Tailoring the IV Characteristics and Quantum Capacitance of Single Layer Graphene; A First Principle Study

Muhammad Suhail[1], Muhammad Rafique[2], Irfan Ahmed[3], Rasool Akhtar[4]

[1-4]Mehran University of Engineering and Technology, SZAB Campus, Khairpur Mir's, Sindh, Pakistan

[1]s.soomro90@yahoo.com, [2]Rafique.naich@muetkhp.edu.pk, [3]Irfanahmed@muetkhp.edu.pk, [4]Rasool.akhtar@muetkhp.edu.pk

***Abstract*– This paper illustrates about electron transmission behaviour / IV characteristics and Quantum capacitance of Single Layer Graphene (SLG) in pure form and defective graphene through doping with Oxygen (O) through Density Functional Tight Binding Plus method. As pure graphene has a zero-band gap, so doping has been done to see the impact on band gap, IV characteristics and Quantum Capacitance of single layer graphene. Then impact of doping has been analysed and compared by varying the concentration of O atoms from 3.125% to 9.37%. The calculated results were compared with pure single layer graphene. Upon doping with O in pure graphene, sufficient band gap appears at Dirac point and the values of IV characteristics and Quantum Capacitance of graphene are enhanced. So making the graphene to be a good semiconductor that can be used as supercapacitor, batteries and storage applications. Moreover, the IV characteristics and Quantum Capacitance values are directly proportional to concentration of impurity in O atoms present in graphene layer. Upon analysing electronic properties of defected graphene layer, it was observed that refractive index of graphene layer was completely changed. As Monolayer graphene termed as a magic bullet for materials engineering suffers zero band gap dilemma, thus making it difficult to be used for real engineering applications. One of major application which has risen in the current decade is its use as super capacitor device. However, quantum capacitance of graphene material varies significantly with a step change in supply voltage. In order to design super capacitor based on graphene material, it becomes imperative to modify the quantum capacitance and electron transmission behaviour of graphene through chemical doping process. Thus appears the need of this study, which is focused on tailoring quantum electrical behaviours at low voltage range.**

***Keywords*— Single Layer Graphene (SLG), IV Characteristics, Quantum Capacitance and Electron Transmission**

I. INTRODUCTION

GRAPHENE is two-dimensional honeycomb lattice of carbon atoms, a single atomic layer of graphite with its own unique properties. In an era when electronics components are becoming progressively smaller and the limits to Moore's Law are frequently considered, the isolation of a single layer graphene represents a major technological advancement [1], [2].

In addition to its physical dimensions, single layer graphene has number of interesting properties. Unlike other 2-D materials, it remains stable in atmosphere and high temperatures [3]. It has a high electron mobility and conductivity, higher thermal conductivity [4].

Like many of these interesting properties taken from behaviour of low energy electronic excitation. Instead of obeying classical equations like other ordinary semiconductors, in graphene quasiparticles obey massless Dirac equation, making it a fundamental member of distinct class of Dirac materials. Other Dirac materials like 1. Graphene nanotubes, 2. Topological insulators, and 3. Cuprate superconductors are 1. Derivatives of graphene, 2. Are not easily modified for industrial applications and 3. Complicated structures that are hard to be understood than a single graphene layer [5], [8].

Much developments in Single Layer Graphene has been done in recent years due to its amazing applicability and scientific importance as a unique model system. Because of its geometric and electronic structure, the IV characteristics and quantum capacitance of single layer graphene (SLG) can be modified in many ways [9]. This modification in properties of graphene can be used in electrical and electronic systems to enhance performance and it allows researchers to study fundamental properties of Dirac Fermions [10]. Most common method to tailor the electronic structure of graphene is by adding a positive or negative bias voltage to graphene layer, which makes modification in the charge carrier density to electronic structure of graphene layer. There is another method to change the electron transmission behaviour and quantum capacitance of graphene layer that is known as chemical doping method. In this method, other elements atoms are chemically doped or adsorbed onto graphene layer [11]. These hetro atoms

can behave as an acceptor or donor impurities in graphene lattice which tends to shift of Fermi energy into the valence or conduction band depending on impurity atoms characteristics. During chemical doping process, foreign atoms chosen carefully, replaces few C atoms in graphene layer to form "Carbon Alloys". Significant work has been done to design graphene based devices by tailoring the band gap, electron transmission and quantum capacitance of graphene by substituting the foreign atoms in graphene [12]. For instance, some studies suggest that graphene can behave as semiconductor, when oxygen (O) atoms are added in graphene lattice.

