Preprint Title	Bandgap Engineering in Iron Doped Graphene Nanosheets: Electrical Performance Boosting for Application in Nano-electronics
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Publication Date	09 Okt. 2020
Article Type	Full Research Paper
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Bandgap Engineering in Iron Doped Graphene Nanosheets: Electrical Performance Boosting for Application in Nano-electronics

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Abstract

The study reports electrical properties of iron atom doped graphene nanosheets using Atomistix Tool Kit- Virtual NanoLab (ATK-VNL) QuantumWise simulation package. Density Function Theory (DFT) has been adopted for the present study. The introduction of iron atoms in a bare graphene nanosheet make changes in the band-structure of otherwise perfectly overlapped bandgap of pristine graphene nanosheets. The controlled amount of iron doping opens a small bandgap in graphene and that enhances gradually with further increase of doping concentration. Chemical potential measurement indicates a steady increase in the magnitude from - 5.661314 eV to - 5.910896 eV. The study depicts that the pristine graphene nanosheet exhibits a DOS value of ~330 eV^{-1} at energy value ~12 eV, but in case of its doped counterpart, the DOS values change to ~290 eV^{-1}, ~270 eV^{-1} and ~250 eV^{-1} respectively for one, two and three atoms doped graphene nanosheets at a specific energy value of ~12 eV. The paper will address the total energy and transmission spectrum of bare and doped graphene nanosheets. The role of iron dopant in tuning the electrical properties of graphene nanosheets are studied extensively for application in nano-electronics. To the best of authors knowledge this is the first report on bandgap engineering in graphene nanosheets by controlled iron doping.

Keywords

Bandgap; Graphene; Doping; Nanosheet; Iron

Introduction

Nanotechnology [1] is a standout amongst the most delicate research territories that cover various orders including biomedical building and development materials. Generally, nanotechnology has been ascribed to the advancements in the field of material science [2], microelectronics [3] and medicines [4]. Nanotechnology is a field that is influenced by the progress in basic chemistry and physics research, where occurrence on molecular and atomic level are used to give structures and materials that execute tasks that are highly impossible for the materials in their typical microscopic form. The enhancement of instrumentation and technology as well as its co related scientific field as Chemistry and Physics are fabricating the research on nanotechnology competitive and progressive. Before the discovery of graphene in 2004, it was assumed that the two-dimensional crystals were not existed as thermodynamic fluctuation does not allow it. Graphene was discovered by a scientist named Andre Geim by the mechanical exfoliation method from graphite [5]. Because of the exceptional property of Graphene, it has been explored for various applications. Graphene is also used to make conductive plates of ultra-capacitors due to its large surface area to mass ratio. Upon doping with different hetero material impurities in bare graphene nanosheets, changes appear in terms of physical and chemical properties [6,7]. Previously the effects of metal atom doping in carbon nanomaterials is already studied [8-12]. Doping of extrinsic impurities to the pristine graphene nanosheets can increase the extent of chemisorptions in a large extent as when compared to physisorption cases. Impurities like N, Al, S and B have been investigated earlier either onto Graphene or Single walled carbon nanotubes by experimentally [13-15] as well as theoretically [16-18]. Chemical potential, band-structure, density of states, total energy, transmission spectrum, optical spectrum, Eigen value, Eigen vector, all these parameters of a pristine graphene nanosheet are expected to get altered when extrinsic impure materials are doped selectively in that sheet. This has led the authors to study the role of iron (Fe) impurity in electrical performance boosting of bare graphene nanosheets for futuristic applications in nano-electronics and photonics.

