

# Charge mobility modification of semiconducting carbon nanotubes by intrinsic defects

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**Abstract.** Charge carrier mobility is a central transport property in nanoscale electronics. Carbon nanotubes (CNTs) are supposed to have high carrier mobility. The preparation methods of CNTs have been greatly improved, but the defects always exist. This work presented first-principle investigations on the charge carrier mobility of carbon nanotubes containing several intrinsic defects. The charge carrier mobilities of zigzag (10, 0) tubes with Stone–Wales, mono vacant and 5/8/5 defects were studied as an example to explore the role of defects. Most carrier mobilities were decreased, but several values of mobility are unexpectedly increased upon the appearance of the defects. This interesting result is discussed based on the changes of the stretching modulus, the effective mass of the carrier and deformation potential constant induced by the defects.

**Keywords:** CNTs, Intrinsic Defects, Carrier Mobility, Charge Transport, DFT

## 1. Introduction

Charge carrier mobility is a central transport property in nano-scaled electronics. As one of the exiting carbon forms, carbon nanotubes (CNTs) are good candidates for the next generation electronics due to high carrier mobility [1-2].

CNTs commonly are fabricated by using various methods, such as arc discharge, chemical vapors deposition and laser vaporization [3]. However, the accuracy of material processing at the atomic scale is still a great challenge currently. The preparation methods are improved a lot, but different kinds of defects always exist in any materials. So defect is also unavoidably in the obtained samples of CNTs [4-6].

It is known that the electronic properties of the materials can be modulated by the geometrical structures. This is also true for CNTs. For instance, the tube diameter, chirality, substitutions, physical or chemical adsorptions and encapsulations are important for tailoring the electronic structures of



CNTs [7-11]. Previous studies also investigated the CNTs containing intrinsic defects, and revealed the impact of the defects on the relative stabilities, electronic properties and young's modulus [12-14]. However, up to date, few understanding is available on the carrier mobility of CNTs induced by defects according to our best knowledge. Thus this paper detailed studies on the carrier mobility of semiconducting zigzag CNTs induced by intrinsic defects are investigated from first-principle point view.

## 2. Models and Computational Details

The charge carrier mobility of the CNTs with and without defects is studied under the framework of deformation potential (DP) theory and effective mass approach [15-18]. The carrier mobility  $\mu$  of 1D crystal can be expressed as:

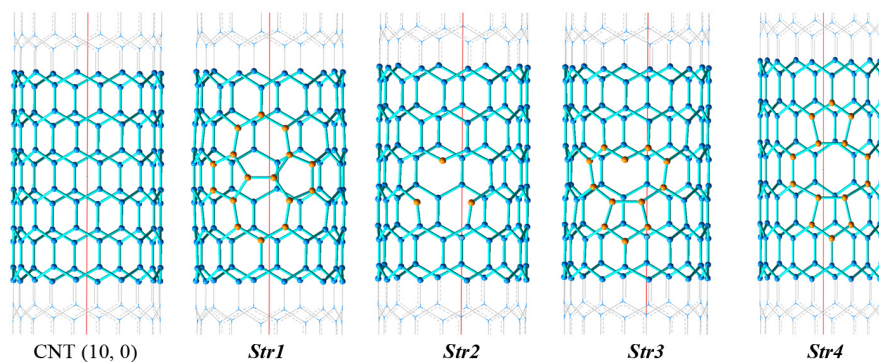
$$\mu = \frac{e\hbar^2 C}{(2\pi k_B T)^{1/2} |m^*|^{3/2} E_1^2} \quad (1)$$

where  $C$  is the stretching modulus of 1D crystal,  $m^*$  is the effective mass of charge carriers and  $E_1$  is DP constants. The detailed descriptions can be seen from our previous studies [17, 18]. It should be aware that only longitudinal acoustic (LA) phonon scattering is considered in the models adopted here. Other scattering mechanisms, such as optical phonon scattering, inter-subband scattering and radial-breathing phonon scattering that may also limit the charge mobility, are not addressed in this work [19].

First-principle studies are conducted based on the Kohn-Sham density functional theory (DFT) combined with self-consistent field crystal orbital (SCF-CO) method. We have chosen hybrid B3LYP method because it is more accurate to explore various carbon-based systems and the methods used here could give rather good results compared with those obtained by various different functional and basis sets according to the previous calculations [20]. All calculations are performed by using the linear combination of atomic orbital (LCAO) technique with CRYSTAL2014 code. A double- $\zeta$  plus polarization basis set 6-21G ( $d, p$ ) implemented in the CRYSTAL program for solid-state calculations and 41 k-points sampling in the first Brillouin zone were adopted in the SCF-CO calculations.