As we know that these hetro atoms have different charge densities that host C atom. Hence, by incorporating foreign atoms, electrons can be added or removed from single layer graphene [13]. Graphene in pure form carries vanishing charge carrier density at Dirac point, which shows significant consequences related to electronic properties. Some studies suggest that, during O (B) atom doping in graphene, the Dirac cone of graphene electronic structure comes below the (E_F) level and sufficient band gap appears at high symmetric K-point. As graphene has a zero band gap and Si atom is the wide band semiconductor, so doping of Si atom is a natural phenomenon to build an ample and wide band in single layer graphene [14]. In addition, a very little work has been done to evaluate the impact of Si atom doping on electron transmission behaviour, IV characteristics and quantum capacitance of single layer graphene.

This study provides new trend in electron transmission behaviour, quantum capacitance, IV characteristics of single graphene layer when Si atoms are incorporated in its lattice. No doubt that Si plays an important role in electronic devices and applications. Now it is playing vital role in graphene nanotubes and graphene thin films and nowadays research on graphene has been fastened to be used in electronic/electrical applications like supercapacitors, batteries and storage devices. Si atom have different number of valence electrons than of constituent C atom of single layer graphene, so we can predict significant band gap in the charge transport behaviour of single layer graphene, that actually alter the quantum capacitance of single layer graphene [15], [16].

This is what we are trying to study in this research using density functional tight binding plus (DFTB+) quantum simulation method. Initially we examine electron transmission behaviour/IV characteristics and quantum capacitance of pure single graphene layer, later, we examine defected graphene by doping of Si atom into the single layer graphene and in next step we will evaluate the difference in band gap after doping in single layer graphene that how much properties have been varied after doping [17]. In last, we will summarize our work and provide some conclusions.

II. DETAILS OF COMPUTATION

This research work has been done using first principles calculations through density functional tight binding plus (DFTB+) method to investigate electron transmission behaviour/IV characteristics and quantum capacitance of pure single layer graphene and defected single layer graphene within generalized gradient approximation (GGA) in materials studio software package. DFTB+ is quantum simulation method for the study of electronic properties of materials significantly in much less time [18].

The cut-off for kinetic energy was set to 450 eV that was used for expansion of wave function. The single layer graphene model was used of 4 x 5 graphene supercell with variable concentration of impurity atoms arrangement for single layer graphene having 15 Å vacuum thickness in Z direction to avoid interface between neighbouring layers. Since it was essential to get accurate results, so the convergence point was very critical to K-points, for that we have used 15 x 15 x 1 K-points mesh for better convergence criteria.

All structures were optimized till Hellmann-Feynman effect was less than 0.04 eV/ Å and the total change in energy was observed which was less than 10^{-6} eV [19]. Gaussian smearing toll was used to tackle partial occupancies graphene layer. We emphasized on frequency-dependent GW technique to calculate electron transmission/IV characteristics and quantum capacitance of Oxygen and Nitrogen doped single layer graphene structures. In Brillouin Zone (BZ), to achieve authentic and reliable results, we used 18 x 18 x 1 Γ k-points mesh [20].

III. RESULTS AND DISCUSSIONS

IV Characteristics, Quantum Capacitance and band structure properties of pure single layer graphene

Initially, we investigated the pure single graphene layer and described its geometry in Fig. 1(a). In geometry letters A and B defines to sub lattices A and B. Achieved lattices constants having value of 2.445 Å, which is approximately equal to experimental value of 2.46 Å and carbon atoms bond distance was about