To study the underlying interaction mechanism of iron dopant and bare graphene nanosheets semi empirical DFT based ATK-VLN QuantumWise software is used. Iron atoms are introduced by ab-initio approach and by Van der Waals force at different interstitial position of bare graphene nanosheets for estimating various electrical, chemical and electronic properties. In comparison to the earlier study by Wang et al. (2009) [19], the present study will throw light on defect free graphene for Fe doping to study its influence over the DOS analysis, band structure modulation and transmission spectrum. Through the controlled doping of iron, it is expected to observe band gap morphology modulation from metallic to semi-metal and semi-metal to semi-conductor like behavior. This possibility has been explored comprehensively through this analytical study.

Simulation Methodology

In this work, the authors have utilized a nano-simulation software, Atomistix Tool Kit-Virtual Nano Lab (ATK-VNL) [19]. (Density Functional Theory (DFT) can be used to correct the self-interaction error by defining an atomic self-energy potential, which is calculated for atomic sites in the system, that cancels the electron–hole self-interaction energy [20]. This potential can be calculated as the difference between the potential atom and that of a charged ion which is formed by the removal of a fraction of its charge of the range between 0 and 1 electrons. Self-energy potential is can be defined as the sum of these atomic potentials.

ATK-DFT generally uses the energy level of conduction band and it eliminates the self-interaction energy effect and as a result an accurate study of electronic properties can be obtained. Numerical Linear Combination of Atomic Orbitals (LCAO) is utilized for all the analyses at fixed algorithm parameters of ATK- DFT. The LCAO Calculator [21] uses DFT and norm-conserving pseudo potentials to give a brief description of electronic structures. In the DFT method, the exchange- correlation term is used to approximate the quantum mechanical part of the electron- electron interactions. A large number of different approximate exchange- correlation density functions exists in DFT.

Defect creation in Graphene upon doping Iron atoms

The doped Iron defects could be observed at different excited charge conditions shown by ‘q’ in Graphene systems. The energy formation denoted by ‘E_F’ of distorted defect comprising of K_{Fe} Iron atoms in varied proportion of KFe_1 to KFe_3 inserted to replace $K(C)_n$ atoms of Graphene, viz. $KFe_1 + KFe_2 + KFe_3 = K(C)_n$ could be represented by the expression as shown in Equation (1).

$$E_F\left[K^q_{(Fe)_{(1-3)}}\right] = E_{Total}\left[K^q_{(Fe)_{(1-3)}}\right] - E_{Total}(C)_n + K(C)_n\mu(C)_n - \left(K_{Fe}\mu_{Fe}\right)_{(1-3)} + q(\mu_e - E_v) \tag{1}$$

where, $E_{Total}\left[K^q_{(Fe)_{(1-3)}}\right]$ and $E_{Total}(C)_n$ are the analysed total energies containing distorted and defect pristine Graphene architecture, respectively. ‘q’ represents the charge condition of the defect architecture; Energy position of the valence band is denoted by E_v; and μ_e represents the electronic chemical potential, defined under the bandgap in relation to E_v [22].

$\mu(C)_n$ and $(\mu_{Fe})_{(1-3)}$ denotes the net chemical potentials of the prevalent elemental components in the systems. When equilibrium condition is reached, the expression of the doped system could be shown as in Equation (2),

$$\mu(C)_n = (\mu_{Fe})_{(1)} + (\mu_{Fe})_{(2)} + (\mu_{Fe})_{(3)} \tag{2}$$

where, $\mu(C)_n$ is defined as the net cumulative energy per hexagonal ring of carbon in the Graphene architecture. Selection of $\mu(C)_n$is described by the net growth conditions of Graphene, and it is very helpful to aid in maintaining the stoichiometry between the Iron atoms in the Graphene network.

Electron temperature is taken as 300 K, the grid mesh-cut value is considered as 20 Hartree, charge is zero, spin is unpolarized, k-points (a, b, c) are (9, 9, 1) and the Carbon energy is 0.0 eV.

