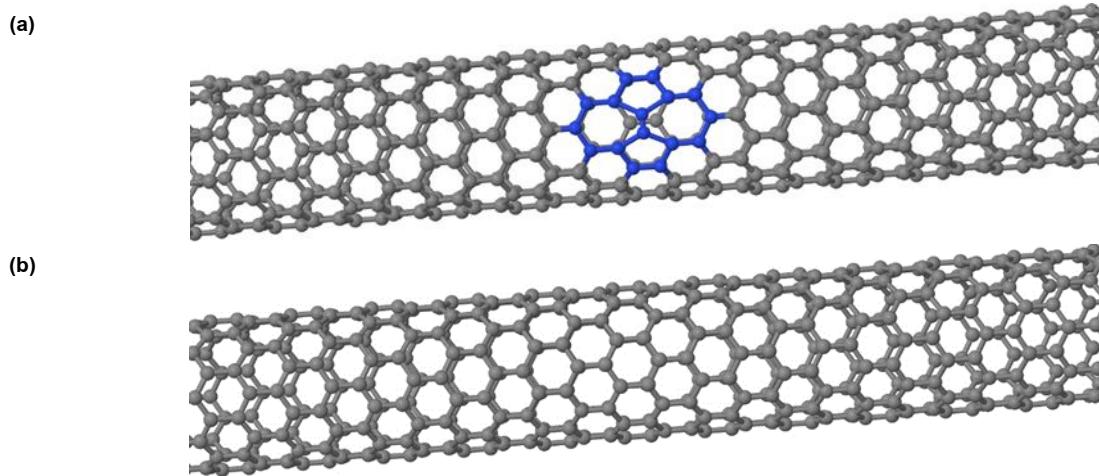


Figure 3. Two types of carbon nanotube used as an electrode (a) defective carbon nanotube (b) pristine carbon nanotube

The computer utilized in this work consisted of an Intel Core i7-4790 (3.60 GHz) of CPU. The graphic card was NVIDIA Quadro K620. The memory of the computer was 32 GB. The operating system was Ubuntu 14.04 LTS. The larger calculations have been performed using a high performance computer. The quantum capacitance in pristine carbon nanotube and defective carbon nanotube are compared after all calculations are completed.

Results and discussion

Figure 4 shows the quantum capacitive behaviors of two types of the carbon nanotubes. The vertical axis is the simulated quantum capacitance which is in the unit of attofarad (aF) and the horizontal axis is carrier density in the unit of electron per length in Angstrom (\AA^{-1}). The carrier density can be calculated by dividing the total charge in nanotube by the length of the nanotube. For the pristine nanotube, the results show quantum capacitance continuously decreases into the negative value until the carrier density is 0.1148 \AA^{-1} , at higher carrier density the sign of quantum capacitance switches into large positive values and converts into nearly zero. In the case of the defective nanotube, the sign of quantum capacitance switches when carrier density is 0.1387 \AA^{-1} . These results show that the effects of Stone-Wales defect can enhance the critical carrier density.

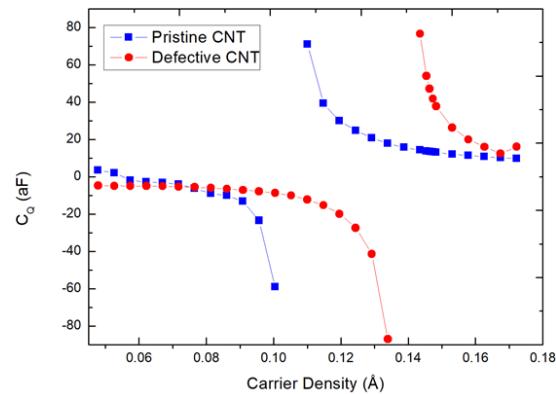


Figure 4. The effect of Stone-Wales defect on quantum capacitance

The quantum capacitance of pristine carbon nanotube and defective carbon nanotube shows negligible different values until the carrier density of approximately 0.09 \AA^{-1} . The quantum capacitance of pristine structure continuously decreases and switches into the positive value at 0.11 \AA^{-1} of carrier density. The quantum capacitance of defective structure continuously up to the carrier density of 0.11 \AA^{-1} , and decreases, and switches abruptly into the positive value at 0.14 \AA^{-1} . Hence, the quantum capacitances of defective carbon nanotubes are greater than the pristine structure when carrier density is more than 0.09 \AA^{-1} until the carrier density of approximately 0.10 \AA^{-1} .

The effects of Stone-Wales to quantum capacitance are clear when considering C_Q at 0.12 \AA^{-1} of carrier density. The quantum capacitance of the pristine structure possesses a positive sign, while the quantum capacitance of a defective nanotube is negative. This demonstrates that a single Stone-Wales defect can switch the sign of quantum capacitance. As an implication of Eq. (2), the increasing overall capacitance may appear when the sign of quantum capacitance is switched from positive to negative. The ability to increase the range of negativity of quantum capacitance by introducing more defects into the structure thus enhances the probability of increasing the overall capacitance. The relations between Stone-Wales defects and quantum capacitance is worth further investigation.