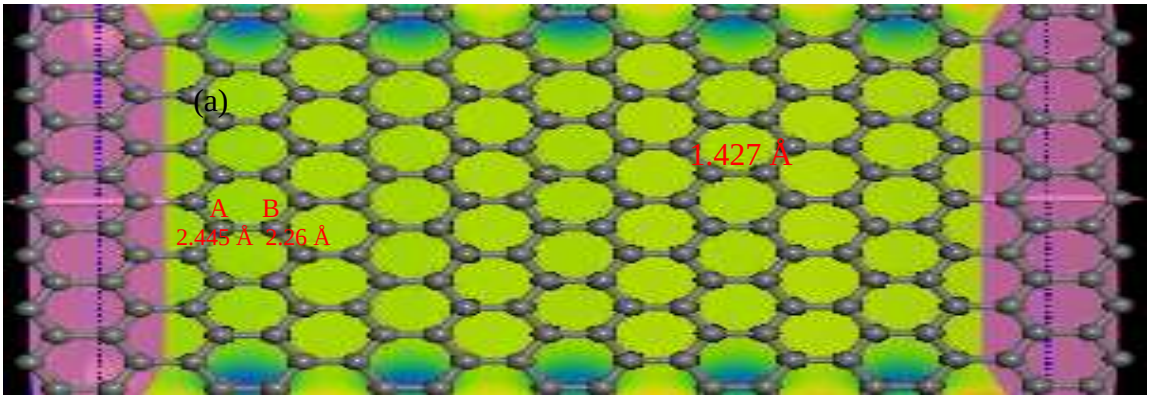

Fig. 1(a): Structure of pure single graphene layer

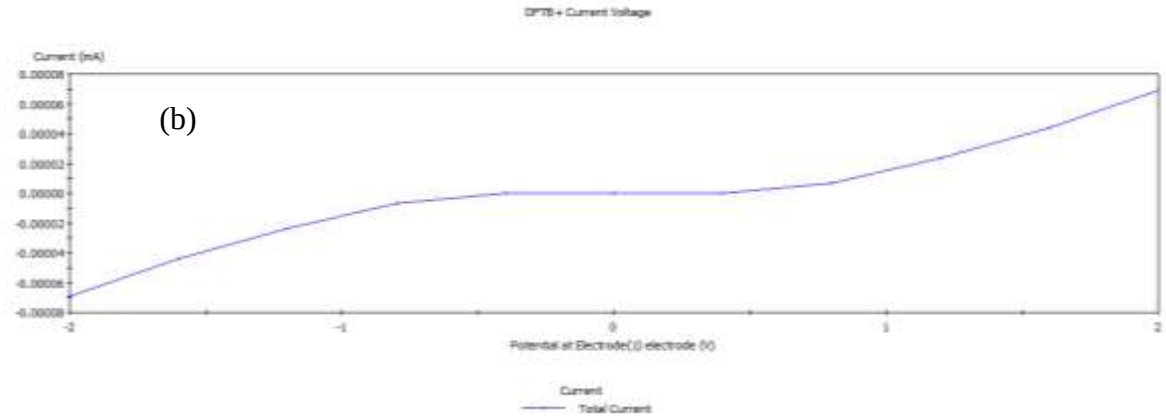

Fig. 1(b): IV characteristics of pure graphene layer

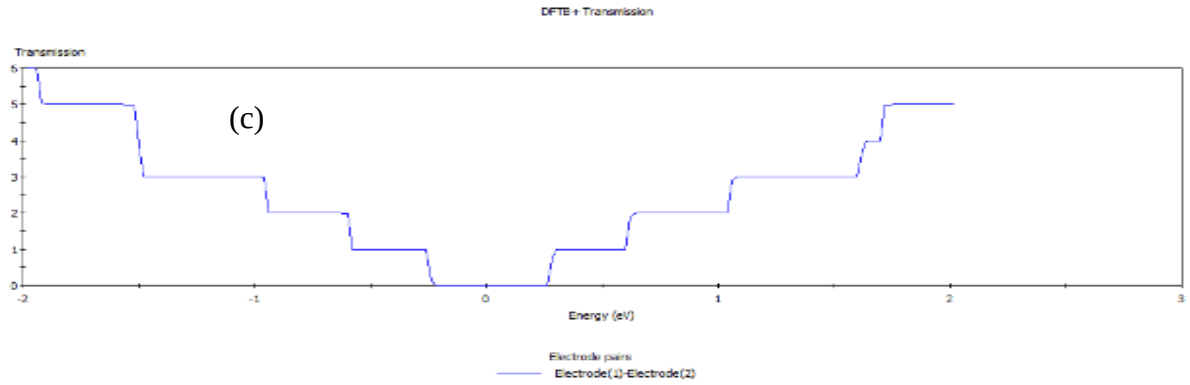

Fig.1(c): Quantum Capacitance of pure graphene

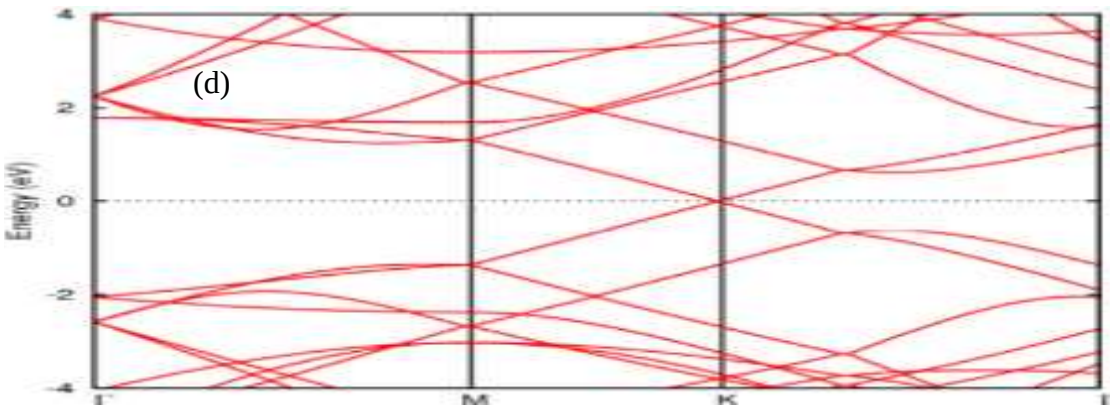

Fig.1(d): Band structure of pure graphene layer

1.427 Å [21], which matches with previous study. We also calculated the IV characteristics, quantum capacitance and band structure of pure single layer graphene, shown in Fig. 1(b), Fig. 1(c) and Fig. 1(d) using first principles study. In Fig. 1(a) it is shown the single graphene layer structure and in Fig.1 (b) is the calculated IV characteristics, where we can see that without applying any external source, the current has a value of -0.00007 A and potential difference at electrode side is -2 V, so current goes on to 0.00008 A. And voltage is 2V, as the voltage V increases the, the current I increases linearly [22]. So we can say that pure graphene has value of current I and voltage V and it also has a negative current and voltage value, so we have to modify that characteristic of single graphene layer to make it good semiconductor to be used as supercapacitor application. In Fig. 1(c), the quantum capacitance of single graphene layer is investigated, here we can see that pure graphene has some value of capacitance 6 eV at electrodes even without any external supply and it starts decaying in steps till it goes to 0 eV and starts charging itself, till the value goes to 6 eV again [23]. This phenomenon is rapid So we can see that pure graphene layer has self-charging and discharging mechanism of quantum capacitance. We have to control this property of pure graphene layer through doping so that we can control charging and discharging of energy stored in its electrodes due to high electron mobility. Fig. 1(d) depicts the band structure of pure graphene layer, here we can notice that pure graphene layer has zero band gap. Here we have used 60-K points grid with the path Γ- M - K – Γ in irreducible Brillouin zone to achieve very fine grid. We will modify the band structure of pure graphene layer through doping with oxygen O to create band gap in graphene layer [24].

IV characteristics, Quantum Capacitance and band structure properties of 2-O doped single layer graphene (SLG)