Results and Discussions

Band Structure Analysis

Graphene is generally a zero-band gap material because the valence band and conduction band of graphene are overlapped in nature. Figure 1 shows the device configurations of all the variants. Figure 2 show the effect of iron doping on band gap modulation in undoped graphene nanosheets. Bare graphene exhibits zero band gap, i.e. overlapping of valence band and conduction band. Introduction of impurity dopant changes the bending pattern in doped graphene by lowering the sub-band from lowest valence region in comparison to its undoped band diagram where significant crossing of sub-bands takes place between lower valence band and upper conduction band at the Fermi level. Figure 2 indicates this observation. With increase in the doping concentrations of the iron atom, also the band gap gets increased. It indicates the semi conducting nature, deviating from its metallic nature.

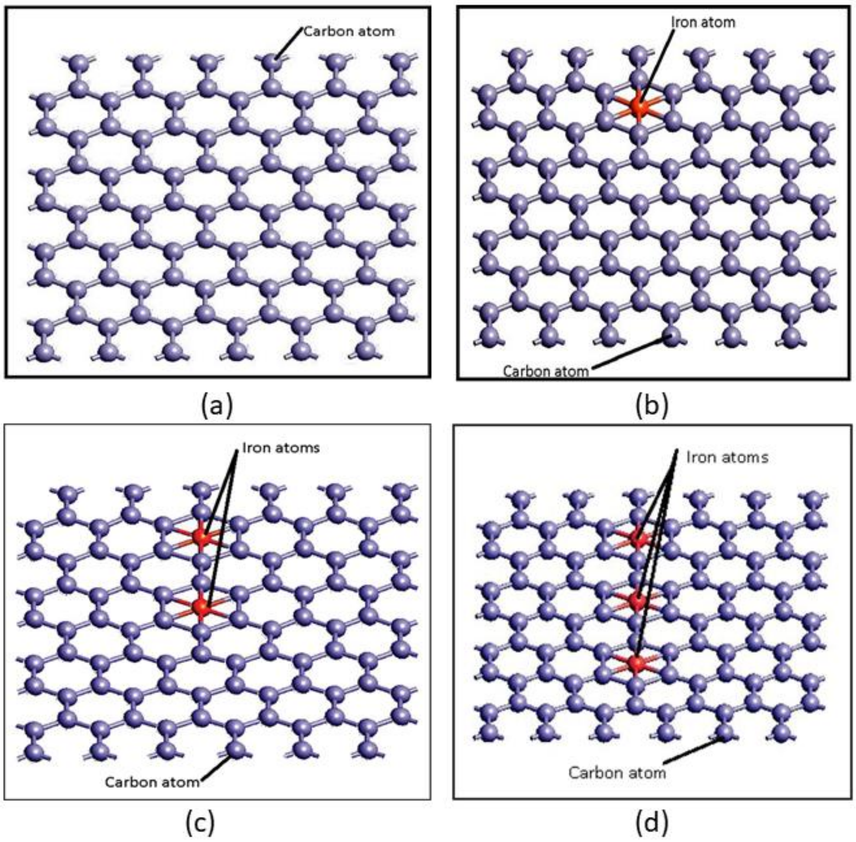
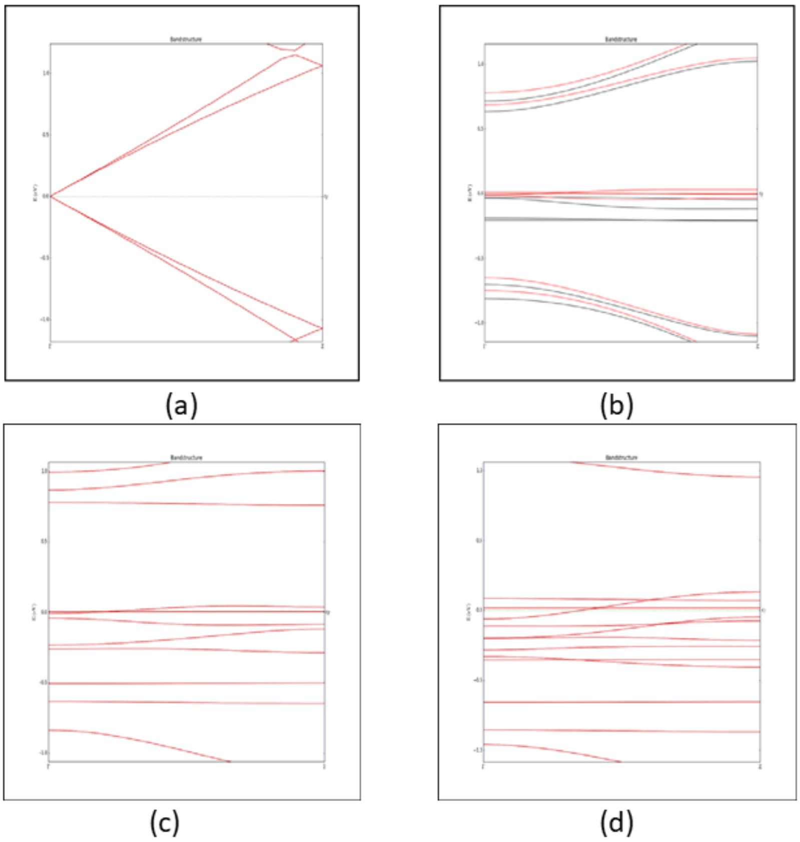