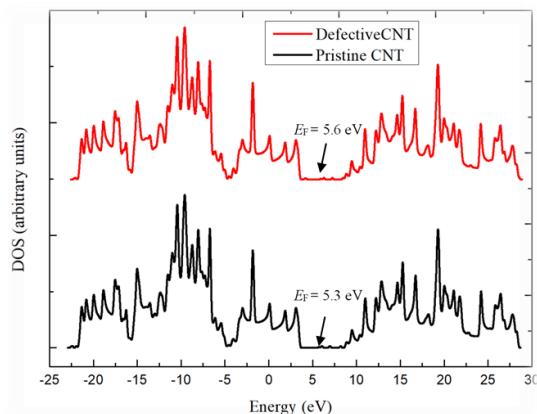


Figure 5. The density of state of a pristine nanotube and a nanotube with a Stone-Wales defect.

It is well-known that the electronic properties of materials are governed by the behavior of electrons such as energy levels that electrons occupies, and the highest state that electrons can be excited. An essential data that demonstrates electronic properties is the density of states (DOS). DOS represents the possible number of occupations on each energy level. Figure 5 shows the DOS's of both pristine and defective nanotubes. In this work a DOS is computed using a nanotube which consists of 2,160 atoms, and is covered by a tetragonal supercell of the size $30.00 \times 30.00 \times 229.33 \text{ \AA}^3$. In Figure 5, the vertical axis is the simulated DOS in the unit of arbitrary unit (arb. unit) and the horizontal axis is energy in the unit of electron volt (eV). Both DOS's are different from other published data due to the greater magnitude of carbon atoms [16]. As shown in Eq. (4), the quantum capacitance depends on both C_{DOS} and C_{XC} . As evident

from Figure 5, the DOS of pristine and defective nanotube show some differences. We can observe a new state appearing at 4.8 eV at the DOS of the defective structure, indicating the reduction of the energy gap of nanotube in the defective CNT. The capacitance due to the DOS is determined by the location of Fermi energy of the electron, according to Eq. (3). The location of the Fermi energies are marked on Figure 5, and they are 5.3 eV and 5.6 eV for pristine and defective CNT respectively. It should be noted that there is only a small shift of 0.3 eV in this Fermi energy. On the other hand, it is widely accepted that the electrostatic interactions among a collection of electrons is revealed by the exchange-correlation energy [17]. According to Hanlumyung, Li, et al. [15], homogenous strain field can significantly alter the contribution of the exchange-correlation to the quantum capacitance in nanotube. Though a Stone-Wales defect does not lead to a homogeneous deformation, it triggers a local bond stretching/shrinkage. It is then believed the alteration of quantum capacitance behavior in this work is governed by such heterogeneous deformation. As implied by [15], the functional dependence of the effect of exchange-correlation energy to the heterogeneous strain field could be rather complicated. The mechanism of strain effects to quantum capacitance has been theoretically demonstrated by considering an electron gas on the surface of a one-dimensional nanowire. In the case of homogeneous strain, the inverse of the quantum capacitance has been shown to be proportional to the second derivative of exchange energy (E_x): $1/C_Q \propto n_1 r_s^2 d^2 E_x / dr_s^2$ [18], where r_s is the inter-particle distance and n_1 is the one-dimensional electron density. The parameter r_s is correlated with the distance among electrons while viewing an electron gas as a collection of electronic particles. From this perspective, inducing a strain field into the CNT structure could alter the quantum capacitance. Nardelli et al. has demonstrated that the critical strain for a formation of a Stone-Wales defect in a zigzag (10,0) CNT is about 10% [19,20]. Therefore, it is believed that a Stone-Wales defect acts as a localized storage of the elastic energy. This heterogeneous strain could play a role similar to the homogeneous strain, affecting the inter-particle distances. Hanlumyung, Li, et al. have revealed the effects of homogenous strain levels of -0.3%, 0.3% and 1.5% to exchange-correlation energy, and found significant shift in the quantum capacitance [15]. It is believed that the stored energy caused by strain the critical strain of 10% around Stone-Wales defect in CNT may

influence quantum capacitance through the exchange-correlation term as well.

Conclusion

We have investigated the quantum capacitance of (10,0) pristine carbon nanotube and the corresponding structure with a Stone-Wales defect. We found that the Stone-Wales defect alters the behavior of quantum capacitance. First, it switches the sign of quantum capacitance from the large positive into the negative values. Second, it increases the negative range of quantum capacitance. Lastly, it enhances the critical carrier density. Generally, the quantum capacitance is contributed by the DOS and the exchange-correlation energy. By examining the DOS of both pristine and defective nanotube, it is inconclusive whether the DOS plays a role in the sign switching behavior due to the existence of defects. On the contrary, it has been argued that the influence of heterogeneous strain field, caused by the existence of the Stone-Wales defects, plays an important role in shifting the values of quantum capacitance. The amount of the strain energy stored by the Stone-Wales defects is about the formation strain energy caused by the critical strain of 10%. This level of strain is much higher than reported values of a few percentages where a significant contribution of the exchange-correlation effect to the quantum capacitance has been found.

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