In this section, we try to investigate the doped single layer graphene with 2-O atoms and see the effect of doping on single layer graphene IV characteristics, Quantum capacitance and band gap structure. Fig. 2(a) shows the 2-O atoms doped single layer graphene having the geometry letters A and B defines to sub lattices A and B. Achieved lattices constants having value of 2.445 Å, which is approximately equal to experimental value of 2.46 Å and carbon atoms bond distance was about 1.427 Å and the O-C bond length is formed 1.409 Å in case of 2 atoms doping [25]. When oxygen is doped in single graphene layer it interacts through sp^2 hybridization and makes three σ bonds with neighbouring carbon atoms. Therefore, there is no distortion in planner structure of single layered graphene sheet. Fig. 2(b) illustrates the effect of 2 oxygen atoms doping on IV characteristics through DFTB+ simulations. Here we can see that as defective graphene has changed the IV behaviour after doping. Pure graphene IV behaviour was in negative but after doping with 2 oxygen atoms the current starts rising from 0.00000 and it goes up till 0.00006 ampere as potential at electrodes is increased from -1 to -0.8 but as potential at electrode side is increased the current I starts decaying. In this way the charging and discharging cycle goes on, but we have to modify the IV characteristics more so that energy stored in electrode side do not dissipate quickly [26]. In next case IV characteristics are more enhanced and discussed. The fig.2 (c) depicts the quantum capacitance of 2-O doped single graphene sheet and here we can see that after doping with oxygen, the quantum capacitance value has been decreased to 1.6 eV as in previous case it was 6 eV. Here can observe that the quantum capacitance is not decreasing rapidly as compared to it was in pure graphene case. Doping creates the band gap because of that electron transmission behaviour is little slowed [27]. During discharging period, the quantum capacitance does not decrease rapidly and during charging period the energy is stored in no time. That is all we want in defective graphene layer to be used as supercapacitor applications. Fig. 2(d) shows the band structure behaviour of single graphene layer after doping with 2 oxygen atoms. Here we used 60 Q-points with the path Γ- M - K – Γ in irreducible Brillouin zone to achieve band structure with very good grid.