Figure 1: Device configuration of (a) pristine Graphene nanosheet; (b) one iron atom doped graphene nanosheet, (c) two iron atom doped graphene nanosheet and (d) three iron atom doped nanosheet.



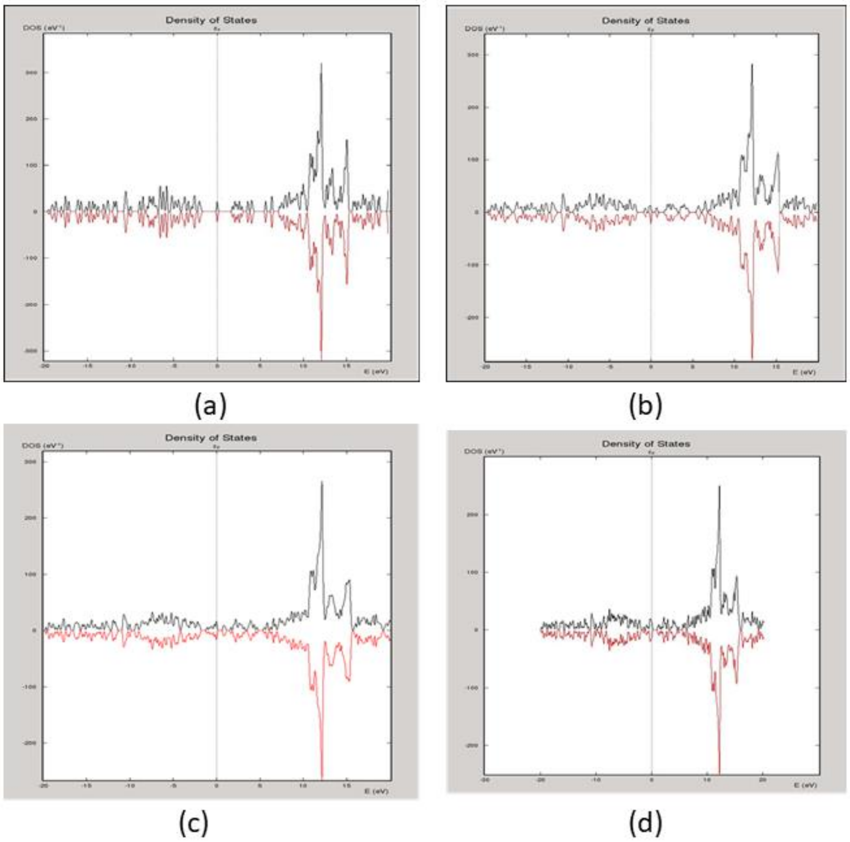
(a) (b)