## 3. Results and Discussion

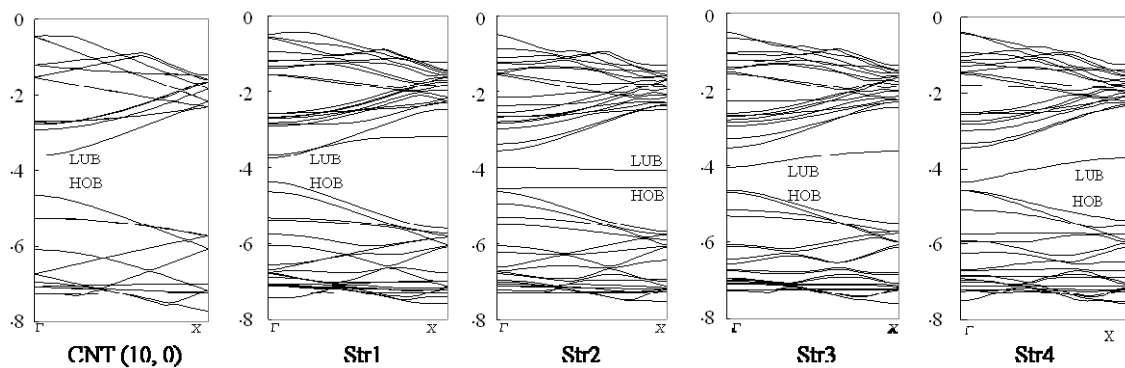
It is known that the structure and physical property of SWCNT mainly depend on the diameter as well as chirality. We limit to semiconducting CNTs with zigzag edges in this work, following previous studies [2]. The armchair tubes are not considered since they all exhibit metallic property. The semiconducting zigzag CNT (10, 0) was selected as a case study to explore the carrier mobility induced by defects. A super-cell was adopted to avoid interaction between adjacent defects; thus, each defect is presented in three unit cells of CNT (10, 0). The obtained structures with fully geometrical optimizations of pristine CNT (10, 0) and four defective structures are shown in **Figure 1**.



**Figure 1.** The structures of pristine CNT (10, 0) and four defective tubes.

Among them, **Str1** is the model containing Stone–Wales (SW) defect. A SW defect occurs when one C–C bond rotates  $90^\circ$  and forms two 5-membered rings and two 7-membered rings. It is also the most commonly observed defects in carbon-based materials with  $sp^2$  hybridization, such as fullerenes, CNTs and graphene. **Str2** is the original mono vacant defected structure. It can be obtained by removing one carbon atom from the hexagonal network directly, with three unsaturated bonds left. **Str3** can be seen as the configurations derived from **Str2** by geometrical reconstructions. **Str4** is the 5/8/5 defect, which can be seen as the structure derived from double vacant defect by geometrical reconstructions. To confirm the stability of these defective structures, molecular dynamics (MD) simulations are conducted by using the density functional based tight binding (DFTB) method. We performed MD simulations at 300 K with each for 3 ps under the constant-temperature constant-volume condition with the time step size as 1 fs. It is found that the geometries of these tubes with mono-vacant or related defects are well kept according to the snapshot images of the equilibrium structure at the end of each MD simulation as well as the potential energies with time evolution. Thus there is no sign of these structures studied here according to the MD simulations.

The calculated electronic band structures are plotted in **Figure 2**. We can see that pristine (10, 0) tube is a semiconductor with a direct band gap of 1.064 eV, which agrees quite well with previous DFT calculations [7]. As the defect is introduced into the tube, it is observed that the semiconducting property is well maintained for all the defective tubes. Nevertheless, the obtained band gaps are all obviously reduced compared with that of pristine tube.



**Figure 2.** Band structures of pristine CNT (10, 0) and four defective tubes.

The calculated electron and hole mobilities for the semiconducting tubes at room temperature are listed in **Table 1**. The electron and hole mobilities ( $\mu_e$  and  $\mu_h$ ) of the pristine (10, 0) tube were calculated to be  $1.096 \times 10^4$  and  $1.390 \times 10^3$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ , respectively, which agree well with previous DFT calculations by Wang and co-workers [7]. Furthermore, the obtained electron mobility is one order larger than the hole. Thus, electron is the majoring carrier, for which the transport is more favorable in pristine (10, 0) tube than hole carrier.