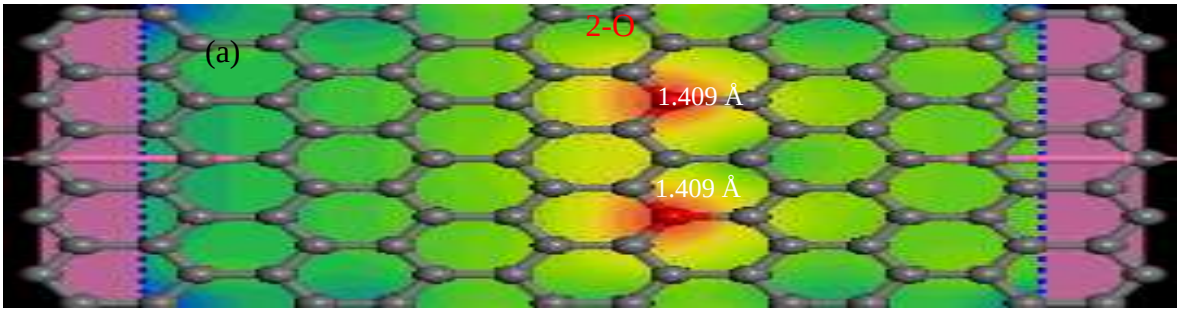

Fig.2(a): 2-O doped single layer graphene structure

However, oxygen doping preserves the energy dispersion linearly near to Dirac point and band gap of 0.1528 eV is created at high symmetric K-point because of dividing of extra Symmetry of sub lattices of graphene due to doping process. Number of states are pulled down Fermi energy level. So it is possible to modify the band gap structure of single layered graphene sheet through