(c) (d)

Figure 2: Band structure plot of (a) pristine Graphene nanosheet; (b) one iron atom doped graphene nanosheet, (c) two iron atom doped graphene nanosheet and (d) three iron atom doped nanosheet

Density of States Analysis

The specific value of DOS at a characteristic energy level in eV explains the number of states available for occupation by the electrons in a system. Figure 3 show that undoped graphene nanosheet exhibits a DOS value of ~330 eV-1 at energy value ~12 eV. But in case of doped graphene nanosheets, the DOS values are ~290 eV^{-1}, ~270 eV^{-1}, ~250 eV^{-1} respectively for one, two and three atoms doped graphene nanosheets at a same energy value of ~12 eV. It implies that the peak value is decreasing with the increasing number of doped atoms. The doping concentration in the basic and stable construction of graphene conveys a charge transfer reaction at the electronic sites of the graphene between carbon and iron atom, which is ascribed to the ensuing retort in the plot. So, with increase in the doping atom concentration in graphene the band structure behavior also changes.



(a) (b)

(c) (d)

Figure 3: Density of States plot of (a) pristine Graphene nanosheet; (b) one iron atom doped graphene nanosheet, (c) two iron atom doped graphene nanosheet and (d) three iron atom doped nanosheet

Chemical Potential Analysis

The chemical potential of a species in a mixture is defined as the rate of change of free energy of a thermodynamic system with respect to the change in the number of atoms or molecules of the species that are integrated to the system. In present study, in

Figure 4 the authors have observed a decrease in chemical potential value by ~2% (for single Fe atom doping), ~3.5% (for double Fe atom doping) and ~ 5% (for triple Fe atom doping) in comparison to its undoped counterpart. It depicts that with decreasing chemical potential, the stability of the system is increasing. The fall in chemical potential values could be ascribed due to the fact that, with the doping of Fe atoms, the basic electronic properties of pristine graphene nano-sheet is changing and that in turn affects the chemical potential of the systems. This change in chemical potential changes the band diagram of undoped graphene and that has also been verified in figure 2.

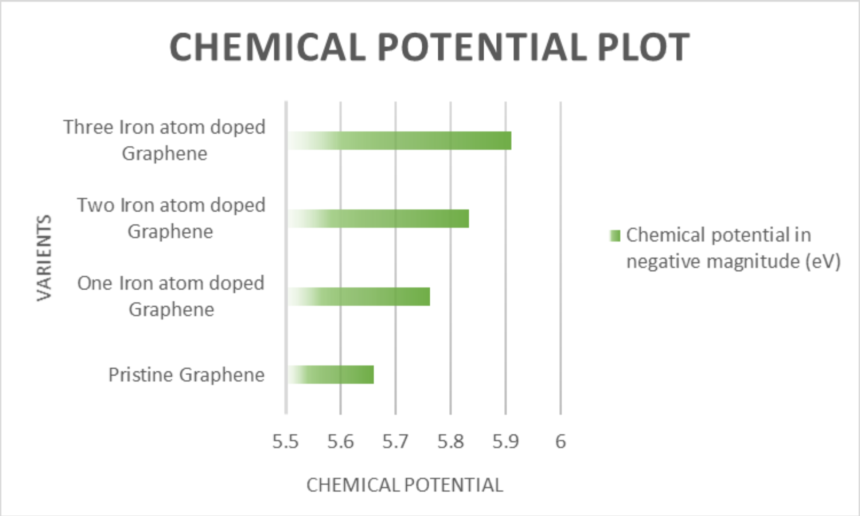


Figure 4: Chemical potential plot of (a) pristine Graphene nanosheet; (b) one iron atom doped graphene nanosheet, (c) two iron atom doped graphene nanosheet and (d) three iron atom doped nanosheet

