First Principles Study on Electronic and Optical Properties of Single Walled Carbon Nanotube for Photonics Application

S N M Halim1*, M F M Taib2, F Ahmad1

1Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Malaysia
2Faculty of Applied Science, Universiti Teknologi MARA, Malaysia

*Corresponding author: siti.nabilah@graduate.utm.my

Abstract. Recent research works on single-walled carbon nanotube (SWCNT) based material has witnessed a great technological importance in photonic applications due to their unique optical characteristics. Present work aims to employ theoretical first principles study to explore the electronic and optical properties of SWCNT in the form of armchair nanotube. The theoretical simulation is done by using density functional theory (DFT) as implemented in the CASTEP computer code. Similar to almost gapless nature of graphene, formation of Fermi level of a relaxed SWCNT structure is found to be at a value approaching zero. The calculated electronic band structure shows a direct band gap of 0.259 eV with Dirac cone form between conduction and valence band. The optical spectrum shows a variation of real and imaginary of dielectric function with inter-band transition taking place along with frequency of the incident light. The absorption spectrum exhibits a significant degree of anisotropic characteristic with almost transparent nature ranging from near infrared to ultraviolet energy range. These optical spectra show excellent nonlinear optical features which remark the suitability in optoelectronic applications.

1. Introduction

Graphene, a unique two-dimensional material made up of carbon atoms has proven to be among the most promising material applied in many fields [1, 2]. Extensive research works have been done to explore its full potential including exploitation of derivative form of graphene and its carbon allotrope [1]. The cylindrically rolled-up planar graphene sheet is being called as carbon nanotube or CNT which is well known to have identical properties with graphene due to its atomic structural similarities [3]. As such, CNT also receives as much attention like graphene by both experimental and theoretical means [1, 3, 4]. Even after more than twenty years of research works, there is still a continuous interesting discovery for its potential novel phenomena and properties.

In terms of structural characteristic, CNTs, like graphene, are made up of sp2 bonded carbon atoms with a diameter of nanometer range and length of microns to centimeters range which making them a low dimensional nanostructures. Generally, CNTs have different types which characterized by chiral structures (end of the tube) and number of tubes (or walls) that are arranged concentrically [5]. These types of CNTs are zigzag, armchair, chiral, single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotube (MWCNT). The SWCNT, the subject of this paper, is especially interesting due to excellent characteristics. According to existing research findings from others [6], electronic
properties show sensitivity to its atomic arrangement that cover a wide spectrum of energy range. Depending on the chirality, SWCNT structures can be either semiconducting or metallic with variation in energy band gaps [7]. Particularly for photonic application, the semiconducting nanotube with direct band gap is more suitable compared to metallic nanotube that is considered as ideal for electronic application. At this point, a subtle difference of structure can lead to opening or closing of energy band gap. Additionally, the SWCNT with different chirality had different levels of optical absorption that can benefit specific desirable photonic application.

Few studies on electronic properties of SWCNT material can be found in the literature [6]. However to the best of knowledge, conceptual investigation on the optical characteristics in atomistic level of relation toward photonic application is less reported theoretically. In this paper, the electronic and optical properties of SWCNT were analyzed comprehensively by first principles calculation in the framework of density functional theory (DFT). Herein, the unique anisotropic effects in various optical properties like dielectric function, refractive index, optical absorption, and loss function of SWCNT is reported as a reference for future research study. This will be remarkable in determining the amount of SWCNT to be a dopant in any kind of compound material that results in optimum photonic characteristics for specific device applications.

2. Computational Details

Computational technique is used to simulate the molecular structure based on fundamental descriptions of density functional theory. The principle lies behind this theory comes from determination of the electron density and its derivation which has been discussed in [8, 9]. A simple model structure of SWCNT with value of chirality (10, 10) under the armchair nanotube was constructed and optimized successfully. The structure is cylindrically rolled with diameter of 1.2 nm as shown in Figure 1. The structure was relaxed using CASTEP computer code as implemented in Material Studio. DFT simulation was performed on SWCNT structure by using planewave pseudopotential within the generated gradient approximation formulation with Perdew-Burke-Ernzerhof (PBE). The structure was successfully optimized with specific parameters setting. The cut-off energy was set to 400 eV and plane wave k-point generated by Monkhorst-Pack grid for integration of Brillouin zone was sampled by $1 \times 1 \times 2$. The valence electron states considered in ultrasoft pseudopotential calculation of SWCNT atomic structure is denoted by C $2s^2 2p^2$ and have been relaxed with convergence criteria such as SCF tolerance of $5.0 \times 10^{-6}$ eV/atom, force of 0.01 eV/Å, and displacement of $5.0 \times 10^{-4}$ Å. In order to avoid periodic interaction between atoms, a vacuum slab of 10 Å is applied into DFT calculation.