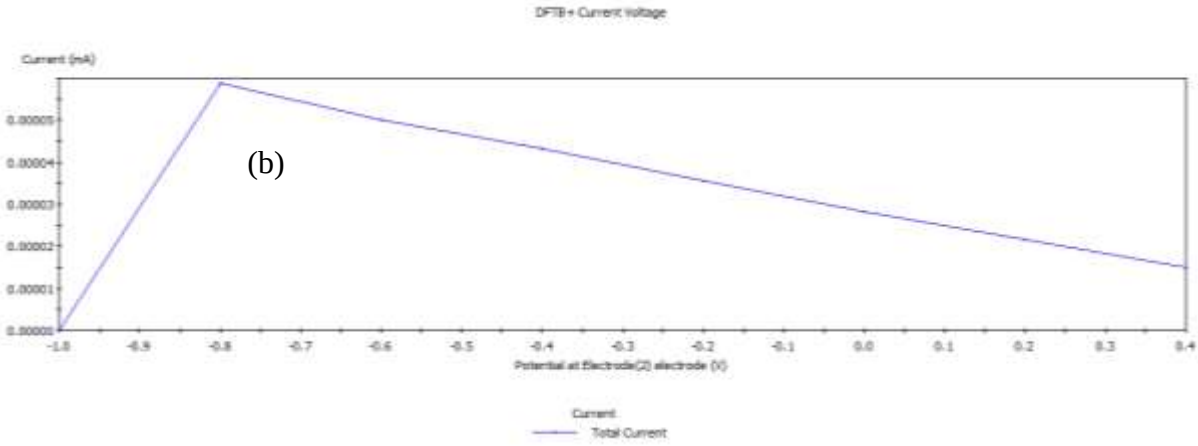

Fig. 2(b): IV characteristics of 2-O doped single layer graphene

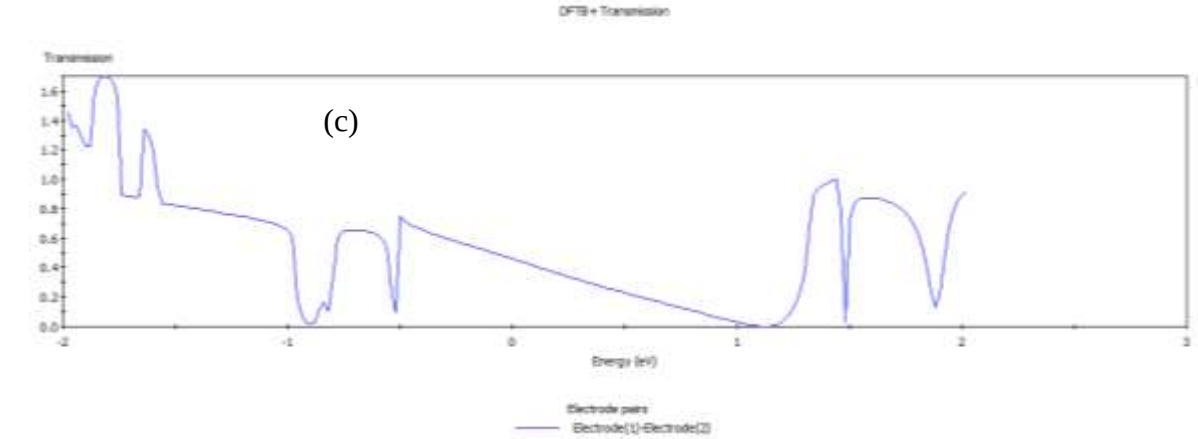

Fig.2(c): Quantum Capacitance of 2-O doped single layer graphene

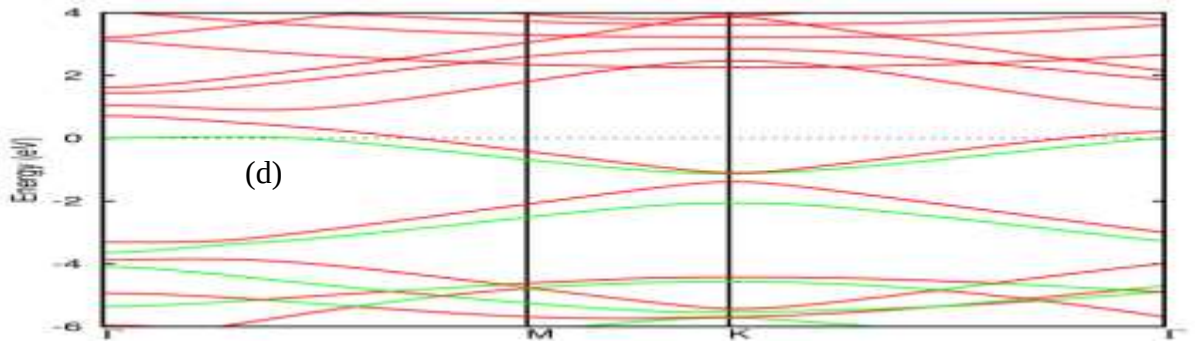

Fig.2 (d): Band gap structure of 2-O doped single layer graphene

doping graphene sheet through doping of foreign atoms [28], which can affect the IV properties and quantum capacitance of single layered graphene sheet.

IV characteristics, Quantum Capacitance and band structure properties of 3-O doped single layer graphene (SLG)

In this section, we try to investigate the doped single layer graphene with 3-O atoms and see the effect of doping on single layer graphene IV characteristics, quantum capacitance and band gap structure. Fig. 3(a) shows the 3-O atoms doped single layer graphene having the geometry letters A and B defines to sub lattices A and B. Achieved lattices constants having value of 2.545 Å, which is approximately equal to experimental value of 2.56 Å and carbon atoms bond distance was about 1.438 Å and the O-C bond length is formed 1.429 Å in case of 3 atoms doping. When oxygen is doped in single graphene layer it interacts through sp^2 hybridization and makes three σ bonds with neighbouring carbon atoms. Therefore, there is no