Total Energy Analysis

Total energy can be defined as the summation of entropy term, external field, Hθ, Hartree, pair potential and spin. Here entropy and Hθ are the total contributing factors of the total energy value. For pristine graphene, the total energy is equal to Hθ= -

5661.22916 eV, entropy is equal to -0.001785 eV, and all other values are zero. Total energy is -5661.23094 eV. For one iron atom doped case, Hθ = -5771.08286 eV and entropy is = -0.07504 eV, Hartree is 0.15842 eV and spin are -0.06999 eV, all other energy parameters are zero, so the total energy is equals to -5771.06946 eV. For two iron atom doped case, Hθ = -5881.75654 eV and entropy is - 0.07600 eV, Hartree is 0.30736 eV and spin are -0.0000 eV, all other energy parameters are zero, So the total energy is equals to -5881.52518 eV. For three iron atom doped case, Hθ = -5991.94177 eV and entropy is = -0.07372 eV, Hartree is 0.42731eV and spin is -0.0000 eV, all other energy parameters are zero, so the total energy is equals to - 5991.58818 eV.

Here the total energy value is decreased from -5661.23094 eV for pristine graphene to -5771.06946 eV for one iron atom doped to - 5881.52518 eV for two iron atoms doped to -5.991.588185 eV for three iron atoms doped graphene as shown in the figure. The steady increase in negative magnitude of total energy is suggesting additional stability in the system with amplified band gap with boosted doping.

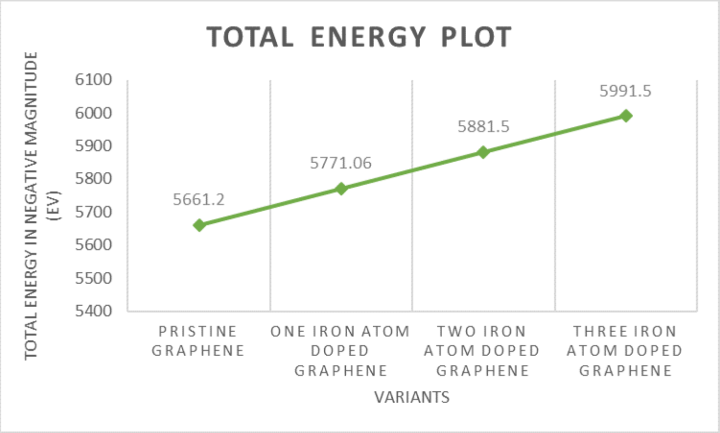
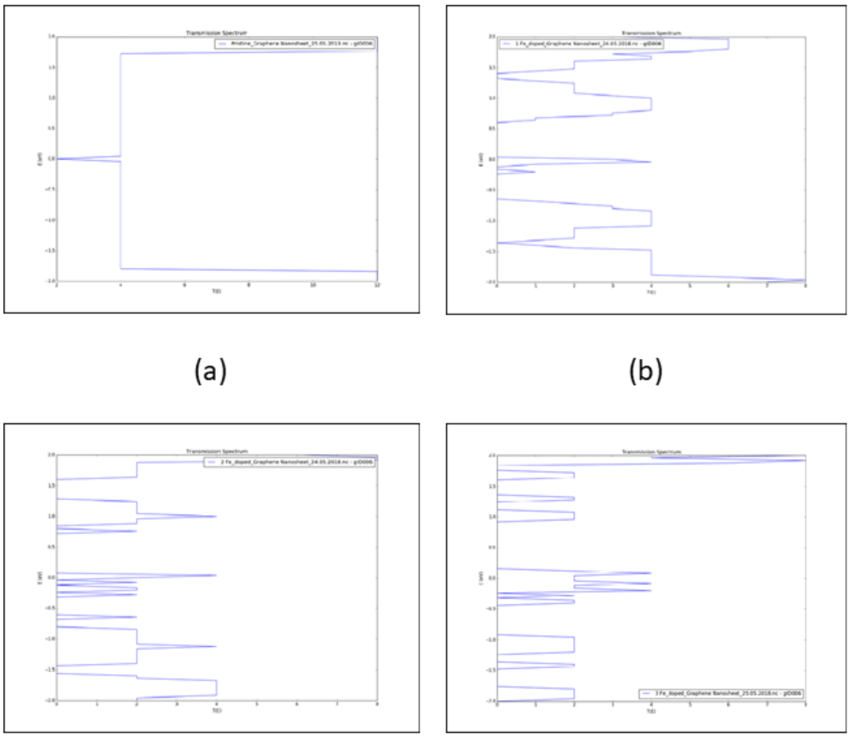