![Figure 1. Relaxed structure of SWCNT inside the Brillouin zone](image)

3. Results and Discussions

3.1. Electronic structure

The electronic band structure calculation of SWCNT has been simulated inside the CASTEP software by taking into account energy derivation based on density functional theory summarized in
Once band structure is plotted, the energy band gap that lies between the top valence band (VB) and bottom conduction band (CB) can be achieved. The calculated band gap of SWCNT is found to be 0.259 eV which is in agreement with other theoretical works [6, 11]. As shown in the Figure 2, the band structure shows a direct band gap as the highest and lowest occupied state is in the same position. As a result, electrons can directly emit photon between the CNT’s band gap, which attribute to its conducting nature [12]. The electron transport inside the energy band gap plays important role in many photonic principles.

Figure 2. Energy band structure of SWCNT with Fermi level start at 0 eV

3.2. Optical properties

The optical characterization of material which related to the wavelength and frequency of electromagnetic radiation have drawn significant importance. In this section, the optical properties of SWCNT obtained from the calculation are plotted with function of energy wavelength from 0 to 10 eV. As incoming light falls on material, it can be absorbed, transmitted, and reflected. The optical properties of SWCNT from DFT calculation are analysed by the initial frequency-dependent complex dielectric function which consist of real and imaginary part from Kramers-Kronig transformation denoted by \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \). In general, the constant dielectric function at low energy region arises due to polarization and dipole mechanism inside the material which is also influenced by the response to electric field. At some frequency, the dipole does not able to response to electric field anymore. Consequently, dielectric constant rapidly goes down with energy as the material’s net polarisation drops. This phenomenon can be well observed at the real part of dielectric function of simulated SWCNT as plotted in Figure 3.

Figure 3. Real and imaginary part of dielectric function of SWCNT
Among the energy region, telecommunication band at 0.8 eV is the most preferable in most photonic application which is considered as low energy region. The calculated real dielectric constant of SWCNT at 0.8 eV is 3.0 which is consistent with other report [13]. Refractive index is a function of frequency or energy of the incoming photon and can be defined as how fast light travels in medium. The refractive index recorded at 0.8 eV is 1.75 and goes down to lower values in the visible region and above. Such value can be fitted into experimental measurement. The refractive index of lower energy region or infrared region is larger than other energy region signifies a large permittivity of SWCNT behaviour.

![Figure 4. Real and imaginary part of refractive index of SWCNT](image)

The incident light penetrate into material depends on the frequency of electromagnetic waves. The penetration of electromagnetic radiation at a particular energy (wavelength) into a material before being absorbed can be described by optical absorption. This optical absorption or absorption coefficient is important properties as it demonstrates which region of wavelength that material can has optimal light absorption character. The calculated optical absorption of SWCNT is shown in Figure 5 considering incident photons of energy from 0 to 20 eV. In general, absorption spectra show an optical gap at lower energy region of 0.2 eV which equivalent to infrared region and suitable operation wavelength for telecommunication field. In addition, highest peak can be observed at 4 eV regions with sudden drop as energy increase. This can be inferring to the efficiency of SWCNT to have an excellent absorption properties at value of 4 eV region.

![Figure 5. Absorption spectra of SWCNT](image)
4. Conclusion

By implementing theoretical framework using DFT calculation, intrinsic characteristics of SWCNT were discussed thoroughly. Representation of band structure is the direct evidence of nanotube having almost similar properties with its parent material, graphene. With only small opening in the band gap, SWCNT is suitable for operation wavelength at telecommunication band. Simulated band gap result of 0.2 eV contributes to the effort for tunability and potential coverage of larger wavelength ranges. The nonlinear optical properties with anisotropic characteristic remark the suitability of SWCNT to be used in the photonic applications. This atomistic level of study contribute to the description on setting parameters for first principles simulation of structural model as well as its electronic, and optical properties that can be as reference for future photonic research.

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