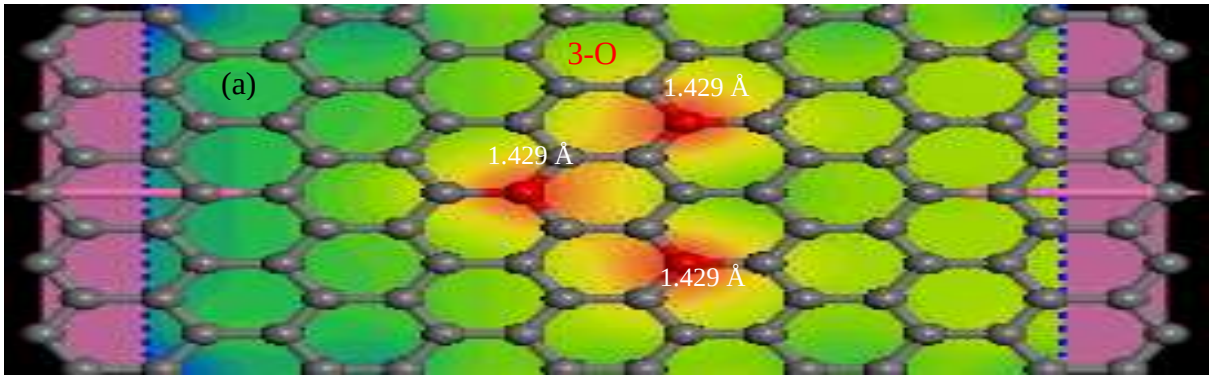

Fig. 3(a): 3-O doped single layer graphene structure

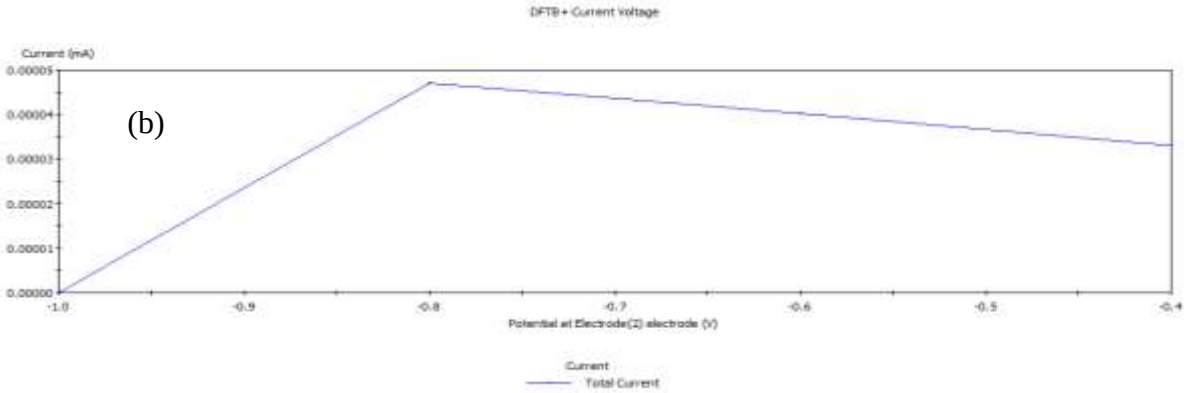

Fig. 3(b): IV characteristics of 3-O doped single layer graphene

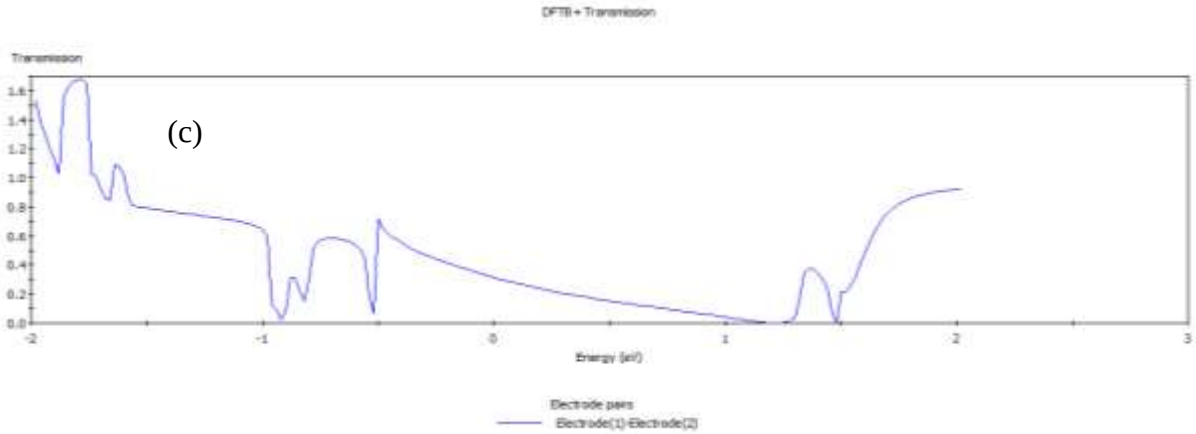

Fig. 3(c): Quantum Capacitance of 3-O doped single layer graphene

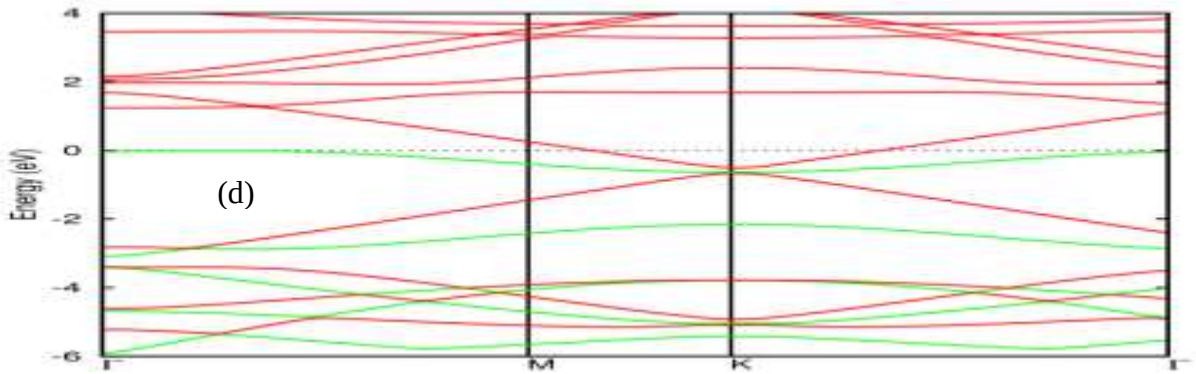

Fig. 3(d): Band gap structure of 3-O doped single layer graphene

distortion in planner structure of single layered graphene sheet. Adding of third oxygen atom in doping makes slight change in properties of single layer graphene Fig. 3(b) illustrates the effect of 3 oxygen atoms doping on IV characteristics through DFTB+ simulations. Here we can see that IV behaviour of defective graphene is slightly changed. Pure graphene IV behaviour was in negative but after doping with 3 oxygen atoms the current starts rising from 0.00000 and it goes up till 0.00005 ampere as potential at electrodes is increased from -1 to -0.8 but as potential at electrode side is increased the current I starts decaying slightly slowly as compared to previous case. Increased concentration of doping expands the charge cycle and discharge cycle at electrodes. The fig. 3(c) depicts the quantum capacitance of 3-O doped single graphene sheet and here we can see that after doping with oxygen, the quantum capacitance value has been decreased to 1.5 eV as in previous case it was 1.6 eV [29]. Here we can observe that the quantum capacitance is not decreasing rapidly as compared to it was in pure graphene case. Increased concentration of dopants in single layer graphene enhances the life cycle of graphene sheet and holds the charge for long time span and doping creates sufficient band gap to control because of that electron transmission behaviour is little slowed. During discharging period, the quantum capacitance does not decrease rapidly and during charging period the energy is stored in no time. That is all we want in defective graphene layer to be used as supercapacitor applications. Fig. 3(d) shows the band structure behaviour of single graphene layer after doping with 3 oxygen atoms. Here we used 60 Q-points