Figure 5: Total Energy plot of (a) pristine Graphene nanosheet; (b) one iron atom doped graphene nanosheet, (c) two iron atom doped graphene nanosheet and (d) three iron atom doped nanosheet

Transmission Spectrum Analysis

Transmission of electron of a system is defined as the upward direction in which electron is transmitted from the valence band to the conduction band. Transmission spectrum comparison of undoped vs doped graphene nanosheets is shown in figure 6. Electrons are generally spin polarized in nature, so the transmission of electron is found to increase due to the application of bias voltage. The transmission spectrum peaks in the conduction band region get sharper as when compared to the peaks in the un-doped case of graphene. That steepness in the conduction band curvature implies a profuse amount of transmission behavior. It is observed that due to the increase in interstitial doping in bare graphene, the sharing of outer electrons from the iron atom to the graphene network takes place. This results into the delocalization of electrons in the overall system and it causes the heightening of transmission spectrum. It is also observed that, for bare graphene, there is lack of development of peaks at the conduction band. When one Iron atom is doped, there is an incidence of development of narrow peaks around the Fermi level. The concentrations of peaks are getting more distinct due to the charge transfer mechanism happened at graphene-iron inter-phase. This result due to a partial formation of forbidden gap around defined Fermi level.



(a) (b)

(c) (d)

Figure 6: Transmission spectrum plot of (a) pristine Graphene nanosheet; (b) one iron atom doped graphene nanosheet, (c) two iron atom doped graphene nanosheet and (d) three iron atom doped nanosheet

Conclusion

In this study, the effect of doping of iron atom over graphene nanosheet has been investigated. Using the ATK-VNL Quantum Wise software, the demonstration of heavy doping using iron atoms is carried out in-silico means by the DFT mode. The study shows that with increase in the concentration of iron atom in the basic architecture of graphene, the tendency of metallic property of graphene change to shift towards semi-conducting behavior. It could be justified from the studies that upon increase in doping concentration of iron atom, the band gap gets gradually broadened as when compared to the pristine case. Chemical potential study also shows a coherent change in its values. The dynamics of band gap opening could be seen with a change in the doping concentration of iron atom. Transmission spectrum too shows the changes in values with introduction of extrinsic iron atom. Due to such attributes, the tuning of band gap of the pristine graphene has been achieved upon doping with impure iron atoms. The density of states also changed with the increasing number of iron atoms. This whole study reconnoiters the inter- phase of quantum mechanical interactions between a metallic atom and graphene, which could pave the way in exploring and devising significant carbonaceous nano-electronic applications. Sensors play the most vital role to design any non-invasive biomedical device. The efficiency of such devices is basically judged by the accuracy and precision of the sensor, used in that device. Graphene is a well-known Bio compatible nano-material, with the help of which highly accurate and precise sensors can be designed. We want to design a bio-compatible photo sensor with Graphene, through ab-initio study, which sensors can be implemented in non-invasive diagnostics.

Acknowledgements

The authors would like to express their deep-felt thanks to Maulana Abul Kalam Azad University of Technology, India, The Neotia University, India and Adamas University, India for giving necessary support and infrastructure to carry out this research work.

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