**Table 1.** Stretching modulus ( $C$ , in  $\text{eV}/\text{\AA}$ ), deformation potential constant ( $E_1$ , in eV), effective mass of carrier ( $m^*$ , in  $m_e^0$ ) and mobility ( $\mu$ , in  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ ) for defective and pristine tubes.

tubes	$C$	$E_{1V}$	$E_{1C}$	$m_h^*$	$m_e^*$	$\mu_h$	$\mu_e$
CNT(10, 0)	573	11.907	4.242	0.0812	0.0812	$1.390 \times 10^3$	$1.096 \times 10^4$
<b>Str1</b>	560	11.592	3.429	0.0653	0.0663	$1.986 \times 10^3$	$2.219 \times 10^4$
<b>Str2</b>	558	3.641	1.465	2.604	1.252	$7.971 \times 10^1$	$1.477 \times 10^3$
<b>Str3</b>	563	11.374	1.469	0.0882	0.1265	$1.322 \times 10^3$	$4.614 \times 10^4$
<b>Str4</b>	547	14.150	13.116	0.3026	0.1149	$1.300 \times 10^2$	$6.490 \times 10^2$

Now we turn to the tubes containing defects. It is noticed that carrier mobility is mainly determined by three parameters according to equation, the stretching modulus ( $C$ ), the effective mass of the carrier ( $m^*$ ) and DP constant. Firstly we focus on the stretching modulus of the tubes upon the incorporation of the vacancy or related defects. From **Table 1**, it is found that the obtained the stretching modules of the defective tubes are in the range of 547-563 eV/Å, and a bit smaller than that of the pristine CNT (10, 0). Thus the charge mobility of the CNTs influenced by the mechanical property of CNTs induced by defects is not significant, despite the structure of the different defects. Secondly, we turn to the deformation potential constant.  $E_{1V}$  and  $E_{1C}$  of pristine CNT (10, 0) are 11.907 and 4.424 eV, respectively. For  $E_{1V}$ , it is found that  $E_{1V}$  of **Str2** is greatly reduced, while others are almost unchanged. For  $E_{1C}$ , the values of **Str2** and **Str3** are reduced, while that of **Str4** is increased obviously. Thus these variations induced by different defects would affect the charge carrier transport of the CNTs according to equation (1). For instance, the increased  $E_{1C}$  of **Str4** is unfavoured to the electron mobility. Thirdly, we pay attention to the effective mass of charge carriers.  $m_h^*$  and  $m_e^*$  of pristine CNT (10, 0) are both  $0.0812 m_e^0$ . As the defect is introduced, it is found that  $m_h^*$  and  $m_e^*$  of **Str1** are both decreased to about  $0.066 m_e^0$ . As to other defective structures, the effective mass of charge carriers are all increased. In particular,  $m_h^*$  and  $m_e^*$  of **Str2** are 2.604 and  $1.252 m_e^0$ , which are enhanced by two orders of magnitude. It is noticed that the increased effective mass would reduce the charge carrier mobility according to equation (1). Thus the variation of effective mass induced by different defects would also affect the charge carrier transport of the CNTs.

The calculated electron and hole mobilities for the defective tubes at room temperature are listed in **Table 1**. The hole mobilities ( $\mu_h$ ) of **Str2** and **Str4** are calculated to be  $7.971 \times 10^1$  and  $1.300 \times 10^2$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ , respectively, while electron mobilities ( $\mu_e$ ) of are  $1.477 \times 10^3$  and  $6.490 \times 10^2$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ , respectively. Thus both electron and hole mobilities of **Str2** and **Str4** are decreased by one or two orders upon the defects incorporation. Obviously these two defects would limit the carrier transport of CNT (10, 0). As is expected, this fact comes without much surprise. Furthermore, it is aware that that hole mobility of **Str3** is  $1.322 \times 10^3$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ , which is very close to that of pure (10, 0) tube. As a matter of fact, the change on the hole mobility induced by **Str3** defect is less than 5%. However, it is interesting that  $\mu_h$  and  $\mu_e$  of the tube with SW defects are calculated to be  $1.986 \times 10^3$  and  $2.219 \times 10^4$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ , respectively.  $\mu_e$  of **Str3** is  $4.614 \times 10^4$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ . These values are as high as about 1.5-4.2 times compared with that of the pristine (10, 0) tube. Thus unexpectedly some defects would increase the mobility of the tube. This is a very interesting result. On the basis of our common sense, defects usually are supposed to block the movement of carriers, leading to a decreased mobility. However, theoretical predictions based on DFT studies in this work reveal that the carrier mobilities of zigzag CNTs with some intrinsic defects can be unexpectedly increased compared with those of the pristine tubes. Further understanding with more insights about the roles of the vacancy or related defects on the charge carrier mobility of CNTs is still on going in our research group.

#### 4. Conclusion

The carrier mobilities of zigzag CNT (10, 0) tube with SW, single vacant and 5/8/5 defects are investigated and compared with those of the pristine tube by using first-principle calculations in this work. It is found that the semiconducting properties of the tubes can be well preserved upon the appearance of the different intrinsic defects. It is found that both electron and hole mobilities of **Str2** and **Str4** are decreased by one or two orders due to the defects. The hole mobility of **Str3** is very close to that of pure (10, 0) tube. However,  $\mu_h$  and  $\mu_e$  of the tube with SW defects, as well as  $\mu_e$  of **Str3** are obviously increased compared with that of the pristine (10, 0) tube.

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