with the path Γ- M - K – Γ in irreducible Brillouin zone to achieve band structure with very good grid. However, oxygen doping preserves the energy dispersion linearly near to Dirac point and band gap of 0.2578 eV is created at high symmetric K-point because of dividing of extra Symmetry of sub lattices of graphene due to doping process [30]. Number of states are pulled down Fermi energy level. So it is possible to modify the band gap structure of single layered graphene sheet through doping graphene sheet through doping of foreign atoms, which can affect the IV properties and quantum capacitance of single layered graphene sheet.

IV. CONCLUSION

By using a first principles study, we investigated the IV characteristics, quantum capacitance and band gap structure of pure single graphene layer and we noticed that current in pure graphene sheet increases from negative value linearly with the supply and quantum capacitance at electrode side charges rapidly with supply and also discharges quickly and has a zero band gap due to high electron mobility. So, we doped the graphene layer with 2 oxygen atoms and made it defective, then we saw the behaviour on IV characteristics, quantum capacitance and band gap structure of doped graphene sheet. Then we noticed that value of current was varied from negative and was starting from 0 and was increasing with supply increased but as supply negative supply comes, the current was decreasing little bit slowly. Quantum capacitance doped graphene layer also improved and energy discharging time was also improved. In addition band gap structure was also modified and little band gap was created in defective graphene layer In third case we doped single layer with 3 oxygen atoms and saw the effect on IV characteristics, quantum capacitance and band gap structure of defective graphene layer. We noticed that IV characteristics were little improved and in quantum capacitance charging coefficient was little improved, plus band gap structure is little more improved from previous case and there was little improvement in band gap value as discussed above.

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